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# Bi-TTF, Bis-TTF, and Related TTF Oligomers

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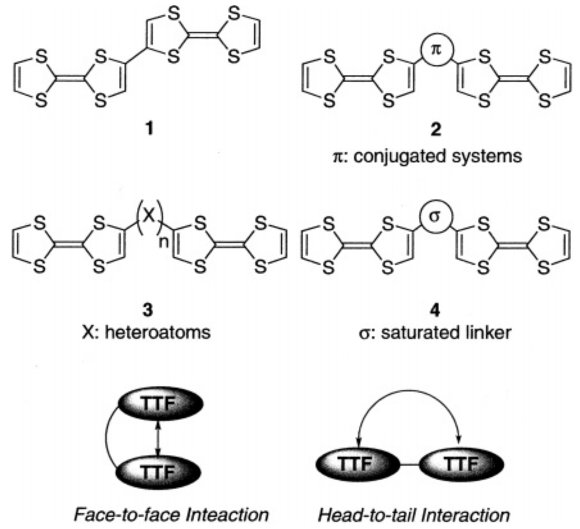
## *Contents*

## *1. Introduction*

Tetrathiafulvalene (TTF) dimers and higher oligomers are currently attracting a lot of interest.[1−5] TTF dimers **1**−**4** linked by $\sigma$-bonds, conjugated $\pi$-systems, chalcogen atoms, or alkyl chains may have intramolecular through-bond or through-space interactions between two TTFs (Chart 1). Thus, the intramolecular through-bond interaction can be made up of the two TTF parts in a head-to-tail manner, although the conjugation of the two neutral and/or TTF parts in **1**−**3** is weak in the ground state. In contrast, an intramolecular through-space interaction can be constructed in **4**, and the face-to-face stacking structure thus formed is stabilized weakly in the neutral state and strongly in the cationic states. As a result of the intramolecular interaction, dimeric TTFs display multistage redox behavior; hence, their CT complexes and ion radical salts might exhibit unique structures and have interesting properties such as unusual electric conductivities, ferromagnetism, electrochromism, solvatochromism, and optical nonlinearity. For example, bi-TTF **1** is a four-electron redox system, and the cation radical, dication, and more highly oxidized species $\mathbf{1}^{\bullet+}$, $\mathbf{1}^{2+}$, $\mathbf{1}^{3+}$, and $\mathbf{1}^{4+}$ can exist in localized or delocalized forms. In addition, dimeric and oligomeric TTFs may be employed for either enhancement of the dimensionality by the extended $\pi$-conjugation or controlling the stoichiometry and band filling in the corresponding conductive complexes to lead to organic metals.[6,7]

**Chart 1**



Recently, dimeric and oligomeric TTFs have come to be regarded as building blocks in supramolecular chemistry, and large “belt-shaped” molecules, cage molecules, “tweezer-like” molecules, dendrimers, and “molecular shuttles” have been investigated in order to realize redox sensors, conducting organic magnets, and novel crystal structures.[8−10] By considering earlier reviews[1−5,7−11] in which dimeric and oligomeric TTFs have been summarized by focusing on specific structures and properties, this review covers a wide range of the chemistry of bi-TTF **1**, bis-TTF **2**−**4**, their derivatives, and related higher oligomers with one or more spacer groups.[11] However, cyclophanes and tetrathiapentalenes are discussed only in a limited number of cases.

## *2. Bi-TTF and Related Compounds*

### 2.1. Synthesis

Among dimeric and oligomeric TTFs, the simplest bi-TTF **1** is a feasible candidate for constructing organic metals with enhanced dimensionality based on a $\pi$-expanded system. It provides the opportunity to control the stoichiometry, band filling, and molecular assembly in the desired conductive complexes.[6] Although bi-TTF **1** was first reported in 1982 in an abstract for a conference, no physical and spectral data were presented.[12] The second synthesis of **1**,

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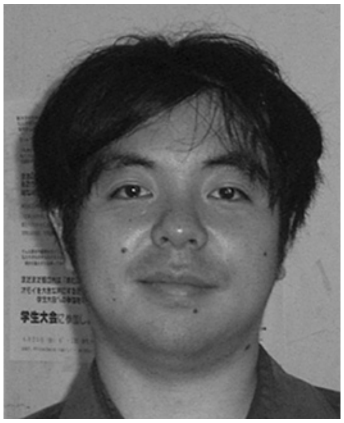
Masahiko Iyoda was born in Okazaki, Japan, in 1946. He received his B.S. (1969) and M.S. (1971) degrees in Chemistry from Nagoya University and his Ph.D. degree in Organic Chemistry from Osaka University in 1974 under the supervision of Professor Masazumi Nakagawa. After postdoctoral work at Osaka University and the University of Cologne (with Professor Emanuel Vogel), he returned to Osaka University in 1977 and became Assistant Professor in 1978. In 1988 he became Associate Professor at the Department of Chemistry, Osaka University. In 1991 he moved to Tokyo Metropolitan University as Full Professor. He was honored with the Chemical Society of Japan Award for Young Chemists (1978). He is currently serving as Associate Editor of *Chemistry Letters*. His current research interests are focused on synthesis of functional $\pi$-electron systems and their applications in material science.



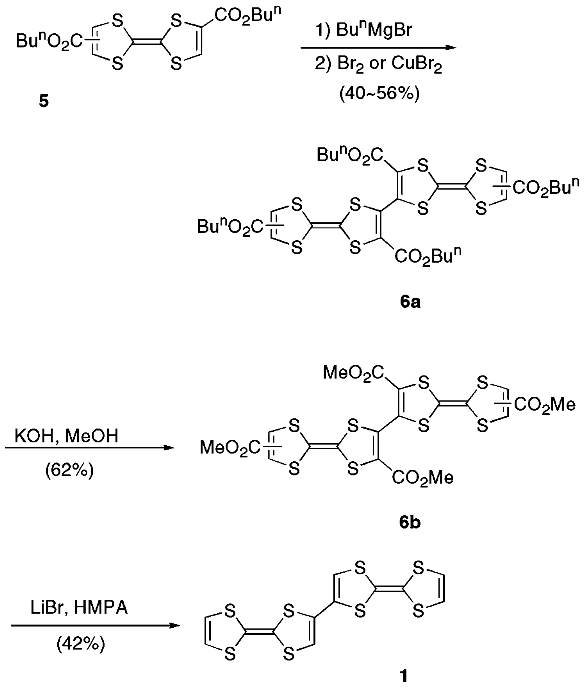
Masashi Hasegawa was born in Tokyo, Japan, in 1977. He graduated from Tokyo Metropolitan University with his B.S. (2000), M.S. (2002), and Ph.D. degrees (2004) under the supervision of Professor Masahiko Iyoda with his thesis titled Construction of Supramolecular Structures Using $\pi$-Extended Tetrathiafulvalene Oligomers. Since 2004 he has worked as a research fellow of the Japan Society for the Promotion of Science. His current research interests are focused on synthesis and supramolecular chemistry of organic $\pi$-donors directed to a construction of functional networks.

with spectral characterization, was reported by Neilands and co-workers in 1989 using coupling of the Grignard reagent and decarboxylation (Scheme 1).[13] Thus, the reaction of **5** with butylmagnesium bromide, followed by treatment with bromine or $CuBr_2$, produced **6a** in 40−56% yield. Transesterification of **6a** with KOH in methanol afforded **6b**, which was converted into **1** by decarboxylation with LiBr in HMPA.

For the synthesis of **1**, Ullmann coupling of iodo-TTF **8** was reported by Becker and Khodorkovsky (Scheme 2).[14a] Lithiation of TTF with LDA (1.5 equiv) followed by treatment with perfluorohexyl iodide afforded iodo-TTF **8**.[14b] The reaction of **8** with copper proceeded at 130−140 °C to give **1** in 22% yield together with a TTF trimer **10** (1−3%). The production of **10** may be due to a small amount of diiodo-TTF **9** contamination in the **8** employed for the Ullmann reaction.

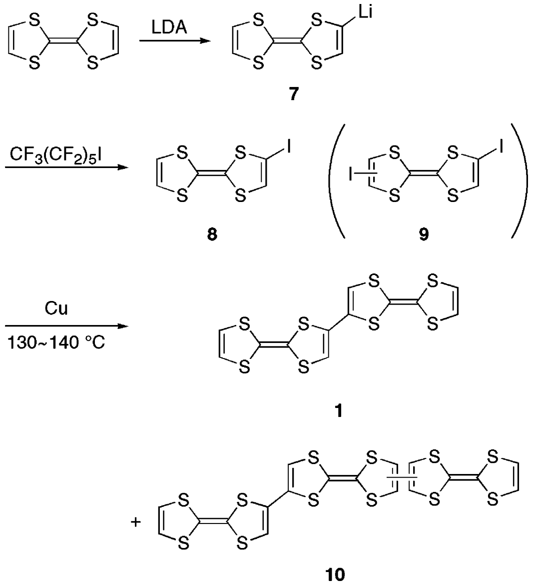
Yoshihiro Miyake was born in Hiroshima, Japan, in 1974. He graduated from Kyoto University, where he received his Ph.D. degree under the supervision of Professor Sakae Uemura in 2002. After postdoctoral research at the Japan Science and Technology Agency for a short time, he has worked as Assistant Professor at the Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, since 2002. His current research interests are focused on novel effective methodologies in organic synthetic chemistry using transition-metal complexes and synthetic and physical studies of multifunctional organic molecules.

**Scheme 1**

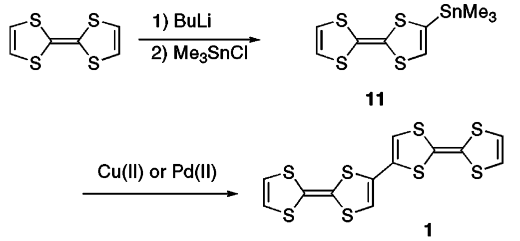


For the synthesis of substituted or dimeric TTFs, we introduced a new methodology based on the copper- or palladium-mediated coupling of trimethylstannyl-TTF **11** (Scheme 3).[15,16] Thus, TTF was first converted into **11** in 86% yield. For the transition-metal-catalyzed homocoupling of **11**, Pd(II) complexes were employed, and the reaction of **11** with stoichiometric amounts of $Pd(OAc)_2$ in benzene at room temperature produced **1** in 67% yield, together with the recovered TTF (20%). Although the reaction of **11** with $PdCl_2(CH_3CN)_2$ in HMPA or $PdCl_2(PPh_3)_2$ in benzene afforded **1** in 62% or 58% yield, respectively,

**Scheme 2**



**Scheme 3**

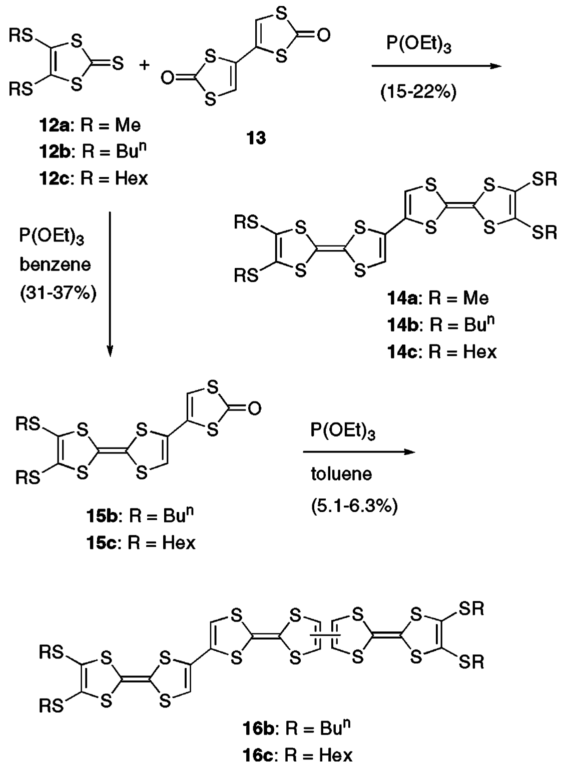


| | |
|---|---|
| $PdCl_2(CH_3CN)_2$ | 62 % |
| $PdCl_2(PPh_3)_2$ | 58 % |
| $Pd(OAc)_2$ | 67 % |
| $Pd(OAc)_2$ / *t*-BuOOH | 8 % |
| $Cu(NO_3)_2$•$3H_2O$ | 70 % |

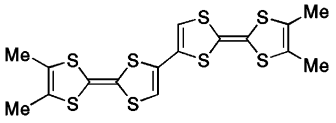
no TTF was recovered in the former reaction and the reaction time required was much longer in the latter case. The homocoupling reaction of tributylstannylbenzene with a catalytic amount of $Pd(OAc)_2$ in the presence of *t*-BuOOH (excess) was reported to produce the corresponding biphenyl in good yield.[17] However, a similar reaction of **11** under similar conditions produced **1** in 8% yield together with 72% yield of TTF (protodestannylation product). In addition, the $Cu(OAc)_2$-mediated homocoupling of **11** in THF at room temperature produced **1** in 70% yield. Although $Cu(OAc)_2$ sometimes oxidizes TTF and its derivatives to the corresponding cation radicals, the reaction of **11** with $Cu(OAc)_2$ proceeds smoothly to afford **1** in a good yield.

For alkylthio derivatives of **1**, Tatemitsu and coworkers reported the synthesis of the tetraalkylthio-bi-TTFs **14a**–**c** using the phosphite-mediated cross-coupling method (Scheme 4).[18,19] Thus, the reactions of **12a**–**c** with **13** in $P(OEt)_3$ at 140 °C yielded the 2:1 coupling products **14a**–**c**. When the $P(OEt)_3$-mediated coupling of **12b**,**c** with **13** was carried out in refluxing benzene, the 1:1 coupling products **15b**,**c** were obtained in 37% and 31% yields, respectively. The homocoupling reactions of **15b**,**c** with $P(OEt)_3$ in refluxing toluene afforded the corresponding trimers **16b**,**c**.

**Scheme 4**



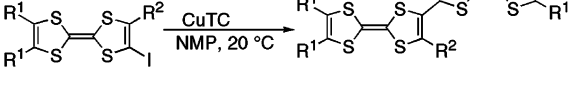
Tetramethyl-bi-TTF **17** was first prepared by a multistep synthesis.[20] Recently, Bryce and co-workers reported a new methodology for the synthesis of bi-TTF derivatives.[21,22] As shown in Scheme 5, the reactions of **18a**–**d** with copper(I) thiophene-2-carboxylate (CuTC) in 1-methylpyrrolidin-2-one (NMP) at 20 °C proceeded smoothly to produce the corresponding coupling products **19a**, **19b**, **19c**, and **19d** in 75%, 65%, 80%, and 72% yields, respectively. Decarboxylation of **19d** with LiBr in DMF at 140 °C afforded **14a** in 59% yield. In the case of **18e**, however, the Ullmann coupling of **18e** with Cu powder produced **19e** in 62% yield.[22]



**17**

To synthesize the bi-TTF derivatives **14a**, **26**, and **27**, we applied palladium-mediated homocoupling similar to that in the synthesis of **1**.[16,23] As shown in Scheme 6, BMT-TTF **20**, EDT-TTF **21**, and EDO-TTF **22** were converted into their corresponding trimeth-

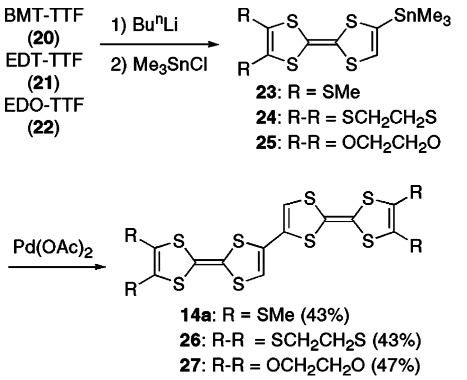
**Scheme 5**



**18a**: $R^1$ = Me, $R^2$ = Me
**18b**: $R^1$ = SMe, $R^2$ = Me
**18c**: $R^1$ = $R^2$ = SMe
**18d**: $R^1$ = SMe, $R^2$ = $CO_2Me$
**18e**: $R_1$ -$R_1$ = $SCH_2CH_2S$, $R_2$ = Me

**19a**: $R^1$ = Me, $R^2$ = Me
**19b**: $R^1$ = SMe, $R^2$ = Me
**19c**: $R^1$ = $R^2$ = SMe
**19d**: $R^1$ = SMe, $R^2$ = $CO_2Me$
**19e**: $R_1$ -$R_1$ = $SCH_2CH_2S$, $R_2$ = Me

**Scheme 6**

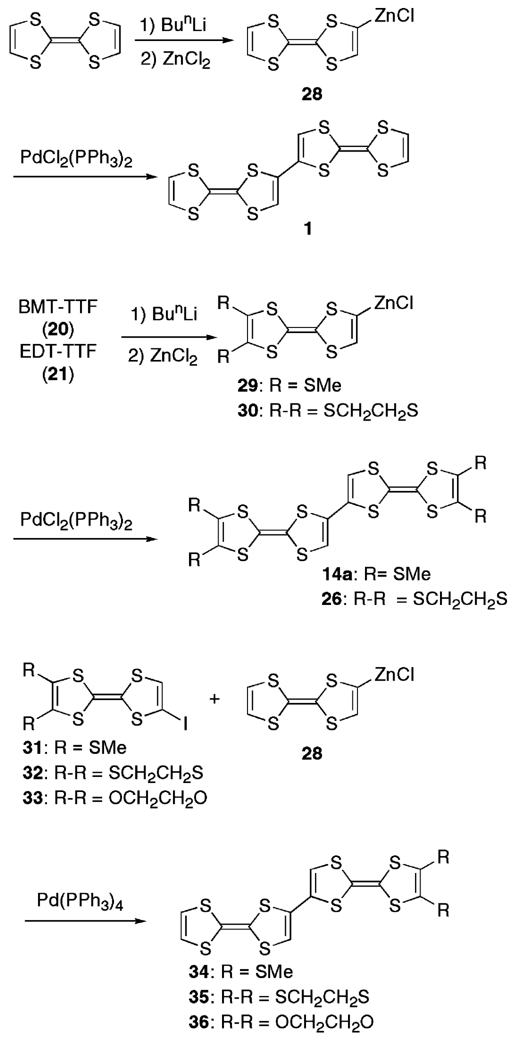


yltin-substituted derivatives **23**, **24**, and **25** in 55%, 48%, and 29% yields, respectively. Although the reactions of **23**−**25** with $Cu(NO_3)_2$ in THF were unsuccessful due to decomposition of the products, the $Pd(OAc)_2$-mediated coupling of **23**−**25** proceeded smoothly in benzene to produce the bi-TTF derivatives **14a**, **26**, and **27** in 43%, 43%, and 47% yields, respectively. All reactions form protodestannylation products, i.e., the starting TTFs **20**−**22**, which can be used again for the synthesis of the organotin(IV) compounds **23**−**25**.

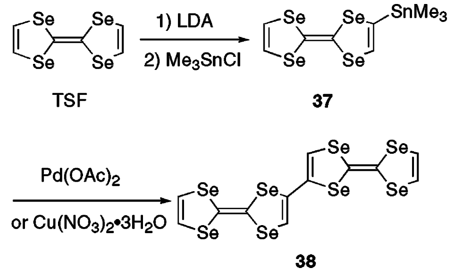
The transition-metal-catalyzed coupling of organozinc species derived from TTF and its derivatives can also be employed for the synthesis of symmetrically and asymmetrically substituted bi-TTF derivatives (Scheme 7).[16,24] Thus, a reddish-brown solution of TTFZnCl **28** in THF is prepared from the monolithiated TTF **7** with 1.2 equiv of anhydrous $ZnCl_2$, and the solution is used for the coupling reactions without further purification. Although TTF-Li **7** is unstable at 0 °C and disproportionates to TTF and $TTFLi_2$,[25] the zinc species **28** is stable in solution at 0 °C and shows no decomposition or disproportionation. For the homocoupling as shown in Scheme 7, a stoichiometric amount of $PdCl_2(PPh_3)_2$ (0.5 equiv) was added to a solution of **28** in THF to produce bi-TTF **1** in 57% yield based on the consumed TTF (13% of the recovered TTF). Similarly, the homocoupling of zinc species **29** and **30** with $PdCl_2(PPh_3)_2$ in THF afforded **14a** and **26** in 70% and 80% yields, respectively. For the cross-coupling, the reaction of **28** (1.7−2 equiv) with the iodo-TTF derivatives **31**, **32**, and **33**[26−29] (1 equiv) in the presence of $Pd(PPh_3)_4$ (10 mol %) in THF led to the asymmetrical bi-TTFs **34**, **35**, and **36** in 88%, 70%, and 20% yields, respectively. The low yield of **36** is presumably due to the difficulty in isolating the product from the reaction mixture.

