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Tetrathiafulvalene Cyclophanes and Cage Molecules

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1. Introduction

For more than three decades tetrathiafulvalene[1] (TTF, **1**) and its derivatives have been intensively studied on account of their unique π-electron-donor properties. They were originally prepared for the development of electrically conducting materials and have, as such, been synonymous with the development of molecular organic metals, and since the discovery of the first metallic charge-transfer (CT) TTF complex,[2] the search for new TTF donor molecules suitable for the formation of molecular organic metals has occupied and continues to occupy a significant part of the scientific community. However, during the past few years the utility of TTF derivatives as building blocks in macrocyclic and supramolecular chemistry[3] has revealed that the TTF unit is useful[1] beyond the field of materials chemistry. In the past decades effective methods have been developed for the preparation of elaborate molecular architectures, and in recent years, TTF has been incorporated into a number of molecular and supramolecular systems, such as macrocycles, cyclophanes, cage molecules, catenanes, rotaxanes, dendrimers, polymers, etc.[1] Consequently, numerous reports describing these kinds of redox-active systems have appeared, and several excellent accounts and reviews have been published.[1] However, one of the interesting aspects of TTF chemistry, namely, that of CT interactions occurring in TTF cyclophanes and cage molecules, has not been reviewed.

This review focuses on TTF cyclophanes and cage molecules. However, it is not a detailed review listing all TTF cyclophanes and cage molecules since Fanghänel and Schukat[1s] very recently (2003) published a comprehensive review on TTF chemistry listing almost all new types of TTF derivatives and their redox properties. Instead, this review will focus on different approaches used to synthesize TTF cyclophanes and cage molecules together with a description of (1) intramolecular interactions observed between different units in suitable designed TTF cyclophanes or cage molecules and (2) intermolecular interactions taking place between acceptor/solvent molecules and TTF cyclophanes or cage molecules.

2. Fundamental Properties of TTF

TTF and its derivatives have been used extensively as electron-donating units in CT complexes.[1] It is well known that TTF can be oxidized reversibly[1] to the radical cation **2** ($TTF^{\bullet+}$) and dication **3** (TTF^{2+}) and that the TTF^{2+} species can act as electron acceptors.[1,4] Although the neutral TTF unit is a planar 14π-electron system, it is nonaromatic according to the Hückel definition because the 14π-electrons lack cyclic conjugation.[1i] Its oxidation to the radical cation **2** and dication **3** occurs (Figure 1) sequentially and reversibly at low potentials. In contrast to the neutral TTF unit **1**, both $TTF^{\bullet+}$ (**2**) and TTF^{2+} (**3**) are aromatic in the Hückel sense as a result of the 6π-electron heteroaromaticity of the 1,3-dithiolium cation. The key properties of TTF that make it an interesting building block in materials, macrocyclic, and supramolecular chemistry are as follows.

(1) TTF is a strong π-electron donor.

(2) Oxidation of the TTF^0 ring system to the radical cation $TTF^{\bullet+}$ and dication TTF^{2+} occurs sequentially and reversibly (see Figure 1).

(3) The oxidation potentials can be finely tuned by attachment of electron-donating or electron-withdrawing substituents.

(4) The TTF radical cation **2** and dication **3** are thermodynamically stable species.

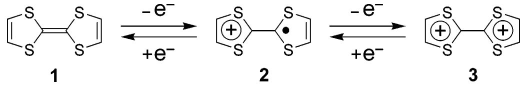

Figure 1. Sequential and reversible oxidation of TTF (**1**) affords stable cationic species **2** and **3**.

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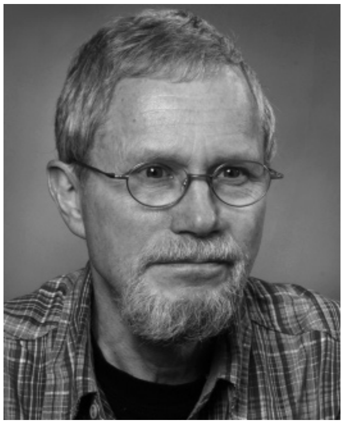
Jan O. Jeppesen was born in Esbjerg, Denmark, in 1972. He received his B.Sc., M.Sc., and Ph.D. degrees in 1996, 1999, and 2001, respectively, from the University of Southern Denmark in Odense for work in molecular, macromolecular, and supramolecular tetrathiafulvalene chemistry under the supervision of Professor Jan Becher. During his Ph.D. studies he spent 10 months in Professor Fraser Stoddart's group at the University of California, Los Angeles (UCLA), working on the design and synthesis of amphiphilic, bistable [2]rotaxanes for use in the fabrication of memory and logic circuits for a chemical computer. In 2003 he was awarded the Hede Nielsen prize for outstanding scientists. Currently he holds a position as Associate Professor at the University of Southern Denmark in Odense supported by the Danish Natural Science Research Council (SNF).

Mogens Brøndsted Nielsen was born in Grenå, Denmark, in 1972. He received his M.Sc. degree at University of Odense in 1997 and his Ph.D. degree in 1999 for work in macrocyclic and supramolecular tetrathiafulvalene chemistry under the supervision of Professor Jan Becher. During his Ph.D. studies he spent 1 year in Professor Fraser Stoddart's group at the University of Califonia, Los Angeles (UCLA). Following postdoctoral studies on acetylenic scaffolding under Professor François Diederich at ETH-Zürich from 2000 to 2002, he returned to the University of Southern Denmark in Odense first as Assistant Professor and in September 2003 as Associate Professor. In February 2004 he became Associate Professor at the University of Copenhagen. He has been awarded the 2004 Knud Lind Larsen prize for his contributions to synthetic and supramolecular chemistry.



Jan Becher was born in Frederiksberg, Denmark, in 1939. He graduated from Professor Ole Buchardt's group, University of Copenhagen, in 1966. He was Assistant Professor at the University of Odense in 1969–1989, awarded Dr. Scient. 1986, and appointed docent (Professor) in 1989, also at University of Odense. He was awarded The Bjerrum Chemistry Award and Gold Medal in 1992 as well as Docteur honoris causa (Université d'Angers, France) in 1998. His research interests cover heterocyclic chemistry, especially sulfur-containing heterocycles, macrocyclic chemistry, macrocyclic ligands, and supramolecular chemistry.

(5) The UV−vis absorption spectra of TTF^0, $TTF^{\bullet+}$, and TTF^{2+} are decisively different from one another.

(6) TTF derivatives readily form dimers, highly ordered stacks or two-dimensional sheets, which are stabilized by intermolecular $\pi-\pi$ interactions and nonbonded sulfur−sulfur interactions.

(7) TTF is stable to many synthetic transformations, although it is important to avoid strongly acidic conditions and strong oxidizing agents.

(8) The contribution from 6π-electron heteroaromaticity in the 1,3-dithiolium cations explains the relatively low oxidation potentials for the parent TTF ($E_{1/2}{}^1 = +0.34$ V, $E_{1/2}{}^2 = +0.73$ V vs Ag/AgCl in MeCN).

Some examples where TTFs have been used[5] are shown in Figure 2.

3. Cyclophanes and Cage Molecules

Cyclophanes[6] are fundamentally important compounds in many aspects of macrocyclic and supramolecular chemistry, and research in this field has expanded rapidly in recent years. On account of their rigid framework, primarily defined by aromatic units, these molecules with very large cavities are ready to accommodate charged or neutral guest molecules.[7] TTF cyclophanes were first synthesized by Staab et al.,[8] and recently there has been increasing interest in this family of compounds. Incorporation of the redox-active TTF unit into cyclophanes may serve a dual purpose, namely, increasing the host−guest interaction with a complementary electroactive guest and at the same time electrochemically signal the complexation event, making such molecules attractive components in, for example, sensor technology. Formally, any aromatic ring bridged by at least one

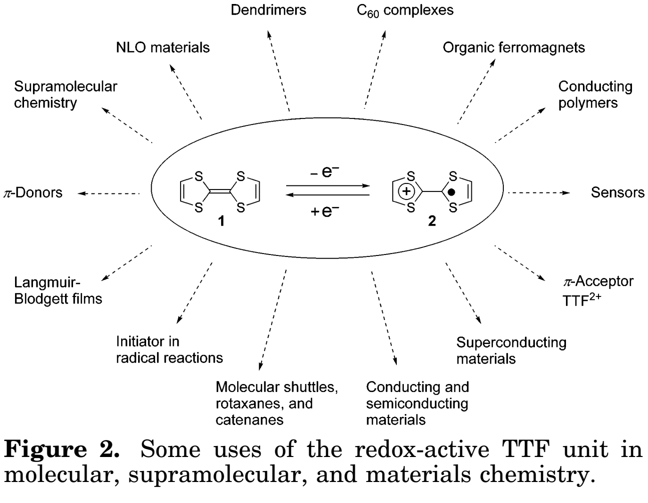


Figure 2. Some uses of the redox-active TTF unit in molecular, supramolecular, and materials chemistry.

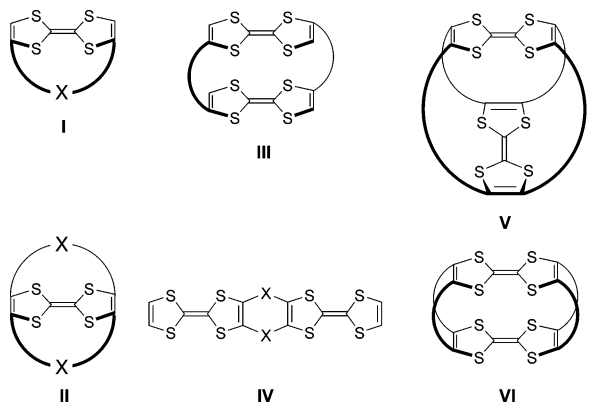


Figure 3. Different types of TTF cyclophanes.

aliphatic *n*-membered bridge ($n \geq 0$) is termed a cyclophane.[9] Therefore, a TTF macrocycle which does not include at least one aromatic unit does not fall under the strict definition of cyclophanes. However, upon oxidation of the TTF unit in a TTF macrocycle, the TTF unit becomes aromatic (vide supra) and as a consequence the TTF macrocycle can be regarded as a cyclophane. Throughout this review the term TTF cyclophane is used for any macrocycle containing a TTF unit, whereas a TTF cage molecule is regarded as a macrobicyclic TTF cyclophane with at least three bridges and at least three TTF units.

3.1. TTF Cyclophanes

The TTF cyclophanes discussed in this section will be composed of one or two TTF units and can be divided into three different classes (Figure 3) depending on the connectivity between the TTF unit and the linkers.

(1) Cyclophanes containing one TTF unit, connected by one linker (type **I**) or by two linkers (type **II**).

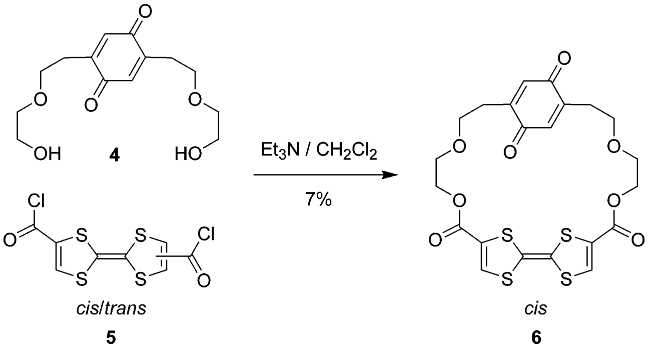
(2) Cyclophanes containing two TTF units connected by two linkers (types **III** and **IV**).

(3) Cyclophanes containing two TTF units connected by four linkers in an orthogonal arrangement (type **V**, crisscross TTFs) or in a parallel fashion (type **VI**, TTF-belts).

