A Flexible Cyclophane: Design, Synthesis, and Structure of a Multibridged Tris-tetrathiafulvalene (TTF) Macrocycle

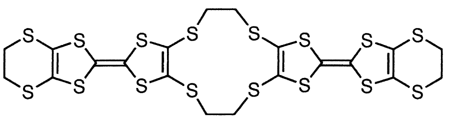
Kazuo Takimiya,[a] Niels Thorup,[b] and Jan Becher*[a]

Abstract: The tris-tetrathiafulvalene (TTF) macrocycles **3** with a large end-cavity were effectively synthesized from the readily available tetrakis(cyanoethylthio)TTF by means of a selective deprotection/realkylation sequence followed by an intramolecular coupling reaction. Crystal structure analyses revealed that the neutral molecules include two (**3a**) or one chloroform molecule (**3b**) as solvent of crystallization inside the cavity, whereas the I_3^- salt of **3b**, obtained by electrocrystallization, has a molecular structure which is different from that of the neutral molecule in that the cavity has completely collapsed.

Keywords: cyclophanes • electrochemistry • electrocrystallization • host–guest chemistry • macrocycles

Introduction

For more than two decades tetrathiafulvalene (TTF) and related derivatives have been studied with the aim of preparing organic conductors and superconductors.[1] Because of the current interest in advanced molecular materials, TTF-based molecules have also gained significance for other purposes:[2] TTF's characteristic redox behavior, that is a facile and reversible two-stage oxidation–reduction couple, makes it attractive as a building block in supramolecular chemistry. Thus the TTF building block has been incorporated into elaborate systems in various molecular devices, such as sensors, switches and shuttles.[3] In addition, owing to its good electron-donating ability, the TTF moiety also appears to be a prime candidate in the syntheses of macrocyclic hosts for electron-deficient compounds. This is documented by the versatile inclusion phenomena of bis-bis(ethylenedithiolo) tetrathiafulvalene (bis-BEDT-TTF) (**1**): in its neutral state,



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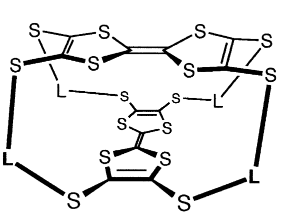
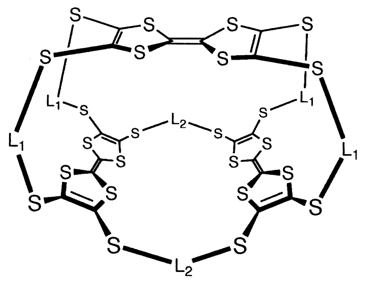
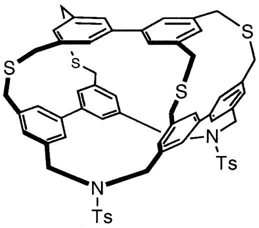


2a L = $(CH_2)_5$
2b L = $(CH_2CH_2O)_2CH_2CH_2$



3a $L_1 = (CH_2CH_2O)_2CH_2CH_2$
$L_2 = CH_2CH_2OCH_2CH_2$

3b $L_1 = (CH_2CH_2O)_2CH_2CH_2$
$L_2 = (CH_2)_3$



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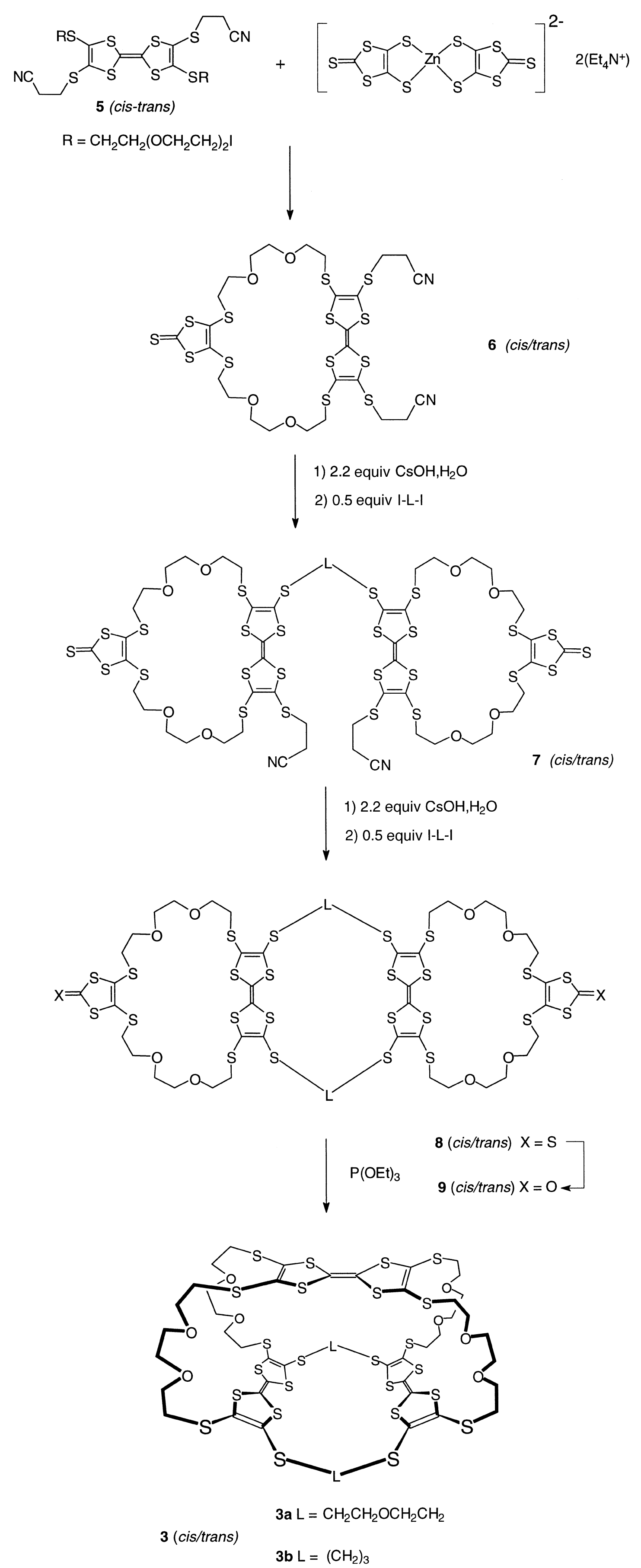
the donor adopts a U-shaped conformation that creates a cavity between the two TTF units which is occupied by a TTF unit of the next donor, whereas in its charge-transfer complex with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), **1** sandwiches the acceptor within the cavity.[4] The donor **1** also forms an inclusion complex with C_{60}.[5] Other examples of inclusion phenomena of TTF-based macrocycles have recently been published for crisscross TTF phanes (**2**) that possess linkers longer than C_5 chains.[6] The neutral molecules of **2a** and **2b** contain one chloroform molecule inside the cavity. In the case of **2a** the inclusion ability is maintained in the radical cation salts which contain one ethanol molecule within the cavity.[6a]