Bi-tetraselenafulvalene (bi-TSF) **38** has been synthesized to design highly conducting CT complexes and radical salts.[30] As shown in Scheme 8, the reaction of TSF with LDA (2 equiv) followed by treatment with chlorotrimethyltin (1 equiv) afforded **37**. The reaction of **37** with $Pd(OAc)_2$ in benzene or $Cu(NO_3)_2$ in THF at room temperature produced **38** in 33% or 39% yield together with the recovered TSF (47% or 56%), respectively. Consequently, **38** was synthesized with an overall yield of 87% based on the consumed TSF.

**Scheme 7**

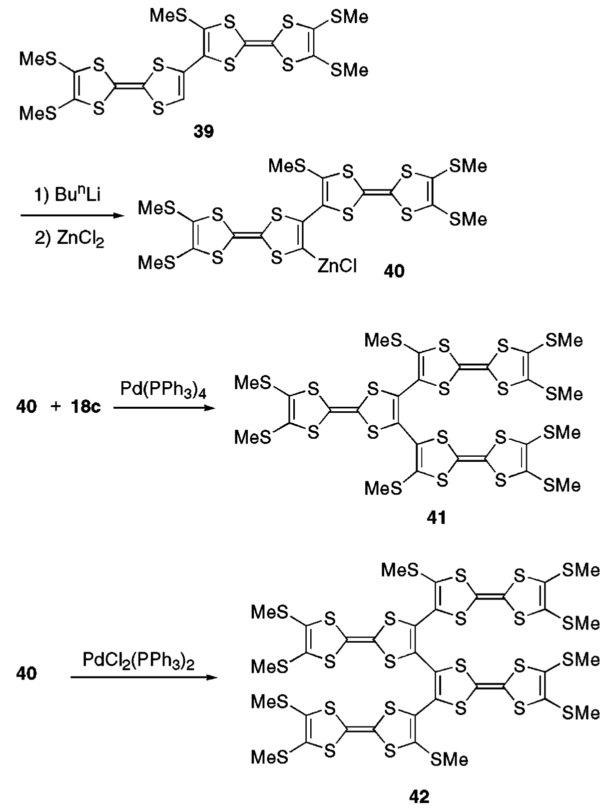


**Scheme 8**

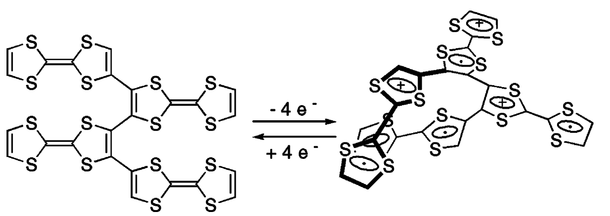


Our procedure for synthesizing dimeric and oligomeric TTFs was applied to the synthesis of ter- and quarter-TTFs **41** and **42** (Scheme 9).[24] Thus, the reaction of **39** with butyllithium, followed by $ZnCl_2$, formed the organozinc intermediate **40**. Cross-coupling of **40** with **18b** in the presence of $Pd(PPh_3)_4$ (20 mol %) produced **41** in 69% yield based on the recovered starting **39**. As for the synthesis of **42**, the homocoupling of **40** using a stoichiometric amount of $PdCl_2(PPh_3)_2$ (50 mol %) resulted in the formation of **42** (52% based on the recovered **39**). The PM3 calculations of **41** and **42** suggest nonplanar structures with a zigzag conformation. The two TTF units at the terminal positions of **41** cannot interact in a face-to-face manner; however, the two

**Scheme 9**

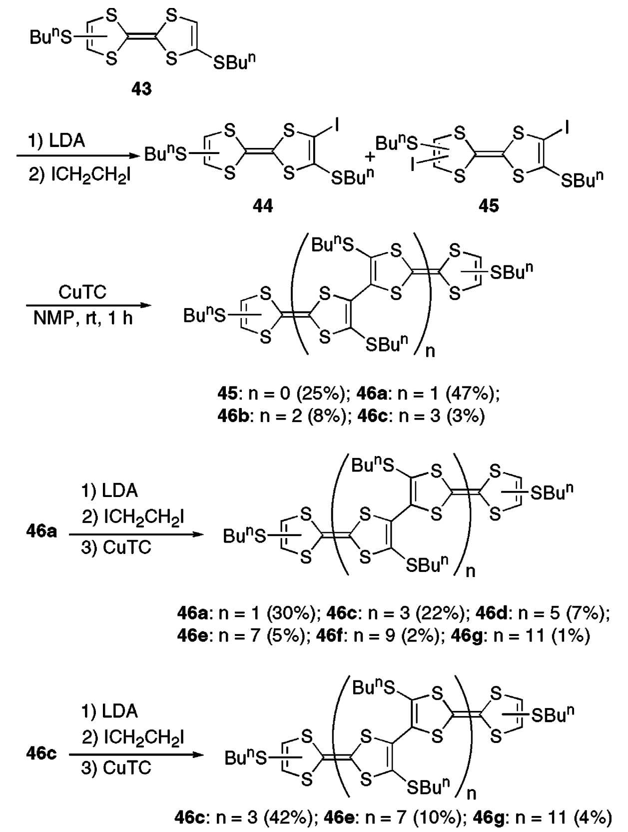


terminal TTFs in **42** may interact with each other by a helical arrangement.

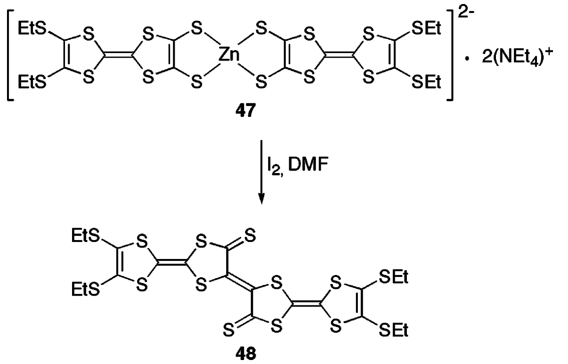


For the linearly extended TTF oligomers, Neiland and co-workers first prepared regioisomeric mixtures of trimers and tetramers as byproducts of the synthesis of **6a**, but no important properties were reported.[13] Recently, Takimiya and Otsubo prepared a series of dimeric and oligomeric TTFs **46a**–**g** (Scheme 10).[31] Although the oligomers **46b**–**g** comprise various isomeric mixtures due to the *E*/*Z* configurations, the structures of these oligomers were well characterized by MS and NMR spectroscopy. The electronic absorption spectrum of monomer **43** exhibits $\pi$–$\pi^*$ transition bands at 306, 321, and 380 nm. The longest shoulder absorption in **46a** is red shifted to 405 nm due to conjugation. However, the electronic spectra of the trimer and higher oligomers **46b**–**g** are nearly superimposable on that of **46a**, although the intensity still increases with increasing TTF units. This means that there is a very limited length for effective conjugation in the oligomeric TTF chain.

**Scheme 10**



**Scheme 11**



Interestingly, treatment of **47** with iodine in DMF resulted in the formation of bis(thioxotetrathiafulvalenylidene) **48** in 63% yield (Scheme 11).[32] The redox process of **48** is composed of four one-electron-transfer steps, i.e., $\mathbf{48}^{\bullet+}$, $\mathbf{48}^{2+}$, $\mathbf{48}^{3+}$, and $\mathbf{48}^{4+}$. The first oxidation potential of **48** shows good donor ability comparable to those of tetrakis(ethylthio)-TTF and BEDT-TTF. In addition, **48** has the longest absorption maximum at 1118 nm ($\epsilon = 6.03 \times 10^3$), reflecting its planar structure.

## 2.2. Structures and Properties

The structures of **1**, **14a**, **19a**, **c**, **27**, **38**, and **48** have been determined by X-ray analysis.[14a,16,21,22,32] As shown in Figures 1 and 2, **14a** and **27** have a crystallographic $C_i$ symmetry and a 2-fold axis passing through the C(1)–C(1*) bond between two TTF units. The central $S_2C_2S_2$ moiety of each TTF unit in **14c** and **27** is exactly planar, and both TTF units have an almost planar structure with a zigzag conformation. Similarly, **1**, **38**, and **48** are planar molecules, whereas **19a** and **19c** have a twisted structure. The torsion angles around the central bond in **19a** and **19c** are 54° and 89°, respectively.

The oxidation potentials of **1**, **14a**, **19c**, **26**, **27**, **34**–**36**, **38** and 4-phenyl-TTF (4-Ph-TTF), together with

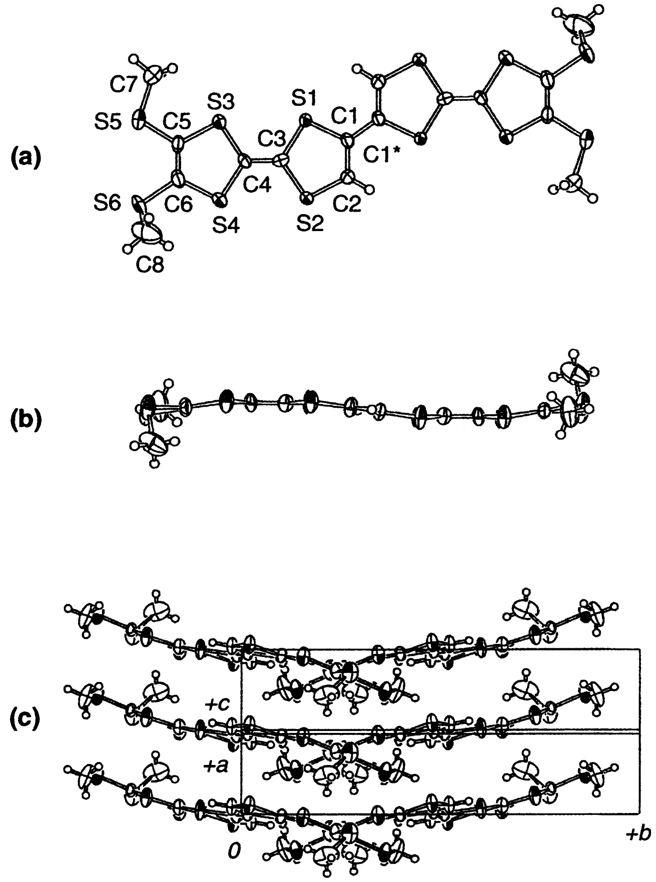


**Figure 1.** X-ray structure of TMT-bi-TTF **14a**. (a) View of the best molecular plane. (b) View perpendicular to that shown in (a). (c) Crystal structure. Selected distances (Å) for **2** are as follows: S(1)–C(1) 1.76(1), S(1)–C(3) 1.76(1), S(2)–C(2) 1.73(1), S(2)–C(3) 1.75(1), C(1)–C(1)* 1.43(2), C(1)–C(2) 1.37(1), C(3)–C(4) 1.34(1). (Reproduced with permission from ref 16. Copyright 2002 Academic Press.)

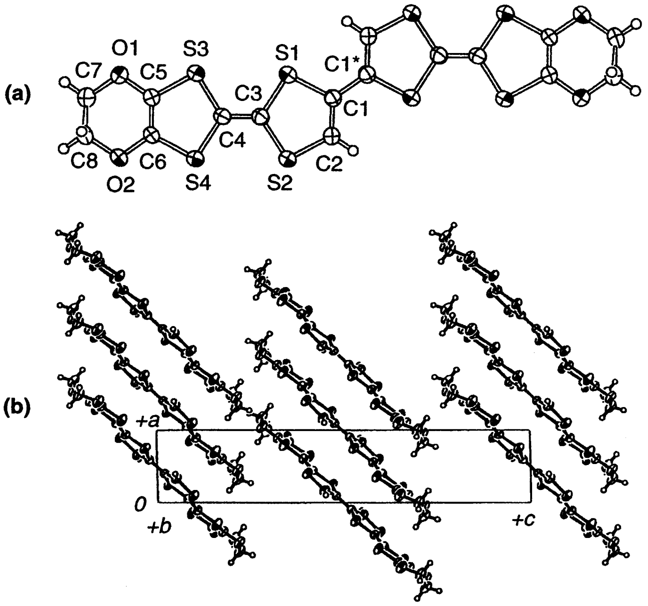


**Figure 2.** X-ray structure of BEDO-bi-TTF **27**. (a) Top view of the molecule. (b) Crystal structure. Selected distances (Å) for **27** are as follows: S(1)–C(1) 1.759(3), S(1)–C(3) 1.758(2), S(2)–C(2) 1.730(3), S(2)–C(3) 1.751(3), C(1)–C(1)* 1.441(4), C(1)–C(2) 1.337(3), C(3)–C(4) 1.331(3). (Reproduced with permission from ref 16. Copyright 2002 Academic Press.)

**Table 1. Redox Potentials of Bi-TTFs 1, 14a, 19c, 26, 27, 34–36, 38, and Related Compounds**[a]

| compound | solvent | $E_1^{1/2}$ | $E_2^{1/2}$ | $E_3^{1/2}$ | refs |
|---|---|---|---|---|---|
| TTF | PhCN | 0.36 | 0.77 | | 16 |
| BMT-TTF | PhCN | 0.44 | 0.77 | | 16 |
| EDT-TTF | PhCN | 0.45 | 0.81 | | 16 |
| EDO-TTF | PhCN | 0.39 | 0.76 | | 16 |
| **1**[b] | $CH_3CN$ | 0.45 | 0.65 | 0.97 | 13 |
| **1** | PhCN | 0.43 | 0.84 | | 15, 16 |
| **14a** | $CH_2Cl_2$ | 0.50 | 0.59 | 0.85 | 19 |
| **14a** | PhCN | 0.52 | 0.63 | 0.87 | 16 |
| **19c**[c] | $CH_3CN$ | 0.53 | 0.60 | 0.77 | 22 |
| **19c** | PhCN | 0.58 | 0.85 | | 24 |
| **26** | PhCN | 0.52 | 0.62 | 0.87 | 16 |
| **27** | PhCN | 0.46 | 0.55 | 0.87 | 16 |
| **34** | PhCN | 0.47 | 0.62 | 0.86 | 16 |
| **35** | PhCN | 0.46 | 0.68 | 0.89 | 16 |
| **36** | PhCN | 0.42 | 0.54 | 0.86 | 16 |
| **38** | PhCN | 0.45 | 0.71[d] | | 26 |
| 4-Ph-TTF | PhCN | 0.38 | 0.80 | | 15, 16 |

[a] Conditions: $Bu_4NClO_4$; 100 m V $s^{-1}$; rt; potentials referred to SCE unless otherwise stated. [b] Reference: Ag/AgCl. [c] Reference: decamethylferrocene. [d] The anodic potential.

those of TTF, BMT-TTF, EDT-TTF, and EDO-TTF, measured by cyclic voltammetry (CV) under similar conditions, are summarized in Table 1. Although the solubilities of **26** and **38** are fairly low in common organic solvents, voltammograms that could be assigned clearly were obtained using benzonitrile as the solvent. As shown in Table 1, the CV analysis of bi-TTFs **1** and **19c** and bi-TSF **38** indicates two redox waves in benzonitrile as the solvent,[15,16] whereas oxidation of **1** and **19c** in acetonitrile was reported as a three-step process.[13,22] By contrast, **14a**, **26**, **27**, and **34**–**36** in benzonitrile show three redox waves in which the third redox process seems to be a two-electron oxidation. 4-Ph-TTF shows a slightly higher first oxidation potential ($E^1{}_{1/2}$ = 0.38 V) than TTF ($E^1{}_{1/2}$ = 0.36 V),[15] whereas bi-TTF **1** has a much higher first oxidation potential ($E^1{}_{1/2}$ = 0.43 V) than TTF, presumably due to the larger electron-withdrawing effect of the TTF moiety as compared to the phenyl group. Although the bond formation between two TTF molecules at the 4 position causes the first oxidation potentials to shift in the positive direction by 0.03–0.12 V, the oxidation potentials ($E^1{}_{1/2}$) of **1**, **14a**, **26**, **27**, and **34**–**36** are much lower than that ($E^1{}_{1/2}$ = 0.55 V) of BEDT-TTF, which is a well-known donor. In the case of bi-TSF **38**, this compound shows lower oxidation potentials than TSF. Therefore, bi-TTFs and bi-TSF can be expected to show good donor ability.

The redox behavior of bi-TTFs and bi-TSF suggests that the through-bond interaction between the two TTF or TSF units is weak in the neutral, cation radical, and dicationic species derived from bi-TTFs and bi-TSF,[33] although the face-to-face through-space interaction between the two TTF units is known to be strong enough to form a mixed-valence state or charge-delocalized $\pi$-dimer in the cation radical or dicationic species, respectively.[34] There are three possible resonance structures for the cation radical $\mathbf{1}^{\bullet+}$ (Figure 3). The first electronic structure shown in Figure 3a has little or no delocalization of the cation radical charge, although a slow migration of the charge occurs [Class I]. In the case of nonplanar bi-TTFs, the weak conjugation through the central

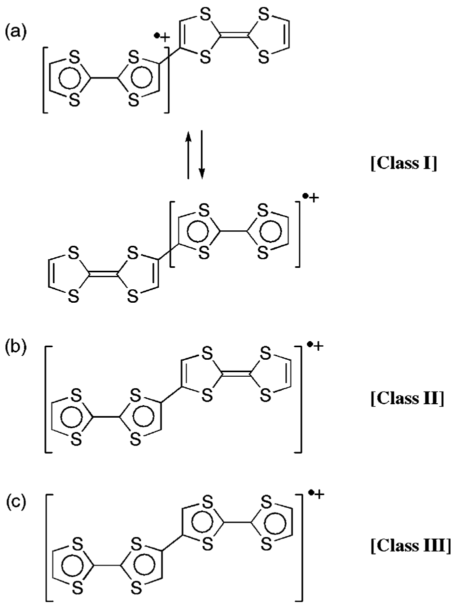


**Figure 3.** Three possible structures of the cation radical $1^{\bullet+}$.

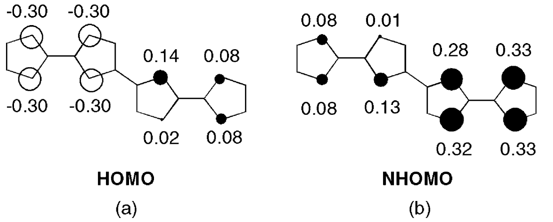


**Figure 4.** Electron density in HOMO (a) and NHOMO (b) ($\Delta E = 0.08$ eV) of **1** calculated by extended HMO.

pivot bond reduces the interaction of the two rings to form the Class I state. The second structure shown in Figure 3b is a slightly delocalized state [Class II]. The major cation radical charge localizes on one ring, whereas the other participates in delocalization to accept a partial charge density. The third one is a strongly or fully delocalized state as shown in Figure 3c [Class III]. Regarding the cation radicals derived from bi-TTFs and bi-TSF, no cation radicals in the Class III state in solution have previously been reported. Interestingly, only one example of a fully delocalized cation radical [Class III] derived from bi-TTFs was observed in the crystal structure of the dimeric cation radical salt of **27**$\cdot$ClO$_4$.[16]

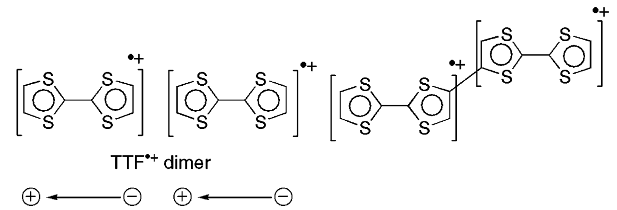


**Figure 5.** Head-to-tail oriented dimer and the bi-TTF dication $1^{2+}$.

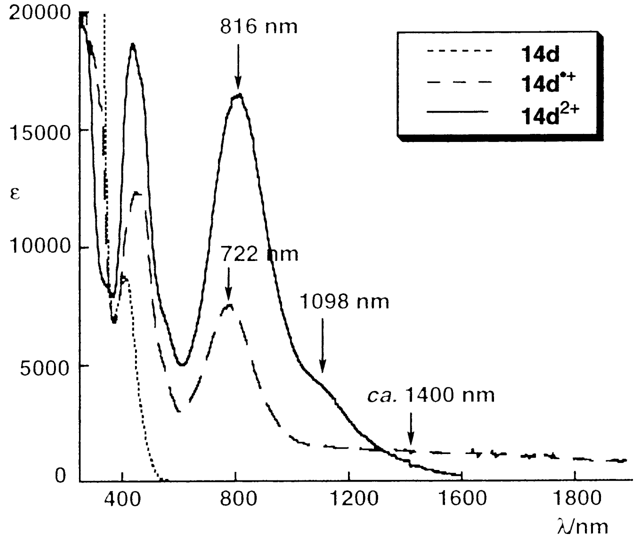


**Figure 6.** Electronic absorption spectra of **14d**, $\mathbf{14d}^{\bullet+}$, and $\mathbf{14d}^{2+}$.

Extended HMO calculations for **1** show that the electron density in the highest occupied molecular orbital (HOMO) is mainly located in the left part of **1** (Figure 4a). On the other hand, the density in the next HOMO (NHOMO) is located in the right part of **1** (Figure 4b). Thus, the extended HMO calculations of **1** indicate the Class II state for $1^{\bullet+}$. Similarly, the weak interaction in the cation radicals of **14a**, **19c**, **26**, **27**, **34**–**36**, and **38** results in the formation of small (or non) [Class I] or slightly [Class II] delocalized states, although the cation radicals derived from the face-to-face fixed bis-TTFs form a strongly delocalized [Class III] species. The cation radical $\mathbf{19e}^{\bullet+}$ seems to possess a Class I state, presumably due to its nonplanar structure with a torsion angle of 77° around the central $\sigma$-bond.[22] In the electrochemical oxidation of bi-TTFs and bi-TSF, $\pi$-dimer formation or aggregation of cation radicals can be excluded due to low solubility of bi-TTFs and bi-TSF in acetonitrile and benzonitrile.

