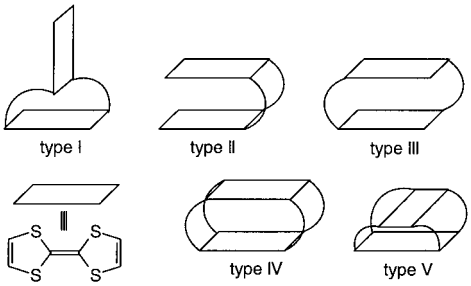
Tetrathiafulvalene Belts with Large Cavities**

Klaus B. Simonsen, Niels Svenstrup, Jesper Lau, Niels Thorup, and Jan Becher*

The ability of the organic chemist to tailor host molecules with specific properties has had a tremendous impact on the development of supramolecular chemistry, which in turn has broadened the understanding of host–guest interactions.[1] In this context, cyclophanes represent an important class of compounds.[2] Owing to their rigid framework, primarily defined by the aromatic units, these molecules exist as conformers with very large cavities that are ready to accommodate charged or neutral guest molecules.[3] The incorporation of redox-active components into these molecules would serve a dual purpose, namely, to increase the host–guest interaction with a complementary electroactive guest and to electrochemically signal the complexation event, making these molecules attractive components for sensor technology.[4] The π-electron donor tetrathiafulvalene (TTF)[5] is a good candidate as a building block for the preparation of electrochemically active macrocyclic systems with specific physical and chemical properties.[6, 7] Bis-tetrathiafulvalenophanes (TTF-phanes) are of particular interest because the two TTF units can adopt a sandwich structure, which enables intermolecular interactions between the two redox units and increases the likelihood of strong noncovalent inter- and intramolecular interactions.[7b] Double-bridged TTFs can exist as one of three stereoisomers (types I, II, or III; Scheme 1).[8–10]



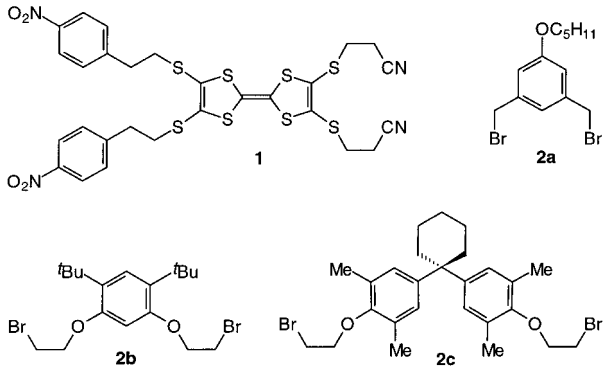
Scheme 1. Possible isomers of the dimeric TTF systems. Types I and III are depicted in the *trans* configuration only.

Two types of quadruple-bridged TTF-phanes can exist: the bis-TTF-belts,[11] where the two TTF units are connected in a parallel fashion (type IV, Scheme 1), and the criss-cross overlaid TTF-phanes, where the two TTF units are orthogonal to each other (type V).[12] Because of the restricted number of available conformers, types IV and V present the best entry to TTF-phanes with large cavities.

The syntheses of nearly all the bis-TTFs known prior to 1995, including the only two known TTF-belts, are based on coupling of a bis-1,3-dithiole precursor[7b] to give the TTF core in the final step of the synthesis (the preparation of one of the TTF-belts also involves an unusual metathesis-like dimerization step).[11a] We have developed a new deprotection–realkylation protocol for the preparation of functionalized TTF derivatives,[13] and this strategy has been used extensively by us[14] and other groups[15] for the incorporation of preformed TTFs into macrocyclic and supramolecular compounds.