3.1.1. Class 1

3.1.1.1. Type I. Moriarty and co-workers[10] prepared a donor−acceptor (D−A) cyclophane utilizing TTF as the donor unit and a quinone moiety as the acceptor unit. This D−A TTF cyclophane of type **I** was synthesized (Scheme 1) from a diol **4** connected to the quinone moiety and a TTF diacid chloride **5** and was isolated as the *cis*-isomer **6** as confirmed by an X-ray crystal structure analysis. Although the cyclophane **6** contains both donor and acceptor moieties, no intramolecular CT interactions were observed.[10]

Scheme 1. Synthesis of a Type I TTF Cyclophane



Several other D−A cyclophanes of type **I** have been prepared, and some examples are shown in Figure 4. The neutral D−A cyclophane **7** is based on a tetrathioTTF as the donor unit and pyromellitic diimide (PMDI) as the acceptor moiety and was isolated as a 1:1 mixture of the cis and trans isomers.[11] The trans isomer was shown[11] to give rise to intramolecular CT interactions in solution as evidenced by the appearance of a clear CT absorption band at $\lambda_{\max} = 590$ nm ($\epsilon = 110$ M^{-1} cm^{-1}) in the UV−vis spectrum recorded of **7** in CH$_2$Cl$_2$. The charged D−A cyclophanes[12] **8**$^{2+}$ have paraquat incorporated as the acceptor moiety, whereas[13] **9**$^{2+}$ has diquat as the acceptor moiety. The charged D−A systems **8**$^{2+}$ showed much stronger intramolecular CT absorption bands in MeCN as compared to the neutral system **7**, and these occurred in the range of 650−675 nm. The extinction coefficient of this absorption band was higher ($\epsilon = 650$ M^{-1} cm^{-1}) in the highly strained *trans*-**8a**$^{2+}$, and the intensity decreased with increased conformational flexibility in analogues **8b**$^{2+}$ and **8c**$^{2+}$. The X-ray crystal structure (Figure 5) of *trans*-**8a**$^{2+}$ provides one of the first solid-state structures of a TTF-acceptor system in which intramolecular CT has been established in solution.[1m,12] The X-ray crystal structure analysis of *trans*-**8a**$^{2+}$ revealed significant bending of the TTF unit induced by the short linkers between the TTF unit and the paraquat moiety, and the bond lengths suggest that the TTF unit is almost neutral.[1m] The UV−vis absorption spectrum[13] recorded of **9**$^{2+}$ in MeCN revealed that the CT absorption band was hypsochromically shifted to $\lambda_{\max} = 540$ nm relative to 675 nm in *trans*-**8a**$^{2+}$. In addition, the intensity ($\epsilon = 1930$ M^{-1} cm^{-1}) of the CT absorption band was almost three times higher in the case of **9**$^{2+}$ as compared to *trans*-**8a**$^{2+}$, a situation which most likely can be accounted for by the presence of the stronger acceptor moiety diquat in **9a**$^{2+}$. In common for all the D−A cyclophanes **6**, **7**, **8**$^{2+}$, and **9**$^{2+}$ is that they can exist

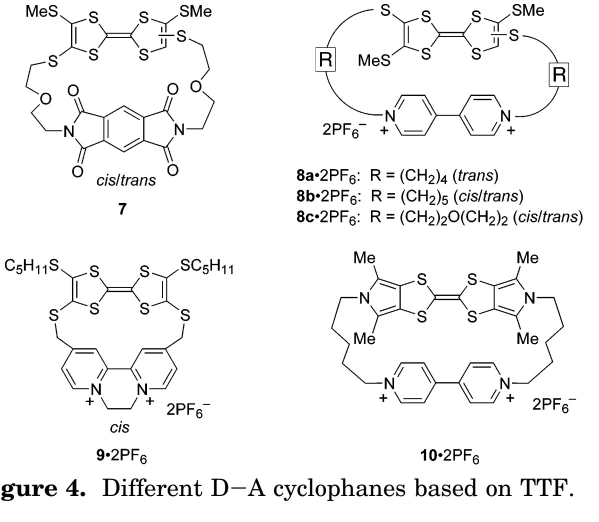


Figure 4. Different D−A cyclophanes based on TTF.

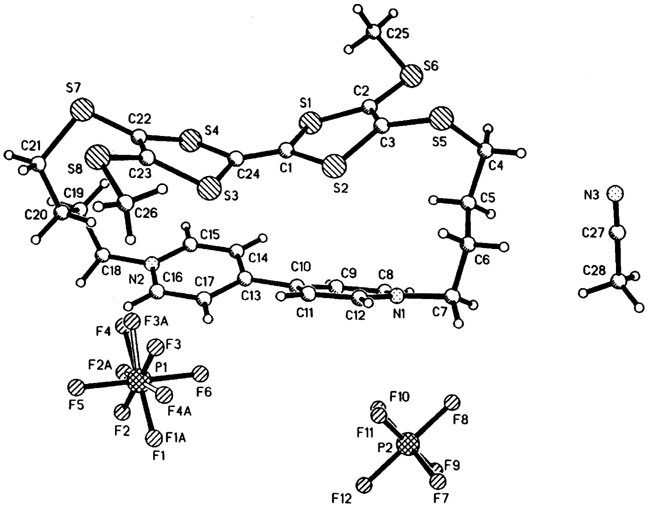
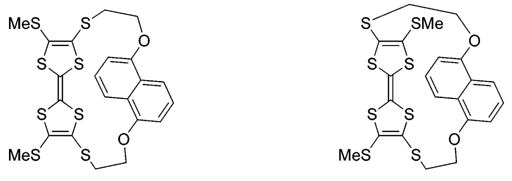


Figure 5. X-ray crystal structure (from ref 12) of **8a**·4PF_6·MeCN.



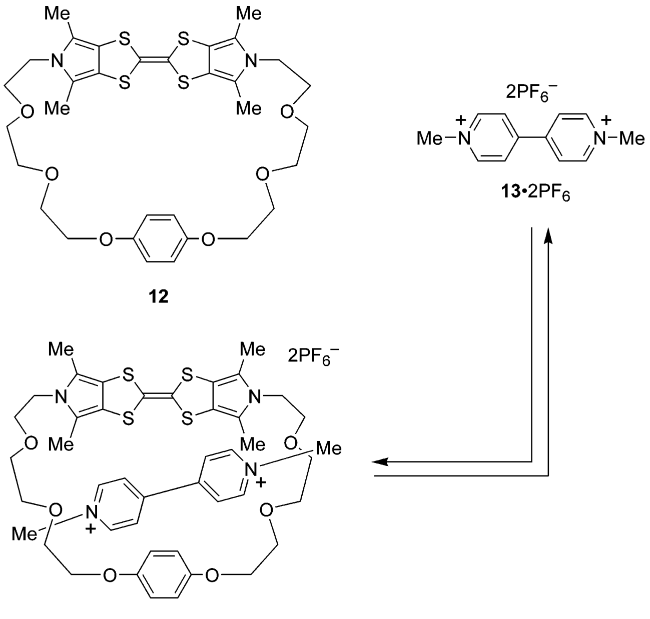
cis-**11** *trans*-**11**

Figure 6. Molecular formulas of the D−D′ cyclophanes *cis*-**11** and *trans*-**11**.

as cis/trans isomeric mixtures. This problem can be circumvented using the bis(2,5-dimethyl)pyrroloTTF unit, and the D−A cyclophane $\mathbf{10}^{2+}$ is an elegant example.[12] It exhibits an intramolecular CT band centered at $\lambda_{max} = 640$ nm.

Intramolecular CT interactions can also be established by oxidation of the TTF unit in rigid D−D′ cyclophanes, where D represents a TTF unit and D′ another π-donor. One example is provided[14] by cyclophanes *cis*-**11** and *trans*-**11** (Figure 6). These type **I** cyclophanes experience a diminished first oxidation potential (by 60 mV) relative to tetramethylthioTTF. This enhanced readiness of oxidation is presumably promoted by favorable intramolecular CT interactions between the dioxynaphthalene donor unit and the TTF radical cation formed upon electrochemical oxidation.[14] In the D−D′ cyclophane **12** (Scheme 2) the cavity is large enough for inclusion of electron acceptors by means of intermolecular CT interactions.[15] Thus, a mixture of **12** and the electron acceptor paraquat $\mathbf{13}^{2+}$ exhibited a broad CT band centered at $\lambda_{max} = 601$ nm in the UV−vis spectrum recorded in a mixture of $CHCl_3$ and MeCN. On the basis of ^1H NMR studies, it was inferred that a 1:1 inclusion complex is formed in solution ($CHCl_3$/MeCN, 1:1) with an association constant of 250 M^{-1} (at 300 K). However, X-ray crystallographic analysis revealed (Figure 7) a solid-state complex consisting of two molecules of **12** per molecule of paraquat. Each of the cyclophanes adopts a conformation in which the angle between the hydroquione moiety and the TTF unit is 70.1, while two of them dimerize to give a box-like structure encapsulating one completely planar paraquat molecule.[15]

Scheme 2. Compelxation of the TTF Cyclophane 12 by 13·2PF$_6$



3.1.1.2. Type II.

Cyanoethyl-protected TTF-tetrathiolates,[1i,16] such as tetrakis(2-cyanoethylthio)TTF, have been widely used as TTF building blocks in macrocyclic and supramolecular chemistry.[1] As an example of a type **II** TTF cyclophane, Simonsen et al.[17] used tetrakis(2-cyanoethylthio)TTF **14** to prepare (Scheme 3) an acceptor−donor−acceptor (A−D−

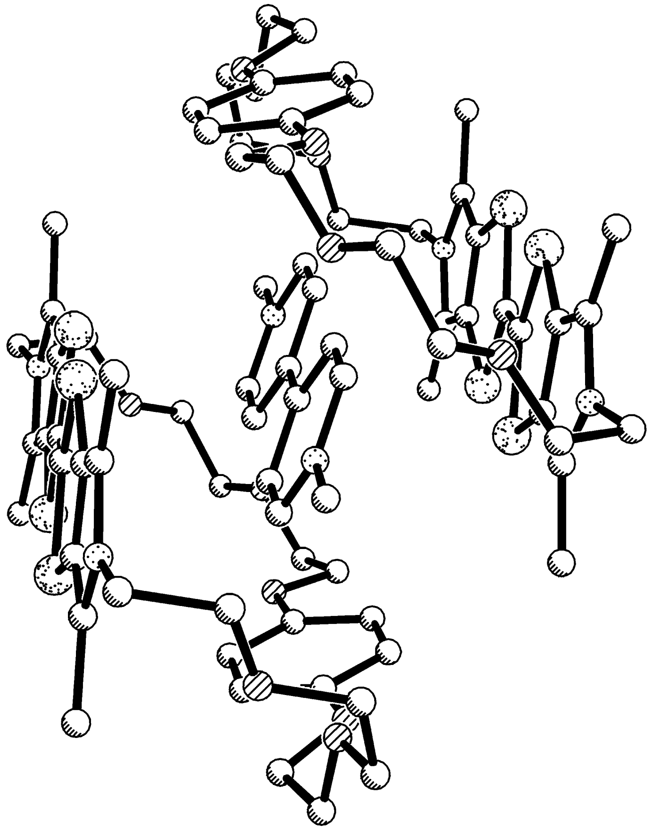
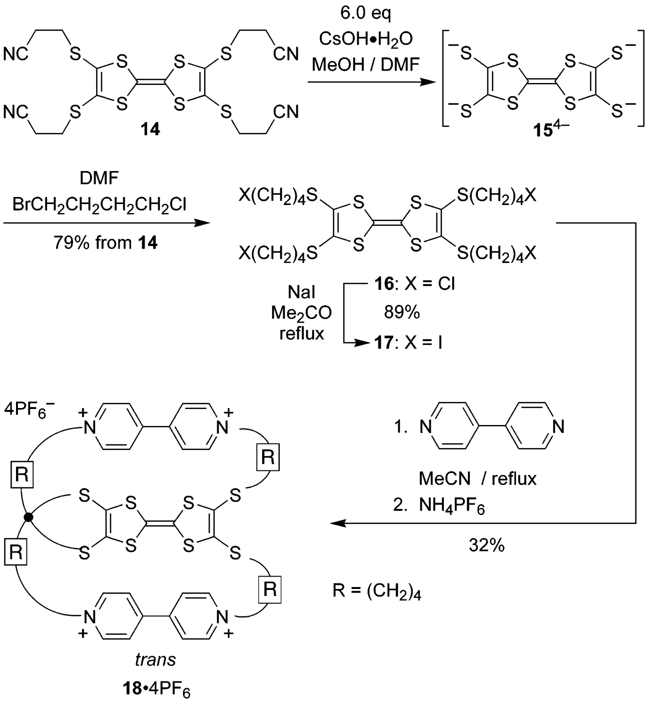


Figure 7. X-ray crystal structure of the $(\mathbf{12})_2$·**13**·2PF_6 complex. Hydrogen atoms, solvent molecules, and counterions are omitted for clarity. (Reprinted with permission from ref 15. Copyright 1999 Wiley-VCH.)