The intramolecular interaction of the two cation radical parts in the dication $1^{2+}$ has undergone very little investigation because $1^{2+}$ is nearly insoluble in common organic solvents and forms no single crystals for X-ray analysis. Torrance and co-workers studied the electronic absorption spectra of TTF$^{\bullet+}$ dimers and presumed a Davydov red shift for a head-to-tail-oriented TTF$^{\bullet+}$ dimer (Figure 5).[35a] Thus, the two TTF$^{\bullet+}$ aligned in a head-to-tail manner makes the dipole interaction attractive; hence, a lower energy is sufficient to excite this transition. Since the interaction between the two cation radical parts in $1^{2+}$ seems to be weak, $1^{2+}$ can be regarded as a model system for the head-to-tail-oriented TTF$^{\bullet+}$ dimer.

Tetraethylthio-bi-TTF **14d**, which can be prepared by palladium-catalyzed coupling of the corresponding zinc species, has good solubility in common organic solvents and shows redox behavior similar to that of **14a**.[33] Therefore, the electronic absorption spectra of the cation radical and dication derived from **14d** were investigated to estimate the interaction between the two cation radical parts. As shown in Figure 6, the cation radical $\mathbf{14d}^{\bullet+}$ shows an absorption of the TTF cation radical ($S_0 \rightarrow S_1$) at 722 nm together with a very broad CT absorption at ca. 1400 nm.[36] In contrast, the dication $\mathbf{14d}^{2+}$ exhibits absorption of the TTF cation radical at 816 nm with a shoulder absorption at 1098 nm. Thus, the $S_0 \rightarrow S_1$ absorption indicates a Davydov red shift of 94 nm. The absorption at 1098 nm may be a forbidden transition.[35b]

**Table 2. Electrical Conductivities of CT Complexes and Radical Cation Salts Derived from 1, 14a, 19a, 19e, 26, 27, and 38**

| donor (D) | acceptor (A) | solvent | D:A | $\sigma_{rt}$/(S cm$^{-1}$) |
|---|---|---|---|---|
| **1** | TCNQ | PhCl | 1:1 | 4.8 (metallic) |
| **1** | $I_3$ | TCE$^a$ | 3:2 | 7.6 |
| **14a** | $ClO_4$ | THF | 1:1 | $9.4 \times 10^{-2}$ |
| **19a** | TCNQ | $CH_3CN$ | 1:1 | $1.2 \times 10^{-2}$ |
| **19e** | $ClO_4$ | TCE$^a$ | 1:1 | $1.6 \times 10^{-3}$ |
| **26** | DDQ | benzene | 2:1 | $8.4 \times 10^{-1}$ |
| **26** | $I_3$ | THF | 2:1 | 125 (metallic) |
| **26** | $AuI_2$ | THF | 1:1 | 778 (metallic) |
| **26** | $BrI_2$ | PhCl | 1:1 | 80 (metallic) |
| **27** | TCNQ | PhCl | 3:1 | 3.6 ($E_a$ = 72 meV) |
| **27** | $ClO_4$ | THF | 1:1 | 6.9 ($E_a$ = 35 meV) |
| **27** | $I_3$ | PhCl | 3:1 | 8.0 (metallic) |
| **38** | $ClO_4$ | $CS_2$-PhCl | 1:1 | 1.2 (semiconductive) |
| **38** | $PF_6$ | $CS_2$-PhCl | 3:2 | 4.2 (semiconductive) |

[a] 1,1, 2-Trichloroethane.

## 2.3. Electric Conductivities and Crystal Structures

Planar bi-TTFs formed CT complexes and cation radical salts.[16,23] As shown in Table 2, the CT complexes derived from **1** and **27** with TCNQ showed fairly high room-temperature conductivities (4.8 and 3.6 S cm$^{-1}$, respectively), and **1**·TCNQ was metallic down to 160 K. However, the **26**·DDQ complex is a semiconductor (0.84 S cm$^{-1}$). Although the $I_3^-$ salt of **1** and the $ClO_4^-$ salt of **14a** were semiconductors, the $I_3^-$, $AuI_2^-$, and $BrI_2^-$ salts of **26** exhibited high conductivities (125, 778, and 80 S cm$^{-1}$) with metallic behavior down to 240, 285, and 240 K, respectively, being transformed at lower temperatures to semiconductors with small activation energies. Furthermore, the $ClO_4^-$ salt of **27** indicated semiconductive resistive temperature dependence (6.9 S cm$^{-1}$) with a small activation energy (35 meV), whereas the $I_3^-$ salt of **27** was metallic (8.0 S cm$^{-1}$) at room temperature. Interestingly, fully substituted bi-TTFs **19a** and **19e** form semiconducting CT complexes and cation radical salts, although these bi-TTFs possess nonplanar structures.[22]

The crystal structures of **14a**·$ClO_4$ and **27**·$ClO_4$ were determined using X-ray diffraction.[16] As shown in Figures 7 and 8, the radical ion salts of **14a** and **27** show unique crystal packings, reflecting a dimeric TTF structure. The net charge on a donor molecule is expected to be +1 due to the 1:1 composition, the charge being half-full in each TTF unit (the band is three-fourths filled). The bi-TTF frameworks in **14a**·$ClO_4$ and **27**·$ClO_4$ exhibit slightly bent and planar structures, the maximum atomic deviations from the least-squares plane of the bi-TTF units except the substituents being 0.46 and 0.18 Å, respectively.

The TMT-bi-TTF molecules are stacked face-to-face to form a dimeric structure (Figure 7), and the dimers are arranged in the so-called $\beta'$-type structure to form a conducting path along the *c* axis. Since the C(3)–C(4) (1.394(9) Å) and C(11)–C(12) (1.343(9) Å) bonds have single- and double-bond character, respectively, the two TTF units **A** and **B** in **14a**·$ClO_4$ have different oxidation states. There are four intra- and interstack interactions between the cation radicals, and the two strong interactions are shown in Figure 7. In contrast to **14a**·$ClO_4$, the cation radical salt **27**·$ClO_4$ has a fairly high conductivity (6.9 S cm$^{-1}$) with a small activation energy (35 meV). The C(3)–C(4) and C(11)–C(12) bonds in the **A** and **B** units are equally long (1.37(1) Å), as shown in Figure 8a, indicating a mixed-valence state. The cation radical salt forms a conducting sheet in the *ac* plane to make a segregated column. There are four intra- and interstack interactions between the cation radicals (Figure 8). Interestingly, the two overlaps are made up of the whole molecules (Figure 8a,b), whereas the other two are constructed by the interaction between only one TTF moiety of the cation radical (Figure 8c). The donor packing in **27**·$ClO_4$ is regarded as a $\beta'$-like dimerized structure. However, **27**·$ClO_4$ shows fairly high conductivity with a small activation energy, reflecting a 2D band structure, in contrast to the 1D $\beta'$-phase.

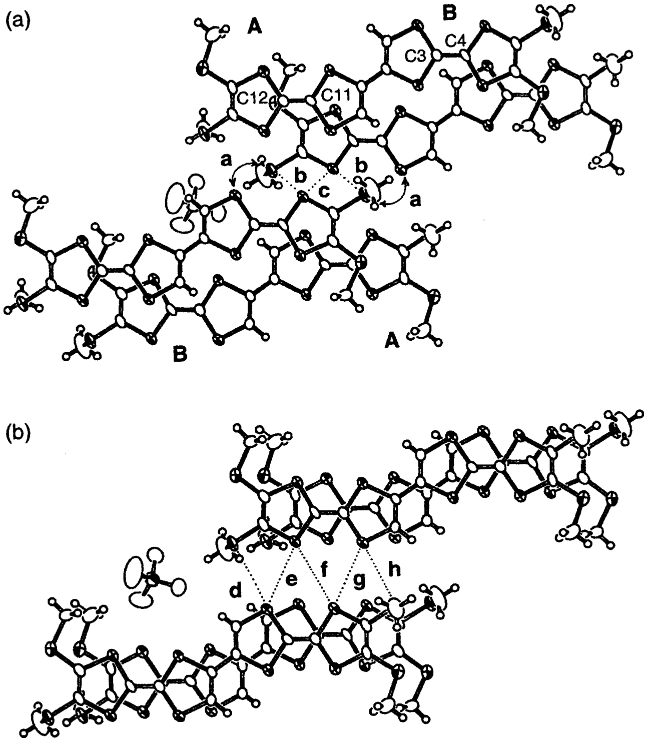


**Figure 7.** The intra- and interstack overlaps of the cation radical **14a**·$ClO_4$. The intercolumnar S···S distances indicated by dotted lines. (a) The intercolumnar S···S distances ($a$ = 3.91, $b$ = 3.79, $c$ = 3.97 Å) with 3.55 Å of the face-to-face stacking. (c) The intercolumnar S···S distances ($d$ = 3.64, $e$ = 3.57, $f$ = 3.79, g = $h$ = 3.50 Å) with 3.50 Å of the face-to-face stacking. (Reproduced with permission from ref 16. Copyright 2002 Academic Press.)

## 3. Conjugated Bis-TTFs Linked by π-Systems

### 3.1. Synthesis

To design superior electronic donors with reduced on-site Coulombic repulsion and increased dimensionality, the conjugated dimeric TTFs **2** have been investigated extensively. Bis-TTFs linked by π-spacers can also be expected to show intramolecular through-bond and through-space interactions between the two TTF units, and hence, these bis-TTF

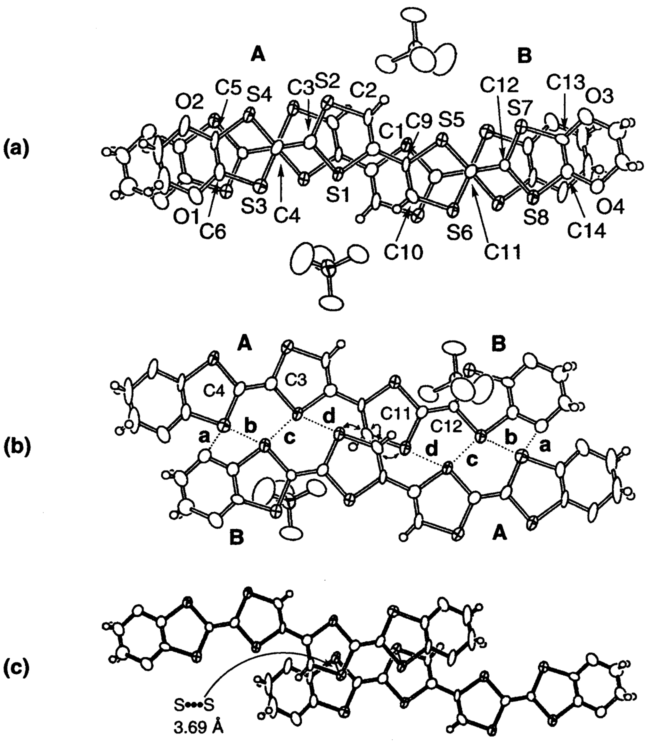


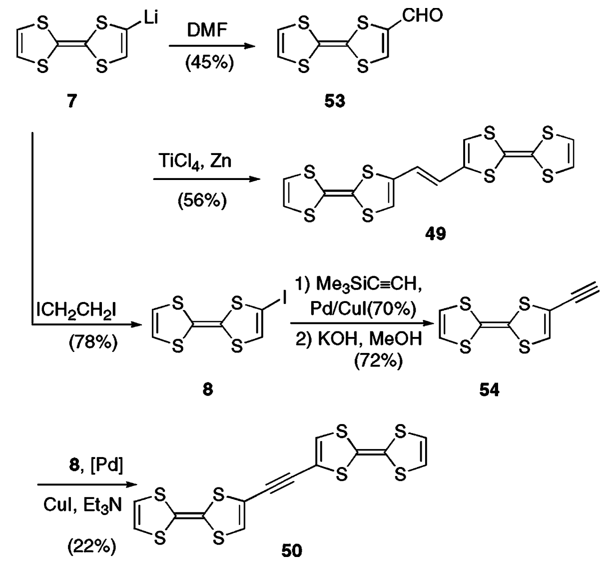
**Figure 8.** The intra- and interstack overlaps of the cation radical **27**·ClO$_4$. The intercolumnar S···S or S···O distances indicated by dotted lines and the intracolumn short S···S contacts indicated by solid lines. (a) The face-to-face overlap and two TTF parts (A and B). (b) The side-by-side overlap and intercolumnar S···S and S···O distances ($a$ = 3.48, $b$ = 3.78, $c$ = 3.70, $d$ = 3.83 Å). (c) The face-to-face overlap between the half TTF moieties. (Reproduced with permission from ref 16. Copyright 2002 Academic Press.)

systems exhibit multifunctionality, such as high electric conductivity, ferromagnetic properties, electrochromism, molecular wire formation, etc. The basic conjugated dimeric TTFs linked by ethylene, acetylene, and diacetylene spacers are **49**–**52**. For the synthesis of **49**,[37] Otsubo and Ogura developed the reductive coupling of 4-formyl-TTF **53** with a low-valent titanium reagent to produce **49** (56%). On the other hand, **50** was prepared by the Sonogashira coupling of **8** with **54** in 22% yield (Scheme 12).[37]

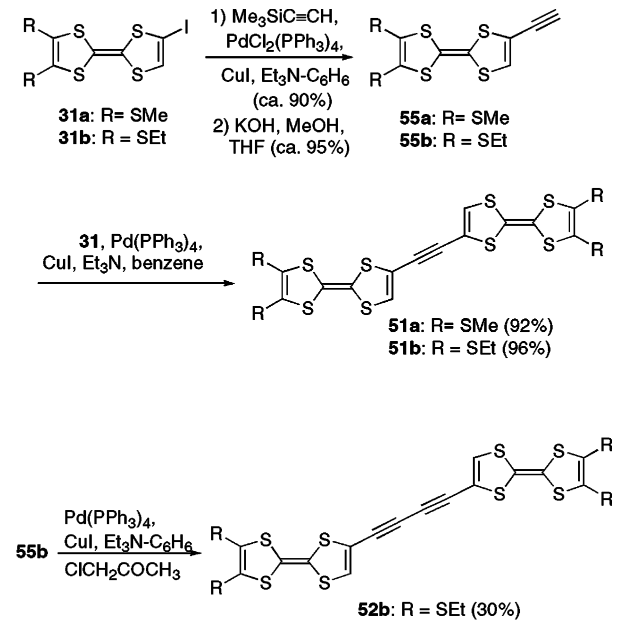
Recently, the synthesis of **51** and **52** has been carried out using palladium-catalyzed couplings (Scheme 13).[33,38] For the Sonogashira coupling of iodo-TTFs, the reaction proceeded smoothly under the conditions reported by Thorand and Krause.[39] Thus, cross-coupling of **55a** with **31a** in the presence of Pd(PPh$_3$)$_4$ and CuI in Et$_3$N–benzene at 65 °C afforded **51a** in 92% yield, whereas a similar reaction of **55b** with **31b** produced **51b** in 96% yield. In contrast, treatment of **55b** with Pd(PPh$_3$)$_4$, CuI, and α-chloroacetone[40] in Et$_3$N–benzene at room temperature led to the homocoupling product **52b** in 30% yield.

The cross-conjugated dimeric TTFs **56**[41] and **57**[42] provide the possibility of a stable triplet ground state, and they can be regarded as simple model compounds for the high-spin system **58** (Figure 9). Fukutome and co-workers predicted theoretically that the dimeric and oligomeric TTFs **56**–**58** give parallel spins upon oxidation and that the radical cation **58** should show

**Scheme 12**



**Scheme 13**



a high-spin ground state.[43] Thus, the dications derived from **56**–**58** have the triplet unrestricted Hartree–Fock (UHF) ground state, whereas trications and tetracations corresponding to the partial structures of **58** have quartet and quintet UHF ground states, respectively.

For the synthesis of bis(tetrathiafulvalenyl)ketones **56a**–**c**, monolithiated TTF **7** was reacted with Me$_2$NCOCl (0.5 equiv) to afford **56a** (9.4%) and **56b** (6.5%) (Scheme 14).[41a] **56a** was also obtained by the reaction of **7** with 1,1′-carbonyldiimidazole in 5.6% yield. On the other hand, **56c** was prepared in 23% yield using MeOCOCl in analogy to Green's method.[25] The redox potentials of **56a**–**c** measured by CV analysis show four-step oxidation, reflecting the intramolecular interaction of the two TTF units.

