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Recent Synthetic Advances of Tetrathiafulvalene-Based Organic Conductors

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The synthetic chemistry of tetrathiafulvalene (TTF)-type electron donors has been markedly promoted by introducing two key reactions, the one-pot preparation of 1,3-dichalcogenole-2-chalcogenones from terminal alkynes and the formation of heterocyclic rings via transalkylation on a chalcogen atom. In combination with a conventional trialkyl phosphite-promoted coupling reaction of 1,3-dichalcogenole-2-chalcogenones, the first reaction constitutes a ready access to the tetrachalcogenafulvalene skeleton. As a result, a number of previously inaccessible TTF-type electron donors were readily obtained. These included tetraselenafulvalene (TSF) derivatives, the selenium/sulfur or selenium/tellurium hybrid systems, dimeric TSFs linked with a single spacer group, and sophisticated stacked TSF phanes. The second reaction is very useful in constructing additional heterocyclic ring(s) on the tetrachalcogenafulvalene skeleton. A wide variety of five-, six-, and seven-membered heterocycle-fused TTF-type compounds were thus synthesized. These were systematically examined for superior electron donors of conductive molecular complexes. This study resulted in the discovery of two novel electron donors, methylenedithio-tetraselenafulvalene and methylenedithio-diselenadithiafulvalene, that form unique superconductors with exceptionally high conductivities at room temperature. The scopes and limitations of these synthetic reactions are described in connection with the recent research trends of TTF-based organic (super)conductors.

Since the discovery of the highly conductive molecular complex of tetrathiafulvalene (**1**, TTF) and tetracyanoquinodimethane (**2**, TCNQ) in 1973,[1] the development of novel TTF-type electron donors has been actively pursed (Fig. 1). As a result of many year's efforts, more than one thousand TTF-type compounds have been synthesized so far.[2] They have been studied not only as electron donors for conductive molecular complexes[3] but also as functionalized building blocks in materials chemistry[4] and supramolecular chemistry.[5] The crystal structure of the TTF-TCNQ complex is comprised of segregated stacking columns of donors and acceptors in the mixed valence states; accordingly, it exhibits an anisotropic conductivity (500 $\mathrm{S\,cm^{-1}}$) along the stacked direction.[6] However, its metallic behavior becomes insulating at a low temperature (59 K) owing to the Peierls instability characteristic of a low-dimensional conductor.[7] Strong intermolecular interactions are required not only to enhance the conductivity but also to suppress the Peierls transition. In the molecular design of superior TTF-type electron donors, two principal guidelines have been proposed: (1) replacement of the sulfur atoms of the TTF skeleton by selenium or tellurium atoms and (2) annelation of additional heterocyclic rings to the TTF skeleton. According to the first guideline, tetraselenafulvalene (**3**, TSF)[8] and tetratellurafulvalene (**4**, TTeF)[9] were synthesized. As expected, the TSF•TCNQ complex showed not only the enhancement of the conductivity (800 $\mathrm{S\,cm^{-1}}$) but also the lowering of the metal–insulation transition temperature (40 K). Furthermore, the TTeF•TCNQ complex showed an extraordinary high conductivity (2200 $\mathrm{S\,cm^{-1}}$) and remained metallic down to a measurable low temperature (2 K). Obviously, strong non-bonded interactions between the introduced heavy chalcogen atoms can strengthen intermolecu-

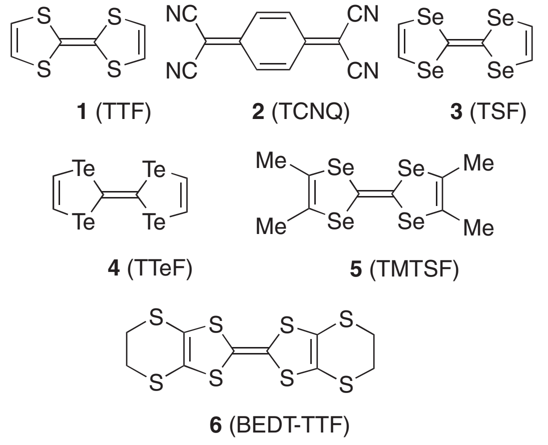

Fig. 1.