Scheme 3. Synthesis of the Type II TTF Cyclophane in the Shape of Acceptor−Donor−Acceptor (A−D−A) Sandwich 18·4PF$_6$



A) sandwich **18**·4PF$_6$ with paraquat as the acceptor moieties. The four cyanoethyl thiolate protecting groups in **14** can be readily deprotected when treated with 6 equiv of cesium hydroxide monohydrate, and the resulting TTF tetrathiolate **15**$^{4-}$ (Scheme 3) can subsequently be realkylated with 1-bromo-4-chlorobutane to afford the TTF derivative **16**, which was converted to the tetraiodide **17** by treatment with sodium iodide. The cyclophane **18**·4PF$_6$ was synthesized by heating a mixture of **17** and 4,4′-bipyridine in MeCN under reflux and was obtained as the trans isomer as a green solid after anion exchange with ammonium hexafluorophosphate. X-ray structure analysis (Figure 8) of **18**·4PF$_6$ clearly revealed that the A−D−A sandwich adopts a trans configuration,[17] and the UV−vis spectrum recorded of **18**·4PF$_6$ in MeCN revealed an absorption band centered around λ_{max} = 645 nm (ϵ = 470 M^{-1} cm^{-1}) assigned to an intramolecular CT band between the TTF unit and the paraquat moieties. Cyclic voltammetry (CV) of **18**·4PF$_6$ recorded in MeCN revealed anodic shifts in both the first (70 mV) and second (90 mV) oxidation potentials which were ascribed to a combination of intramolecular CT interactions and electrostatic repulsion between the paraquat moieties and the oxidized TTF unit.[17]

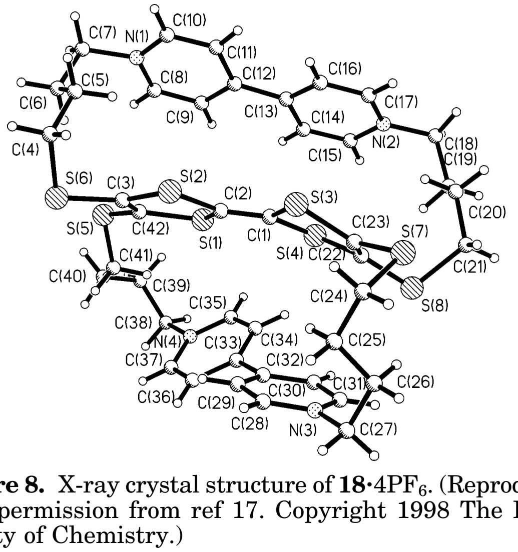
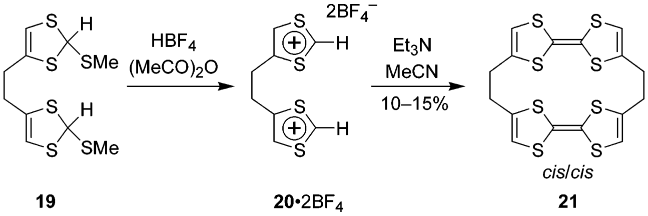
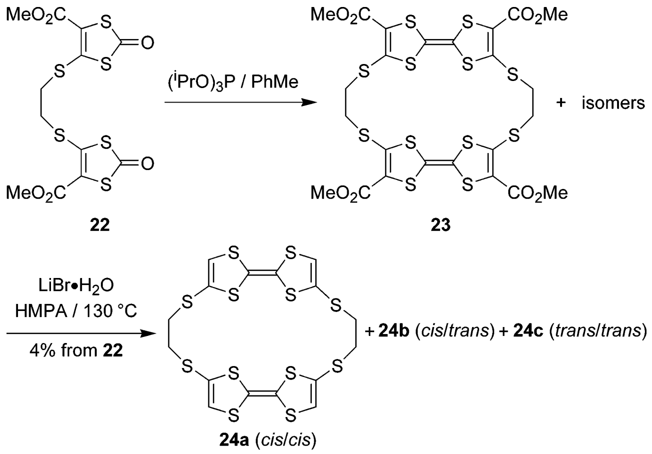


Figure 8. X-ray crystal structure of **18**·4PF$_6$. (Reproduced with permission from ref 17. Copyright 1998 The Royal Society of Chemistry.)

Scheme 4. Synthesis of a Type III TTF Cyclophane by Deprotonation of a Bis-1,3-dithiolium Salt



Scheme 5. Synthesis of the Type III TTF Cyclophanes 24

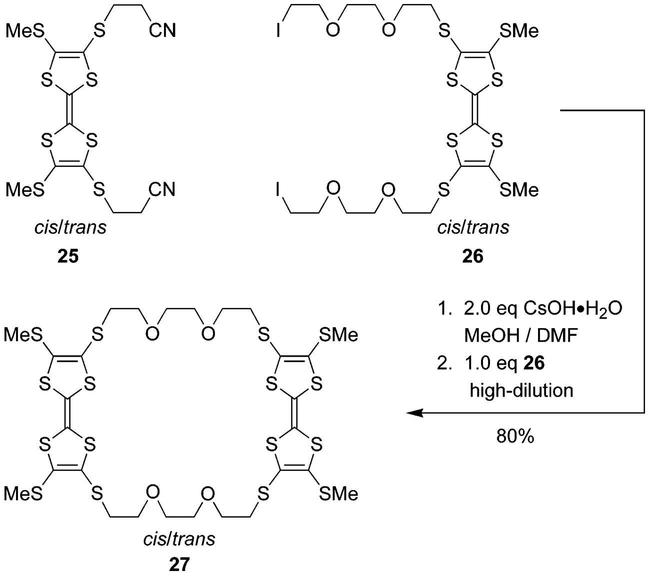


3.1.2. Class 2

3.1.2.1. Type III. Several stereoisomers are possible for type **III** TTF cyclophanes on account of different cis and trans substitution modes. The first example of a type **III** TTF cyclophane **21** was reported by Staab et al.,[8] prepared (Scheme 4) by a base-mediated coupling of the bis-1,3-dithiolium salt **20**·2BF$_4$, and obtained after fractional crystallization as the cis/cis isomer as evidenced by X-ray structural analysis.

Otsubo and co-workers[18] later on succeeded in obtaining (Scheme 5) all three isomers of the ethylenedithio-spaced TTF cyclophane **24** as an isomeric mixture which could be separated by elaborate fractional crystallization. The mixture was prepared in 4% yield by an intermolecular triisopropyl phosphite-mediated coupling reaction of the dimeric 1,3-dithiole-2-one derivative **22** followed by decarboxylation of the tetrakis(methoxycarbonyl)TTF derivative **23**. The CV of compound **24a** showed two reversible one-electron oxidation processes at +0.41 and +0.56 V and one quasi-reversible two-electron oxidation process at +0.83 V. The splitting of the peaks assigned to the first oxidation process of each of the TTF units indicates the existence of an intramolecu-

Scheme 6. Synthesis of a Type III TTF Cyclophane by Macrocyclization of a TTF-Bisthiolate

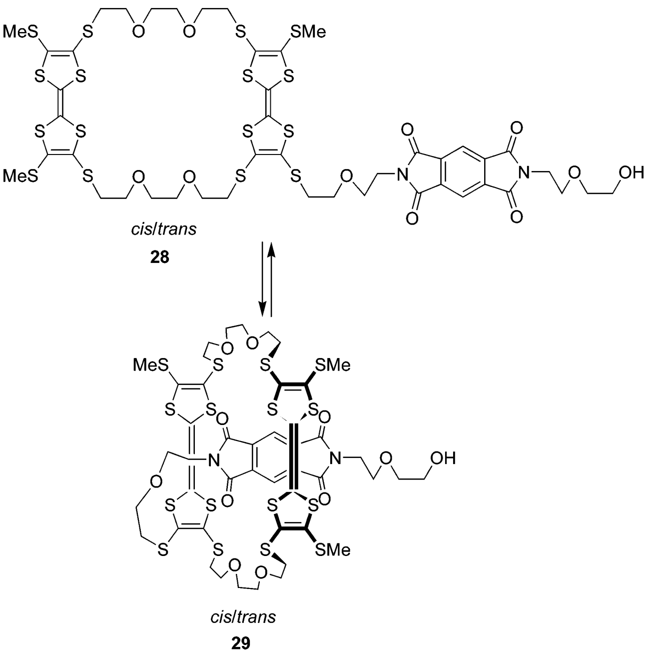


lar interaction between the two TTF units in the monooxidized form of **24a**.

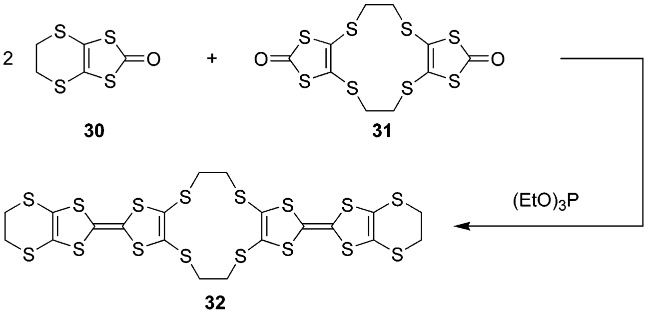
The two examples shown in Schemes 4 and 5 are both based on a strategy in which the central fulvalene bond of the TTF unit is formed in the final cyclization step. However, this approach often results in low yield of the desired TTF cyclophane. Another strategy is based on the cyanoethyl deprotection/realkylation protocol[1i,16] of TTF-tetrathiolates which made it possible to obtain a variety of TTF cyclophanes in high yields, and one example[19] is illustrated by synthesis (Scheme 6) of the TTF cyclophane **27**.

A derivative of **27** containing one cyanoethyl-protected thiolate group allowed further functionalization of the cyclophane via alkylation at this reactive handle after deprotection. From this precursor a TTF cyclophane **28** containing a PMDI moiety attached to one of the TTF units was prepared[20] (Scheme 7). ^{1}H NMR spectroscopic studies were used to establish that **28** can undergo "self-complexation" (Scheme 7) and that the equilibrium between the two conformations **28** and **29** occurred rapidly. In addition, the UV−vis spectrum recorded of **28** in CH_2Cl_2 revealed a CT band observed as a shoulder at approximately 580 nm. This value is slightly blue shifted relative to the position of the CT band of the rigid cyclophane *trans*-**7** (λ_{max} = 590 nm).

Scheme 7. "Self-Complexing" TTF Cyclophane



Scheme 8. Synthesis of a Type IV TTF Cyclophane by an Intermolecular Phosphite Coupling Reaction



3.1.2.2. Type IV. The type **IV** TTF cyclophane bis-bis(ethylenedithiolo)TTF (bis-BEDT-TTF) **32** was synthesized (Scheme 8) by Sugawara and co-workers[21] by an intermolecular triethyl phosphite-mediated cross-coupling of ketones **30** and **31**. This TTF cyclophane exhibited some interesting inclusion properties. The X-ray crystal structure[22] of the neutral TTF cyclophane **32** revealed (Figure 9a) that the molecule adopts a U-shaped conformation creating a cavity between the two TTF units which is occupied with a TTF unit of the next donor. Mixing **32** with the electron-acceptor 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in a 1:1 mixture of THF and CS_2 afforded black plates. X-ray crystal structure analysis[22] of the CT complex **32**·DDQ showed that **32** adopts a conformation in which DDQ is sandwiched within its cavity as depicted in Figure 9b. The UV−near-IR spectrum of **32**·DDQ revealed absorption bands at λ_{max} = 450 and 900 nm associated with the DDQ radical anion and the TTF radical cation, respectively. On the basis of these results and on an analysis of the bond lengths of the DDQ moiety in the CT complex it was deduced that the host donor and guest acceptor afford the radical salt with complete electron transfer. The TTF cyclophane **32** also forms an inclusion complex with the much weaker acceptor C_{60}, and the crystal structure[23] of **32**·C_{60} is illustrated in Figure 10. The crystal structure of **32**·C_{60} showed that the cavity between the two TTF units is larger as compared to the cavity in neutral **32**. A comparison of the absorption spectra (Figure 11) recorded of **32**·C_{60} in a KBr pellet with those of neutral **32** and C_{60} recorded under similar conditions revealed a distinct absorption band centered around 750 nm, which can be assigned to an intermolecular CT band between **32** and C_{60}.