Here we present a new stepwise synthesis of TTF-belts with well-defined large cavities. Our earlier attempts at preparing TTF-belts using a TTF precursor containing only one type of protecting group were unsuccessful, presumably because a sufficient level of selectivity could not be achieved in this system. However, the study of model systems indicated that the sequential stepwise functionalization of the TTF could be performed under complete control using a differentially protected TTF (in which the thiolates of the 2,3-positions are protected by a cyanoethyl group, whereas the thiolates of the 6,7-positions are protected by a 4-nitrophenylethyl group).[16]

2,3-(2-Cyanoethylthio)-6,7-bis[2-(4-nitrophenyl)ethylthio]-tetrathiafulvalene (**1**), the key compound for the assembly of the TTF-belts, was prepared by standard cross-coupling.[13c] The bis-alkylating reagents **2a–c**, chosen to confer rigidity as well as solubility to the belt molecule, were prepared in three steps from 5-hydroxyisophthalic acid, resorcinol, and 2,6-dimethylphenol, respectively.[17]



The TTF-belts **6a–c** were synthesized by a four-step strategy (Scheme 2).[18, 19] Compound **1** was monodeprotected under standard conditions,[13b,c] and the generated monothiolate was realkylated with the dibromides **2a–c** (0.5 equiv). The resulting bis-TTFs **3a–c** were purified by chromatography, isolated, and then treated with cesium hydroxide (2 equiv) in *N*,*N*-dimethylformamide to remove the two remaining cyanoethyl protecting groups. The resulting dithiolate was realkylated with **2a–c** (1 equiv) under high-dilution conditions. Purification by chromatography gave the macrocyclic bis-TTFs **4a–c** as the only isolable products. The structure of **4a–c** was confirmed on the basis of ^{1}H and ^{13}C NMR spectroscopy, plasma desorption (PD) mass spectrometry, and elemental analysis. Next, the two TTF units of

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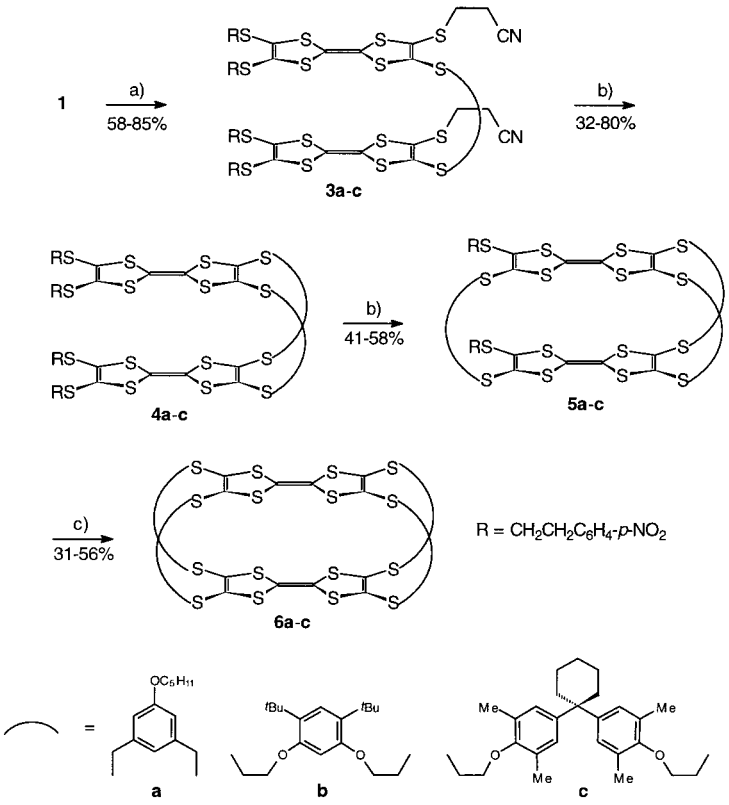

Scheme 2. Synthesis of the TTF-belts **6a–c**. a) 1. $CsOH \cdot H_2O$ (1.05 equiv), MeOH, DMF; 2. **2a–c** (0.5 equiv); b) 1. $CsOH \cdot H_2O$ (2.1 equiv), MeOH, DMF; 2. **2a–c** (1.0 equiv), DMF, high dilution; c) 1. $CsOH \cdot H_2O$ (3 equiv), MeOH, DMF; 2. **2a–c** (1.0 equiv), DMF, high dilution. All reactions were carried out under N_2 at room temperature.