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lar contacts enough to suppress the Peierls instability at low temperature.[10] Further study along this guideline led to the development of tetramethyltetraselenafulvalene (**5**, TMTSF),[11] which gave the first organic superconductors $(TMTSF)_2PF_6$ under pressure in 1980[12] and $(TMTSF)_2ClO_4$ under ambient pressure in 1981.[13] It is worth noting that these quasi-one-dimensional compounds become superconducting only at a very low temperature of around 1 K. According to the second guideline, bis(ethylenedithio)tetrathiafulvalene (**6**, BEDT-TTF) was synthesized.[14] Here the sulfur atoms of the fused heterocyclic rings can also contribute to increase intermolecular contacts and stabilize the metallic state. As a result, the BEDT-TTF donor produced a great number of quasi-two-dimensional superconductive complexes. These have different types of molecular packings: termed α, β, γ, θ, and κ phases.[15] Among them, κ-type superconductors, such as $(BEDT\text{-}TTF)_2Cu(NCS)_2$,[16] $(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$,[17] and $(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$,[18] are unique in terms of having very high critical temperatures $T_c > 10$ K.[19] The κ-type conductors have a quite different packing from the conventional stacking structures of the TTF-based conductors: the BEDT-TTF molecules form face-to-face pairs, and adjacent pairs are almost orthogonally aligned.[20] Short sulfur–sulfur interactions among adjacent molecules form a two-dimensional conduction sheet in the crystal structure.

Following TMTSF and BEDT-TTF, the fourteen TTF-type compounds have so far been found to be able to form superconductors: **7**,[21] **8**,[22] **9**,[23] **10**,[24] **11**,[25] **12**,[26] **13**,[27] **14**,[28] **15**,[29] **16**,[30] **17**,[31] **18**,[32] **19**,[33] and **20**[34] (Fig. 2). Notice that nearly half of these donors are of selenium-containing types. In addition, it should be emphasized that the selenium-containing TTF-type compounds tend to give unique superconductors. Specifically, bis(ethylenedithio)tetraselenafulvalene (**7**, BETS) serves as a source of a genuine organic superconductor, $(BETS)_2(Cl_2TCNQ)$,[35] or of a molecular magnetic superconductor, κ-$(BETS)_2FeBr_4$.[36] Thus, selenium-containing TTF-type compounds are particularly promising if one is searching novel organic superconductors. However, the development of such potential compounds is not easy, because in contrast to the rich synthetic methods of TTF derivatives, only a limited number of methods exist for the selenium-containing counterparts. In particular, it is difficult to synthesize such heterocycle-fused TSF electron donors as BETS. The exploitation of general synthetic methods accessible to such compounds has been long awaited. In this regard, we have recently introduced two key reactions: (1) one-pot preparation of 1,3-dichalcogenole-2-chalcogenones from terminal alkynes and (2) formation of additional heterocyclic rings via transalkylation on a chalcogen atom. The first reaction is very useful for the construction of the skeletal heterocyclic rings of tetrachalcogenafulvalenes, and the second for the construction of the fused heterocyclic rings. In combination with a conventional trialkyl phosphite-promoted coupling of 1,3-dichalcogenole-2-chalcogenone, these reactions offer very useful and versatile methods that allow ready preparations of a variety of sophisticated heterocycle-fused TTF-type compounds including the selenium variants of BEDT-TTF (**6**): BETS (**7**), MDT-ST (**16**), and MDT-TSF (**17**) capable of forming superconductive complexes. Here we would like to review the scopes and limitations of these reactions by demonstrating a number of practical synthetic applications and to discuss the recent research trends of TTF-based organic (super)conductors.

1. One-Pot Preparation of 1,3-Dichalcogenole-2-chalcogenones

Many synthetic methods of TTF derivatives have been developed so far. The representatives involve versatile approaches to 1,3-dithiole-2-thiones (**21**) and, as a common path, the subsequent trialkyl phosphite-induced coupling of **21** (or the ketone alternatives) to the TTF derivatives.[2] Thus, it is not too much to say that the accessibility of the common intermediates **21** is a key to the syntheses of TTFs.[37] Mayer and Gebhardt in 1964 reported a synthetic method of 1,3-dithiole-2-thione (**21**) by the successive treatments of acetylene with so-