Recently a type **IV** TTF cyclophane **37** based on the monopyrroloTTF unit[24] has been prepared[25] as outlined in Scheme 9. A solution of the biscyanoethyl thiolate-protected monopyrroloTTF building block,[24b]

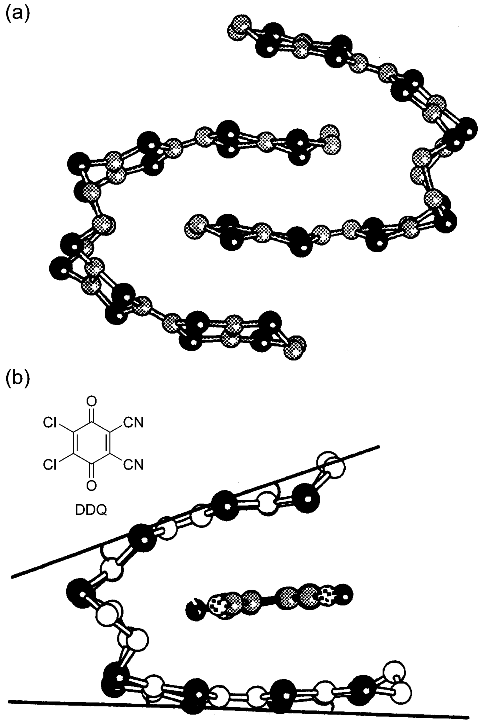


Figure 9. (a) Molecular structure of the neutral TTF cyclophane **32** and (b) its CT inclusion complex with DDQ. Hydrogen atoms are omitted for clarity. (Reproduced with permission from ref 22. Copyright 1993 The Royal Society of Chemistry.)

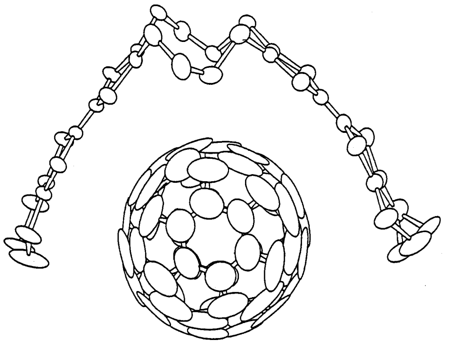


Figure 10. Molecular structure of **32**·C_{60}. Hydrogen atoms are omitted for clarity. (Reprinted with permission from ref 23. Copyright 1992 The Chemical Society of Japan.)

33, was treated with 1 equiv of cesium hydroxide monohydrate. This procedure generated the TTF-monothiolate, which was alkylated with 0.5 equiv of 1,2-bis(2-iodoethoxy)ethane (**34**) to afford the bis-TTF **35** in 85% yield. Subsequently, the two remaining cyanoethyl protecting groups in **35** were deprotected using 2 equiv of cesium hydroxide monohydrate followed by addition of 1 equiv of the diiodide **34**, which effected the second deprotection/alkylation sequence, affording **36** in 64% yield. Deprotection of the tosyl groups was carried out in near quantitative yield by boiling **36** in a 1:1 mixture of THF and MeOH in the presence of an excess of sodium methoxide. The TTF cyclophane **37** was subsequently used to prepare (vide infra) a TTF-belt.

In should be mentioned that several other type **IV** TTF cyclophanes have been prepared.[26] However, it is beyond the scope of this review to describe all of them here.

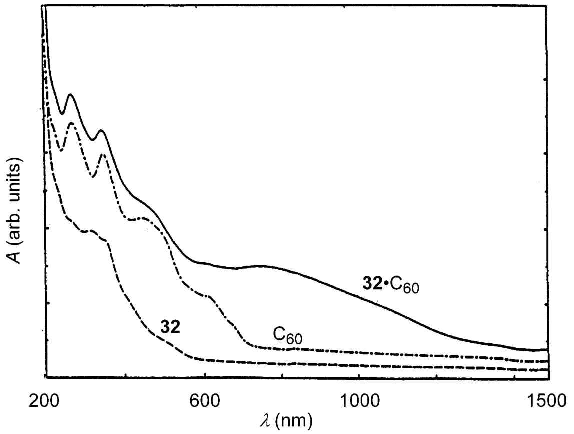
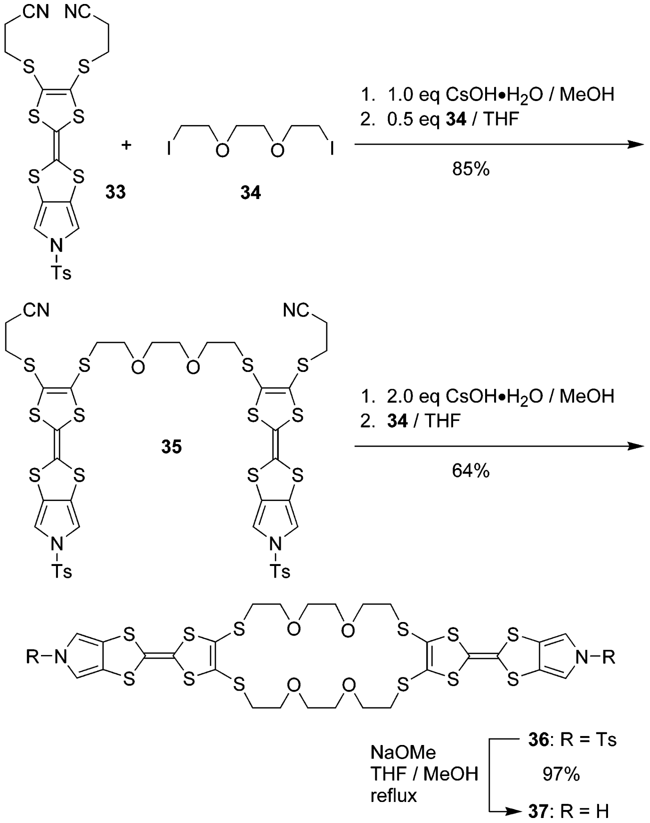


Figure 11. Absorption spectra of **32**·C_{60}, **32**, and C_{60} recorded in KBr pellets. (Reprinted with permission from ref 23. Copyright 1992 The Chemical Society of Japan.)

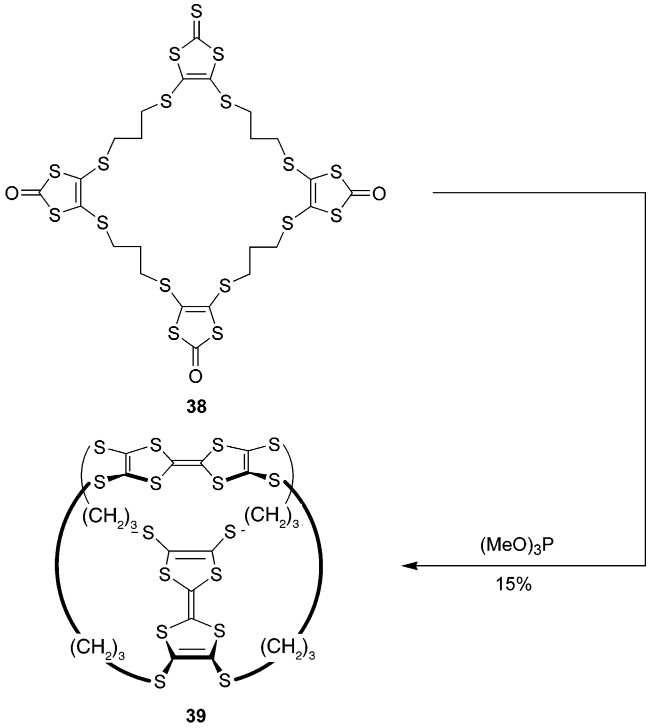
Scheme 9. Synthesis of Type IV TTF Cyclophane 37 Based on a Monopyrrolo TTF Unit



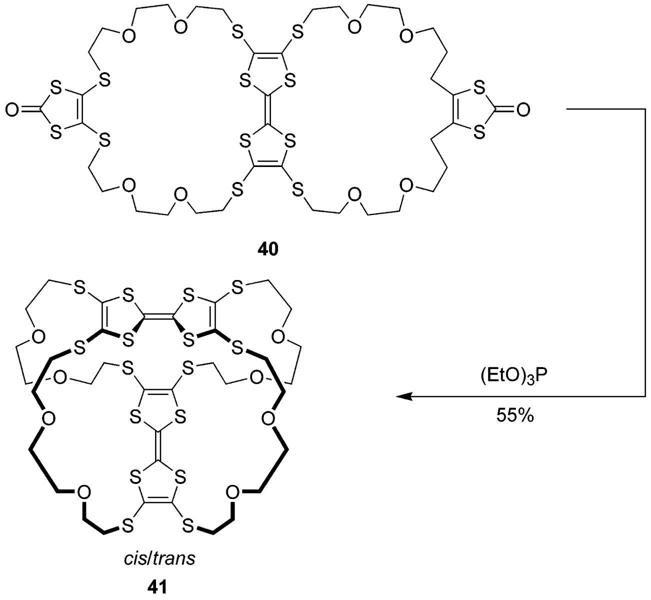
3.1.3. Class 3

3.1.3.1. Type V. Crisscross bis-TTF cyclophanes of type **V** can be obtained by different approaches. Sugawara and co-workers[27] prepared (Scheme 10) the first type of a crisscross bis-TTF cyclophane **39** by an intramolecular trimethyl phosphite coupling of the macrocycle **38** containing three 1,3-dithiole-2-on and one 1,3-dithiole-2-thion moieties. A crystallographic analysis of the CT complex between **39** and the electron-acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) was used to confirm the orthogonal structure of **39**. Surprisingly, the X-ray structure of **39**·TCNQ revealed that the TCNQ acceptor moiety was located outside the cavity of **39**.

Scheme 10. Synthesis of the Crisscross Bis-TTF Cyclophane 39 by Intramolecular Coupling



Scheme 11. Synthesis of the Crisscross Bis-TTF Cyclophane 41 from a Type II TTF Cyclophane



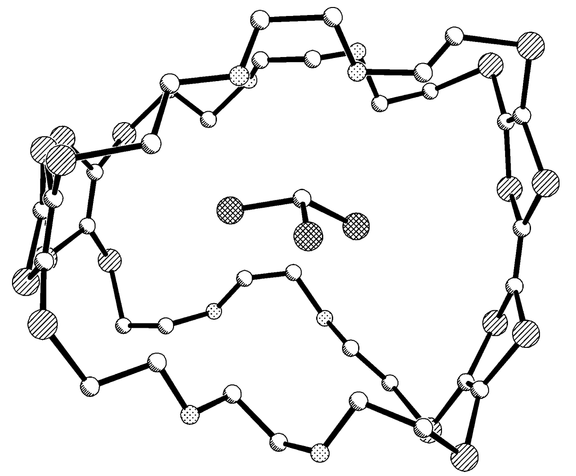
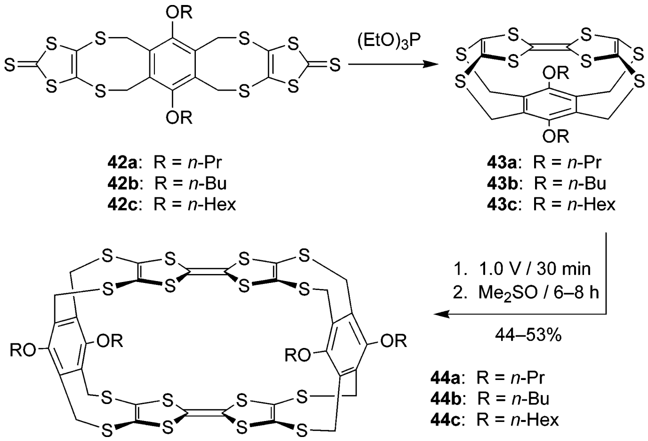


Figure 12. X-ray crystal structure of $\mathbf{41}\cdot CHCl_3$. Hydrogen atoms are omitted for clarity. (Reproduced with permission from ref 28. Copyright 1998 The Royal Society of Chemistry.)

Scheme 12. Synthesis of the First TTF-Belts 44a−c by Electrochemical Oxidations



Another approach reported by Nielsen et al.[28] relied on intramolecular triethyl phosphite coupling of a type **II** TTF cyclophane **40** having one 1,3-dithiole-2-on moiety in each of the two linkers which produced (Scheme 11) the crisscross bis-TTF cyclophane **41** in 55% yield as a cis/trans isomeric mixture. By slow diffusion of MeOH into a $CHCl_3$ solution of the isomeric mixture of **41**, single crystals of the cis/cis isomer were obtained as confirmed by X-ray crystal structure analysis.[28] The molecular structure revealed (Figure 12) that $CHCl_3$ was included inside the cavity of **41**. The redox behavior of the crisscross TTF cyclophane **41** was investigated by differential pulse voltammetry and revealed a splitting of both the first and second oxidation process, and as a consequence, four one-electron oxidation peaks were observed in the voltammogram recorded of **41** in CH_2Cl_2. These results indicate that an interaction is taking place between the two TTF units. The first oxidation potential is lowered (−40 mV) relative to that of the precursor **40**, an observation which can be explained by a stabilization of the monooxidized compound as a result of delocalization of the positive charge over both TTF units. In contrast, the second oxidation potential of **41** is increased (+90 mV) relative to that of **40**. Thus, removal of the second electron from **41** is more difficult, which can be accounted for by the presence of Coulombic repulsion between the two positive charges on the two TTF units present in the bis-oxidized form of **41**.