4a–c were monodeprotected, and the resulting dithiolate (one thiolate group on each TTF) was realkylated with **2a–c** (1 equiv) under high-dilution conditions. The triple-bridged bis-TTFs **5a–c** were isolated as inseparable mixtures of two diastereoisomers differing in connectivity: In one isomer the TTFs are connected through the 6,6′-positions, whereas in the other they are connected through the 6,7′-positions.[20] In the final step of the reaction, the remaining two protecting groups were cleaved with an excess of base (3 equiv). Realkylation with **2a–c** under high-dilution conditions gave **6a–c** in 32–56% yield after chromatography on silica gel.

The positive-ion PD mass spectra of **6a–c** revealed peaks at *m*/*z* 1418.6, 1762.9, and 2171.2 for the parent ions of **6a–c**, respectively; no oligomeric products were detected. NMR spectroscopy confirmed these observations.

The belt structure and large cavity of **6c** can be clearly seen in the X-ray crystal structure (Figure 1).[21] The unit cell contains one centrosymmetric belt molecule, four chloroform molecules, and one methanol molecule (centrosymmetric on average, but disordered). Two of the chloroform molecules (C59-Cl1-Cl2-Cl3 and C59A-Cl1A-Cl2A-Cl3A) reside inside the spacious cavity of **6c**, while the other two (C60-Cl4-Cl5-Cl6 and C60A-Cl4A-Cl5A-Cl6A) are positioned at the rim of

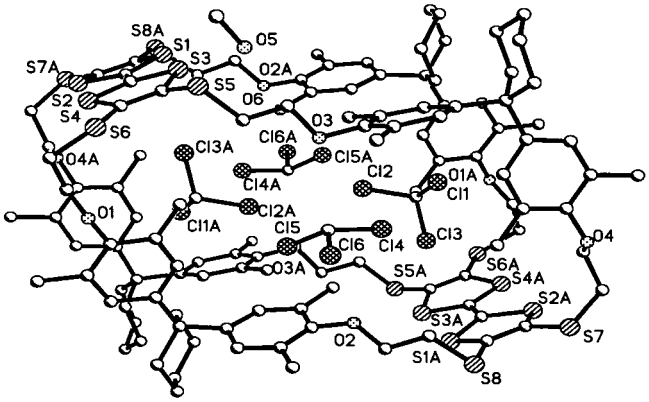

Figure 1. View of the molecular structure of **6c** including solvent molecules. For clarity the hydrogen atoms have been omitted, and atomic labels have been omitted for the carbon atoms.

the macrocycle. None of the chloroform molecules appears to be involved in any strong interactions with the TTF-belt itself. As seen in the packing diagram of **6c** (Figure 2), the packing is defined by intermolecular stacking between one TTF unit of one belt and the inversion-symmetric TTF unit in a neighboring belt molecule. The TTF units are parallel, but shifted somewhat sidewise. The distance between these planes is 3.36 Å, and there are two identical and somewhat short nonbonding S···S contacts of 3.624 Å between S2 and S3 $(1-x,-y,1-z)$ and between S3 and S2 $(1-x,-y,1-z)$.