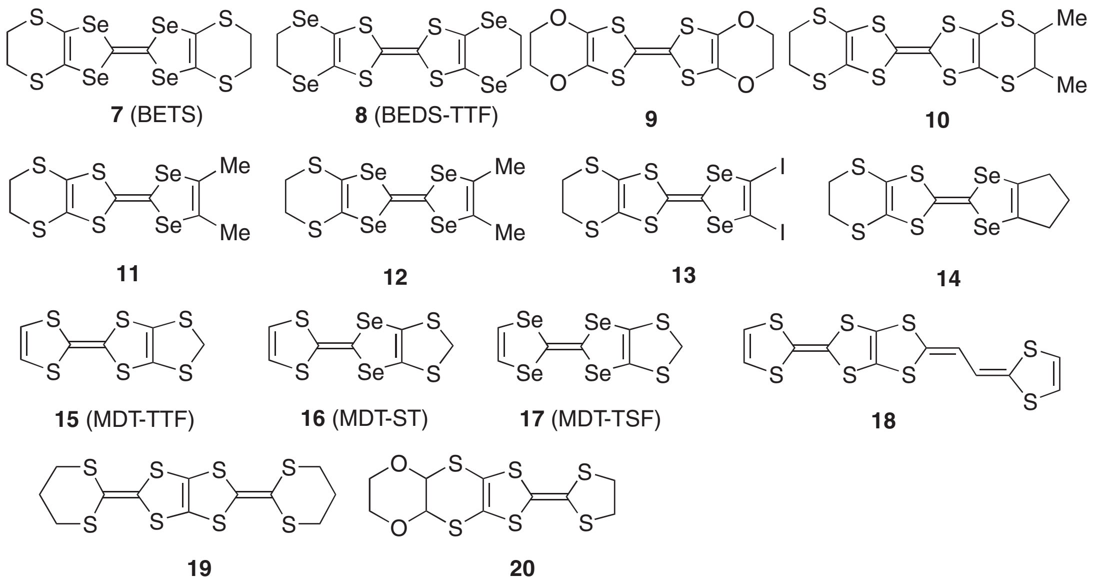
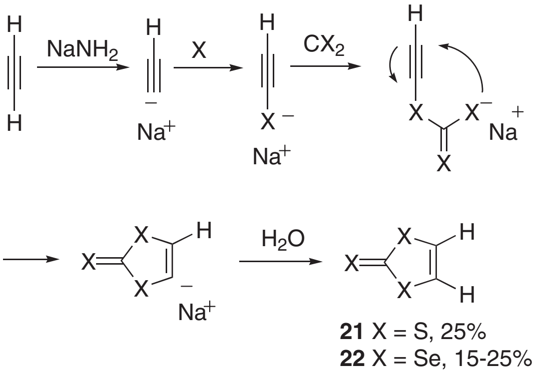


Fig. 2.

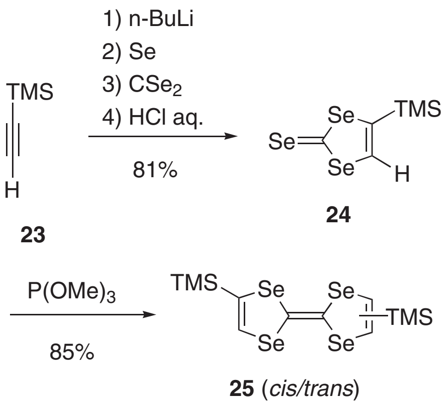


Scheme 1.

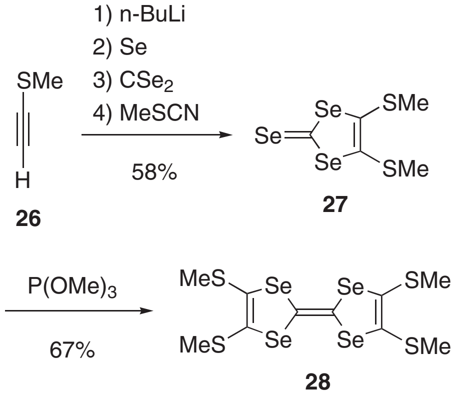
dium amide, sulfur, and carbon disulfide in liquid ammonia (Scheme 1).[38] This one-pot cyclization reaction is straightforward, but previously has attracted little attention for the synthesis of TTF and its derivatives because of the low yield (25%) of **21** as well as the laborious procedure required in using liquid ammonia. It is, however, worth noting that Engler and Patel utilized this reaction to produce 1,3-diselenole-2-selone (**22**) and succeeded in the first preparation of TSF from **22** in 1976.[8] Even then, use of toxic carbon diselenide and the low yield are disadvantages in this reaction. Alternative synthetic methods of TSF without hazardous carbon diselenide were also developed, but none of them contributed to the wide developments of TSF derivatives.[39]