Conventional cyclophanes constitute an important class of synthetic host molecules;[7] thus, it is of interest to develop simple routes to TTF macrocycles that are related to the above-mentioned crisscross TTF phanes. To enlarge the cavity surrounded by TTF groups, we designed the multibridged tris-TTF macrocycles **3**, in which two of the three TTF groups lie in a parallel arrangement and the third is orthogonal to these. It appears attractive to construct such cyclophanes with effective TTF donors, not only for possible host–guest interactions, but also to obtain systems with the potential to undergo a reversible change of structure upon oxidation/reduction.

The molecular structure of a related cage molecule with biphenyl building blocks (**4**) was reported to have a large T-shaped cavity (dimensions of the T: height: 7.25 Å; width at the bottom of the cavity: 3.86 Å; width at the top of the cavity: 7.25 Å). Although **4** crystallizes with one chloroform molecule as solvent of crystallization, the solvent molecule lies outside the cavity.[8] Cory–Pauling–Koltun (CPK) modeling suggests that our target, tris-TTF macrocycles (**3**), have rather larger cavities than those of **2** and **4**.

Herein we describe multibridged tris-TTF macrocycles (**3**), their effective syntheses from readily available tetrakis(cyanoethylthio)TTF, and their electrochemical behavior together with the crystal structures of both the neutral and the oxidized states.



Scheme 1. Strategy for the synthesis of the tris-TTFs (**3**).

Results and Discussion

Synthesis: Retrosynthetically, the tris-TTF cyclophane **3** can be dissected into a reasonable intermediate (**6**) by disconnecting one central C=C bond in the upper TTF group and two linkers between two bottom TTF groups. This disconnection approach is suitable for the stepwise cyanoethyl deprotection/realkylation method[9] followed by a final intramolecular coupling of the resulting bis-TTF macrocycle with two molecules of the 1,3-dithiole-2-(thi)one intermediate (Scheme 1). The common intermediate

(**6**) for both **3a** and **3b** was readily prepared by the reaction of bis(tetraethylammonium) bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate, $(TEA)_2[Zn(dmit)_2]$, and **5** derived by the selective deprotection/realkylation of tetrakis(cyanoethylthio)TTF. Selective deprotection of one cyanoethyl group of **6** with $CsOH \cdot H_2O$ (1.1 equiv) followed by alkylation with 0.5 equivalents of 1,3-diiodopropane or bis(2-iodoethyl)ether gave **7** in moderate yields, which was subsequently deprotected/realkyated under high-dilution conditions to give the bis-TTF macrocycles with two 1,3-dithiole-2-thione moieties (**8**). After *trans*-chalcogenation of **8** into the corresponding ketones (**9**) by the standard procedure (mercury acetate), the intramolecular coupling reaction, mediated by triethylphosphite, gave the desired multibridged tris-TTF macrocycles **3** in relatively high yields of 61% and 53% for **3a** and **3b**, respectively. Although all the intermediates (**5–9**) and the final tris-TTF (**3**) were obtained as a mixture of *cis* and *trans* isomers on each TTF moiety, careful recrystallization of **3** gave reasonable amounts of pure all-*cis* isomers (see the Experimental Section).

Crystal structure: Slow evaporation of a solution of **3a,b** (*cis*/*trans*) in chloroform/light petroleum gave orange platelike crystals. Figure 1 shows the molecular structure of $\mathbf{3a} \cdot 3CHCl_3$. The molecule has an all-*cis* configuration, which is the least strained structure as predicted by a CPK model. The pair of TTF units in the parallel orientation has a double-decker structure which sandwiches one chloroform molecule. The third TTF unit is separated from this pair by the long and flexible bis(ethoxy)ethyl linkers. A large cavity is thus created by the TTF pair, the third TTF unit, and the four linkers, in which a further chloroform molecule is encapsulated.

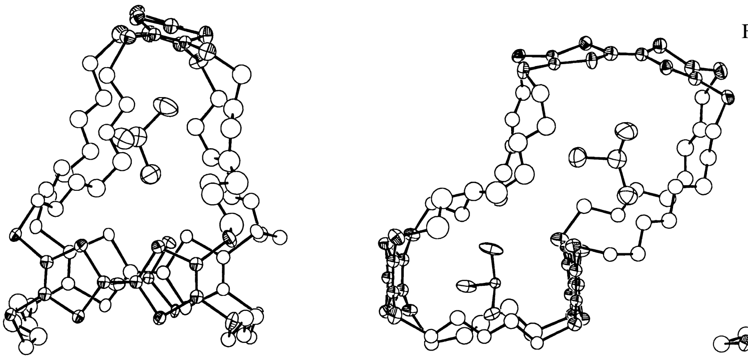


Figure 1. Molecular structure of **3a** (all-*cis*): top view (left) and side view (right).

In the crystal packing, the parallel-oriented TTF pairs stack to give a columnar structure along the *b* axis to give the arrangement -D-D-S-D-D-S- (where D = donor = TTF and S = solvent, Figure 2). This stacking is separated by the third TTF unit and the bis(ethoxy)ethyl linkers. Along the direction of the *c* axis, wedge-shaped **3a** arranges alternately in a complementary packing to minimize the amount of space between the **3a** molecules in this direction. However, there exists a cleft in-between, and this interstitial position is occupied by the third chloroform molecule.