As shown in Scheme 15, trimethylstannyl-TTF **11** was found to be an effective synthon to construct the 1,1-(tetrathiafulvalenyl)ethylene framework **57**.[42] Thus, the Stille coupling of **11** (2 equiv) with 1,1-

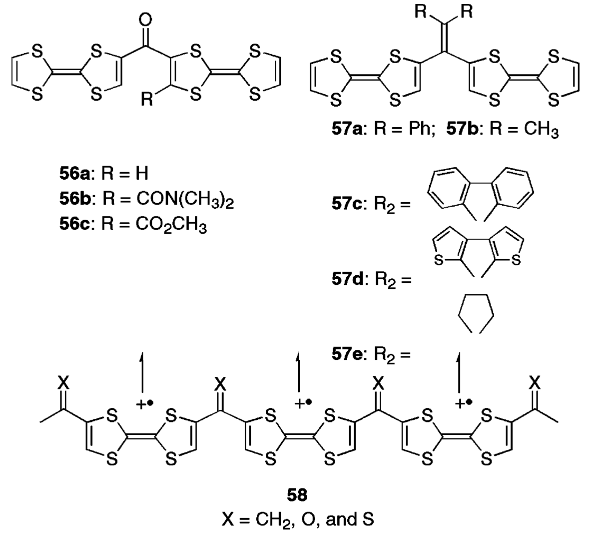
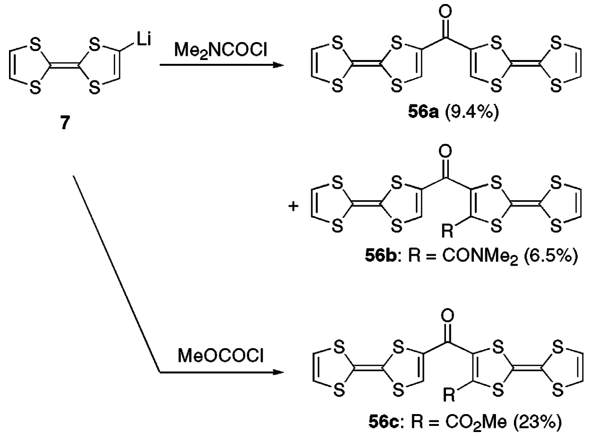
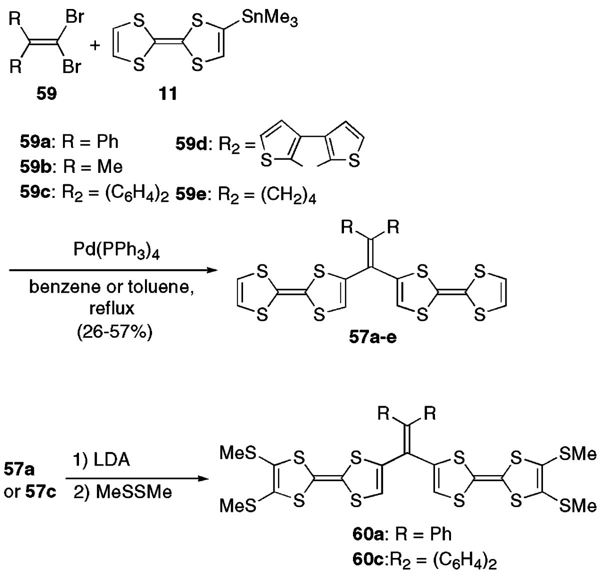


**Figure 9.** Cross-conjugated dimeric TTFs **56** and **57** and their polymer **58**.

### Scheme 14

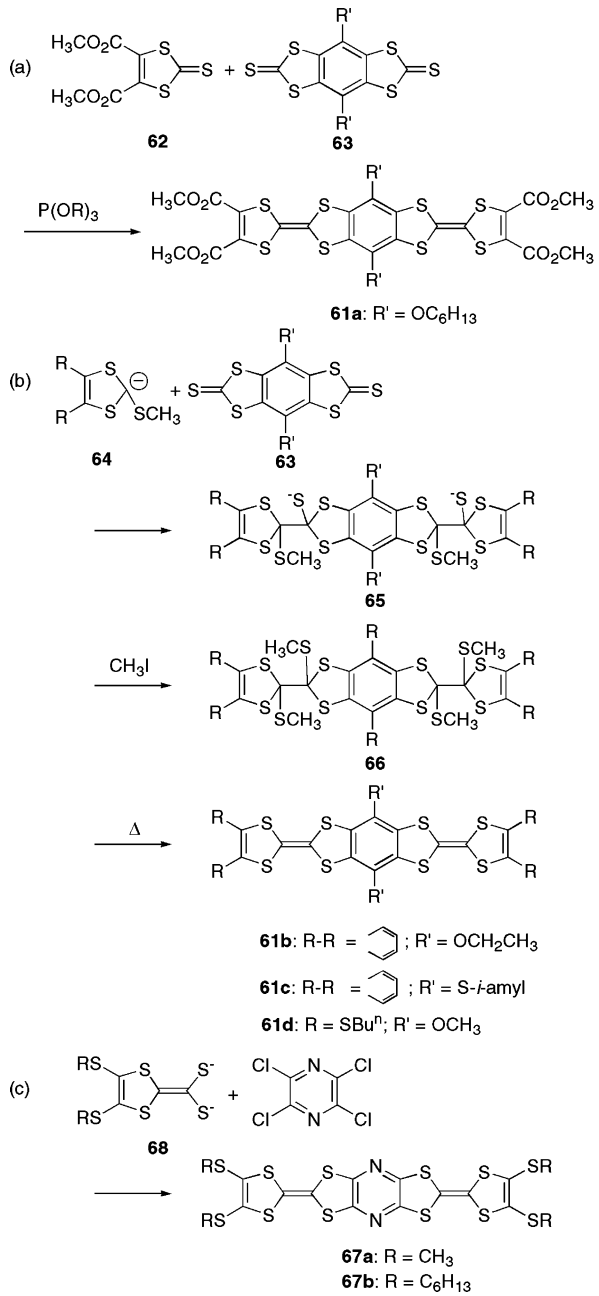


### Scheme 15



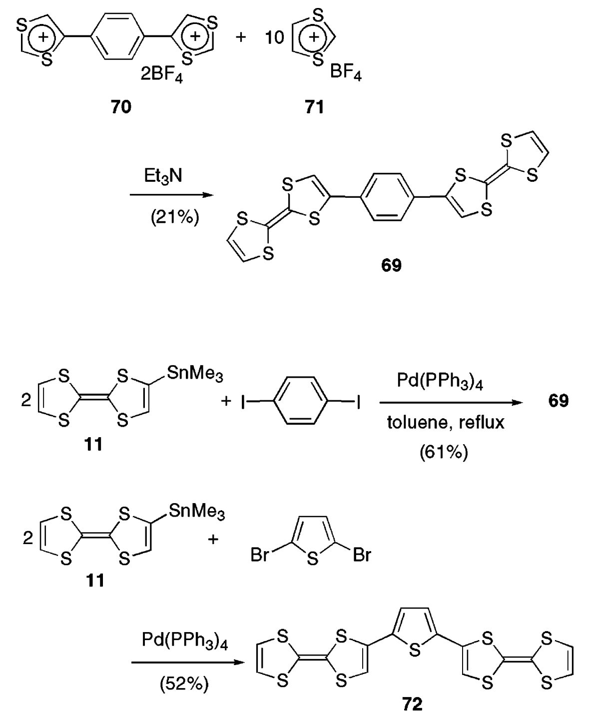
dibromo-2,2-diphenylethylene **59a** in the presence of $Pd(PPh_3)_4$ (10 mol %) proceeded smoothly in refluxing benzene to afford **57a** in 57% yield. Similarly, the palladium-catalyzed reactions of **11** with **59b**, **59c**, **59d**, and **59e** in refluxing benzene or toluene gave the corresponding products in 26%, 52%, 41%, and 28% yields, respectively. Because of the low solubility of **57a**,**c** in common organic solvents, **57a**,**c** were converted into the hexamethylthio derivatives **60a**,**c** by treatment with LDA, followed by reaction with excess dimethyl disulfide.

### Scheme 16



Dimeric TTFs linked by aromatic systems have been studied independently by many different groups. Müllen and co-workers investigated oligomeric systems of benzo-fused bis-TTFs **61a**–**d** (Scheme 16).[1,44–46] For the synthesis of **61a**–**d**, the cross-coupling reaction of **62** with **63** (route a) or the addition–elimination procedure via **65** and **66** (route b) has been reported. Route b was employed effectively for the preparation of benzo-fused bis-TTFs. A simple and efficient synthesis of pyrazine-fused bis-TTFs **67a**,**b** was achieved by Moradpour and co-workers using the aromatic nucleophilic substitution of **68** (route c).[47a] This aromatic substitution is also applicable to the synthesis of **61**.[47b]

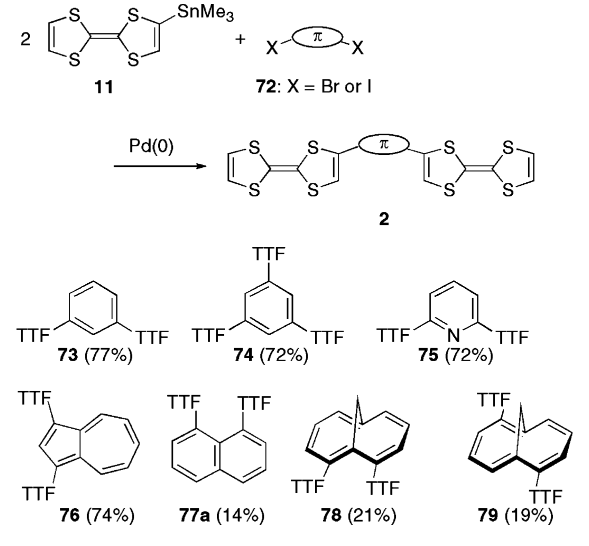
**Scheme 17**



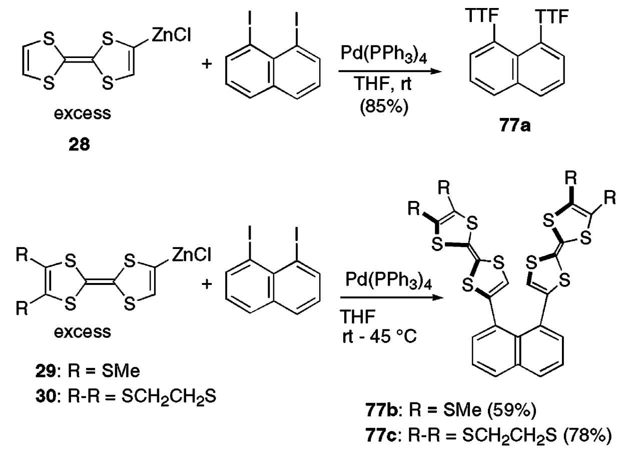
*p*-Phenylene-bis(tetrathiafulvalene) **69** is one of the simplest bis-TTFs linked by a benzene ring. As shown in Scheme 17, the first synthesis was carried out by Wudl and co-workers using the cross-coupling of 1,3-dithiolium tetrafluoroborates **70** and **71**.[48] The Stille coupling was found to be more effective for the synthesis of **69**.[15] Trimethyltin-TTF **11** can be prepared from TTFLi **7** in good yield (Scheme 3). Palladium-catalyzed coupling of **11** with 1,4-diiodobenzene or 2,5-dibromothiophene in refluxing toluene afforded **69** or **72** in 61% or 52% yield, respectively.

The palladium-catalyzed cross-coupling of **11** with dihalide **72** can be widely applied for the synthesis of bis-TTF derivatives.[49] Reaction of **11** with 1,3-diiodo- and 1,3,5-triiodo-benzenes, 2,6-dibromopyridine, and 1,3-dibromoazulene in the presence of $Pd(PPh_3)_4$ (10−20 mol %) in refluxing toluene afforded **73**−**76** in good yields (Scheme 18). However, similar reactions of **11** with 1,8-diiodonaphthalene and 2,10- and 2,7-dibromo-1,6-methano[10]annulenes gave **77a**, **78**, and **79** in lower yields,[50] presumably due to the low reactivity of dihalides.

**Scheme 18**



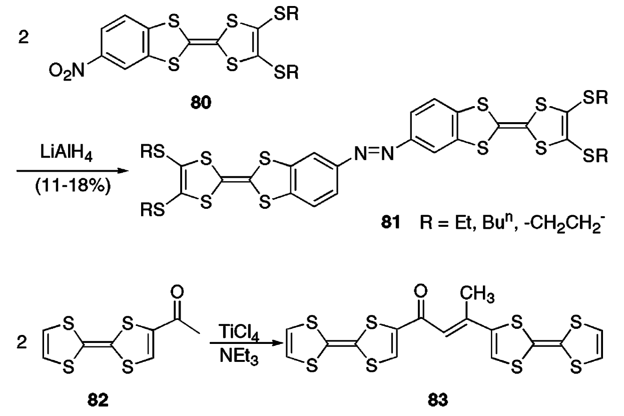
**Scheme 19**



As shown in Scheme 19, the palladium-catalyzed coupling of TTF−ZnCl **28** with dihalide **72** was employed for the synthesis of **77a**. TTF−ZnCl **28** can be generated in situ by reaction of TTFLi **7** with $ZnCl_2$ (Scheme 8). Reaction of **28** (excess) with 1,8-diiodonaphthalene in the presence of $Pd(PPh_3)_4$ (7 mol %) at ambient temperature produced **77a** in 85% yield.[36] Similarly, reaction of **29** and **30** with 1,8-diiodonaphthalene in the presence of catalytic amounts of $Pd(PPh_3)_4$ afforded **77b** and **77c** in 59% and 78% yields, respectively.[51]

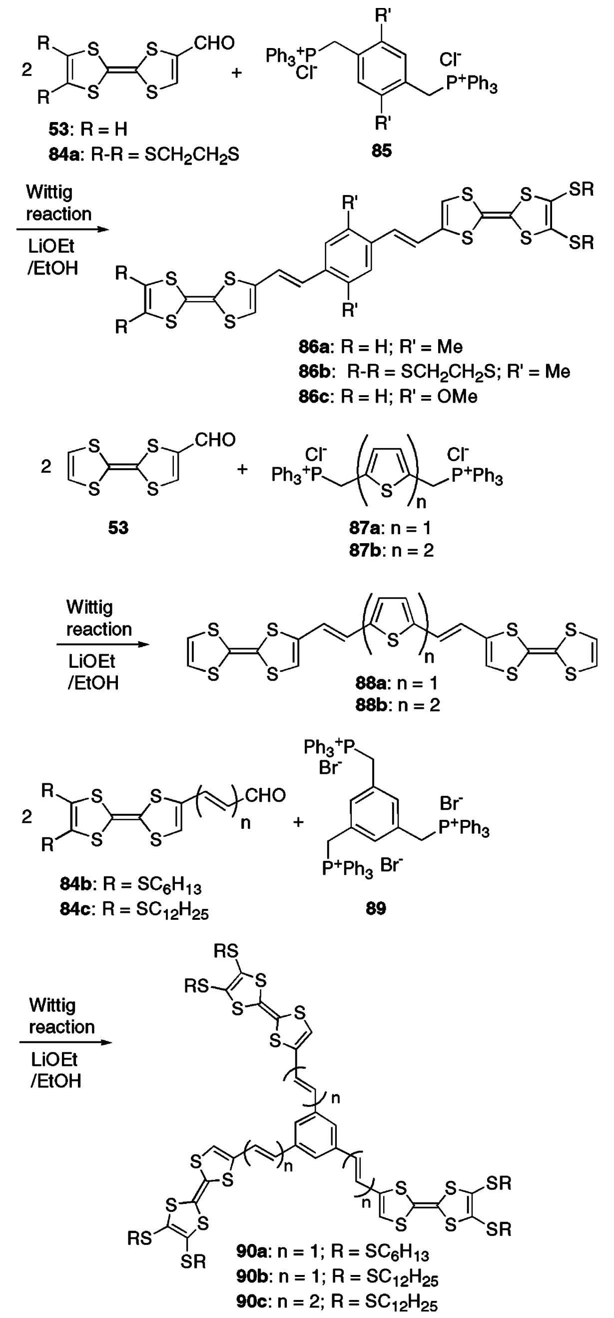
Besides typical bis-TTFs linked by $\pi$-systems, a variety of bis-TTF derivatives with unique structures have been synthesized to date. Bis-TTF **81** containing an azobenzene linkage can be expected to show photoinduced structural change. Tatemitsu and co-workers synthesized **81** using the reductive coupling of **80** with $LiAlH_4$ (Scheme 20).[52] Titanium-mediated self-condensation of **82** was used for the preparation of **83**.[53]

**Scheme 20**



Synthesis of dumbbell-type bis-TTFs **86** and **88** was carried out using Wittig reactions for the construction of the molecular framework, as shown in Scheme 21. Thus, a series of bis-TTFs **86a**−**c** and **88a**,**b** were prepared by the reaction of **53** and **84a** with **85** and **87a**,**b** in the presence of lithium ethoxide.[54,55] Using a similar methodology, Martín and co-workers pre-

**Scheme 21**



pared **90** to investigate conducting and magnetic properties of its cation radical species.[56]

As shown in Chart 2, new chiral bis-TTF **91** was synthesized, and its redox properties were reported.[57] Hudhomme and co-workers prepared a fused perpendicular bis-TTF **92**.[58] CV analysis of **92** showed four sequential reversible redox processes, reflecting an intramolecular interaction between the two different TTF moieties.[58] Frère and Gorgues reported the synthesis of **93**.[59] Dendralene-type bis-TTF **94** was prepared by successive formulation and Wittig reactions.[60] Recently, a similar dendralene bearing a 1,3-diselenole moiety has been prepared.[61] The all-sulfur-containing [4]- and [6]radialenes **95** and **96** were synthesized by Yoshida and co-workers.[60,62,63] Radialenes **95** and **96** can be regarded as dimeric and trimeric TTFs, but they exhibit explicit cyclic properties. Recently, the synthesis of bis-TTF **97** containing tetrathiapentalene units has been carried out to improve the dimensionality of tetrathiapentalenes.[64] Becher and co-workers synthesized TTF-annelated porphyrins **98**.[65] Interestingly, **98** consists of a mixture of the neutral and corresponding cation radical species. **98** stacks very easily to form a columnar structure. Two star-shaped TTFs, a trimer and a tetramer (**99** and **100**), have been synthesized to investigate their supramolecular structures.[66,67] To construct supramolecular structures in solution, we employed terminal TTF units to anchor the star molecules **99** and **100**. Although **99** and **100** have noncyclic structures, the three and four TTF units in **99** and **100** act cooperatively to form stacked dimers in solution.

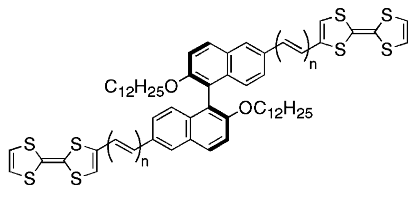
Conjugated bis-TTFs linked to macrocycles and polymers (Chart 3) have been investigated for the construction of multifunctional $\pi$-systems and conducting polymers. The TTF-annelated [12]annulenes **101** and **102** exhibit $\pi$-amphoteric properties based on the TTF donor and [12]annulene acceptor.[68,69] A polymeric TTF derivative **103** and a poly(TTF-thiophene) system **104** have been reported by Yamamoto and Shimizu.[70] Extended $\pi$-conjugation in polymers **103** and **104** is evident from a red shift in their electronic spectra. New poly(arylacetylene) **105** with a TTF unit in the side chain has been prepared using Rh-catalyzed polymerization of TTF−acetylene.[71] Müllen and co-workers synthesized a variety of TTF polymers (**106** and **107**).[72] Rodlike structures were proposed for **106** and **107**.

## 3.2. Structures and Properties

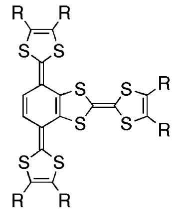
Among bis-TTFs, the benzo- and pyrazine-fused systems **61** and **67** exhibit four reversible one-electron oxidation steps according to CV analysis. In contrast, most of the bis-TTFs, with the exception of the face-to-face-arranged bis-TTF **77c**, show two reversible two-electron oxidations by CV analysis. The redox potentials of the typical bis-TTFs are summarized in Table 3 together with two tris-TTFs **74** and **90a**.