Because we think Engler's approach to 1,3-diselenole-2-selones has synthetic potential, we have reexamined the reaction conditions.[40] We found the following satisfactory modification: successive treatments of trimethysilylacetylene (**23**) with *n*-BuLi in THF at −78 °C, with selenium at 0 °C for 2 h, then with carbon diselenide[41] at −90 °C for 3 min, and finally with water gave 1,3-diselenole-2-selone (**22**) in 94% isolated yield. In this reaction, the trimethylsilyl group was spontaneously eliminated during work-up with water. However, quenching the reaction mixture with acidic water left the trimethylsilyl derivative (**24**) in 81% yield (Scheme 2). The self-coupling of **24** induced by trimethyl phosphite produced the bis(trimethylsilyl) TSF electron donor (**25**) in 85% yield.

Furthermore, versatile acetylene derivatives bearing phenyl, methylthio, hexyl, tetrahydropyranyl (THP)-protected hydroxymethyl, and acetal-protected formyl groups can be used as substrates of this reaction to form the corresponding mono-substituted 1,3-diselenole-2-selone derivatives in good to excellent yields. The tetrahydropyranyloxymethyl and diethoxymethyl groups are readily deprotected with dil. hydrochloric acid to the hydroxymethyl and formyl groups, respectively. These groups may serve as useful anchors for the construction of functionalized TSF systems.



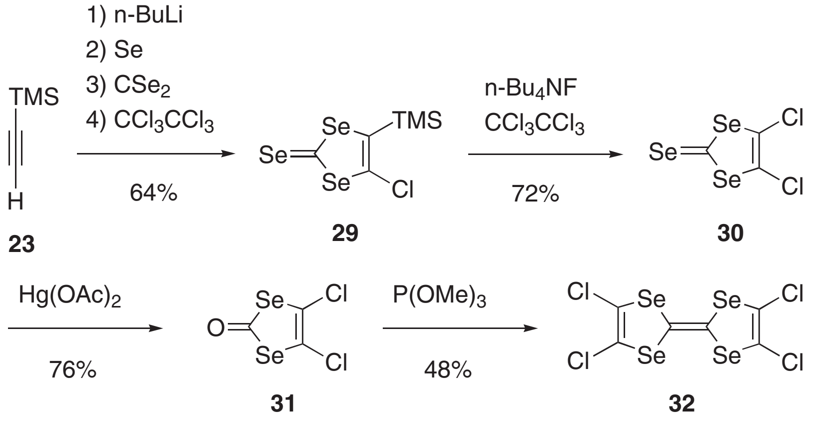
Scheme 2.



Scheme 3.

The disubstituted TSFs such as **25** are usually comprised of a mixture of the *cis* and *trans* isomers, which are readily convertible to each other in solution. The presence of such structural isomers is sometimes responsible for disordering in the crystal structures of molecular complexes. The present one-pot synthetic method can be extended to the synthesis of 4,5-disubstituted 1,3-diselenole-2-selones, which serve as precursors of tetrasubstituted TSFs. In this case, an additional substituent group can be introduced by quenching the one-pot reaction of the terminal alkyne with an appropriate electrophilic reagent instead of water.[42] Scheme 3 demonstrates that, when a reaction mixture from methylthioacetylene (**26**) was quenched with methyl thiocyanate, 4,5-bis(methylthio)-1,3-diselenole-2-selone (**27**) was obtained in 58% yield and converted to tetrakis(methylthio) TSF (**28**) in 67% yield. Such symmetrical tetrasubstituted TSFs are more favorable for complexation studies than the disubstituted TSFs with structural isomers.