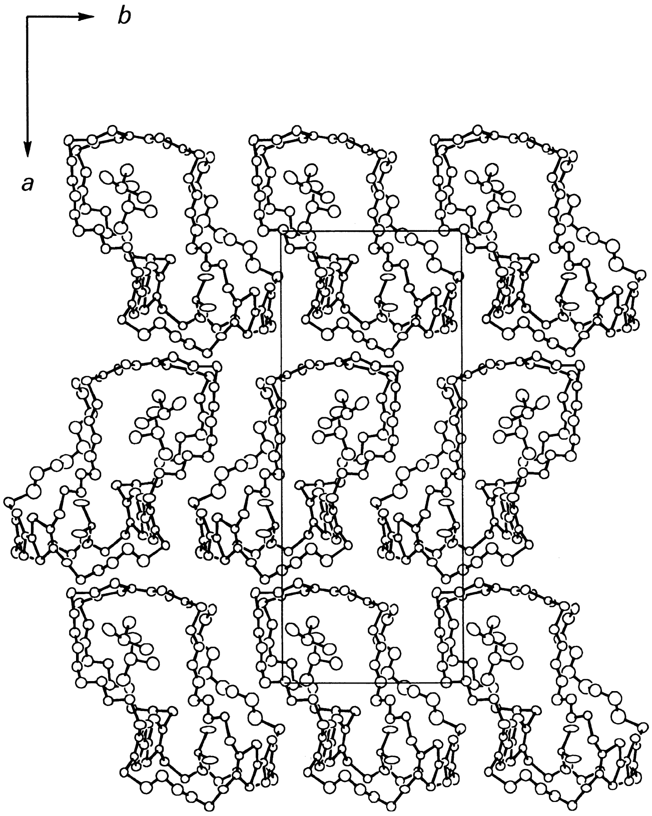


Figure 2. Crystal structure of **3a** along the *c* axis.

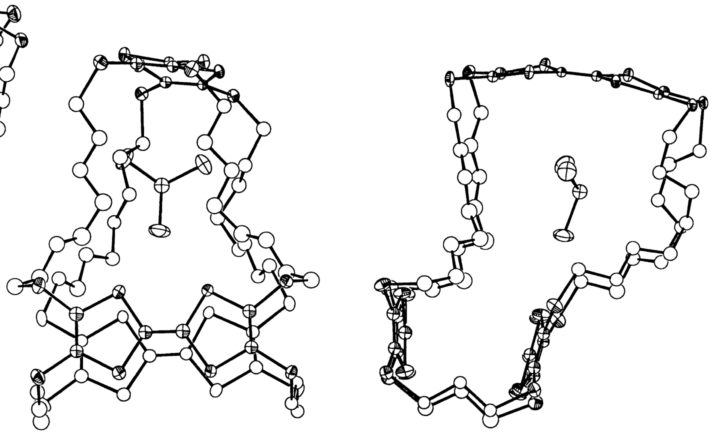


Figure 3. Molecular structure of **3b** (all-*cis*): top view (left) and side view (right). Only one of two crystallographically independent molecules is presented.

The molecular structure of $\mathbf{3b} \cdot CHCl_3$ is shown in Figure 3. Although the crystal contains two crystallographically independent molecules in the asymmetric unit, both have basically the same molecular shape, which is an all-*cis* form and very similar to that of **3a**. In the molecular structure of **3b**, however, the interplanar distance between the parallel-oriented TTF pairs is too short to bind a chloroform molecule, and thus only one chloroform molecule is included in the cavity formed by the TTF pair, the third TTF, and the ether linkers.

The characteristic structural feature of these tris-TTF macrocycles is the stacking arrangement of the parallel-oriented TTFs and the third TTF which is separated from the

TTF stack, to produce a cavity surrounded by three TTF groups. This cavity is large enough to include two (**3a**) or one (**3b**) chloroform molecule(s). In both cases the volume of the cavity is smaller than expected, probably owing to the flexibility of the linkers, which allows two TTFs in parallel orientation to stack intramolecularly.

Electrochemistry: The electrochemical behavior of the TTF macrocycles was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (Figure 4). The redox potentials of **3a** and **3b** are summarized in Table 1 together with those of bis-TTF, **8a**, and **8b.** Both **8a** and **8b** showed a splitting of the peaks assigned to the first oxidation step of each TTF moiety, which indicates the existence of an intramolecular interaction between two TTFs. This intramolecular interaction appears to be affected by the length of the linkers; **8b** with the shorter C_3 linker demonstrates a larger splitting of the first redox wave of both TTFs. These observations are consistent with a similar electrochemical behavior to the related double-bridged TTF phanes.[10] In contrast, the redox behavior of **3** is not so resolved as that of **8**. In both CV and DPV **3a** shows only two redox peaks, and the first one ($E = +0.52$ V) is quite broad. This might be understood by the overlap of close peaks for the first redox processes of all the three TTFs, suggesting weak interactions between them. On the other hand, **3b** shows three well-resolved peaks at $E = +0.49$, 0,57, and $+0.87$ V which qualitatively correspond to a one-, two-, and three-electron process, respectively. It is reasonable to consider the following explanation: i) the first peak which results from a one-electron process may be assigned to the oxidation of one of the parallel-oriented TTFs, ii) the resulting monocation radical is stabilized by intramolecular interaction between the two parallel-oriented TTFs, and iii) the first oxidation processes of the remaining TTFs thus overlap somewhat with the second peak. The different electrochemical behavior observed for **3a** and **3b** arises from the different linkers and corresponds qualitatively well to the interplanar distance between the two parallel-oriented TTFs. Notably, a small modification of the molecular structure, such as a change in the two bottom linkers (L_2), effectively alters both the molecular structure and the electrochemical behavior.