The four one-electron oxidations in **61c**,**d** and **67b** indicate that the cation radical, dication, and trication radical intermediates are stabilized by delocalization of the charged species to form mixed-valence states. However, most bis-TTFs exhibit simple two-step oxidation due to the weak interaction between the two TTF parts, although the electronic spectra of bis-TTFs demonstrate marked red shifts, reflecting extensive conjugation of the $\pi$ system of both TTF units. The through-bond electronic interaction between the TTF units of bis-TTFs is weak in the ground state because the coefficients of atomic orbitals at the 4,5-positions are small in the HOMO, as shown in Figure 4. However, the coefficients at the same 4,5-positions in the LUMO are large enough to lead to red shifts in the electronic spectra. In the case of the face-to-face-arranged bis-TTF system, **77a** exhibits the three-step redox waves corresponding to one-, one-, and two-electron transfers. Therefore, the two TTF units in the cation radical **77a**$^{\bullet+}$ and dication **77a**$^{2+}$ are stabilized by delocalization of the charged species in the mixed-valence and $\pi$-dimer states,[73a]

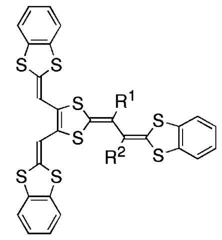
**Chart 2**



**91**

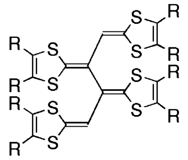


**92**



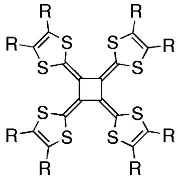
**93a** : $R^1$ = Ph, $R^2$ = H

**93b** : $R^1$ = $R^2$ = Me

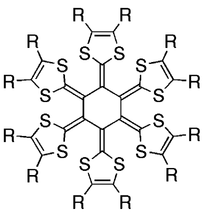


**94a** : R = $CO_2Me$

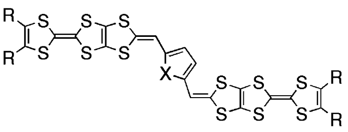
**94b** : R = H



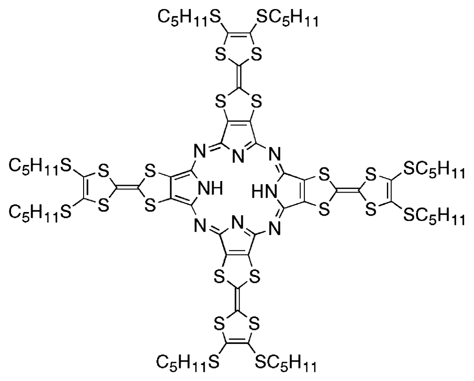
**95**



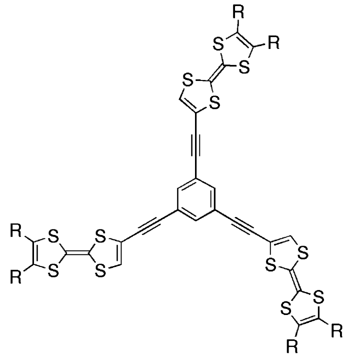
**96**



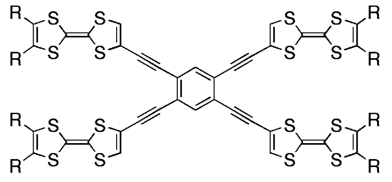
**97** X = S, O



**98**



**99** R = $SCH_3$, $SC_2H_5$, SBu



**100**

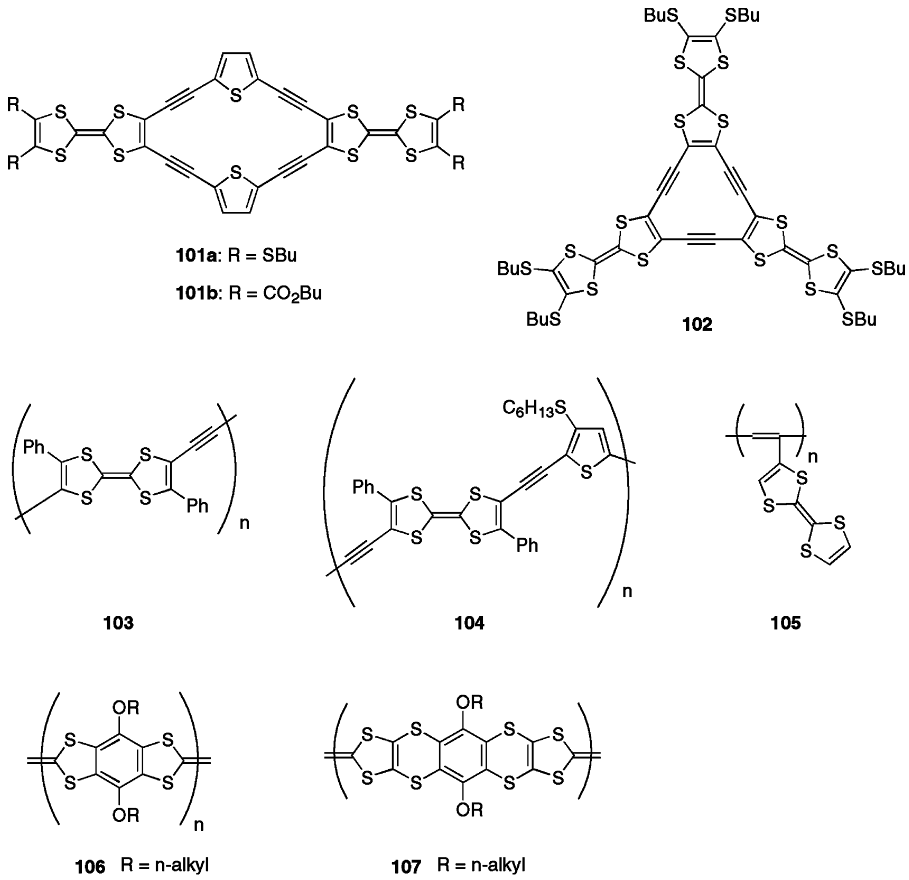
although TTF cation radicals in solutions exist as monomers at room temperature.[73b]

Cation radicals derived from conjugated bis-TTFs can be expected to show a decrease in on-site Coulombic repulsion, enhancement of dimensionality, and control of stoichiometry and band filling. The intramolecular interaction between the TTFs is weak in bis-TTFs. However, **49** and **50** formed 1:1 complexes with DDQ and $TCNQF_4$, even when the acceptors were used in large excess. The powder sample conductivities of the complexes **49**·$TCNQF_4$ and **50**·DDQ were 3.6 and 0.11 S $cm^{-1}$, respectively.[2]

Although the lack of molecular planarity and introduction of bulky alkyl substituents into bis-TTFs diminish the conductivities of CT complexes and cation radical salts, **61b**,**c**, **73**, **74**, and **86a** produced conducting CT complexes and cation radical salts. Thus, the benzo-fused bis-TTFs **61b** and **61c** form 1:2 complexes with DDQ and $TCNQF_4$, and the powder conductivities of complexes **61b**$(DDQ)_2$, **61b**$(TCNQF_4)_2$, and **61c**$(DDQ)_2$ were 0.1, 0.2, and 0.08 S $cm^{-1}$, respectively, without forming a Mott insulator.[45] In the case of the phenylene–TTF system, dimeric **73** produced a 2:3 complex with TCNQ whereas trimeric **74** resulted in the formation of a 1:2 complex with TCNQ. Since the nitrile vibrational frequencies of $(\mathbf{73})_2(TCNQ)_3$ and **74**$(TCNQ)_2$ are 2195 and 2201 $cm^{-1}$, both CT complexes reveal a partial charge transfer of 0.68 and 0.59, respectively.[74]

It is worth noting that bis-TTFs **86a**,**b** formed 1:1 metallic cation radical salts with $I_3^-$ and $IBr_2^-$.[54] The room-temperature conductivities of **86a**·$I_3$ and **86b**·$IBr_2$ were 140 and 80 S $cm^{-1}$, and they showed metallic behavior down to 180 and 230 K, respectively. The high electrical conductivities are ascribable to the dimeric structure of the donors, which increases dimensionality and controls the stoichiometry and band filling. Other conjugated bis-TTFs **83** and **88a**

**Chart 3**



**101a**: R = SBu

**101b**: R = $CO_2Bu$

**102**

**103**

**104**

**105**

**106** R = n-alkyl

**107** R = n-alkyl

**Table 3. Redox Potentials of Bis-TTFs 49–52, 57, 61, 67, 69, 72–74, 77, 86, 88, and 90**

| compd | solvent | $E_1^{1/2}$ | $E_2^{1/2}$ | $E_3^{1/2}$ | $E_4^{1/2}$ | refs |
|---|---|---|---|---|---|---|
| **49** | $CH_2Cl_2$ | +0.41 | | +0.71 | | 37 |
| **50** | $CH_2Cl_2$ | +0.56 | | +0.78 | | 37 |
| **51b** | PhCN | +0.57 | | +0.88 | | 33 |
| **52b** | PhCN | +0.58 | | +0.78 | | 33 |
| **57a** | PhCN | +0.40 | | +0.79 | | 42 |
| **57b** | PhCN | +0.39 | | +0.72 | | 42 |
| **61c** | $CH_2Cl_2$ | +0.44 | +0.68 | +1.10 | +1.29 | 45 |
| **61d** | $CH_2Cl_2$ | +0.39 | +0.61 | +1.07 | +1.23 | 45 |
| **67b** | $CH_2Cl_2$ | +0.49 | +0.71 | +1.24 | +1.50 | 47 |
| **69** | PhCN | +0.35 | | +0.82 | | 15 |
| **72** | PhCN | +0.38 | | +0.81 | | 15 |
| **73** | PhCN | +0.40 | | +0.81 | | 49 |
| **74** | PhCN | +0.29 | | +0.77 | | 49 |
| **77c** | PhCN | +0.28 | +0.41 | +0.90 | | 51 |
| **86a** | PhCN | +0.56 | | +0.93 | | 54 |
| **88a** | $CH_2Cl_2$ | +0.39 | | +0.67 | | 55 |
| **90a** | $CH_2Cl_2$ | +0.48 | | +0.85 | | 56 |

gave 1:1 CT complexes with $TCNQF_4$ and TCNQ, and powder conductivities of **83**·TCNQ and **88a**·$TCNQF_4$ were 0.16 and 0.1 S $cm^{-1}$, respectively.[53,55]

The cross-conjugated bis-TTFs **56** and **57** and 1,3-phenylene-bis-TTF **73** provide the possibility of a stable triplet ground state, as shown in Figure 9. The dication radical and trication radical states $\mathbf{73}^{2+}$ and $\mathbf{74}^{3+}$ derived from **73** and **74** can be expected to show a ferromagnetic interaction between $TTF^{\bullet+}$ units. In the case of $\mathbf{74}^{3+}$, both doublet and quartet ground states should exhibit ferromagnetic interactions (Figure 10). However, the through-bond interaction between the $TTF^{\bullet+}$ units in $\mathbf{73}^{2+}$ and $\mathbf{74}^{3+}$ is weak in the ground state, and almost no spin–spin interaction was observed in these cases.

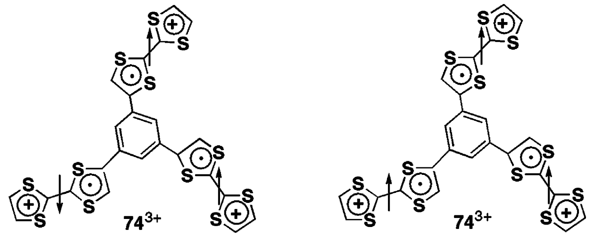
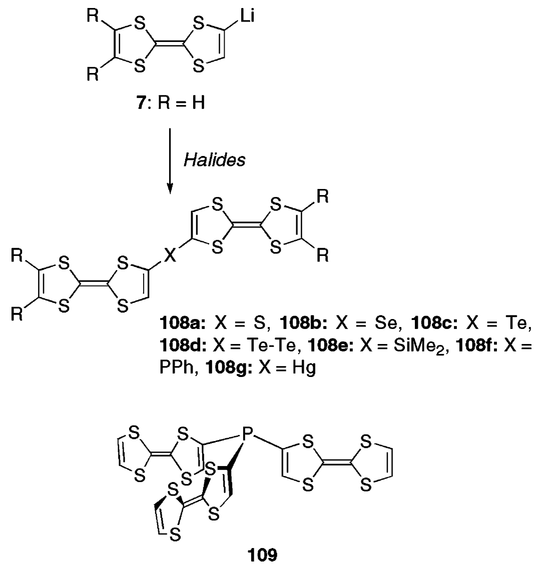


**Figure 10.** Possible interaction between TTF cation radicals.

The dications $\mathbf{56a}^{2+}$ and $\mathbf{57}^{2+}$ derived from cross-conjugated bis-TTFs were expected to show a triplet ground state because the theoretical prediction suggests a high-spin ground state in these molecules. Sugimoto and co-workers reported that the dication radical of **56a** possesses a singlet ground state, which is not in agreement with the prediction of a triplet state from the theoretical calculations, presumably because it is fairly well stabilized.[41] The calculations do predict the observed small singlet–triplet difference in $\mathbf{56}^{2+}$ compared with those in other bis-TTFs such as the 1,1-bis(tetrathiafulvalenyl)ethylene dication and the bis(tetrathiafulvalenyl)thioketone dication. Taking these results into consideration, we designed and synthesized the 1,1-bis(tetrathiafulvalenyl)ethylene derivatives **57a–e** in order to examine the spin–spin interactions in their oxidation states.[42,75] The redox processes of **57a**,**b** shown in Table 3 display no separation in either of the two-electron transfers in their CVs, presumably due to the weak interaction between the two TTF moieties

**Scheme 22**



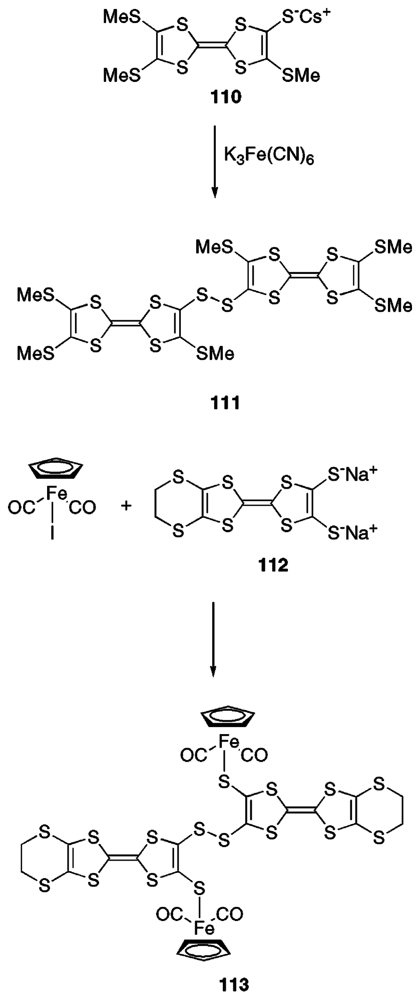
in these molecules. This weak interaction reflects the twisted structure, which was elucidated by X-ray analysis of **57a**.[42] Treatment of **57a** with iodine produced the corresponding cation radical salt, which shows interesting magnetic behavior. The ESR spectrum of the powdered sample of the cation radical salt of **57a** consists of a broad signal at the center and a fine structure ($g = 2.0074$, $D = 108$ G at 163 K) together with signals of $\Delta m_s = 2$ corresponding to a triplet species. The distance between the two spins, as estimated from the $D$ value by the point-dipole approximation (6.36 Å), seems to be comparable to the distance between the two TTF units in the radical salt. This result paves the way for the synthesis of polymeric analogues such as **58** (Figure 9), which exhibits the more preferred triplet ground state.

## 4. Bis-TTFs Linked by Heteroatoms

Incorporation of heteroatoms as connecting spacers is mainly aimed at enhancement of intermolecular orbital overlap in the solid state.[76a] The resulting high-dimensional network would suppress the Peierls distortion for a metal−insulator transition, which is characteristic of a one-dimensional conducting system. In addition, highly polarized TTFs containing electron-withdrawing heteroatoms are advantageous for constructing organic conductors because intermolecular interactions can be enhanced by electrostatic interactions.[77] Main-group elements such as sulfur, selenium, tellurium, silicon, phosphorus, and mercury have been employed to link TTF units.

Heteroatom-bridged bis-TTFs involving S (**108a**),[78] Se (**108b**),[78] Te (**108c**),[79,80] Te−Te (**108d**),[80,81] Si (**108e**),[82] P (**108f**),[81−83] and Hg (**108g**)[82] have been prepared from lithio-TTFs (Scheme 22). Similarly, Fourmigué and Batail reported the reaction of TTF−Li **7** with $PBr_3$ as a trivalent phosphine source to afford the corresponding trimeric TTF **109** in 40% yield.[83b] Moreover, the bis-TTF **111** connected with two sulfur atoms was synthesized in 87% yield by oxidative homocoupling of the thiolate **110** with potassium hexacyanoferrate(III).[84] The reaction of **112** with iron (II) complex in ethanol produced the disulfide-linked bis-TTFs **113** containing the two iron complex moieties (Scheme 23).[85]

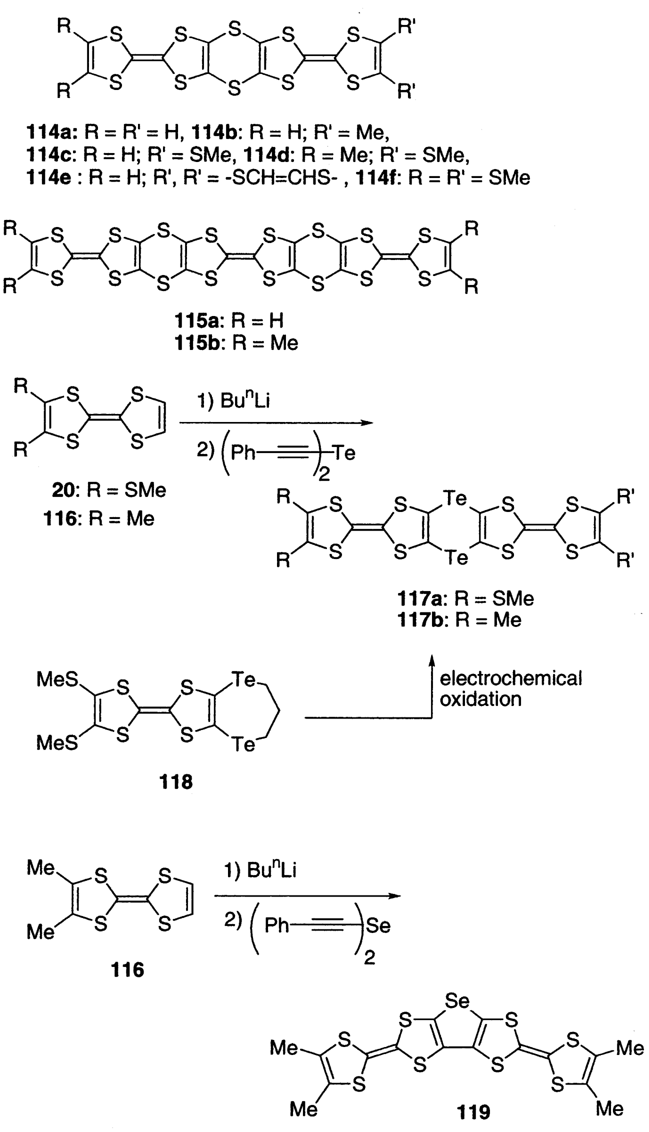
**Scheme 23**



Bis-TTFs in which two TTF units are fused to 1,4-dithiine and ditellurine have been synthesized to enhance molecular rigidity (Scheme 24). Thus, **114**[86,87] and **115**[87b] containing 1,4-dithiine rings were prepared by phosphite-mediated homo- or cross-coupling reactions of 1,3-dithiole-2-ones having a 1,4-dithiine ring. Becker and Bernstein reported bis-TTFs fused to 1,4-ditellurine.[88] The reaction of lithio-TTFs derived from **20** and **116** with bis(phenylacetylenyl) telluride in THF resulted in the formation of **117a** and **117b** in 26% and 63% yields, respectively.[88,89] Interestingly, Kobayashi and co-workers obtained the cation radical of **117b** by electrochemical oxidation of **118**.[89] Bis-TTF **119** bearing a central selenophene ring was prepared by a one-pot procedure.[90] The reaction of **116** with butyllithium in THF, followed by treatment with an equimolar amount of bis(phenylacetylenyl)selenide, formed **119** in 37% yield (Scheme 24).[90]

As for bis-TTFs with unique structures, Fujiwara and Kobayashi reported the synthesis of **121**.[91] The reaction of the dithiolate complex **120** with $SCl_2$ in acetonitrile at 55 °C produced the TTF dimer **121** as air-stable black plates (Chart 4). Martín and Seoane synthesized dimeric TTF **122** with a $p$-quinodimethane

**Scheme 24**



structure.[92] Bis-TTFs **122,** which are connected by an oxygen bridge, were obtained in 45−56% yields using the Wittig−Horner reaction of the corresponding anthraquinone precursor.[92]

**Chart 4**

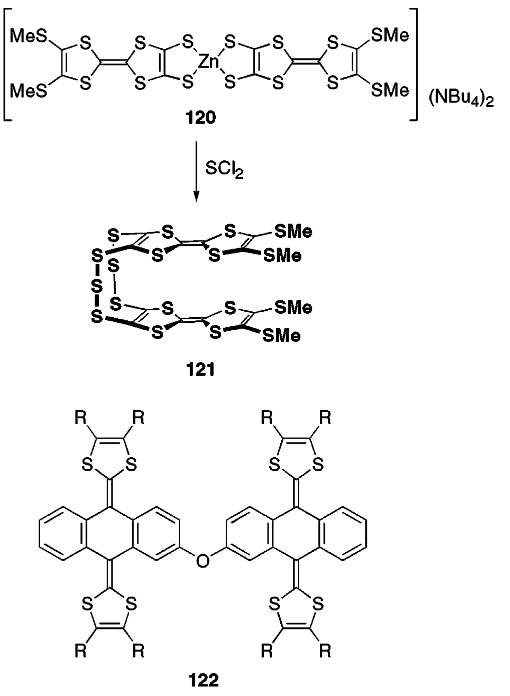


**Table 4. Redox Potentials of Bis-TTFs Linked by Heteroatoms**[a]

| compound | solvent | $E_1^{1/2}$ | $E_2^{1/2}$ | $E_3^{1/2}$ | $E_4^{1/2}$ | refs |
|---|---|---|---|---|---|---|
| **108a** | $CH_2Cl_2$ | 0.49 | 0.61 | 0.86 | | 77 |
| **108c** | $CH_3CN-THF$ | 0.47 | 0.85 | 1.0[c] | | 88b |
| **108e** | $CH_2Cl_2$ | 0.29 | 0.38 | 0.77 | | 81 |
| **108f**[b] | $CH_2Cl_2$ | 0.37 | 0.47 | 0.84 | | 81 |
| **108g**[b] | DNF | 0.35[d] | 0.68[d] | | | 81 |
| **109**[b] | $CH_3CN$ | 0.47 | 0.86 | | | 82 |
| **111**[b] | $CH_2Cl_2$ | 0.61[e] | 0.93[e] | | | 84 |
| **113** | PhCN | −0.07[f] | 0.17 | 0.33 | 0.66 | 85 |
| **114a** | PhCN | 0.47 | 0.67 | 0.89 | | 87a |
| **114b** | PhCN | 0.43 | 0.64 | 0.88 | | 87a |
| **114c** | PhCN | 0.49 | 0.75 | 0.89 | | 87a |
| **114d** | PhCN | 0.47 | 0.76 | 0.87 | | 87a |
| **117a** | PhCN | 0.57 | 0.84 | | | 88b |
| **117b** | PhCN | 0.48 | 0.83 | | | 88b |
| **119** | PhCN | 0.40 | 0.56 | 0.93[e] | 0.96[e] | 90 |
| **121** | PhCN | 0.57 | 0.67 | 1.15 | | 91 |
| **122**[b] | $CH_2Cl_2$ | 0.50 | | | | 92 |

[a] Potentials (V) vs Ag/Ag$^+$. [b] Reference: SCE. [c] Irreversible oxidation of the Te bridge. [d] Broad peak. [e] The anodic potential. [f] Redox potential of the iron(II) complex moieties.