Here we have described a new strategy for the preparation of belt-type bis-TTFs starting from a new protected TTF, and

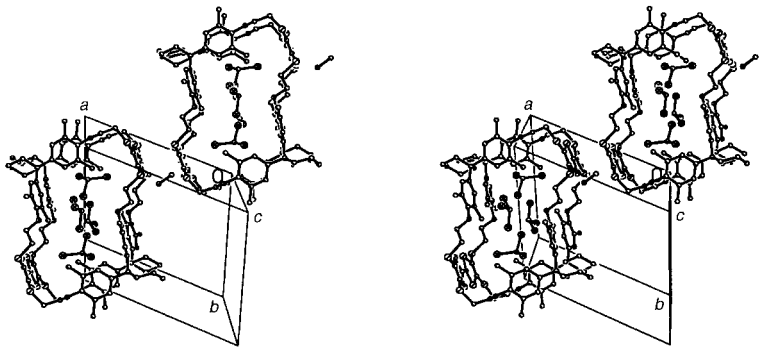

Figure 2. Stereodrawing of the packing diagram of **6c**.

demonstrated the synthetic utility of this method by synthesizing three TTF-belts. The TTF-belts **6a–c** are stable and isolable compounds that show some promise as host molecules, as indicated by the solid-state structure of **6c**, which crystallizes with two molecules of chloroform inside its spacious cavity. Preliminary complexation studies (^{1}H NMR) with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and **6a** indicate that there is an interaction; when **6a** (1 equiv) was added to a solution of TCNQ in $CDCl_3$, the signal from TCNQ disappeared and the signals from the belt experienced a broadening. However, these results do not provide any

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information regarding whether the guest (TCNQ) is complexed inside the cavity of the host molecule (**6a**) or if the interaction is on the outside of the TTF-belt; a solid-state structure determination of the complex is required.

Experimental Section

The synthesis of **6c** represents a general procedure for the deprotection–realkylation reactions.

6c: Compound **5c** (180 mg, 0.09 mmol) in dry DMF (23.0 mL) was degassed with N_2 for 15 min and then treated dropwise with a solution of $CsOH \cdot H_2O$ (46 mg, 0.27 mmol) in dry MeOH (2.0 mL) over a period of 30 min and left to stir for 30 min. This solution and a degassed solution of **2c** (48 mg, 0.09 mmol) in dry DMF (25.0 mL) were added simultaneously to 30 mL of dry degassed DMF under N_2 in a 250-mL three-necked flask under high-dilution conditions (3.0 mL h^{-1}) by means of a perfursor pump (Perfuser, Secura, Braun AG). After complete addition the reaction mixture was stirred for 4 h, the solvent was removed in vacuo, and the resulting orange solid was subjected to column chromatography (silica gel, CH_2Cl_2/cyclohexane 3/1, $R_f = 0.5$) to give **6c** as a pale orange crystalline powder upon removal of solvent. Recrystallization from $CHCl_3$/MeOH gave **6c** as orange crystals (0.060 g, 32%). M.p. > 250 °C (decomp.); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.83-6.80$ (2 × s, 12H; ArH), 4.40–3.70 (m, 12H, OCH_2CH_2S), 3.30–2.95 (m, 12H, OCH_2CH_2S), 2.17 (brs, 24H, CH_3), (brs, 16H, CH_2CCH_2), 1.43 (brs, 24H, $CH_2CH_2CH_2$); PD-MS: *m*/*z*: 1085 [M^{2+}], 2172 [M^+]; Elemental analysis calcd for $C_{116}H_{136}O_8S_{16} \cdot 3\,CHCl_3$ (2171.3): C 55.50, H 5.54; found: C 55.90, H 5.42; CV (in CH_2Cl_2, vs. Ag/AgCl): $E_{1/2} = 0.58$, 0.91 V.