3.1.3.2. Type VI. The first type **VI** TTF cyclophanes were prepared (Scheme 12) by Müllen and co-workers.[29] Intramolecular triethyl phosspite-mediated coupling of the bis-1,3-dithiole-2-thiones **42a**−**c** gave[30] the strained type **II** TTF cyclophanes **43a**−**c** which upon electrochemical oxidation followed by dissolution of the electrolysis product in Me_2SO afforded the TTF-belts **44a**−**c**. The formation of **44a**−**c** is most likely a result of a reverse reduction of the generated bis-radical cation to the neutral

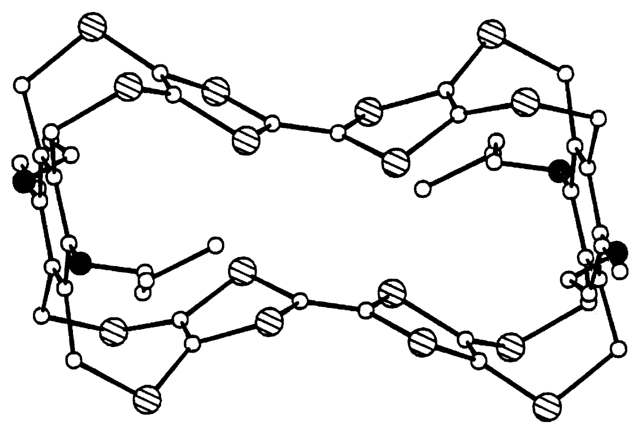
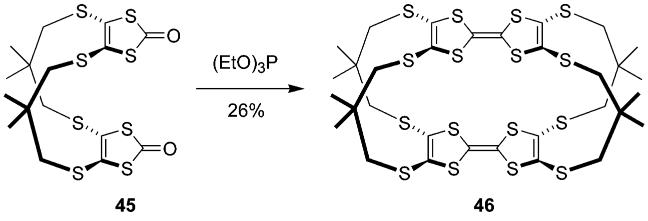


Figure 13. X-ray crystal structure of **44b**. Hydrogen atoms are omitted for clarity. (Reprinted with permission from ref 29. Copyright 1992 Wiley-VCH.)

Scheme 13. Synthesis of a Bis-TTF-Belt 46 by an Intermolecular Coupling

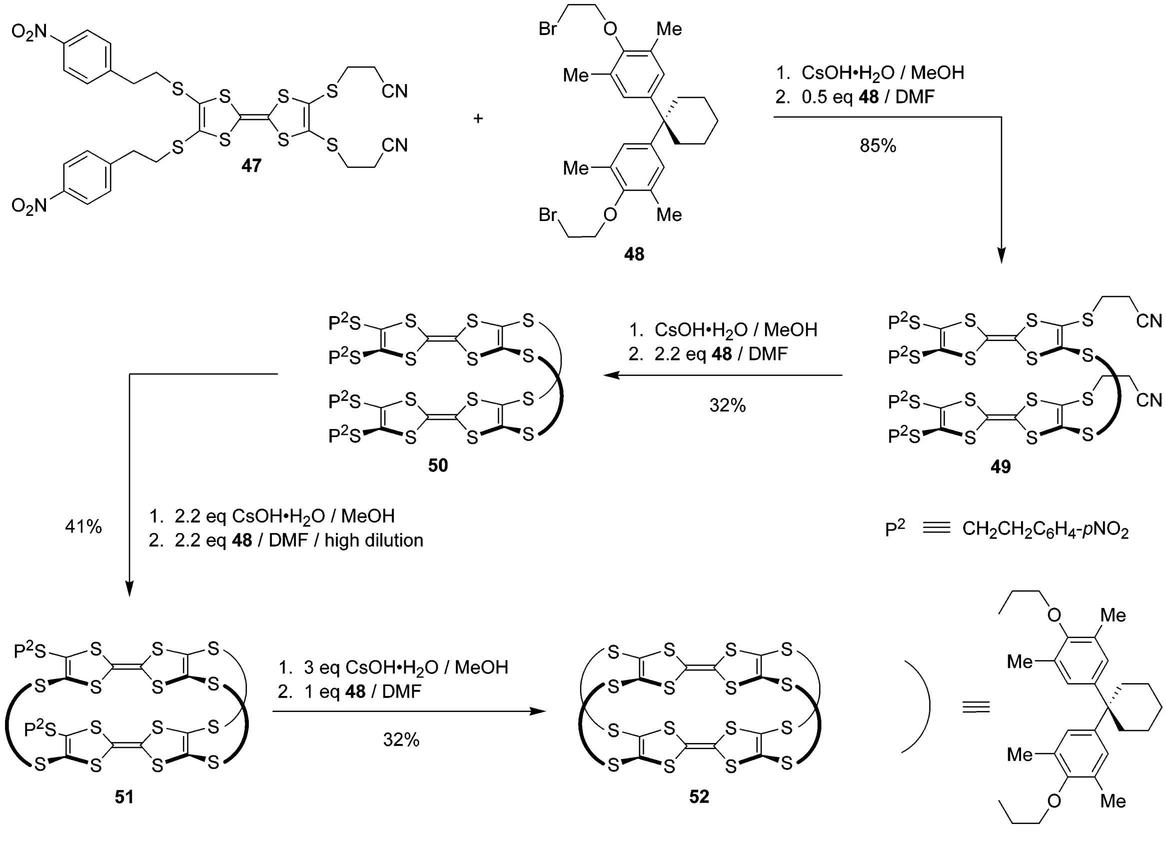


compound. The driving force leading to dimerization products is probably the release of strain from **43a**–**c**. The crystal structure (Figure 13) of **44b** revealed that the two TTF units are bent out of planarity toward the center of the cavity, resulting in a dumbbell-shaped structure.

Later Otsubo and co-workers developed a more conventional synthetic strategy[31] for the preparation of type **VI** TTF cyclophanes, which is based on an intermolecular triethyl phosphite-mediated coupling of a dimeric 1,3-dithiole-2-on derivative **45** producing (Scheme 13) the TTF-belt **46** in 26% yield. The relatively short 2,2-dimethylpropylene linkers were chosen in order to prevent intramolecular coupling and to enhance the solubility of the product formed. The molecular structure[31] of the TTF-belt **46** clearly shows that the two TTF units are stacking in a face-to-face overlap. The CV of **46** recorded in a 1:1 mixture of CS_2 and PhCN revealed only two reversible oxidation processes at $+0.68$ (2 e^-) and $+1.00$ V (2 e^-) associated with the TTF units.[31] These results indicate that no intramolecular interactions are taking place between the two TTF units in **46**, which is surprising since the TTF units are situated close to each other. Similar electrochemical results[29] were obtained in the case of the TTF-belt **44a**.

Using the stepwise cyanoethyl protection/deprotection protocol, it has been possible to prepare TTF-belts in high yields. Two retrosynthetic routes to TTF-belts are shown in Figure 14. Using rigid linkers and the protection/deprotection method it is in some cases possible to prepare an all-*cis*-TTF cyclophane. Route A includes a triethyl phosphite coupling in the final macrocyclization step. The alternative Route B requires the use of two orthogonal[32] protecting groups, P^1 and P^2. An example of the last strategy is illustrated in Scheme 14 using P^1 = cyanoethyl and P^2 = 2-(*p*-nitrophenyl)ethyl, producing the TTF-belt **52** via a multistep protection/deprotection sequence.[33] The belt-like structure of **52** and the appearance of

Scheme 14. Sequential Synthesis of the Rigid TTF-Belt 52



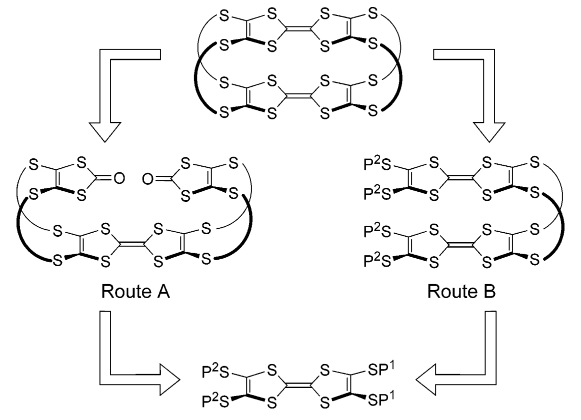


Figure 14. Two different retrosynthetic approaches for the preparation of TTF-belt molecules. P^1 = cyanoethyl and P^2 = 2-(*p*-nitrophenyl)ethyl.

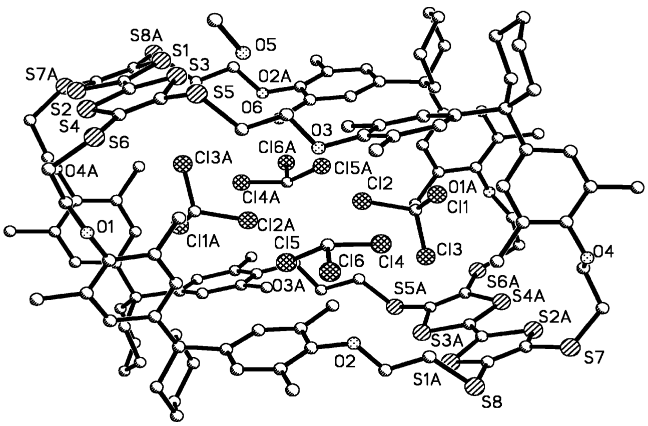


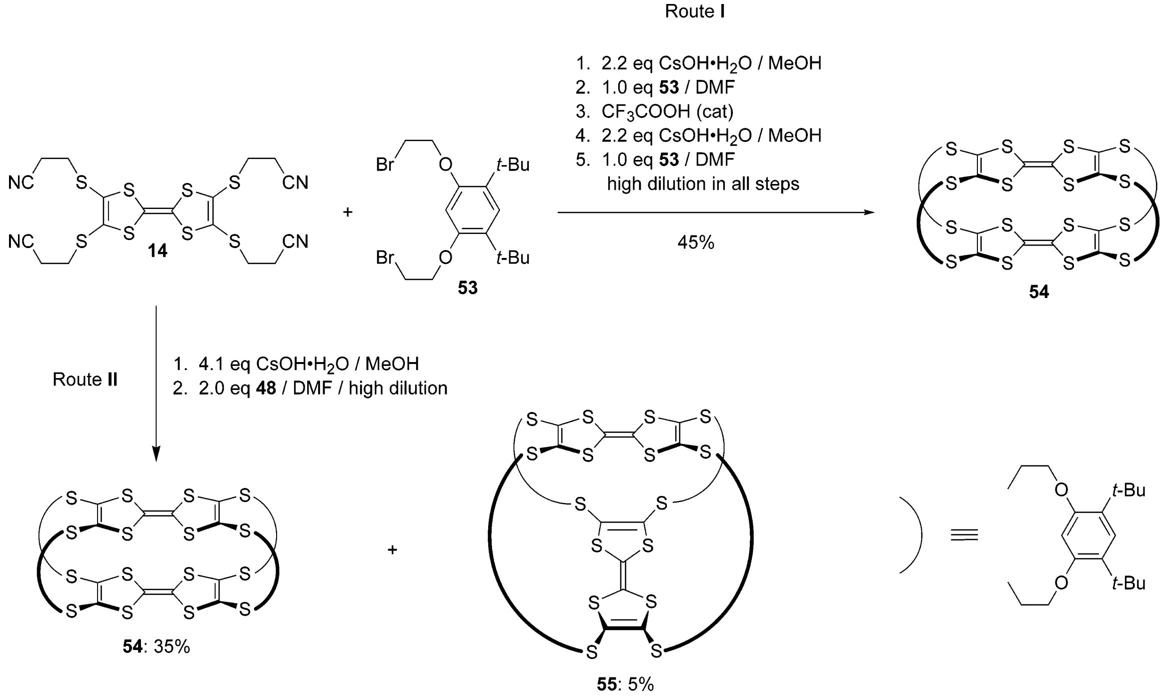
Figure 15. Molecular structure of the TTF-belt **52**·4CHCl$_3$·MeOH. Hydrogen atoms are omitted for clarity. (Reprinted with permission from ref 33. Copyright 1999 Wiley-VCH.)

a large cavity inside **52** is clearly seen from the X-ray crystal structure (Figure 15). The unit cell contains one molecule of **52** together with four CHCl$_3$ molecules and one MeOH molecule. Two of the CHCl$_3$ molecules are positioned inside the cavity of **52**, whereas the other two are located at the rim of the TTF cyclophane.[33] However, none of the CHCl$_3$ molecules seem to be involved in any strong interactions with the TTF-belt **52**. On account of the rigid linkers the two TTF units can only interact intermolecularly in the solid state, resulting in a compact packing in the crystal.[33] Some complexation studies between the TTF-belt **52** and the electron-acceptor TCNQ were conducted,[33] and some weak interactions between the donor and acceptor molecules were observed. However, the results did not provide any information regarding whether the guest (TCNQ) was complexed inside or outside the cavity of the host molecule (i.e., **52**) or outside **52**.