Although compounds **108c**, **108g**, **109**, **111**, and **117a**,**b** showed two pairs of reversible two-electron redox waves in their cyclic voltammograms, **108a**,**b**, **108e**,**f**, **114a**−**d**, and **121** showed two pairs of reversible one-electron and one pair of reversible two-electron waves, suggesting sequential formation of the mono- and dicationic species followed by a further two-electron oxidation to form the tri- and tetracationic species (Table 4). The cyclic voltammogram of **113** is similar to the latter case mentioned above but with an additional redox wave ($E_{1/2}$ = −0.07 V) for the iron(II) moieties. In the case of **119**, CV analysis showed four redox waves consistent with the sequential formation of **119**$^{\bullet+}$, **119**$^{2+}$, **119**$^{3+}$, and **119**$^{4+}$. Therefore, the redox process of **119** seems to be similar to that of **61** with the central benzene ring. In contrast, CV analysis of **122** exhibited only one redox wave, involving a four-electron process, to form the corresponding tetracation **122**$^{4+}$. Thus, the sequential formation of cationic states clearly indicates that heteroatom bridging can easily allow cation radicals to adopt the electron delocalization state [Class II] or [Class III]. However, extended Hückel MO calculations for **108a**−**g** indicated that both the through-space and through-bond orbital overlaps between the two TTF moieties are weak and hence unable to account for the observed redox behavior.[80,82] It was thus concluded that the dominant interaction can be ascribed to Coulombic repulsions between the two TTF units, which depend mainly on the nature of the bridging atom and the distances between the two redox centers.

X-ray analyses of **108a**,[78] **108c**,[79,80] **108d**,[80,81] **114c**·TCNQ,[87a] **117a**,[88b] **117b**,[88a] **117b**·$[Au(CN)_2]_{0.42}$,[89] **119**,[90] and **121**[91] have been reported. All crystal packings revealed remarkable two-dimensional networks through S···S, S···X, and X···X (X = heteroatom) contacts. The molecular structures are affected mainly

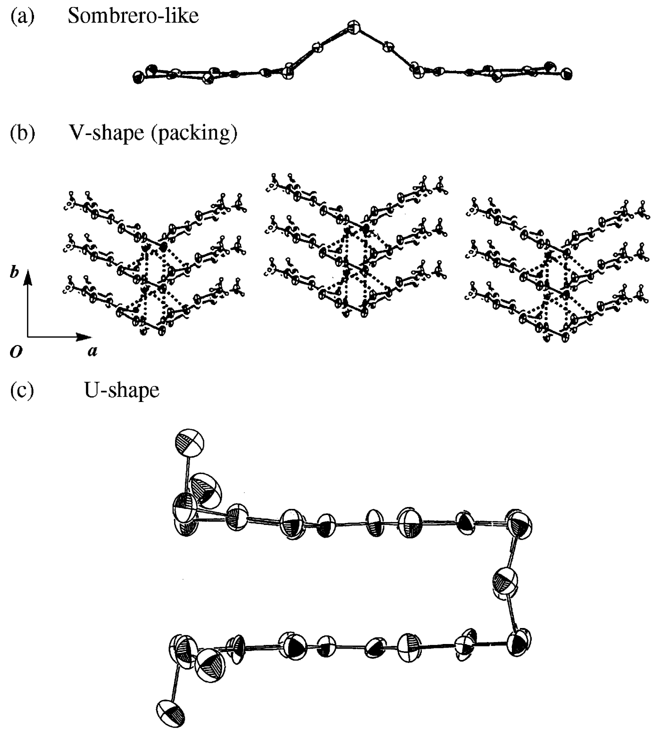


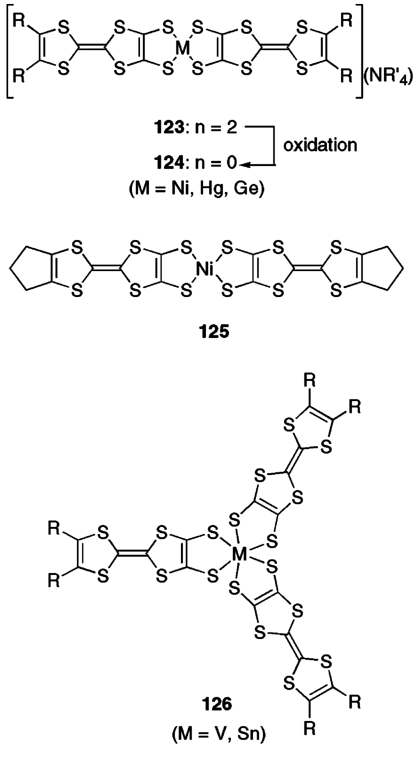
**Figure 11.** X-ray crystal structures of Heteroatom bridged dimers. (a) The crystal structure of **117b** (Sombrero-like). (Reproduced with permission from ref 88a. Copyright 1994 Royal Society of Chemistry.) (b) Stacking columns of **117b**·$[Au(CN)_2]_{0.42}$ (V-shape). (Reproduced with permission from ref 89b. Copyright 1999 Wiley–VCH.) (c) The crystal structure of **121**·$(ClO_4)_2$ (Sombrero-like). (Reproduced with permission from ref 91. Copyright 1998 Royal Society of Chemistry.)

by heteroatom spacers. For instance, two TTF units in **108a**, **108c**, and **108e** are almost mutually perpendicular due to repulsion of the lone pairs of the sulfur atoms, while crystalline **108d** adopts a V-shaped structure. The tellurocycle-fused **117a** and **117b** exhibit nonplanar “sombrero-like” conformations in the neutral state, whereas the **117b**·$[Au(CN)_2]_{0.42}$ salt adopts a V-shaped structure (Figure 11).[89] In the case of **121**, the molecule has a cyclophane-like U-shaped structure attributed to the flexible trisulfide linkage. Interestingly, the dication **121**·$(ClO_4)_2$ derived from **121** also exhibits a U-shaped structure, with TTF moieties that are almost perfectly eclipsed, in a manner similar to $\pi$-dimers (Figure 11).[91]

**Table 5. Electrical Conductivities of CT Complex and Radical Salts**

| donor | acceptor | D:A | $\sigma_n$/S cm$^{-1}$ | refs |
|---|---|---|---|---|
| **108d** | TCNQ | 1:1 | 0.3 ($E_a$ = 62 meV) | 94 |
| **108d** | TCNQ | 1:2 | 8.4 | 94 |
| **108d** | DCNQI | 1:1 | $<10^{-9}$ (insulator) | 94 |
| **108e** | TCNQ | | $(3-5) \times 10^{-5}$ (semiconductive) | 81 |
| **108g** | TCNQ | | $<10^{-2}$ | 81 |
| **113** | iodine | (excess) | $1.7 \times 10^{-4}$ | 85 |
| **113** | iodine | | $8.7 \times 10^{-6}$ | 85 |
| **114c** | TCNQ | 2:1 | 6.0 (semiconductive) | 87a |
| **117b** | DMTCNQ | | 6.0 | 88a |
| **117b** | $Au(CN)_2^-$ | 1:0.42 | 13 | 89 |
| **117b** | $ClO_4^-$ | | 6.6 ($E_a$ = 37 meV) | 89 |
| **117b** | $PF_6^-$ | | 3.3 ($E_a$ = 57 meV) | 89 |
| **119** | TCNQ | 4:3 | 32 ($E_a$ = 53 meV) | 90 |
| **121** | $ClO_4^-$ | 1:2 | insulator | 91 |
| **122** | TCNQ-$F_4$ | 1:3 | $<10^{-6}$ | 92 |

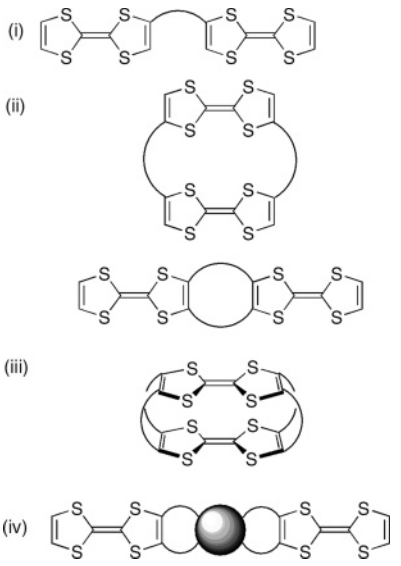
**Chart 5**



Due to the large overlap resulting from chalcogen–chalcogen and/or heteroatom–chalcogen interactions, some bis-TTFs linked by one or two heteroatoms show high conductivities. In fact, **108d** shows semiconductive behavior ($5 \times 10^{-5}$ S cm$^{-1}$) even in the neutral state.[80,93] Electrical conductivities of typical CT complexes and cation radical salts are summarized in Table 5. The CT complex derived from **108d**,[94] which is linked by two flexible heteroatoms, shows fairly high conductivities, whereas the CT complexes derived from **108e** and **108g** show lower conductivities.[94] The cation radical salts of **117a** exhibited semiconductive resistivities with small activation energies ($E_a$ = 30–60 meV). However, their room-temperature electrical conductivities are relatively high ($\sigma_{rt}$ = 1–10 S cm$^{-1}$).[89] The electrical conductivity of the CT complex of **119** with TCNQ is high (32 S cm$^{-1}$), reflecting the presence of a number of Se···S and S···S contacts.[90] IR spectroscopy indicated that the CT complex incorporates three differently charged TCNQ species. In contrast, the cation radical salt **121**·$(ClO_4)_2$ is an insulator.[91]

Metal-bridged bis-TTF dithiolates **123**–**126** have attracted much recent attention in the field of organic conductors and superconductors (Chart 5).[76b] Complexes **123** and **124**, involving Ni,[95,96a] Hg,[96b] and Ge[97] atoms, have already been reported by several groups. Although intramolecular interactions between the two TTF units are very weak in the neutral state, the crystals of these complexes adopt three-dimensional intermolecular interactions. Kobayashi and coworkers reported a single-component synthetic metal based on the neutral complex **125,** which showed a high conductivity ($\sigma_{rt}$ = 400 S cm$^{-1}$).[98] Metal complexes of **126** with tri-TTF dithiolate groups were

**Scheme 25**



reported independently by Sugimoto[99] and Matsubayasi.[100]

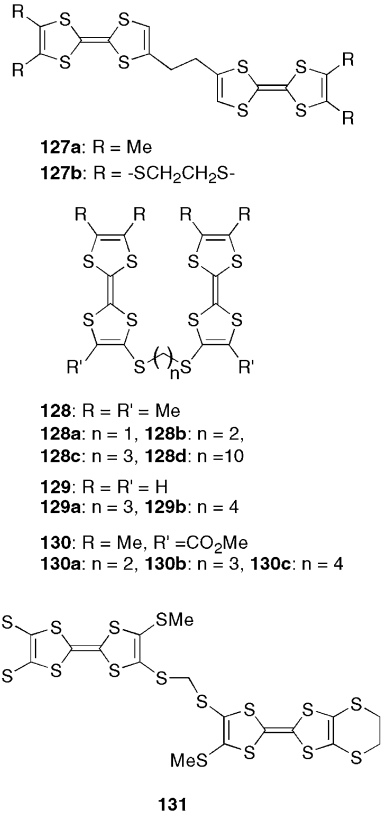
## 5. σ-Bond-Linked TTF Oligomers

A number of non-conjugated bis-TTFs and oligo-TTFs in which the TTF units are connected with σ-bond linkers, such as, for example, alkyl and thioalkyl chains, have been researched recently. Compared with the conjugated compounds, these generally have more flexible structures due to the conformational change resulting from the σ-bond linkers. As a result of this flexibility, their conformations can easily be converted into the dynamically favorable conformers by using the intramolecular through-space interactions between the TTF units in the neutral and oxidation states. These electron donors can be used as building blocks for the effective construction of supramolecular architecture in material science and nanochemistry. Moreover, multi-TTFs connected with other functional moieties, such as crown ether units, fullerenes, and chromophores, are also synthesized for use as functional materials. Bis-TTFs and oligo-TTFs linked by σ bonds are divided into the following four classes based on the junction type and the characteristic features: (i) linear molecules with a single linkage, (ii) macrocycles and cyclophanes with a double linkage, (iii) cyclophanes with a quadruple linkage, and (iv) systems that are radially expanded from the central core (Scheme 25). Syntheses and properties of these classes are reviewed in the following sections.

### 5.1. Linear Molecules with a Single Linkage

Linear bis-TTFs with a single linkage can be defined as dimeric compounds with the connection between the two TTF units at the 4-position. These types of molecules have been widely investigated from the viewpoint of controlling stoichiometry and band filling in the conductive complex. Since **127a** was synthesized by Bechgaard and co-workers in 1990,[101a−d] several groups have reported the nonconjugated dimeric TTFs **127b**,[101e,f] **128**,[102] **129**,[103] **130**,[104] and **131**[105] (Chart 6). Bechgaard and

**Chart 6**



**127a**: R = Me
**127b**: R = -$SCH_2CH_2S$-

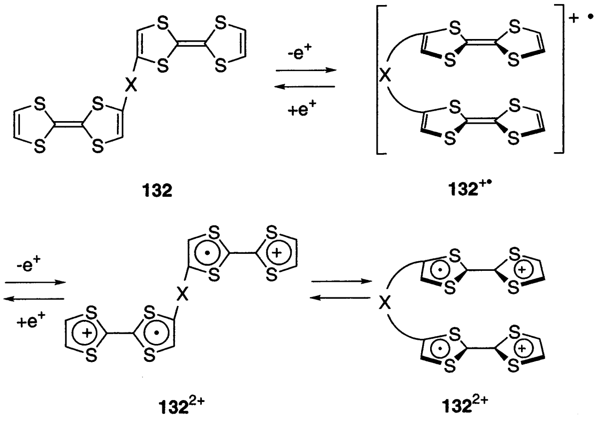
**128**: R = R' = Me
**128a**: n = 1, **128b**: n = 2,
**128c**: n = 3, **128d**: n =10

**129**: R = R' = H
**129a**: n = 3, **129b**: n = 4

**130**: R = Me, R' =$CO_2Me$
**130a**: n = 2, **130b**: n = 3, **130c**: n = 4

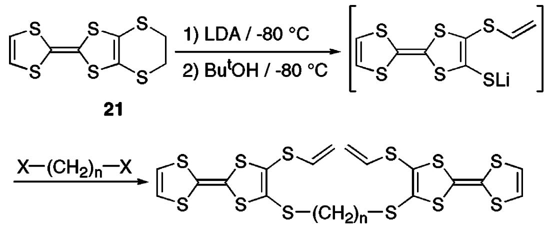
**131**

**Scheme 26**



Jørgensen's group studied the electrochemical behavior of a series of bis-TTFs **128** with different chain lengths.[102] Bis-TTFs **128a** and **128b**, having methylenedithio and ethylenedithio linkers, respectively, showed three reversible redox waves which suggested two one-electron-transfer stages and one two-electron-transfer stage, while **128c** and **128d** with longer σ-linkers ($n = 3$ and 10) showed two two-electron redox waves like the monomeric TTFs. Similar multiredox behaviors were also found for **127a**, **130b**, and **131**. These multiredox stages can be explained by postulating a sandwich structure via the through-space interactions for the stabilization of the monocationic species (Scheme 26). One-electron oxidation of **132** may give the mixed-valence intermediate **132**$^{+\bullet}$ followed by the removal of the second electron to afford the dicationic **132**$^{2+}$ so that the first and second oxidation waves are split, in contrast to the non-splitting of the third and fourth ones.

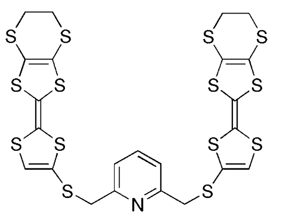
**Scheme 27**



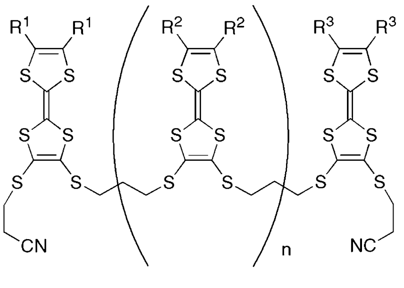
**133**

Sugawara and co-workers reported the unique properties of the radical salts in the crystalline state.[105] Electrocrystallization of **131** gave two polymorphic ion radical salts with $ClO_4^-$. One has 2:1 donor to acceptor stoichiometry and a conductivity of 0.1 S cm$^{-1}$ in which the donor molecules exist in a twisted U-shaped conformation. The other has 1:1 donor to acceptor stoichiometry and is insulating, with the donor molecules existing in a cyclophane-like eclipsed U-shaped conformation.

In recent years, several groups have synthesized other, unique spacer-linked bis-TTFs **133**[106] and **134**[107a] and the linear oligo-TTFs **135**.[107b−d] The bis-TTFs **133** were synthesized from EDT-TTF **21** by unique methods (Scheme 27). Treatment of **21** with LDA followed by alkylation with α,ω-dihaloalkane afforded the bis-TTFs **133** via the unexpected ring opening of the ethylenedithio unit. Fabre and co-workers synthesized oligo-TTFs **135** via stepwise connection with the TTF moiety and found that one of the oligo-TTFs **135** has a similar multiredox behavior to bis-TTF **128a**. In addition, Otsubo's group reported the syntheses and structures of single-linkage bis-tetraselenafulvalenes.[108]

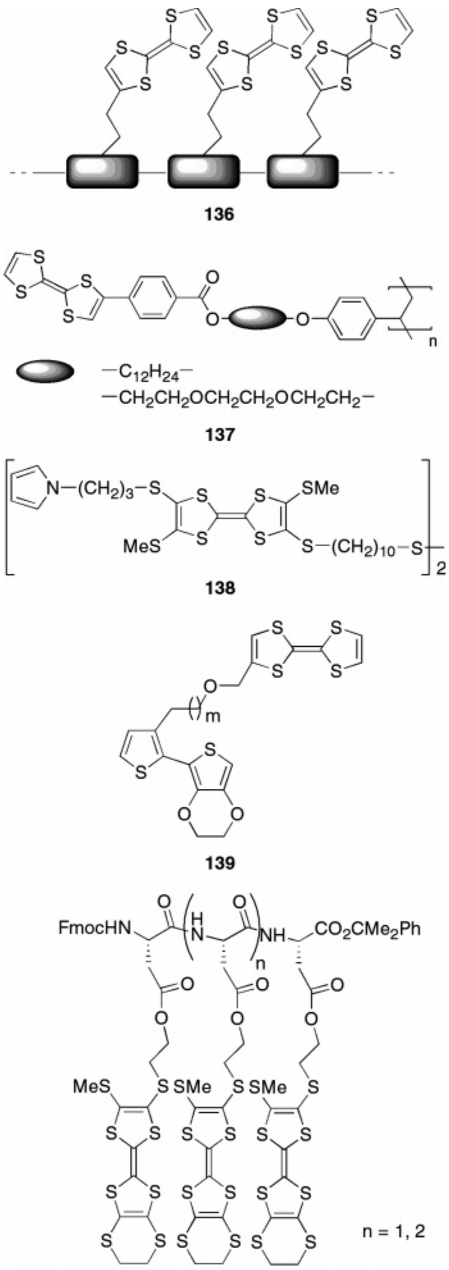


**134**



**135**

**Chart 7**



**136**

**137**

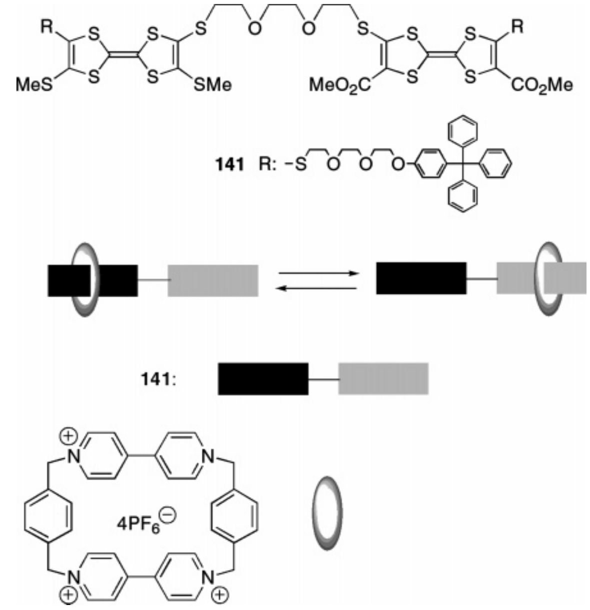
**138**

**139**

**140**

Functional polymers **136** incorporating TTF units in their side chains have been studied intensively. A TTF-side-chain polymer could provide partial stacking of the TTF subunits[109] similar to the crystal lattice arrangement of its monomeric counterpart if a smectic phase were achieved. Moreover, a variety of other functional moieties linked to TTF units can be combined and polymerized because monomers including TTF units may be easy to prepare. Poly(*p*-hydroxystyrene) **137** incorporating TTF units was synthesized from poly(*p*-hydroxystyrene), namely, TTF units were introduced to the polymer after polymerization.[110] Although $^1$H NMR spectra of **137** suggested quantitative formation, IR spectra showed weak OH absorption, which unfortunately corresponded to uncovered poly(*p*-hydroxystyrene). Other groups researched the concept of combining TTF systems connected with linear π-conjugated polymers. Bifunctional monomers such as pyrrole combined with TTF **138**[111] and bithiophene combined with TTF **139**[112] were prepared, and successful electrochemical polymerizations were demonstrated. Peptides **140** with a TTF side chain were also synthesized, and electrochemical studies of **140** indicated that they might undergo conformational reorganization upon oxidation of the TTF units.[113] (See Chart 7.)