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[16] The 2-cyanoethyl group is cleaved in preference to the 2-(4-nitrophenyl)ethyl group upon exposure to cesium hydroxide. Therefore a stepwise cleavage can be performed by slow addition of the base in four subsequent steps.
[17] Compound **1** was prepared by standard cross-coupling methodology[13] by heating a 1:1 mixture of 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-one and 4,5-bis[2-(4-nitrophenyl)ethylthio]-1,3-dithiole-2-thione in freshly distilled triethylphosphite. Experimental details of the synthesis of **1** and **2a–c** will be reported elsewhere.
[18] Compounds **3–6** were purified by chromatography on silica gel to give analytically pure products upon evaporation of solvent. All new compounds gave satisfactory spectroscopic data (^{1}H and ^{13}C NMR), spectrometric data (PD-MS), cyclic voltammetries, and elemental analyses.
[19] The intermediate compounds **3–5** as well as the final TTF-belts **6** can be manipulated in air without any precautions; this is in contrast to the case for a number of other bis-TTF sandwiches. This is probably a consequence of the rigidity of the belts, which prevents intramolecular interactions between the two redox-active units, which is known to lower the redox potential.
[20] The latter isomer is chiral, but no attempt to separate the two enantiomers was carried out.
[21] Deep orange crystals, suitable for X-ray crystallography, were prepared by allowing a hot solution of **6c** in $CHCl_3$/MeOH to cool slowly to room temperature in a Dewar flask. Crystal data for of **6c** · $4\,CHCl_3 \cdot CH_3OH$ ($C_{121}H_{144}Cl_{12}O_9S_{16}$): $M_r = 2680.72$, triclinic, space group $P\bar{1}$, $a = 16.002(3)$, $b = 16.203(3)$, $c = 16.415(3)$ Å, $\alpha = 114.68(3)$, $\beta = 117.82(3)$, $\gamma = 93.25(3)°$, $V = 3248.4(11)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.370$ g cm^{-3}, $F(000) = 1402$, graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K; crystal size: $0.30 \times 0.13 \times 0.10$ mm. $\mu = 0.567$ mm^{-1}, min./max. transmission: 0.85/0.95. The intensities of 26379 reflections were measured on a Siemens SMART CCD diffractometer covering 99.7% of a complete hemisphere with $\theta_{max} = 23.26°$; $R_{int} = 0.0664$. Structure solution and refinement and production of the crystallographic illustrations was carried out with the Siemens *SHELXTL* package (G. M. Sheldrick, *SHELXTL Users Manual*, Version 5.0, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, **1994**) and *SHELX-97* (G. M. Sheldrick, *SHELX-97*, Universität Göttingen, Germany, **1997**). The refinement of 706

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parameters with all 9299 unique reflections converged at $R_1 = 0.0824$ (for $F_o > 4\sigma(F_o)$). Hydrogen atoms were included in calculated positions; max./min. residual electron density $1.06/-0.89$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115498. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

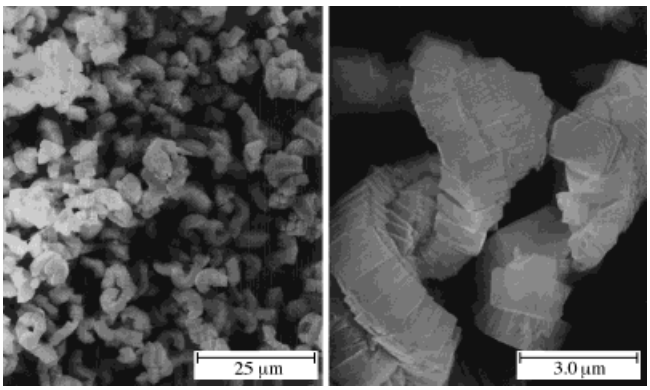

Figure 1. Two scanning electron micrographs of the novel silicate material obtained from run 1 (Table 1).