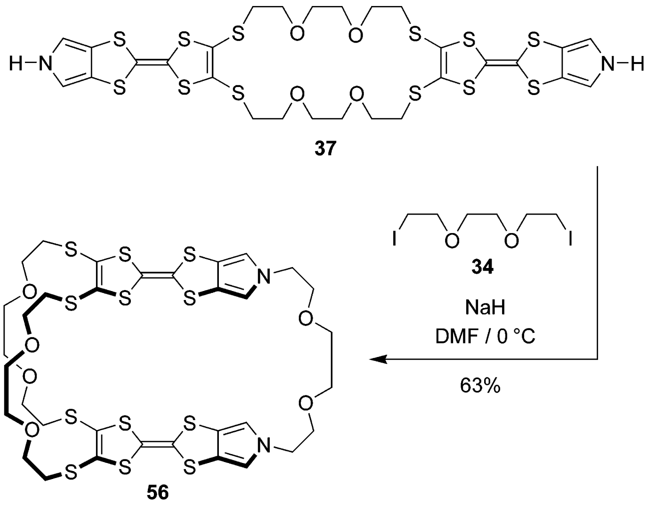
As a result of the effective S-alkylations of TTF-thiolates, it is even possible to prepare TTF cyclophanes of type **VI** in a one-pot reaction as shown in Scheme 15. By employing the rigid linker **53** it has been demonstrated[34] that it is possible to prepare TTF-belts in up to 45% yield when a sequential one-pot reaction is used. Note that step 3 in Route **I** involves isomerization of the initial mixture of cis and trans isomers with a catalytic amount of acid. The rigidity of the linker **53** forces the intermediate to adopt a correct cis/cis conformation before its final ring closure to complete the synthesis of the belt-molecule **54**. This reaction procedure only works when rigid linkers, such as dibromide **53**, are used—flexible and longer linkers result in the formation of complex reaction mixtures.[34] Note also that if the reactions are *not* carried out sequentially but directly in one step without isomerization of the fulvalene double bond, a small amount of the crisscross isomer **55** is formed as a byproduct.

Almost all TTF cyclophanes described in this review have so far resulted in a mixture of cis and

Scheme 15. One-pot Preparation of the TTF-Belt 54 Using the Rigid Linker 53



Scheme 16. Synthesis of the TTF-Belt 56 Incorporating the MonopyrroloTTF Unit



trans isomers as a consequence of the four attachment sites of TTF unit. This problem can be circumvented using the biscyanoethyl thiolate-protected monopyrroloTTF building block **33** possessing only three attachment sites as illustrated in Scheme 9. By employing high dilution conditions a 63% yield of the TTF-belt **56** was obtained[25] (Scheme 16) following *N*-alkylations of the pyrrole units in the type **IV** TTF cyclophane **37** with the diiodide **34**.

Figure 16 shows the X-ray structure of the TTF-belt **56**. The TTF-belt **56** was designed to allow complexation of the electron-acceptor TCNQ inside its cavity. Addition of 1 equiv of TCNQ to a CH_2Cl_2 solution of **56** resulted in an immediate color change from orange to green and the appearance of two CT absorption bands centered on $\lambda_{max} = 749$ and 849 nm in the UV–vis spectrum (Figure 17), indicating that two different forms of complexation exist in solution, most likely an inside and outside (alongside) form. In addition, electron paramagnetic resonance (EPR) spectroscopy of **56**·TCNQ recorded in CH_2Cl_2 revealed radical signals at $g = 2.009$ and 2.004 consistent with the presence of a TTF radical cation and a TCNQ radical anion, respectively. These results indicate that a CT interaction between the host and guest is taking place in solution.[25] However, these results do not provide any information regarding the stoichiometry of the complexation or whether TCNQ is complexed inside the cavity of **56** or outside **56**.

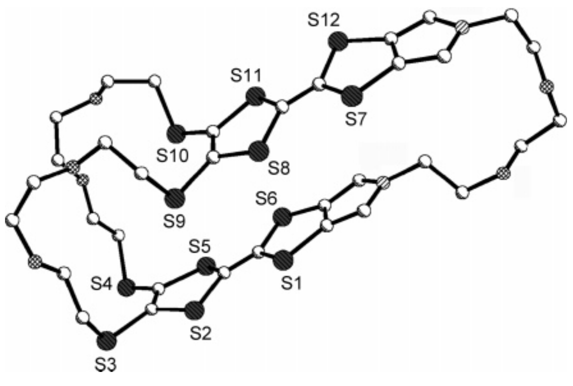


Figure 16. Crystal structure (from ref 25) of the TTF-belt **56**. Hydrogen atoms are omitted for clarity.

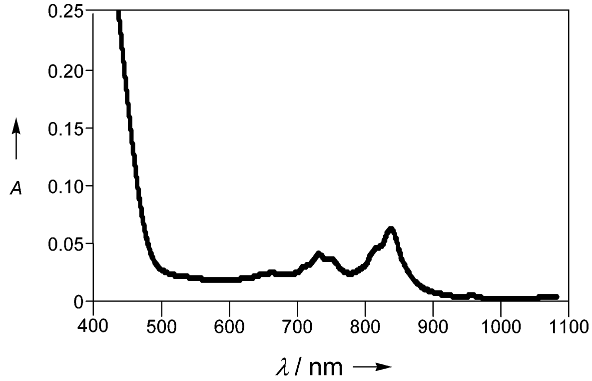


Figure 17. Absorption spectrum (from ref 25) recorded in CH_2Cl_2 at 298 K on a 1:1 mixture of **56** and TCNQ.

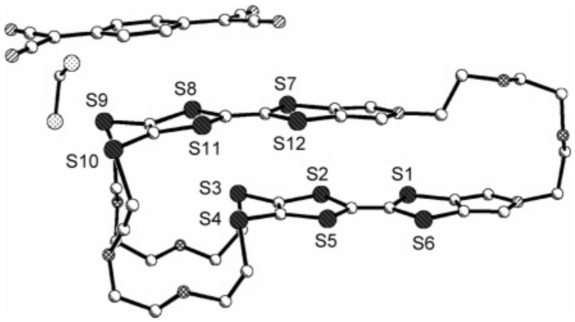


Figure 18. Crystal structure (from ref 25) of the CT complex **56**·TCNQ. Hydrogen atoms are omitted for clarity.

Some of these questions were answered by solid-state X-ray crystal structure analysis (Figure 18) of the CT complex **56**·TCNQ. Surprisingly, the structure revealed that the TCNQ acceptor is associated outside (alongside) one of the electron donors, reflecting that the complicated and subtle balance between all the individual noncovalent forces acting in cooperation are difficult to predict.[25]

3.2. TTF Cage Molecules

As illustrated in the previous section, TTF cyclophanes constitute an important class of synthetic host molecules. To enlarge the cavity surrounded by TTF units, several TTF cage molecules have been prepared[35] using the cyanoethyl protection/deprotection protocol, and some examples are shown in Figure 19.

An elegant example of a TTF cage molecule **65** (Scheme 17), able to undergo a reversible change of its structure upon oxidation, has been reported by Takimiya et al.[36] In contrast to the TTF cage molecules **57** and **58** (Figure 19), **65** has a molecular structure in which two of the three TTF units lie in a parallel arrangement and the third is orthogonal to these and was synthesized as illustrated in Scheme 17. Compounds **60**–**64** and the TTF cage molecule **65** were obtained as a mixture of cis and trans isomers on each of the TTF units. However, by careful recrystallization of **65** it was possible to obtain an all-*cis*-isomer, and its structure was confirmed by X-ray crystal structure analysis. Crystals of *cis*-**65**·$CHCl_3$ were obtained by slow evaporation of a solution of a cis/trans mixture of **65** in $CHCl_3$/light petroleum, and the molecular structure (Figure 20)

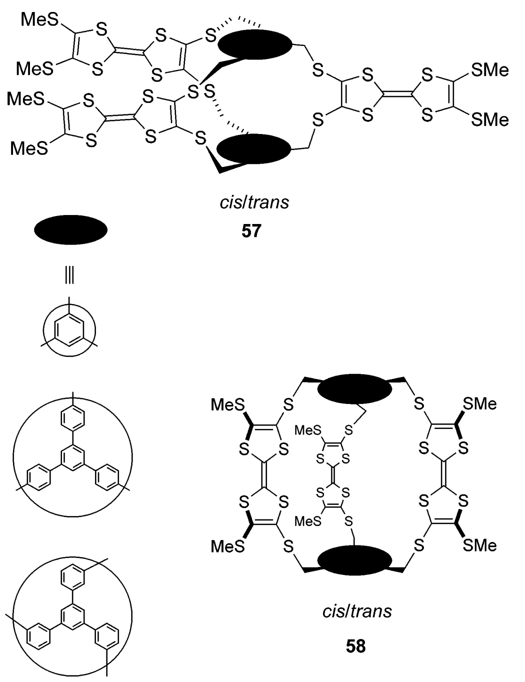


Figure 19. Different TTF cage molecules.

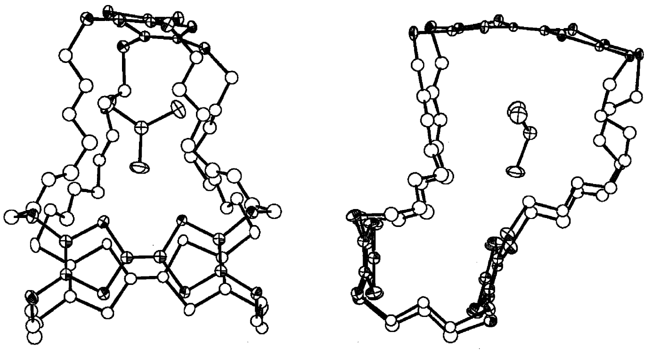
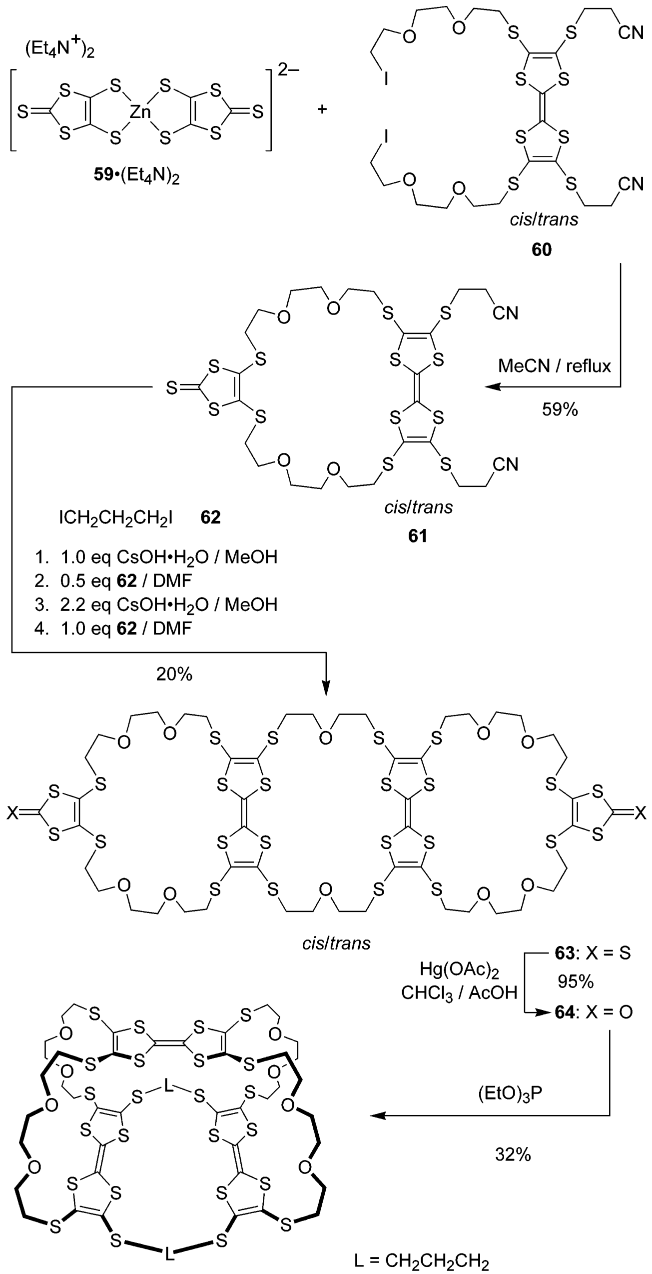


Figure 20. X-ray crystal structure of *cis*-**65**$\cdot CHCl_3$: top view (left) and side view (right). Hydrogen atoms are omitted for clarity. (Reprinted with permission from ref 36. Copyright 2000 Wiley-VCH.)