**Scheme 28**

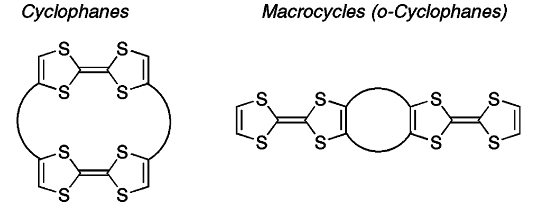


Becher and co-workers synthesized the linear bis-TTF **141** from the viewpoint of molecular machines (Scheme 28).[114a] [2]Rotaxanes containing a TTF unit have been studied intensively as potential molecular shuttles.[114b−h] The shuttling process in supramolecular structures of this type has been controlled by chemical, photochemical, and electrochemical methods. Therefore, [2]rotaxane **141** derived from linear oligo-TTFs provides the possibility of creating new molecular machines. Bryce and co-workers used the donor properties of bis-TTFs to construct a stopperless [2]pseudorotaxane and reported the formation of a [3]pseudorotaxane.[114i]

## 5.2. Cyclophanes and Macrocycles with a Double Linkage[115]

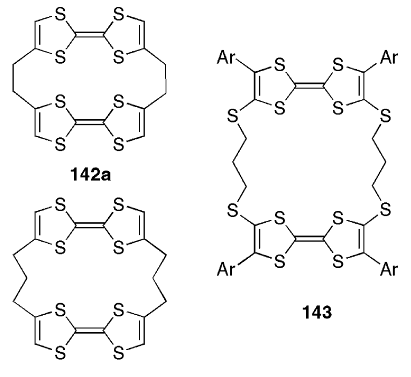
Bis-TTFs containing a double linkage can be roughly divided into the following two types, based on the junction positions on the TTF units (Scheme 29):

**Scheme 29**



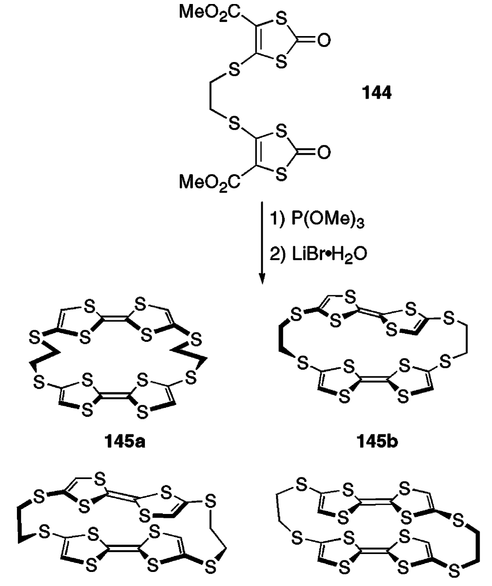
(i) *m*- or *p*-cyclophanes, where one connection position on a TTF unit is at one dithiole ring and the other is at the other one, (ii) macrocycles (*o*-cyclophanes), where two connection positions on a TTF unit are on the same dithiole ring.

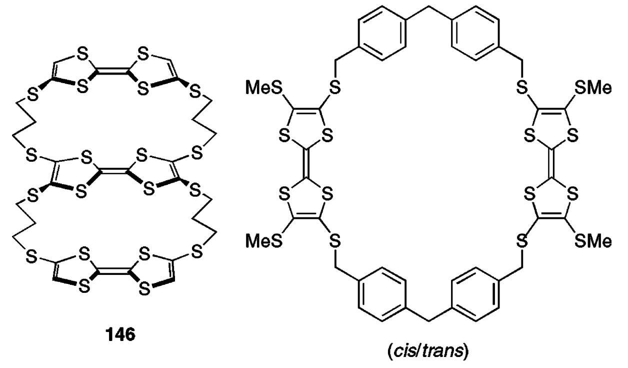
The first examples of cyclophane-type bis-TTFs **142** were reported by Staab in 1980.[116a] The structure of **142a** was determined by X-ray analysis. This result suggests that **142a** has a steplike anti conformation. Although **143** with longer double bridges was synthesized, no information on its structure was described.[116b]



Cyclophane-type bis-TTF has essentially four regioisomers, i.e., meta-meta, meta-para, and two para-para isomers. Otsubo's group synthesized all possible isomers **145a**−**d** of the bis-TTF-cyclophane (Scheme 30).[117] The homocoupling of the bis-dithiole precursor **144** with trimethyl phosphite followed by decarboxylation afforded a mixture of **145a**−**d**. Bis-TTFs **145a**, **145b**, and **145c** were successfully purified as crystals, and these structures were determined by X-ray analysis. However, the fourth isomer **145d** could not

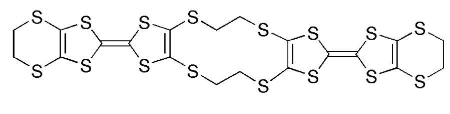
**Scheme 30**



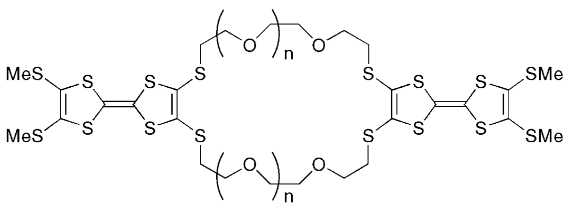


**146**

**147**



**148**



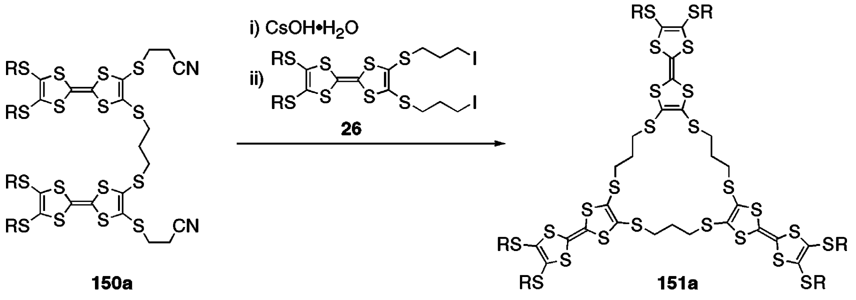
**149a:** n = 1
**149b:** n = 2

be isolated in a pure form. These isomers were stable in the solid state but gradually converted into isomeric mixtures in solution. The same group also succeeded in synthesizing the steplike cyclophane trimer **146**[118] and the selenium analogues of these cyclophane-type dimers.[119] Compounds **147** with longer spacers have been reported and include cis/trans isomers.[120] The crystal structures of **147** revealed that *cis*-**147** possesses a planar TTF moiety while *trans*-**147** has a distorted TTF unit.

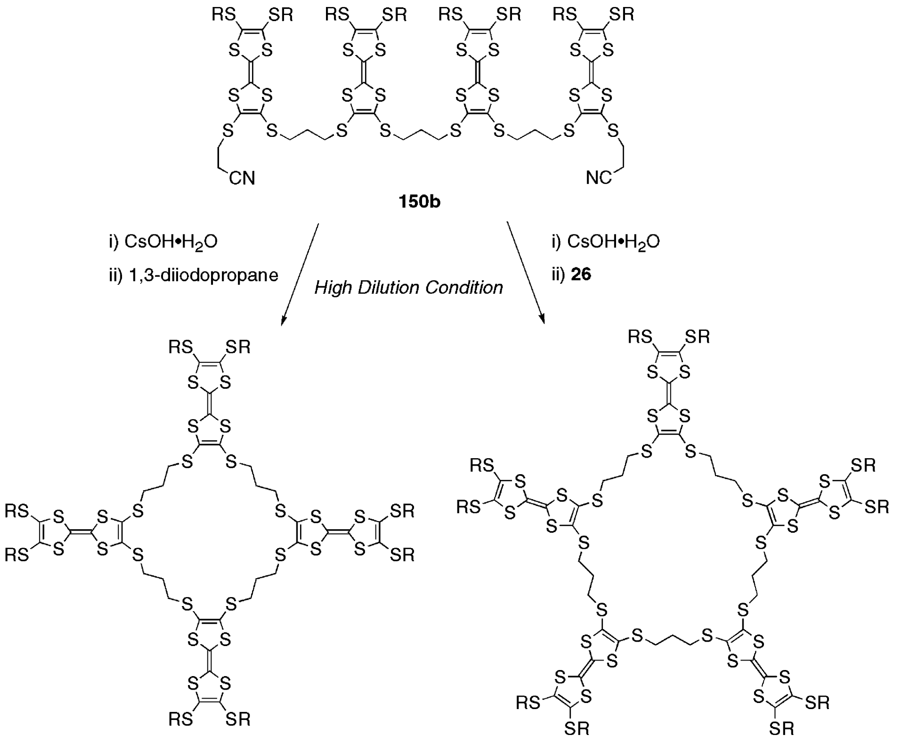
Among macrocycles containing oligo-TTF moieties, an intriguing macrocyclic bis-TTF **148**, which can behave like a molecular tweezer, was synthesized.[121] The neutral **148** has a U-shaped conformation, so that it has a cavity which can include an electron acceptor through a CT electronic interaction. Because the cavity size is very flexible, it affords inclusion complexes not only with planar $\pi$-acceptors such as DDQ[121c] but also with the giant molecule $C_{60}$.[121b]

Recently, many macrocyclic bis-TTFs with a variety of spacers, such as alkyl chains,[122] dialkylpyridine,[123] dialkylbiphenyl,[124] dialkylbutadiyne,[124] and crown ether,[125] have been studied. Crown ethers **149a**,**b** containing two TTF units were prepared, and the crystal structures of the divalent cations and the CT complexes were described.[125] These X-ray analyses suggest that **149a**$^{2+}$ takes a Z-type intramolecular $\pi$-dimer structural conformation and the magnitude of intramolecular $\pi$–$\pi$ overlap depends on the ring size of the macrocycles. Multiannulated macrocycles **150a**–**c** were also synthesized from linear oligomers **151a**,**b** (Schemes 31 and 32).[107c,126] The intermolecular ring-closure reactions of the linear oligomers **151a**,**b** under high dilution conditions afforded the corresponding **150a**–**c** in good yields. This modular

**Scheme 31**

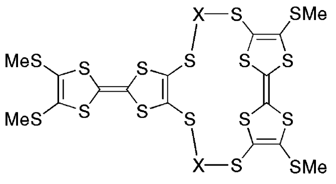


**Scheme 32**

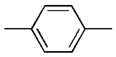


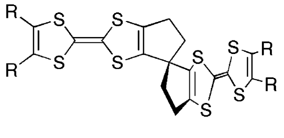
and convergent methodology is quite versatile and may be extended to a variety of different spacers and substituents.

Bryce's group reported the synthesis of the cyclophane-macrocycle-mixed dimer **152**, and CV analysis of **152** showed three redox waves, reflecting the intramolecular interaction in $\mathbf{152}^{\bullet+}$ and $\mathbf{152}^{2+}$.[127] Tatemitsu and co-workers designed and synthesized the unique TTF dimers **153** where the two TTF units are annulated on a spirocyclic system and hence rigidly fixed in the orthogonal directions.[128] Cyclic voltammetry of **153** showed four reversible redox potentials, and all the observed redox waves of **153** were assigned to one-electron-transfer processes on the basis of peak-to-peak separation.



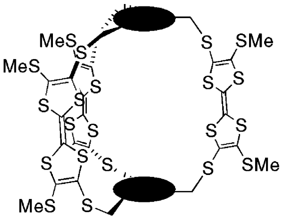
**152** X = $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_2O(CH_2)_2$



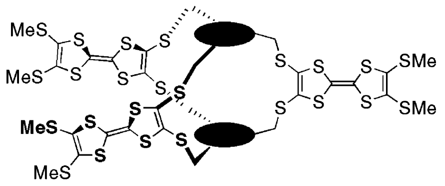


**153a**: R = H
**153b**: R, R = $SCH_2CH_2S$

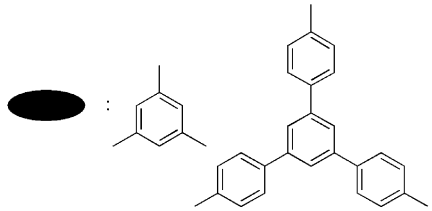
Becher's group studied the synthesis and properties of cage-type molecules such as **154** and **155** intensively.[129] These molecules have a cavity inside the cyclophane, so they are expected to be applicable for supramolecular chemistry. Pyrrole annulated cage-type molecules were also reported, and the excellent results obtained are reviewed in their accounts.[130]



**154**



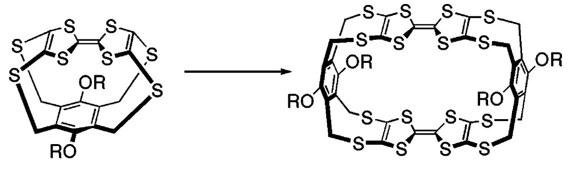
**155**



## 5.3. Cyclophanes with a Quadruple Linkage[115]

In bis-TTFs containing a quadruple linkage, one TTF unit is connected to the other TTF unit at four positions. Compared to the single- and double-linkage types, this type of bis-TTF has a more fixed conformation, so that it is expected that sandwich TTF cyclophanes[122,131−133] such as **157**, **159**, and **160** have an obvious interaction between the TTF units. Müllen and co-workers reported that the cyclophanes **157a**−**c** were formed via a metathesis-like dimerization of the precursors **156** under anodic oxidation conditions (Scheme 33).[131] The molecular structure of **157b** indicates that both TTF units are stacked face-to-face in a parallel arrangement. Each TTF moiety has a nonplanar, bent structure and curves unexpectedly toward the direction of the center of the cavity. The TTF cyclophane **159** was synthesized using phosphite-mediated homocoupling of the cyclic bis(1,3-dithiole-2-one) **158** (Scheme 34).[132] The face-to-face interaction was also observed by X-ray analysis and in electronic spectra.

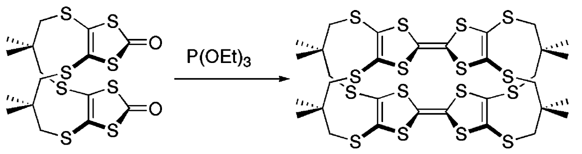
**Scheme 33**



**156**

**157a**: R = n-propyl
**157b**: R = n-butyl
**157c**: R = n-hexyl

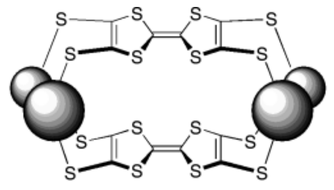
**Scheme 34**



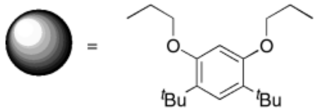
**158** **159**

Becher's group designed the cylindrical bis-TTFs **160a**,**b** having larger cavities as host molecules.[133] The compounds **160a**,**b** were synthesized by a stepwise strategy so that a variety of large spacers could be introduced into the cyclophane skeleton. The cylindrical structure and large cavity of **160b** was confirmed by X-ray analysis. One molecule of **160b** in one unit cell includes four chloroform molecules and one methanol molecule.

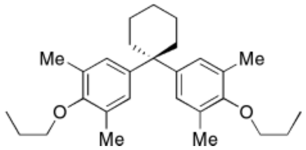
In contrast to eclipsed TTF cyclophanes, orthogonal bis-TTFs with a quadruple linkage have been prepared and are called crisscross bis-TTFs.[122,134,135] In 1995 Ostubo's group[134] and Sugawara's group[135] independently reported the first examples of crisscross bis-TTFs **161a**−**d**. X-ray analysis of **161c** showed that two TTF moieties overlap each other in a crisscross manner. Cyclic voltammograms of **161a**−**d** provided interesting information on the different types of intramolecular interactions. The compound **161b** showed four reversible one-electron redox waves,



**160**

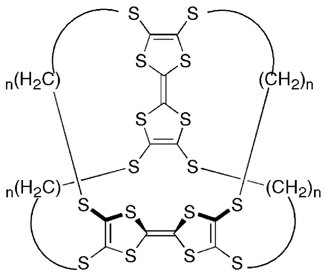


**160a**



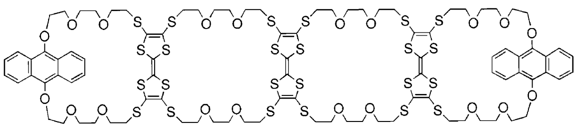
**160b**

similar to the TTF dimer **153** that has an orthogonal interaction between the two TTF units. Although **161c** only showed two two-electron redox waves, the cyclic voltammogram of **161d** exhibited interesting behavior, i.e., a single wave for the first two-electron oxidation and a split wave for the second one. Recently, interesting properties of the ion-radical salt derived from **161b** have been reported.[135e] The cation radical salt, **161b**·Br·(1,1,2-trichloroethane)$_2$ prepared by electrocrystallization, exhibited a ferromagnetic interaction on the basis of the through-bond coupling even when the dimeric donor was singly oxidized. Although the degree of the coupling is weak, the phenomenon opens up the possibility of designing a new organic ferromagnetic metal.



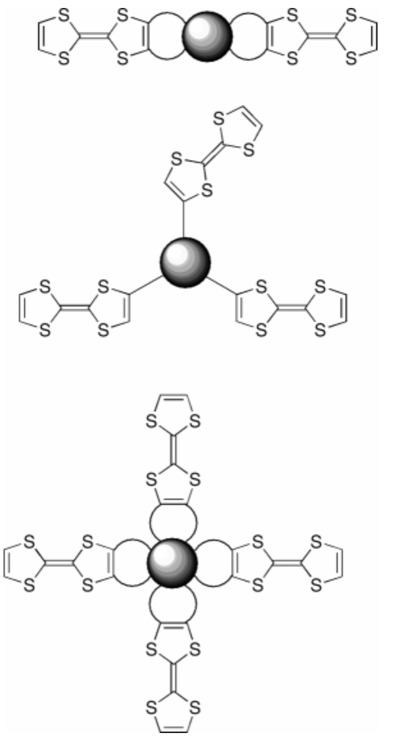
**161a**: n = 2
**161b**: n = 3
**161c**: n = 4
**161d**: n = 5

The unique macrocyclic TTF trimer **162** that has a quadruple linkage was prepared by Becher's group.[136] The compound **162** includes four crown ether moieties and is expected to be applicable for use as a partial unit for catenanes. CV analysis of **162** also showed complex electrochemical properties.