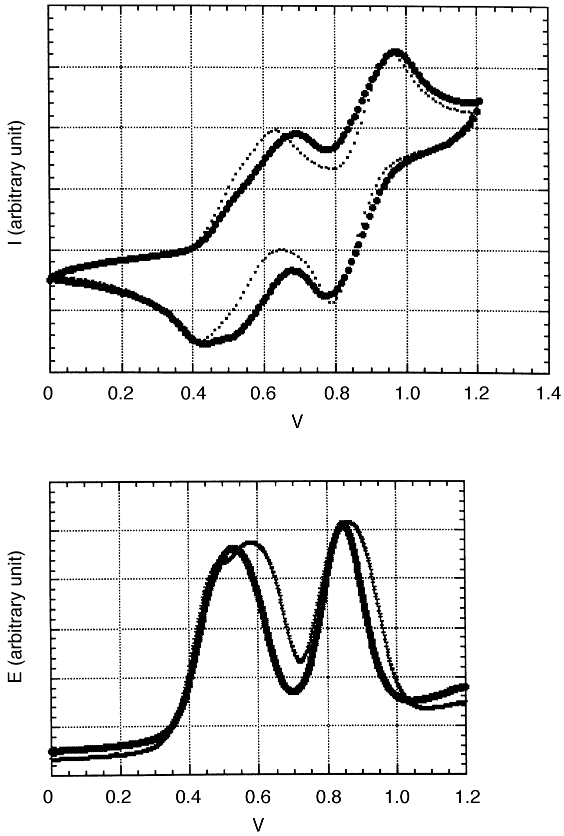


Figure 4. Top: Cyclic voltammogram (CV) for compound **3a** (bold) and compound **3b** (thin). Bottom: Differential pulse voltammogram (DPV) for compound **3a** (thin) and **3b** (bold).

Table 1. Oxidation potentials E [V] and number of electrons (ne) as determined by differential pulse voltammetry.[a]

Compound	E^1 [V]	E^2 [V]
3a	+0.52 (3e)	+0.85 (3e)
3b	+0.49 (1e), +0.57 (2e)	+0.87 (3e)
8a	+0.49 (1e), +0.55 (1e)	+0.87 (2e)
8b	+0.50 (1e), +0.62 (1e)	+0.85 (2e)

[a] Differential pulse voltammetry was carried out with Pt working and counter electrodes and an Ag/AgCl reference electrode in 3×10^{-4} mol dm^{-3} dichloromethane solution containing 10^{-1} mol dm^{-3} tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

Electrochemical crystallization: The electrochemistry results proved that the present tris-TTFs (**3a,b**) retain the facile oxidation ability observed for simple TTF derivatives. In order to compare the molecular structures of these TTF macrocycles upon oxidation with those of the neutral state, standard electrocrystallizations were examined in the presence of various tetrabutylammonium (TBA) salts as the electrolyte: these included linear (I_3^-, I_2Br^-), tetrahedral (ClO_4^-), and octahedral (PF_6^-) anions. However, only the electrocrystallization of **3b** with TBA · I_3 gave crystalline salts as black lustrous plates.[11] The room-temperature conductivity for two single crystals of the **3b** · I_3 salt was measured by the two-probe method, and gave a conductivity of 2.8×10^{-6} S cm^{-1} and 3.1×10^{-6} S cm^{-1}. Notably, even though the identical conditions for the successful electrocrystallization of **3b** · I_3 were applied to the electrocrystallization of **3a** or **3b** with other counteranions (i.e. the same concentration and applied current in the same solvent), no crystalline radical salt of good quality was obtained. This implies that the crystal packing is severely influenced by the geometry of the TTF macrocycle as well as the size and shape of the counteranions.

An X-ray crystallographic analysis revealed the crystal structure of **3b** · I_3 · (1,2-dichloroethane) (Figure 5): the oxidized **3b** has an all-*cis* structure, as in the neutral state. The molecular shape, however, is completely different from that of the neutral molecule:[12] the neutral end-cavity that encapsulates one chloroform molecule has completely collapsed, while the molecule itself folds to effectively minimize the volume of the cyclophane cavity (Figure 6).

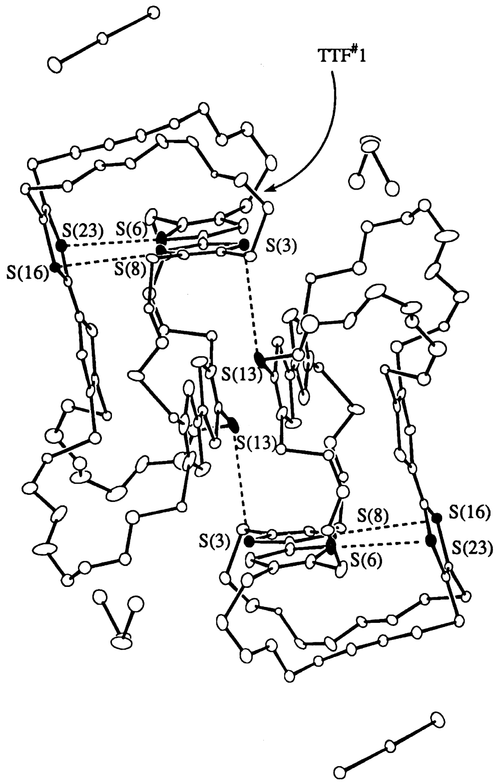


Figure 5. Dimeric pair of **3b** seen in the X-ray structure of **3b**$\cdot I_3 \cdot$(1,2-dichloroethane), showing one of the two possible conformations of the linkers. For the sake of clarity the ellipsoids are represented with 30% possibility. Intramolecular contact distances [Å]: S(6)–S(23) 3.735, S(8)–S(16) 3.520. Intermolecular contact distances S(3)–S(13) 3.379 Å.