A variety of tetrasubstituted TSFs are thus accessible. A special example of the application of this approach is the synthesis of the tetrahalogen-substituted derivatives of TSF.[43] We initially attempted the synthesis of tetrachloro TSF (**32**) from direct tetralithiation of TSF: successive treatments of TSF with four equivalents of lithium di(isopropyl)amide and then with excess hexachloroethane gave only 2,3-dichloro TSF as an isolated product. The absence of any formation of the desired tetrachloro derivative (**32**) indicates that the generation of the expected tetralithio TSF in the initial step was difficult.[44] Alternatively, we tried the synthesis of **32** via 4,5-dichloro-1,3-diselenole-2-selone (**30**) from trimethylsilylacetylene (**23**). As shown in Scheme 4, 4-chloro-5-trimethylsilyl-1,3-diselenole-2-selone (**29**) was obtained by quenching the one-pot reaction of **23** with hexachloroethane. Then its trimethylsilyl group was converted to the second chloro group by treatment with tetrabutylammonium fluoride and hexachloroethane. Finally the resulting key intermediate **30** is converted via the ketone **31** to the desired tetrachloro TSF (**32**). It is also possible to prepare the tetrabromo and tetraiodo TSFs in a similar manner. These halogen-substi-



Scheme 4.

tuted TSF derivatives are expected to show strong non-bonded interactions due to the halogen groups, being potentially useful in studying crystal engineering in molecular complexation.[27,45]

Reaction conditions found for the synthesis of 1,3-diselenole-2-selones are also effective in the formation of 1,3-dithiole-2-thiones using a combination of sulfur and carbon disulfide reagents.[40] Unlike the original method of Mayer and Gebhardt, this modified method is practical for large-scale preparation and nicely complements the preceding synthetic methods of TTF derivatives.

2. Hybrid Tetrachalcogenafulvalenes

Another advantage of the one-pot synthetic method of 1,3-dichalcogenole-2-chalcogenones is to provide a tool for the synthesis of hybrid systems by use of different kinds of chalcogen for the combined reagents of elemental chalcogen and carbon dichalcogenide. Actually, Engler's group used this methodology in the synthesis of hybrid diselenadithiafulvalene (**33**),[46] and our group used it in the syntheses of a number of the heterocycle-fused hybrid derivatives discussed later (Fig. 3).

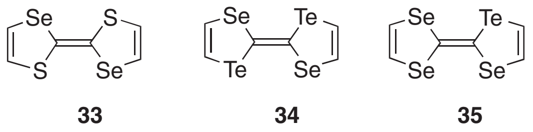
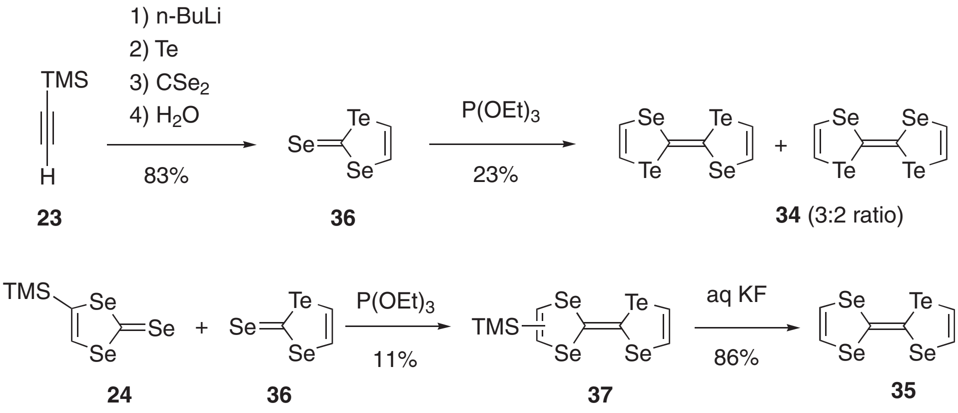


Fig. 3.