**162** (*cis/trans*)

**Scheme 35**



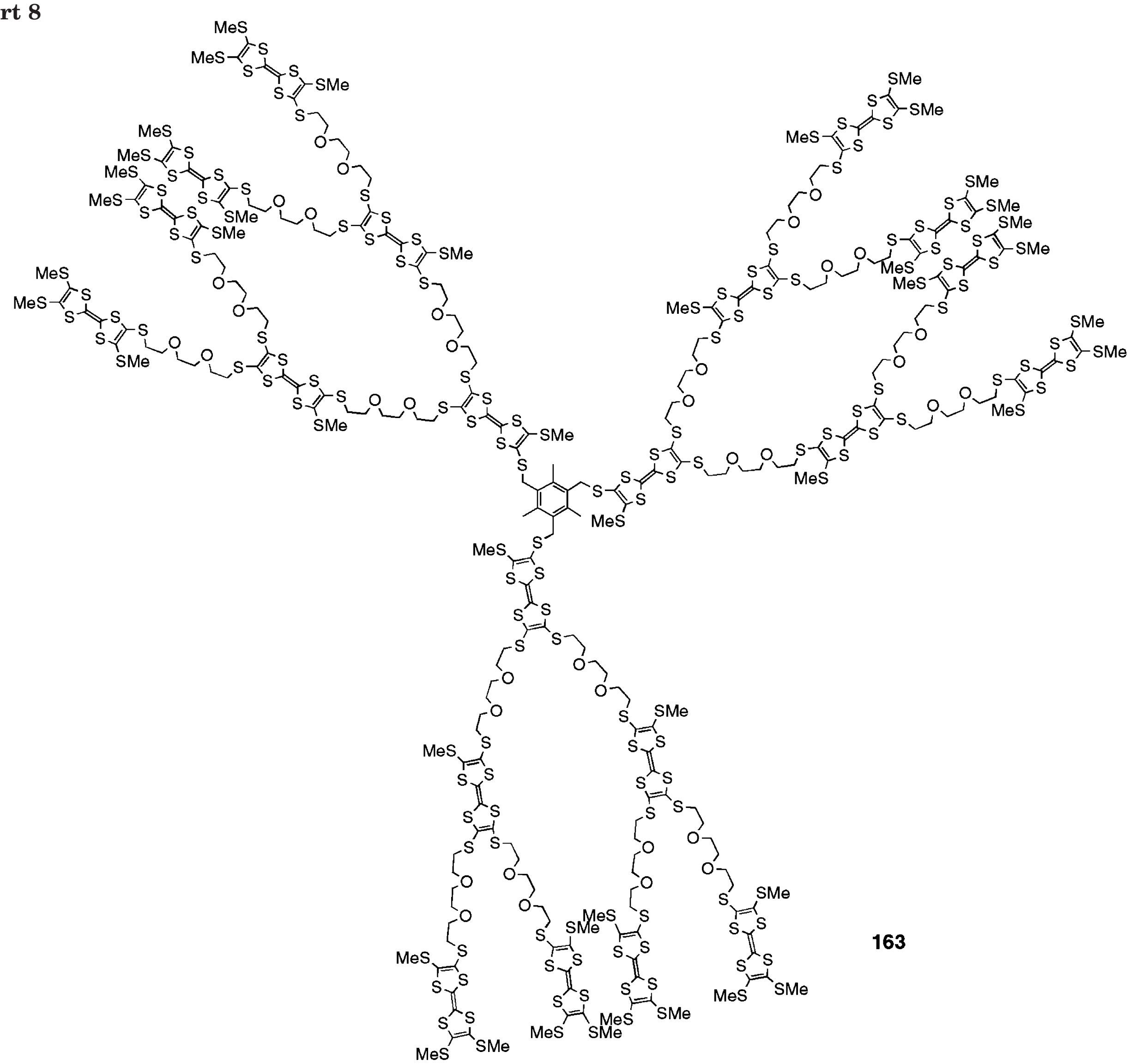
## 5.4. Radially Expanded Systems

Multi-TTFs with radially expanded structures can be defined by a characteristic feature in which TTF units radiate from the central core (Scheme 35). These types of oligo- and multi-TTFs may be expected to demonstrate multifunctionality because a central core and TTF branches exhibit individual and/or cooperative functionalities. Dendrimers incorporating TTF units are cited as representative examples.

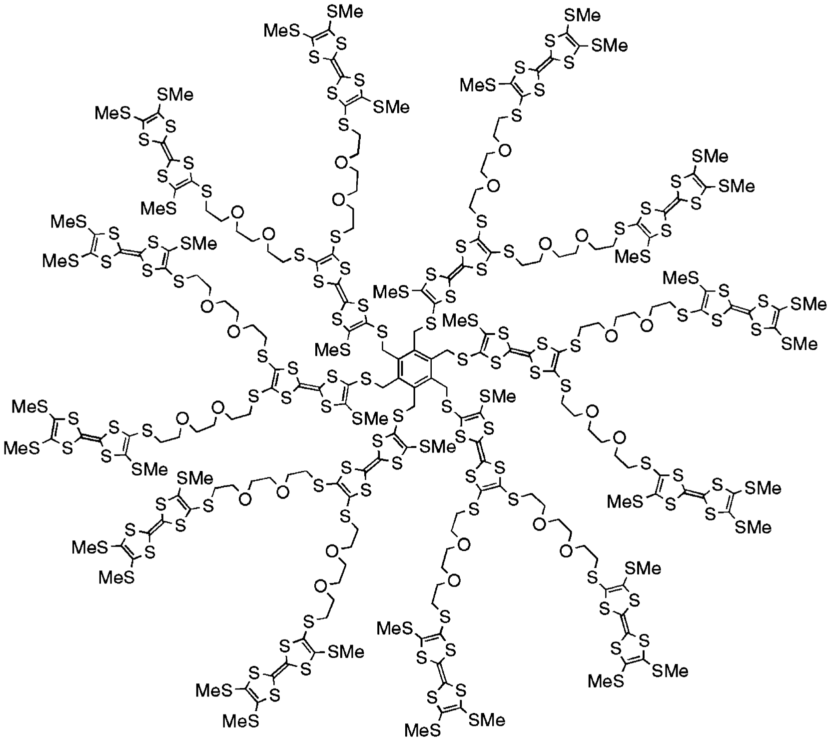
A variety of radial multi-TTFs with a benzene core have been reported.[137−139] Bryce and Becher's group reported several TTF−glycol dendrimers containing a benzene core (Chart 8). Dendrimer **163** with 21 TTF units in one molecule was synthesized by the convergent method.[137a] Electrochemical analysis of **163** showed two redox waves, successively generating $\mathbf{163}^{21+}$ and $\mathbf{163}^{42+}$. Electronic spectra of the oxidized $\mathbf{163}^{21+}$ revealed intra- and intermolecular $\pi$-dimer interactions between partially oxidized TTF units. The bigger dendrimer **164**, which branches in six directions, can also be prepared by a similar method.[137c]

Compound **165** is a dendrimer with aryl ester tethers and a functionalized surface with 12 TTF units (Chart 8). Bryce and co-workers synthesized **165** by using a convergent strategy based on a receptive coupling/deprotection sequence with 4-(hydroxymethyl)−TTF as the starting monomer. They also reported the similar aryl ester dendrimer **166** incorporating both $\pi$-donor TTF units and $\pi$-acceptor anthraquinone units. Dendrimer **166** showed a clean amphoteric redox behavior with reversible switching between cationic and anionic states under electrochemical conditions. These donor−acceptor systems

**Chart 8**

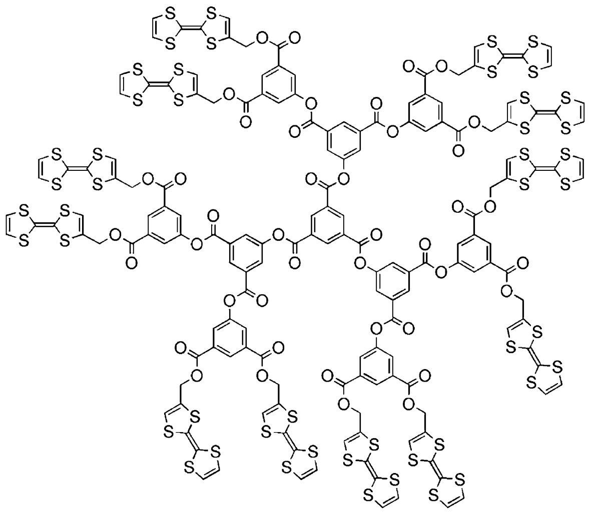


**163**

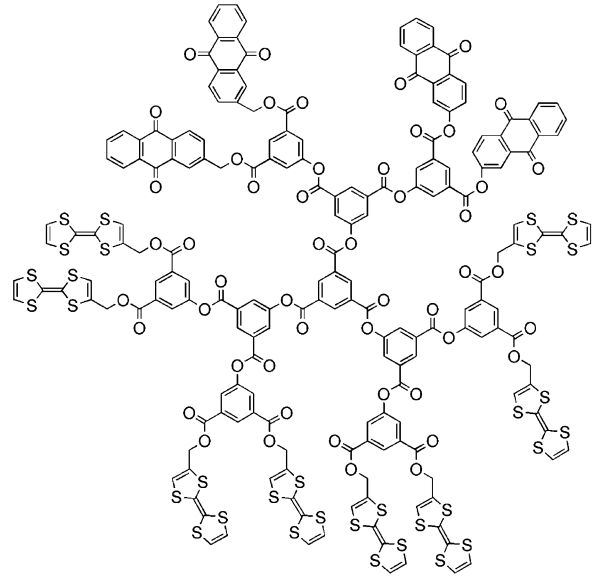


**164**

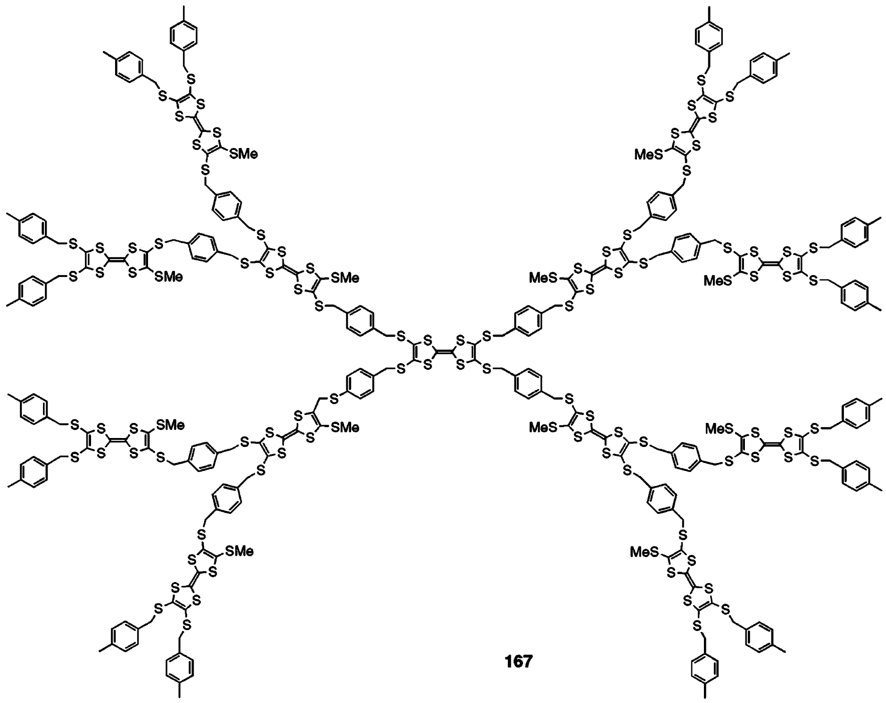
**Chart 8 (continued)**



**165**

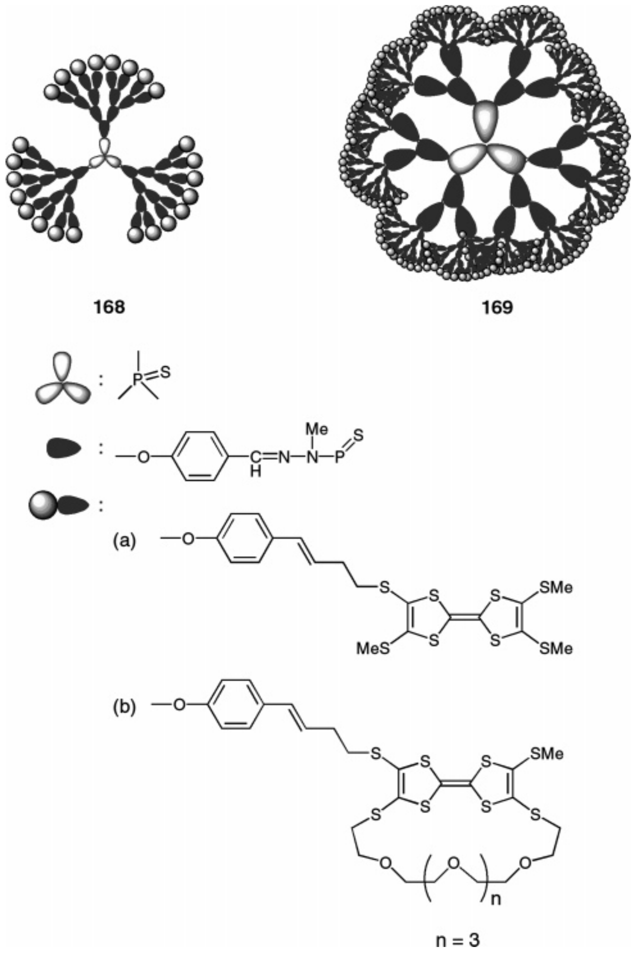


**166**



**167**

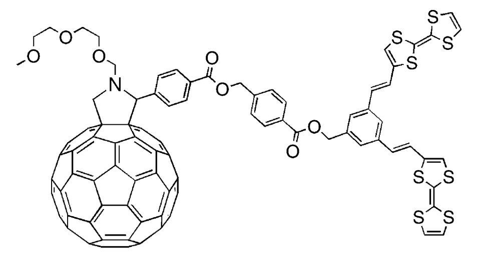
**Chart 9**



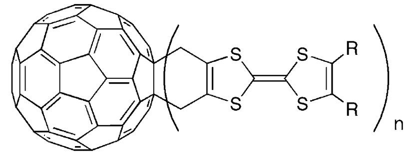
may enable the study of intramolecular charge-transfer interactions within a dendritic microenvironment. Another type of dendrimer, the radial multi-TTF **167** with a TTF core, has also been synthesized.[125b,137c,140]

Sallé, Majoral, and co-workers reported the unique properties of dendrimers **168a**,**b** and **169a**,**b**.[141] Dendrimer **169a** has 96 redox-active TTF moieties on its periphery, which allows the generation of a polycationic species bearing 192 positive charges on its surface. This work was extended to construct novel devices in nanochemistry, and **168a**,**b** and **169a**,**b** were incorporated in a modified electrode by using electrodeposition. The modified electrode incorporating immobilized dendrimer **168b** can be used for the electrochemical sensing of metal cations such as $Ba^{2+}$ (Chart 9).

Other functional units such as fullerenes,[142,143] cyclodextrins,[144] and phthalocyanine[145−148] can also be introduced into the core of radial multi-TTFs. Recently, extensive efforts have been dedicated to the development of a $C_{60}$-based donor−acceptor system which leads to light-induced intramolecular charge separation, i.e., a solar battery. To construct new systems, the fullerene triad **170** containing a bis-TTF unit was synthesized by a stepwise procedure.[142] Hudhomme's group prepared the $(TTF)_n$−$C_{60}$ polyads **171** using [4 + 2] cycloaddition of bismethylidene TTF with $C_{60}$.[143]



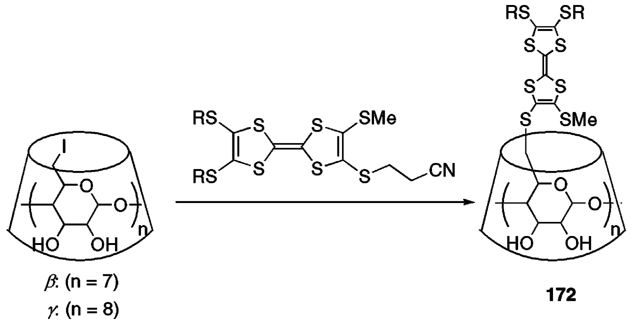
**170**



**171**

Cyclodextrins (CDs) have been used as platforms to carry TTF units, and CDs functionalized with an alkyl chain at the primary OH position have been shown to form Langmuir−Blodgett (LB) films. Sallé and co-workers carried out the synthesis of CD-connected multi-TTFs **172** according to a convergent method (Scheme 36).[144] These systems are interesting because they have both the complexing ability of the CD cavity and the redox properties of TTF units. Furthermore, the ability of the CD moiety to promote film transfer was transmitted successfully to produce high-quality LB films incorporating TTF units.

**Scheme 36**

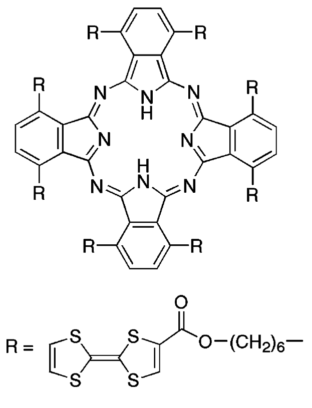


Since phthalocyanines are very important chromophores with electronic, optical, structural, and coordination properties, they have attracted considerable attention in chemistry and physics. Phthalocyanines incorporating multi-TTF units such as **173**,[145] **174**,[146] and related molecules[147,148] are expected to demonstrate multifunctionality in the fields of nonlinear optics (NLO) and liquid crystals, LB films, and electrochromic devices (Chart 10).

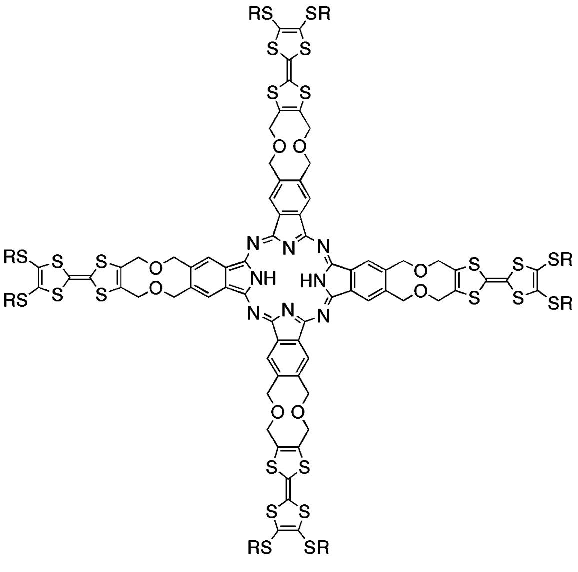
## 6. Summary

Although molecular engineering based on TTF oligomers and hybrid systems containing TTF units has expanded during the last 15 years, the main efforts have been focused on the "properties-directed synthesis" of large molecules and molecular assemblies. Thus, supramolecular chemistry in

**Chart 10**



**173**



**174**

thisfield has developed rapidly, and the transition from supramolecules to materials has gradually proceeded with the realization of molecular switches, devices, and machines. In contrast to the stubborn, traditional means, the flexibility of designing supramolecular materials may make it possible to couple two or several optimized properties into the same material.

Bi-TTFs, bis-TTFs, and related TTF-oligomers summarized in this review are a relatively new class of donors that play an important role in the basic science of organic conductors. In contrast to the parent TTF and its derivatives, dimeric and oligomeric TTFs exhibit intramolecular electronic interactions between the TTF units, and hence, the stoichiometry of the desired complexes can be controlled depending on the nature of the spacer groups. In addition, they have versatile molecular shapes such as linear, crooked, butterfly-shaped, star-shaped, helical, cyclic, and dendritic structures, which can lead to the formation of a variety of CT complexes and radical cation salts with unique molecular arrangements.[2,10] Dimeric TTFs and related compounds thus provide an opportunity for designing novel organic conductors having interesting properties such as ferromagnetism, electrochromism, solvatochromism, optical nonlinearity, and chirality.[149]

Multi-TTF systems constructed using dimeric and oligomeric TTFs also provide an opportunity for supramolecular chemistry and nanotechnology. Redox-active molecular wires, belts, capsules, and shuttles have recently been synthesized using oligo-TTFs as building blocks. Since dimeric and oligomeric TTFs have been employed as macrocyclic ligands, LB film-forming amphiphilic molecules, and dendritic macromolecules,[150−152] molecular memories, electronic devices based on multistage redox systems, and nanomachines could be designed using multi-TTF systems in the future.[153−155]

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