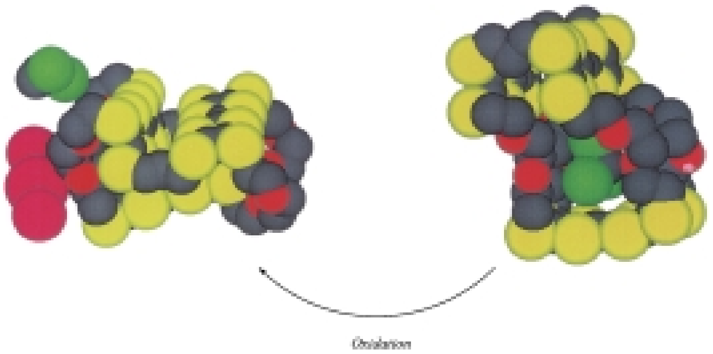


Figure 6. A CPK model description of the change in the shape of the cavity in cyclophane **3b** upon oxidation.

The length of the central C=C bond in a TTF system is very sensitive to the oxidation state of the TTF.[13] Thus, in order to evaluate the oxidation state of each TTF group in the **3b**$\cdot I_3$ salt, the length of their central C=C bonds are compared with those of neutral **3b** (1.325(12)–1.366(14) Å). The total charge transfer is assumed to be close to unity for stoichiometry reasons and judging from the bond order, it is assumed that TTF#1, which has the longest central bond (1.395(9) Å), is cationic and carries more charge than the two remaining, neutral TTFs with central bond lengths of 1.347(10) and 1.351(11) Å. There is a face-to-edge intramolecular interaction between the cationic TTF and one of the neutral TTF moieties through short S–S contacts (3.735 and 3.520 Å). Thus, it is clear that the cohesive force between the cationic and neutral TTFs plays an important role in the stabilization of the collapsed molecular shape and consequently the solvent molecule that lies in the neutral cavity in **3b** is expelled.

The packing diagram normal to the *ab* plane is shown in Figure 7. The two L-shaped **3b** molecules have a complementary arrangement through short intermolecular S–S contacts (3.379 Å) between the cationic and the neutral TTF moieties. These dimers are repeated along the direction of the *a* axis to create infinite donor arrays; the channels created between these arrays are occupied by solvent molecules and I_3 anions.

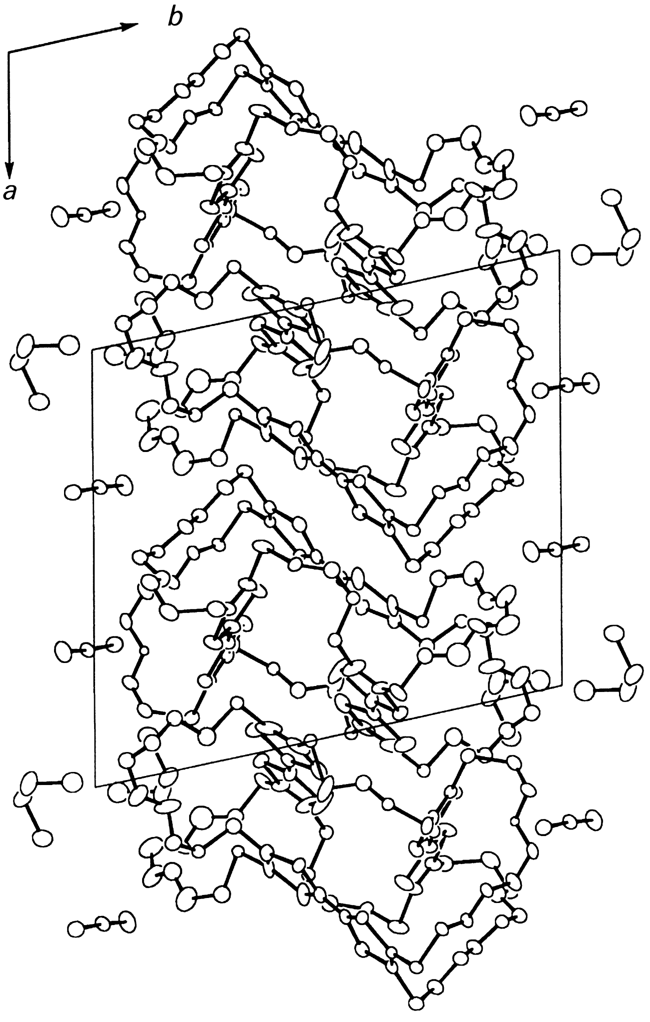


Figure 7. Crystal packing in **3b**$\cdot I_3 \cdot$(1,2-dichloroethane) viewed down [001].

Conclusions

Combination of the deprotection/realkylation sequence of the protected TTF tetrathiolate followed by an intramolecular coupling reaction is effective for the synthesis of unprecedented multibridged tris-TTF macrocycles. Single-crystal X-ray analyses of the neutral tris-TTFs have indicated that they have large end-cavities which are able to encapsulate chloroform molecules. The volume of the end-cavity is influenced by the length of the bottom linkers: with short tri(methylene) linkers the TTF macrocycle can include only one chloroform, whereas with bis(ethylene)ether linkers the macrocycle cavity is large enough to include two chloroform molecules.

In contrast to the inclusion phenomena observed in the neutral molecules **3a** and **3b**, the structural analysis of the oxidized form, **3b**$\cdot$I$_3$$\cdot$(1,2-dichloroethane), revealed that the end-cavity has completely collapsed, probably driven by the cohesive force between the cationic and the neutral TTF moieties. Although we initially expected that $\mathbf{3}^{+\bullet}$ might behave as a host for anionic species upon oxidation, this was found not to be the case. The observed expulsion of solvent molecules on oxidation can be regarded as a kind of "stimulus-response"-type phenomenon; in other words the inclusion ability of **3b** can be controlled by the oxidation state of the TTF building blocks. This is attributed to the long and flexible linkers between the TTF tetrathiole moieties, which make it possible to take arbitrary molecular shapes depending on the circumstances, namely the crystal packing and oxidation state of TTF moieties. The present synthetic pathway is basically applicable for all types of linkers. Furthermore, on account of the stepwise procedure, it will be easy to use two different linkers (L$_1$ and L$_2$) to enable a fine tuning of the molecular structure and electrochemical properties.