Scheme 17. Synthesis of the Tris-TFF Cage Molecule 65



clearly shows that the TTF cage molecule **65** adopts an all-*cis*-configuration, which is the least strained structure as predicted by Corey–Pauling–Koltun (CPK) models. The $CHCl_3$ molecule is included in the cavity formed by the TTF pair, the third TTF, and the glycol linkers. Electrochemical investigations carried out on **65** revealed three well-resolved redox peaks: a one-electron oxidation process at +0.49 V, a two-electron oxidation process at +0.57 V, and a three-electron oxidation process at +0.87 V. These results were explained as follows: (1) the first peak can be assigned to the oxidation process of one of the parallel-oriented TTF units, (2) the resulting monoradical cation is stabilized by intramolecular interaction between the two parallel-oriented TTF units, and (3) the first oxidation processes of the remaining TTF units thus overlap somewhat with the second peak.[36] By electrochemical crystallization of **65** in the presence of $(n\text{-Bu})_4NI_3$, crystals of the radical salt **65**$\cdot I_3 \cdot (ClCH_2CH_2Cl)$ were obtained. The structure was solved by X-ray crystallography and revealed that the oxidized TTF cage molecule **65**$^+$ has an all-cis configuration, as in the neutral state. A comparison of the structure of the neutral TTF cage molecule **65** with the structure of the oxidized **65**$^+$ showed that the two forms adopt completely different molecule shapes. The neutral end cavity that encapsulated one $CHCl_3$ molecule in the neutral **65** collapses completely upon oxidation as depicted in Figure 21, and the oxidized molecule **65**$^+$ folds to effectively minimize the volume of cavity.[36] These observations clearly illustrate that intramolecular interactions between the cationic and neutral TTF units are taking place and play an important role in the stabilization of the collapsed molecular shape of **65**$^+$.

As seen in the previous examples, incorporation of the tetrathio-TTF unit into cage molecules often results in the isolation of cis/trans isomeric mixtures. This inherent cis/trans isomerism may alter the complexing ability of the host.[37] By extension of the synthetic methodology used for the preparation

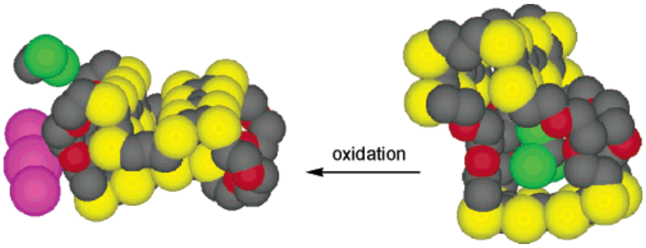


Figure 21. CPK model describing the change in the shape of the cavity in the tris-TTF cage molecule **65** upon oxidation. (Reprinted with permission from ref 36. Copyright 2000 Wiley-VCH.)

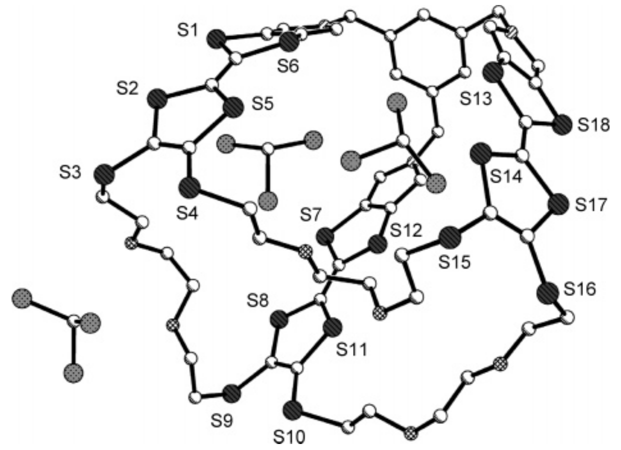
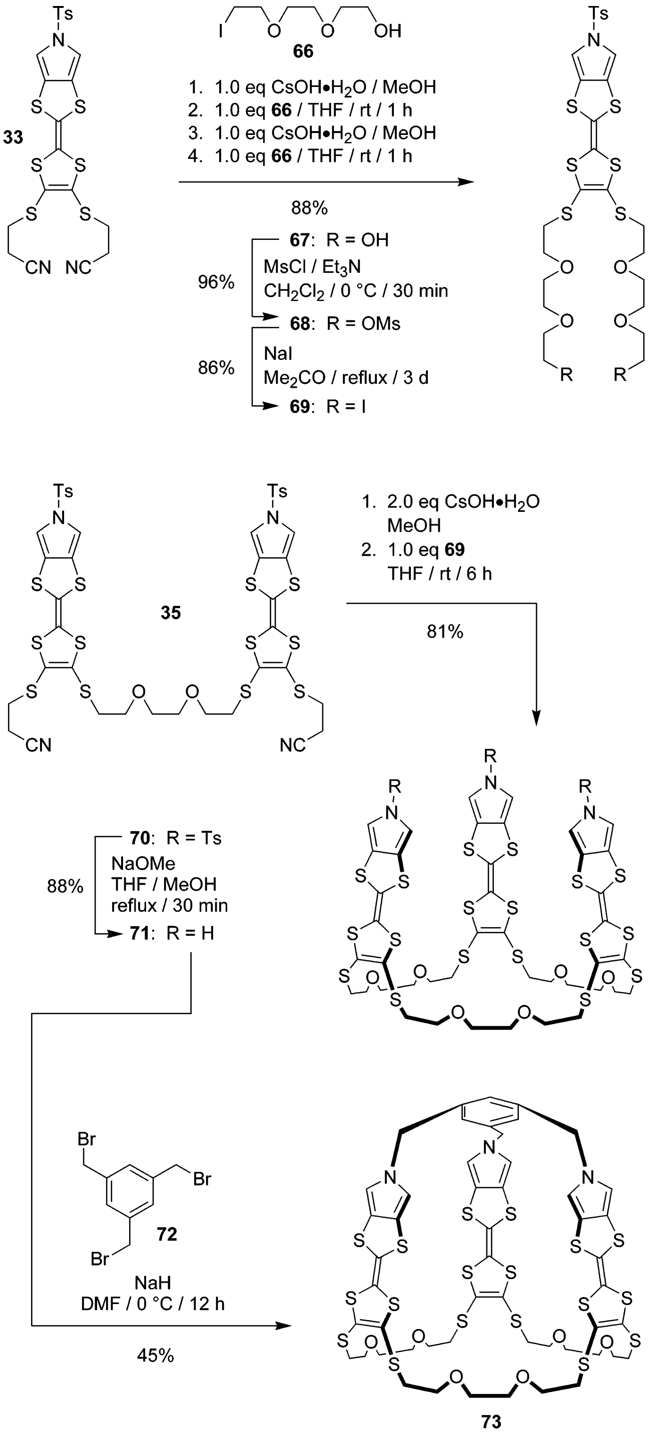


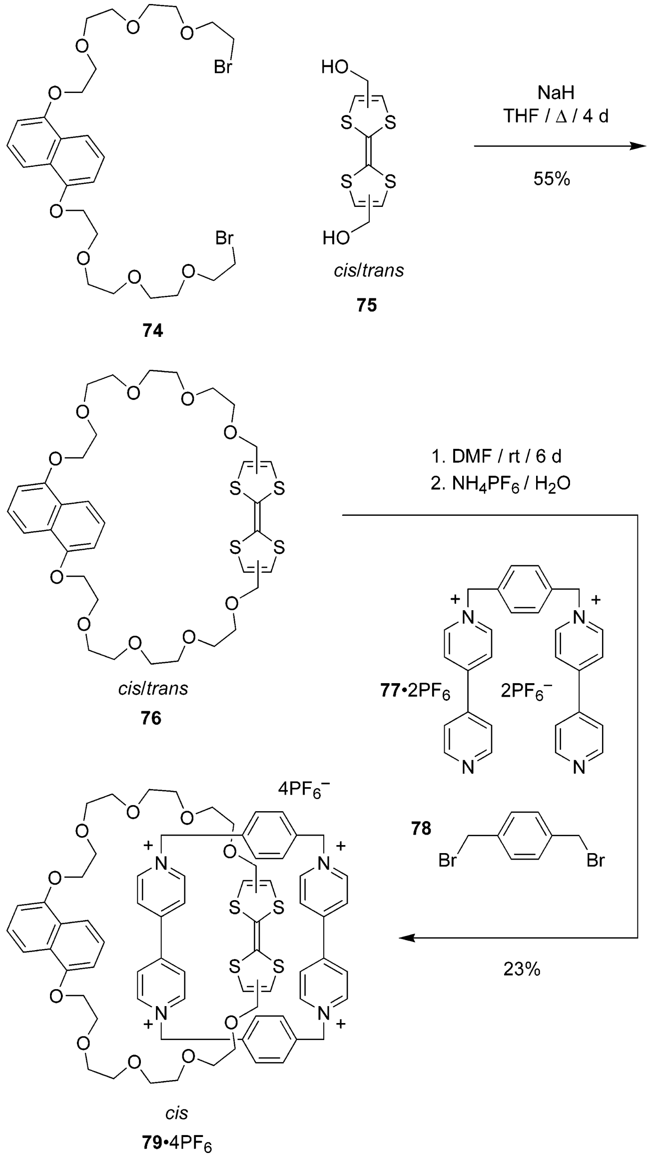
Figure 22. Crystal structure (from ref 38) of the tris-TTF cage molecule **73**. Hydrogen atoms are omitted for clarity.

Scheme 18. Synthesis of the Tris-TFF Cage Molecule 73 Devoid of *cis/trans* Isomerism



(Schemes 9 and 16) of the TTF-belt **56**, a general and efficient method for the synthesis of TTF cage molecules devoid of cis/trans problems have been developed.[38] The tris-TTF cage molecule **73** (Scheme 18) was designed to participate in host–guest chemistry,[3] and a CPK model suggests that **73** has a larger and more flexible cavity that that of the TTF-belt **56**, thereby increasing the likelihood for **73** to act as a host molecule for electron-deficient guests such as 1,3,5-trinitrobenzene. The tris-TTF cage molecule **73** was synthesized as illustrated in Scheme 18. A THF solution of the cyanoethyl-protected monopyrroloTTF building block **33** was treated with 1 equiv of cesium hydroxide monohydrate. This procedure generated the TTF-monothiolate, which was alkylated with 1 equiv of 2-[2-(2-iodoethoxy)ethoxy]ethanol (**66**). Subsequently, deprotection/alkylation with 1 equiv of cesium hydroxide monohydrate and 1 equiv of **66** gave (Scheme 18) the TTF derivative **67** in 88% yield. Mesylation (96%) of **67** in CH_2Cl_2 followed by treatment of **68** with sodium iodide in Me_2CO gave (86%) the TTF derivative **69**. Macrocyclization of the 36-membered ring system **70** was performed using high dilution conditions. A THF solution of **35** was treated with 2 equiv of cesium hydroxide monohydrate. This procedure generated the TTF-bisthiolate, which was alkylated with 1 equiv of the TTF derivative **69** under high dilution conditions, affording (Scheme 18) the tris-TTF macrocycle **70** in 81% yield. Removal of the tosyl protecting groups was carried out in 88% yield by boiling **70** in a 1:1 mixture of THF and MeOH in the presence of an excess of sodium methoxide. Finally, the tris-TTF cage molecule **73** was obtained in 45% yield following *N*-alkylations of the three pyrrole units in **71** with 1,3,5-tris(bromomethyl)benzene (**72**) in DMF containing sodium hydride. The structure of the tris-TTF cage molecule **73** was determined from mass spectrometry, NMR spectroscopy, and, above all, X-ray crystallography. The molecular structure of **73** is illustrated in Figure 22. The unit cell contains two TTF-cage molecules and six $CDCl_3$ molecules—three per tris-TTF cage molecule. Two of the $CDCl_3$ molecules reside inside the cavity of **73**, while the other is positioned outside the cage, indicating that the tris-TTF cage molecule is able to accommodate guest molecules. The fact that two $CDCl_3$ molecules reside inside the cavity of the solid-state structure of **73** may indicate that **73** can act as a host molecule for other guest molecules as well.[38] However, such experiments have yet not been reported.