A Novel Layered Silicate with a Helical Morphology

Yoshikatsu Akiyama, Fujio Mizukami,* Yoshimichi Kiyozumi, Kazuyuki Maeda, Hiroyuki Izutsu, and Kengo Sakaguchi

Some layered silicate materials such as kanemite and magadiite (a mineral clay) are formed from silica under hydrothermal conditions.[1] Various silicate phases can be formed only by calcination.[2] When small amounts of aluminum hydroxide and tetramethylammonium hydroxide (TMA-OH) are added to a silica source and treated under hydrothermal conditions, high-silica zeolites such as Nu-1[3], Fu-1,[4] (Na, TMA)-E,[5] and sodalite[6] are formed. Furthermore, it was reported recently that the TMA ion is a template for the formation of the zeolite precursor RUB-15,[7, 8] in which hemihedral cavities constitute a layered structure; however, the precise role of the TMA ions is still obscure. We considered that comparing products obtained with and without TMA or an aluminum component in organic or aqueous solution under hydrothermal conditions might give insights into this subject, and also provide an opportunity to elucidate the difference between the transformation of amorphous silica into layered and microporous structures. In the course of our investigations, under aluminum-free conditions, we found a novel silicate phase, the scanning electron micrograph of which (Figure 1) showed a helical morphology consisting of stacked layers. This morphology differs strongly from those of traditional layered silicates such as kanemite and magadiite[1, 2] and from those of more recently reported layered silicates.[7, 8]

Table 1 lists the reaction conditions under which the helix layered silicate (HLS) was formed. As indicated in runs 1–3 and 7–9, besides silica, NaOH, TMA-OH, and 1,4-dioxane are essential for the formation of HLS, which is also favored by low H_2O:1,4-dioxane ratios. Under the conditions investigated here, TMA-OH did not transform silica into a layered silicate, whereas NaOH transformed silica into a magadiite phase. Consequently, it can be concluded that silica sol is transformed into the HLS by the cooperative action of both TMA-OH and NaOH. The elemental analysis of the HLS gave a TMA content of 13.2 wt%, consistent with the value obtained by thermogravimetric differential thermal analysis (TG-DTA), and the water content as determined by TG-DTA was 10.8 wt%. The silicon and sodium contents calculated from elemental analysis and energy dispersive analysis of X rays (EDAX) were 30.4 and 0.48 wt%, respectively. When a 0.1-g sample of the HLS was treated with 30 mL of 0.05 N HCl in aqueous solution, the EDAX peak of sodium disappeared completely, and the TMA content by elemental analysis decreased to 4.2 wt%. This indicates that both TMA and sodium ions in the HLS are easily replaced with protons.

Table 1. Products obtained under different reaction conditions.[a]

Run	Composition of the reaction mixture				Product[c]
	SiO_2 [10^{-2} mol]	TMA-OH [10^{-3} mol]	NaOH [10^{-3} mol]	H_2O:1,4-dioxane[b]	
1	3.60	4.80	3.00	2.20	HLS
2	3.60	4.80	3.00	3.77	HLS
3	3.60	4.80	3.00	4.46	HLS
4	3.60	4.80	3.00	6.61	Amo
5	3.60	4.80	3.00	9.71	Amo
6	3.60	4.80	3.00	34.3	Amo
7	3.60	4.80	3.00	∞	Amo
8	3.60	0	3.00	2.45	Mag
9	3.60	4.80	0	34.3	Amo

[a] The reaction was carried out at 150 °C for 10 d. [b] In all runs, the total amount of 1,4-dioxane and H_2O was 18.0 g. [c] HLS = helix layered silicate, Amo = amorphous silica, Mag = magadiite. These phases were evaluated by means of XRD patterns.

We then investigated whether the HLS is a single phase or a mixture of different layered silicates. Figure 2 shows the ^{29}Si MAS NMR and ^{13}C CP-MAS NMR spectra of the HLS. The ^{29}Si MAS NMR contains a strong signal at $\delta = -104.4$, which can be assigned to $-Si(OSi)_3$ (Q^3) units, and weak broad signals, probably due to unchanged amorphous silica. This Q^3 connectivity is characteristic of layered silicates. The ^{13}C CP-MAS NMR spectrum displays a strong signal for TMA at $\delta =$ 57.9. When TMA is trapped in a confined space, its ^{13}C NMR

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