Experimental Section

General: All reactions were carried out under a nitrogen atmosphere. Solvents and reagents were purified according to standard procedures when necessary. Silica gel "Kieselgel 60, Merck" was used as the stationary phase for column chromatography. Melting points were determined in open capillary tubes on a Büchi apparatus and were uncorrected. Microanalyses were performed at the Microanalytical Lab., University of Copenhagen. ^{1}H NMR were recorded on a Varian Gemini 2000 (300 MHz) with tetramethylsilane as the internal reference. IR spectra were recorded on a Perkin – Elmer 580 spectrometer either neat or in a KBr disk. PDMS (plasma desorption mass spectra) were recorded on a Bio-Ion 20 K on the basis of 500000 fission events. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out with an Autolab PGSTAT10 potentiostat (ECO CHEMIE BV) in a single-compartment cell with a platinum disk working electrode, a platinum wire counter-electrode, and an Ag/AgCl electrode as the reference electrode. High-dilution addition was performed by means of a perfuser pump (Perfuser, Secura, Braun AG).

2,7(6)-Bis(2′-cyanoethylthio)-3,6(7)bis{2-[2-(2-iodoethoxy)ethoxy]ethylthio}tetrathiafulvalene (*cis/trans*) (5): To a solution of 2,3,6,7-tetrakis(2′-cyanoethylthio)tetrathiafulvalene (3.0 g, 5.5 mmol) in DMF (140 mL) was added CsOH$\cdot$H$_2$O (1.94 g, 11.6 mmol) in methanol (20 mL) at room temperature over a period of 45 min with stirring. The mixture was then stirred for 1 h and 1,2-bis(2-iodoethoxy)ethane (40.74 g, 110 mmol) was added. The mixture was stirred overnight and then concentrated under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ (200 mL), washed with water (2 × 50 mL), and dried over MgSO$_4$. The concentrated organic phase was subjected to column chromatography (silica gel): excess 1,2-bis(2-iodoethoxy)ethane was eluted with CH$_2$Cl$_2$, and the desired product obtained as an orange solid (4.73 g, 93 %) with CH$_2$Cl$_2$/AcOEt (10:1). Recrystallization from acetone/methanol gave orange crystals. M.p. 93.5 – 94.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 2.74$ (t, ^{3}J(H,H) = 6.9 Hz, 4H; CH$_2$), 3.06 (t, ^{3}J(H,H) = 7.1 Hz, 4H; CH$_2$), 3.08 (t, ^{3}J(H,H) = 6.7 Hz, 4H; CH$_2$), 3.29 (t, ^{3}J(H,H) = 6.9 Hz, 4H; CH$_2$), 3.60 – 3.80 (m, 16H; CH$_2$); IR (KBr): $\tilde{\nu} = 2919$ (C–H) 2874 (C–H), 2249 (CN), 1132 – 1108 cm^{-1} (C-O-C); MS (PD): *m*/*z*: 922 [*M*]$^+$; anal. calcd for C$_{24}$H$_{32}$N$_2$O$_4$S$_8$I$_2$ (922.8): C 31.24, H 3.50, N 3.04; found: C 31.34, H 3.30, N 2.95.

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)bisthio]tetrathiafulvalene (*cis/trans*) (6): The solution of **5** (2.15 g, 2.33 mmol) and zincate (943 mg, 1.31 mmol) in acetonitrile (350 mL) was refluxed overnight. After the mixture had cooled to room temperature, the solvent was evaporated to give a semisolid residue, which was dissolved in CH$_2$Cl$_2$ (250 mL). An insoluble inorganic solid was filtered off by passing through a Celite pad. The filtrate was washed with water (3 × 70 mL), dried over MgSO$_4$, and then concentrated. The residue was taken up to the top of a silica gel column, which was eluted with CH$_2$Cl$_2$/AcOEt (10:1) to give **6** (1.20 g, 59 %) as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 2.76$ (t, $^{3}J = 6.9$ Hz, 4H; CH$_2$), 3.04 – 3.11 (m, 12H; CH$_2$), 3.64 – 3.75 (m, 16H; CH$_2$); IR (KBr): $\tilde{\nu} = 2921$ (C–H), 2862 (C–H), 2250 (CN), 1132 – 1104 (C-O-C), 1060 cm^{-1} (C=S); MS (PD): *m*/*z*: 865 [*M*]$^+$; anal. calcd for C$_{27}$H$_{32}$N$_2$O$_4$S$_{13}$ (865.3): C 37.47, H 3.73, N 3.24; found: C 37.57, H 3.56, N 3.29.

2,2′-Bis[7(6)-{(2′-cyanoethylthio)-3,6(7)-[2-thioxo-1,3-dithiole-4,5-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalen-2-ylethio}ethyl ether (*cis/trans*) (7a): To a solution of **6** (1.92 g, 2.2 mmol) in DMF (80 mL) at room temperature was added CsOH$\cdot$H$_2$O (372 mg, 2.2 mmol) in methanol (10 mL) over a period of 45 min with stirring. The mixture was stirred for a further 1 h, 1,2-bis(2-iodoethyl)ether (361 mg, 1.1 mmol) in DMF (10 mL) was added, and the mixture was stirred overnight. The reaction mixture was concentrated in vacuo, and the residue was taken up into CH$_2$Cl$_2$ (200 mL), washed with water (2 × 70 mL), dried over MgSO$_4$. Column chromatography of the concentrated organic phase with CH$_2$Cl$_2$/AcOEt (8:1) as eluent, gave **3a** (717 mg, 38 %) as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 2.74$ and 2.76 (t, $^{3}J = 7.4$ Hz, 4H; CH$_2$), 2.98 – 3.12 (m, 24H; CH$_2$), 3.60 – 3.80 (m, 36H; CH$_2$); IR (neat): $\tilde{\nu} = 2921$ (C–H), 2862 (C–H), 2250 (CN), 1132 – 1094 (C-O-C), 1067 cm^{-1} (C=S); MS (PD): *m*/*z*: 1695 [*M*]$^+$; anal. calcd for C$_{52}$H$_{64}$O$_9$N$_2$S$_{26}$ (1694.7): C 36.85, H 3.81, N 1.65; found: C 37.11, H 3.67, N 1.50.