Scheme 19. Synthesis of the [2]catenane 79·4PF$_6$



3.3. Miscellaneous

3.3.1. Catenanes

Catenanes (from the greek word catena meaning chain) are molecules containing two or more interlocked rings which cannot be separated without breaking a covalent bond. Since the mechanically interlocked components of suitable designed catenanes can be induced to change their relative positions, as a result of some well-chosen external stimulus, they are ideally suited for the construction of nanoelectronic devices because large-amplitude motion can be envisaged within such architectures without the risk of damaging the chemical structure of the system. The relative movements of the interlocked components can be triggered by chemical, electrochemical, and photochemical stimuli (input signal), forcing the molecule to switch between its two nondegenerate states. Stoddart and co-workers[39] developed a strategy for the formation of both catenanes and rotaxanes based on molecular recognition between π-electron donors and acceptors assisted by hydrogen bonding, and as consequence several TTF cyclophanes[15,19,28,40,41] have been used as the ring component in the preparation of catenanes based on the electron-poor tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}). The synthesis of a switchable [2]catenane,[41] **79**·4PF$_6$, is shown in Scheme 19. This catenane is composed of a type **I** cyclophane containing a TTF unit and a dioxynaphthalene (DNP) moiety catenated with CBPQT^{4+}. The design and synthesis of this switchable [2]catenane was guided by the fact that in solution, TTF and its derivative carrying polyether chains display[42] strong binding (K_a > 8000 M^{-1}) toward CBPQT^{4+}, whereas substrates incorporating similarly derivatized DNP moieties[43] are more weakly bound (K_a < 5000 M^{-1}). While the DNP moiety is difficult to oxidize, TTF units are readily oxidizable. The type **I** TTF cyclophane **76** was obtained[41b] as a cis/trans isomeric mixture by heating a mixture of the dibromide **74** carrying the DNP unit and the TTF derivative **75**. To complete the synthesis (Scheme 19) of **79**·4PF$_6$, the cyclophane CBPQT^{4+} was introduced by a clipping reaction.[44] Using the cyclophane **76** as the template for the formation of the encircling CBPQT^{4+} tetracation, the [2]catenane was self-assembled in 23% yield from the cyclophane **76**, the dicationic precursor **77**·2PF$_6$, and the dibromide **78**. X-ray crystal structure analysis (Figure 23a) was used to confirm[41b] that the TTF unit is encircled by the tetracationic cyclophane and that the TTF unit adopts a cis configuration in the catenane **79**·4PF$_6$. Under normal conditions the TTF unit is encircled exclusively by CBPQT^{4+} as result of CT interactions between the TTF unit and the paraquat moieties and hydrogen-bonding interactions between the oxygen atoms in the TTF cyclophane and the α-bipyridinium protons in CBPQT^{4+}. However, upon electrochemical (or chemical) oxidation of the TTF unit to the corresponding dication, circumrotation of the cyclophane occurs—as a consequence of electrostatic repulsion between charges—and the TTF unit inside CBPQT^{4+} is replaced by the DNP moiety. This process (Scheme 20) is completely reversible upon electrochemical (or chemical) reduction of the TTF dication and hence provides the basis for a reversible molecular switch. The spectroscopic properties of **79**·4PF$_6$ change according to the oxidation state of the TTF unit, and the absorption spectra recorded of the different oxidation states of **79**·4PF$_6$ are depicted in Figure 24. When the TTF unit is in its neutral oxidation state (i.e., TTF^0), a broad absorption band is observed (Figure 24a) at λ_{max} = 835 nm which can be associated with the CT interaction that occurs when the TTF unit is located inside CBPQT^{4+}. In agreement with this interpretation, the CT absorption band characteristic of a DNP moiety (λ_{max} = 515 nm) being encircled by CBPQT^{4+} is absent in the spectrum. After oxidation of the TTF unit, the absorption band at 835 nm disappears and the absorption features of the TTF radical cation (Figure 24c) and TTF dication (Figure 24d) appear. Ultimately, the CT absorption

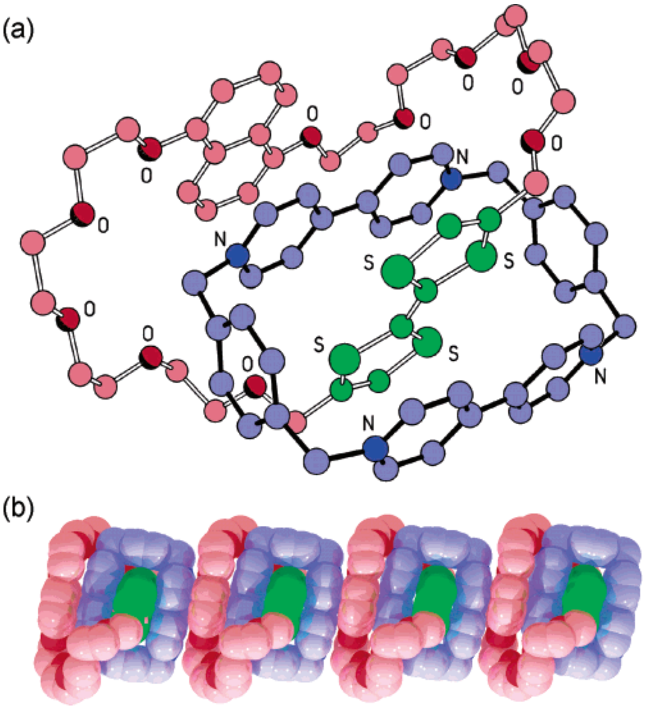
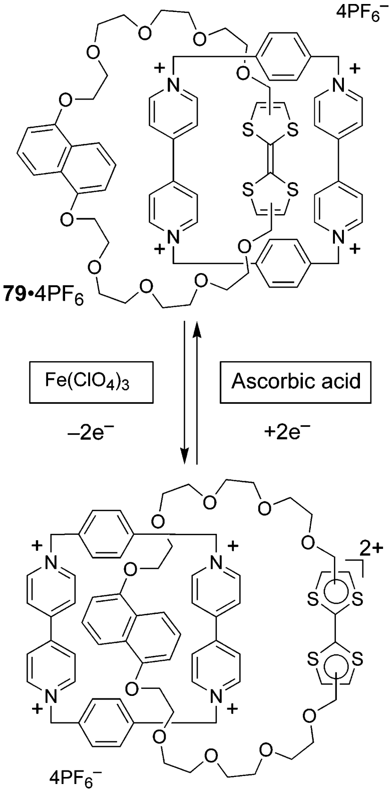


Figure 23. (a) Molecular structure (from ref 45) of the [2]catenane **79**·4PF$_6$ and (b) its packing in the solid state. Hydrogen atoms are omitted for clarity.

Scheme 20. Switching of the [2]catenane 79·4PF$_6$



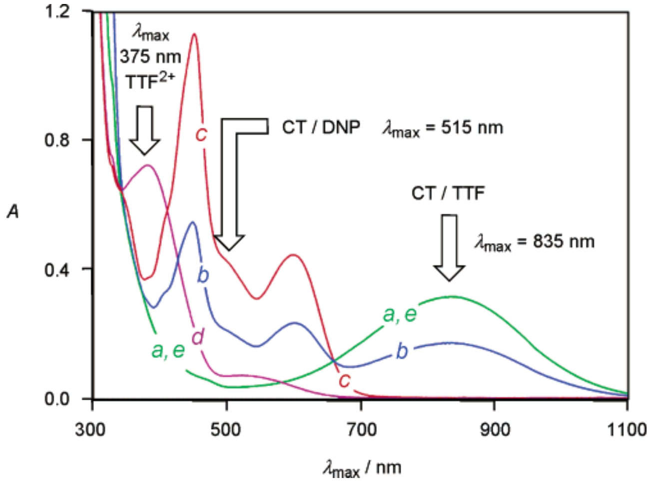
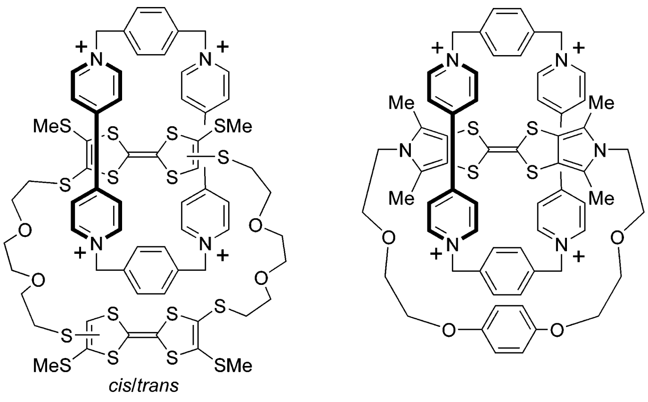


Figure 24. UV–vis spectra (from ref 45) recorded at room temperature in MeCN of the [2]catenane **79**·4PF$_6$: (a) starting [2]catenane, (b and c) progressive addition of 1 equiv of Fe(ClO$_3$)$_4$, (d) after addition of 2 equiv of Fe(ClO$_3$)$_4$, and (e) after further addition of 2 equiv of ascorbic acid.



80•4PF$_6$ **81**•4PF$_6$

Figure 25. Molecular formulas of the TTF-encircled [2]catenanes **80**·4PF$_6$ and **81**·4PF$_6$.

band for a DNP moiety being located inside CBPQT^{4+} appears at λ_{max} = 515 nm. In the solid state (Figure 23b) the [2]catenane **79**·4PF$_6$ is arranged as continuous polar π-electron D–A stacks. This arrangement of largely hydrophilic molecules can be transformed into a monolayer on a Langmuir trough using hydrophobic dimyristoylphosphatidic (DMPA$^-$) counterions. This act of self-assembly provides the opportunity to prepare molecular junctions[45–47] where these electroactive molecules are sandwiched between two metal electrodes. The device fabricated from the [2]catenane **79**·4PF$_6$ is stable, and it can be cycled over approximately a 2-month period before there is any appreciable decrease in its performance.[46]

Encirclement of one of the TTF units in the type **III** TTF cyclophane **27** by CBPQT^{4+} affords the [2]catenane **80**$^{4+}$ (Figure 25), which showed a CT absorption band centered at λ_{max} = 799 nm in its UV–vis spectrum recorded in MeCN.[19] This CT band is significantly red shifted relative to that observed for the related D–A cyclophanes **8**$^{2+}$ (λ_{max} = 650–675 nm).

In the case of the bis(2,5-dimethylpyrrolo)TTF-based catenane **81**$^{4+}$, a CT absorption band is observed at λ_{max} = 699 nm in the UV–vis spectrum recorded in MeCN,[15] a value which should be compared to 640 nm found for the D–A cyclophane **10**$^{2+}$.

4. Conclusions

Since the first TTF cyclophanes were prepared by Staab and co-workers in 1980, an immense number of TTF cyclophanes and TTF cage molecules have been prepared. In particular, the cyanoethyl deprotection/realkylation protocol has allowed the ready incorporation of TTF-thiolates into cyclophane structures via stepwise procedures. Rigid TTF cyclophanes have contributed to a fundamental understanding of CT interactions involving TTF and different acceptors, such as paraquat, diquat, and PMDI. Larger cyclophanes and cage molecules have been successfully exploited for inclusion of electron-poor guest molecules; yet the stoichiometry of these complexes was often found to differ in the solid and solution states. TTF cyclophanes have also been employed for the template-assisted formation of interlocked cyclobis(paraquat-*p*-phenylene) with the formation of catenanes as the result. Taking advantage of the three reversible redox states of the TTF unit, these mechanically interlocked molecules are ideally suited for the construction of nanoelectronic devices since controlled switching between different translational isomers can be controlled by the oxidation state of the TTF unit.

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