1,3-Bis[7(6)-{(2′-cyanoethylthio)-3,6(7)-[2-thioxo-1,3-dithiole-4,5-diylbisthiobis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]tetrathiafulvalen-2-ylethio}propane (*cis/trans*) (7b): The same procedure as that used for **7a** gave **7b** as an orange oil. Yield: 39 %; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 1.99$ (m, 2H; CH$_2$), 2.73 and 2.77 (t, $^{3}J = 7.4$ Hz, 4H; CH$_2$), 2.95 – 3.15 (m, 24H; CH$_2$) 3.59 – 3.80 (m, 32H; CH$_2$); IR (neat): $\tilde{\nu} = 2919$ (C–H), 2861 (C–H), 2250 (CN), 1107 (C-O-C), 1064 cm^{-1} (C=S); MS (PD): *m*/*z*: 1665 [*M*]$^+$; anal. calcd for C$_{51}$H$_{62}$O$_8$N$_2$S$_{26}$ (1664.6): C 36.80, H 3.75, N 1.68; found: C 36.71, H 3.63, N 1.66.

Bis-TTF macrocycle with bis(1,3-dithiole-2-thione) (*cis/trans*) (8a): To a stirred solution of **7a** (700 mg, 0.41 mmol) in DMF (40 mL) was added dropwise a solution of CsOH$\cdot$H$_2$O (144 mg, 0.86 mmol) in methanol (10 mL) at room temperature over a period of 20 min. Stirring was continued for a further 45 min. This solution and a solution of 1,2-bis(2-iodoethyl)ether (134 mg, 0.41 mmol) in DMF (50 mL) at room temperature were added simultaneously into DMF (50 mL) over a period of 20 h under high-dilution conditions by means of a perfusor pump. The mixture was stirred for an additional 3 h, and then concentrated in vacuo. The resulting residue was taken up into dichloromethane (200 mL), washed with water (2 × 50 mL), and dried over MgSO$_4$. Evaporation of the solvent and subsequent column chromatography (silica gel, CH$_2$Cl$_2$/AcOEt 5:1) gave **8a** (414 mg, 61 %) as an amorphous orange solid. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 2.98$ – 3.12 (m, 24H; CH$_2$) 3.60 – 3.80 (m, 40H; CH$_2$); IR (neat): $\tilde{\nu} = 2921$ (C–H), 2861 (C–H), 1104 (C-O-C), 1066 cm^{-1} (C=S); MS (PD): *m*/*z*: 1659 [*M*]$^+$; anal. calcd for C$_{50}$H$_{64}$O$_{10}$S$_{26}$ (1658.6): C 36.21, H 3.89; found: C 36.42, H 3.69.

Bis-TTF macrocycle with bis(1,3-dithiole-2-thione) (*cis/trans*) (8b): Yield: 52 %; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 2.00$ (m, 4H; CH$_2$), 2.70 – 3.15 (m, 24H; CH$_2$) 3.59 – 3.81 (m, 32H; CH$_2$); IR (KBr): $\tilde{\nu} = 2921$, 2862 (CH), 1137 – 1099 (C-O-C), 1059 cm^{-1} (C=S); MS (PD): *m*/*z*: 1598.0 [*M*]$^+$; anal. calcd for C$_{48}$H$_{60}$O$_8$S$_{26}$: C 36.06, H 3.78; found: C 36.38, H 3.61.

Bis-TTF macrocycle with bis(1,3-dithiol-2-one) (*cis/trans*) (9a): To a solution of **8a** (360 mg, 0.22 mmol) in CHCl$_3$ (30 mL) was added Hg(OAc)$_2$ (320 mg, 1.0 mmol) and then acetic acid (2 mL). The mixture was stirred for 2 h, and the white solid which had precipitated was filtered off onto a Celite pad and washed with additional CHCl$_3$ (2 × 25 mL). The combined filtrate was washed with saturated aqueous NaHCO$_3$ solution (2 × 30 mL) and water (30 mL), and then dried over $MgSO_4$. Chromatography on a short column (silica gel, CH_2Cl_2/AcOEt 5:1) gave **9a** as an amorphous orange solid. Yield: 360 mg (100 %); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.95-3.15$ (m, 24H; CH_2) 3.60–3.80 (m, 40H; CH_2); IR (neat): $\tilde{\nu} = 2921$ (C–H), 2861 (C–H), 1667 (C=O), 1104 cm^{-1} (C-O-C); MS (PD): m/z: 1626 [M^+]; anal. calcd for $C_{50}H_{64}O_{12}S_{24}$ (1626.5): C 36.92, H 3.97; found: C 37.00, H 3.82.

Bis-TTF macrocycle with bis(1,3-dithiol-2-one) (*cis/trans*) (9b): Yield: 95 %. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.00$ (4H, m, CH_2), 2.70–3.15 (m, 24H; CH_2), 3.59–3.81 (m, 32H; CH_2); IR (KBr): $\tilde{\nu} = 2861$ (CH), 1664 (C=0), 1106 cm^{-1} (C-O-C); MS (PD): m/z: 1566 [M]$^+$; anal. calcd for $C_{48}H_{60}O_{10}S_{24}$ (1566.4): C 36.80, H 3.86; found: C 36.71, H 3.78.

Tris-TTF macrocycle (*cis/trans*) (3a): A mixture of **9a** (305 mg) and triethylphosphite (7 mL) in toluene (10 mL) was refluxed for 2 h. The solvent and the excess phosphite was evaporated off under reduced pressure, and the resulting residue separated by chromatography (silica gel, CH_2Cl_2/AcOEt 10:1) to afford **3a** as an amorphous orange solid. Yield: 185 mg (61 %); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.80-3.18$ (m, 24H; CH_2) 3.58–3.80 (m, 40H; CH_2); IR (KBr): $\tilde{\nu} = 2918$ (C–H), 2859 (C–H), 1104 cm^{-1} (C-O-C); MS (PD): m/z: 1594 [M]$^+$; anal. calcd for $C_{50}H_{64}O_{10}S_{24}$ (1594.5): C 37.66, H 4.05; found: C 37.75, H, 4.07. Recrystallization of the isomeric mixture (123 mg) from chloroform/petroleum ether (≈1:1) gave **3a** (40 mg) as orange prisms (all-*cis* isomer confirmed by an X-ray analysis); m.p. 89–91 °C; anal. calcd for $C_{53}H_{67}O_{10}S_{24}Cl_9$ (**3a** · 3 $CHCl_3$; 1952.6, the ratio was also confirmed by an X-ray crystal analysis): C 32.60, H 3.46; found: C 33.33, H 3.39.

Tris-TTF macrocycle (*cis/trans*) (3b): Amorphous orange solid; yield: 53 %; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.98$ (m, 4H; CH_2), 2.70–3.15 (m, 24H; CH_2), 3.59–3.81 (m, 32H; CH_2); IR (KBr): $\tilde{\nu} = 2916$, 2857 (CH), 1109 cm^{-1} (C-O-C); MS (PD): m/z: 1534 [M]$^+$; anal. calcd for $C_{48}H_{60}O_8S_{24}$ (1534.4): C 37.57, H 3.94; found: C 37.77, H 3.86. Orange plates (23 mg, all-*cis* isomer confirmed by an X-ray diffraction analysis) were obtained by recrystallization of the mixture (58 mg) from chloroform/petroleum ether (≈1:1); m.p. 118–119 °C; ^1H NMR (300 MHz, CDCl3, 25 °C, TMS): $\delta = 1.98$ (q, $^3J = 6.9$ Hz, 4H, CH_2), 2.83–3.17 (m, 24H; CH_2), 3.60–3.78 (m, 32H; CH_2); anal. calcd for $C_{49}H_{61}O_8S_{26}Cl_3$ (**3b** · $CHCl_3$; 1716.9): C 35.58, H, 3.71, found: C 36.02, H 3.55.

Electrocrystallization of 3b: In an H-shaped cell with sintered glass dividing the two compartments, **3b** (5 mg) and nBu$_4$NI$_3$ (50 mg) were placed into the anodic compartment and the supporting electrolyte (50 mg) was placed into the cathodic compartment. Dry dichloroethane (15 mL) and dry ethanol (1.5 mL) were then poured into the cell, and the resulting solution was degassed with a stream of nitrogen for 10 min. The platinum electrodes were introduced, and a constant current of 3–5 µA was applied. Within several days black platelike crystals grew on the surface of the anodic electrode. They were collected by filtration and washed with dichloromethane.

Crystal structure analyses: Suitable single crystals were mounted in a thin protecting layer of oil on glass fibers and transferred to the cold stream of nitrogen (Oxford Cryostream) on the diffractometer. Data was collected on a Siemens SMART CCD diffractometer at 120 K. An almost complete sphere of reciprocal space was covered by a combination of several sets of exposure frames; each set with a different φ angle for the crystal and each frame covering a scan of 0.3° in ω. Data collection, integration of frame data, and conversion to intensities corrected for Lorenz, polarization, and absorption effects were performed with the programs SMART,[14] SAINT,[14] and SADABS.[15] Structure solution, refinement of the structures, structure analysis, and production of crystallographic illustrations was carried out with the programs SHELXS97,[16] SHELXL97,[17] PLATON,[18] and SHELXTL.[19] In **3a** and **3b** · I_3 H atoms were included in calculated positions. The refinements were complicated by conformational disorder of linker atoms and of the solvent molecules. This disorder was modeled by placing some atoms in split positions (A and B) with isotropic displacement parameters. The structure of **3b** was refined with mostly isotropic displacement parameters on account of the size of the structure with two independent macromolecules. The large residual electron density in that structure determination is probably caused by additional solvent, which, however, could not be identified. A summary of the crystal data, X-ray data collection parameters, and structural refinement results is given in Table 2. The final atomic coordinates and other crystallographic data have been deposited with CCDC.[20]

Table 2. Crystal data and structure refinement parameters.

	3a	**3b**	**3b** · I_3
chemical formula	$C_{50}H_{64}O_{10}S_{24} \cdot 3\,CHCl_3$	$C_{48}H_{60}O_8S_{24} \cdot CHCl_3$	$C_{48}H_{60}O_8S_{24} \cdot I_3 \cdot C_2H_4Cl_2$
T [K]	120(2)	120(2)	120(2)
crystal system	orthorhombic	orthorhombic	triclinic
space group	$Pna2_1$	$Pca2_1$	$P\bar{1}$
a [Å]	30.3759(7)	39.336(8)	17.3594(10)
b [Å]	12.2830(4)	12.520(3)	19.6212(10)
c [Å]	21.5012(5)	30.977(6)	12.5898(10)
α [°]	90	90	110.878(10)
β [°]	90	90	105.512(10)
γ [°]	90	90	95.114(10)
V [Å^3]	8022.3(4)		15256(5)
	3778.8(4)		
Z	4	8	2
ρ_{calcd} [g cm^{-3}]	1.617	1.440	1.770
Mo$_{K\alpha}$ radiation [Å]	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.990	0.821	2.021
crystal size [mm]	0.28 × 0.18 × 0.06	0.40 × 0.15 × 0.10	0.35 × 0.23 × 0.03
transmission range	0.769–0.943	0.735–0.922	0.538–0.942
θ range for data collection [°]	1.34–23.25	1.04–26.42	1.13–26.37
no. of measured reflections	62880	156941	39656
no. of unique reflections	11527	31172	15298
completeness of unique refl.	1.000	0.998	0.990
R_{int}	0.0997	0.0760	0.0413
data/restraints/parameters	11527/60/856	31172/19/1513	15298/86/770
no. of refl. with $I > 2\sigma(I)$	9065	25234	10935
R (F, $I > 2\sigma(I)$)	0.0772	0.0841	0.0571
wR (F^2, all)	0.2125	0.2521	0.1430
goodness-of-fit (S)	1.020	1.117	1.023
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	1.28, −0.89	4.73, −1.05	2.26, −1.64

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