Furthermore, we found that this protocol is applicable to the syntheses of a new kind of selenium/tellurium hybrids **34** and **35**.[47,48] Such hybrid systems are very useful for the research of still unripe tellurium-based organic conductors. Scheme 5 demonstrates the synthetic route to these hybrid systems. Thus, 1,3-selenatellurole-2-selone (**36**) was readily obtained in 83% yield by successive treatments of trimethylsilylacetylene (**23**) with 1 eq. *n*-BuLi, 1 eq. tellurium powder, 1 eq. carbon diselenide, and finally water. The triethyl phosphite-promoted coupling reaction of **36** afforded diselenaditellurafulvalene (**34**) in 23% yield, which exists as a mixture of *trans* and *cis* isomers in a ratio of 3:2. Triselenatellurafulvalene (**35**) was also obtained by a cross-coupling reaction between **24** and **36**, followed by desilylation of the coupling product **37** with aqueous potassium fluoride.[48]

The TCNQ complex of the hybrid compound **34** showed a high conductivity of $1400\ \mathrm{S\,cm^{-1}}$, which is just in between those of TSF•TCNQ and TTeF•TCNQ. Figure 4 demonstrates its variable temperature resistivities, which steadily decrease to one-fourth down to 4 K. There is no metal–insulator transition, as seen for the case of TTeF•TCNQ. On the other hand, the TCNQ complex of **35** showed a further higher conductivity of $2000\ \mathrm{S\,cm^{-1}}$, but underwent a metal–insulator transition at 80 K. Both crystal structures of the two TCNQ complexes are characterized by segregated stack columns of donors and acceptors, but have quite different packing motifs. As shown in Fig. 5, the stack columns of the **34**•TCNQ complex are ar-



Scheme 5.

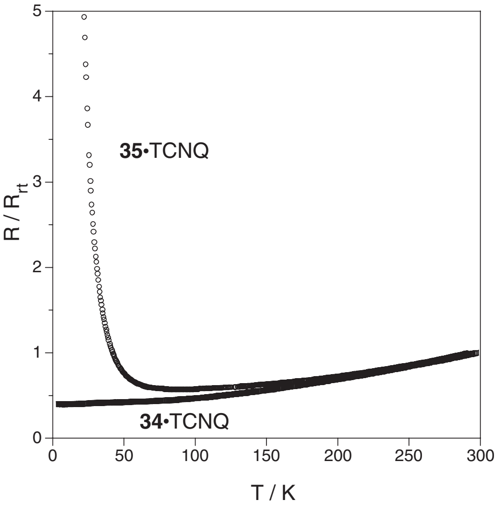


Fig. 4. Temperature-dependent resistivities of the TCNQ complexes of diselenaditellurafulvalene (**34**) and triselenatellurafulvalene (**35**).

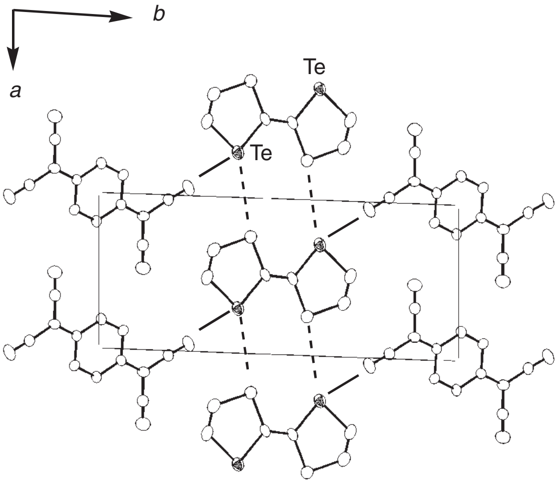


Fig. 5. Crystal structure of the TCNQ complex of diselenaditellurafulvalene (**34**) viewed along the stacking direction.

ranged side-by-side with the same kind of columns. This structure is essentially the same as the packing motif of TTeF•TCNQ complex.[10b] All donor molecules in the complex take *trans*-conformation, and the tellurium atoms strongly interact with the selenium atoms of the neighboring donor molecule. The intercolumnar interactions through Te–Se contacts in the transverse direction thus serve to suppress the Peierls transition and to stabilize the metallic state down to a measurable low temperature. Evidently, replacement of two selenium atoms of TSF by tellurium is enough to suppress the Peierls instability. On the other hand, the donor columns of the **35**•TCNQ complex are surrounded by the acceptor columns, and vice versa. This structure is reminiscent of the packing motifs of TTF•TCNQ[6] and TSF•TCNQ[8] complexes, and lacks intercolumnar interactions in the transverse direction. Replacement of only one selenium atom of TSF by tellurium can not induce a structural change significant enough to suppress the Peierls instability.

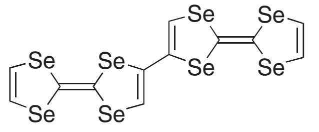


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Fig. 6.

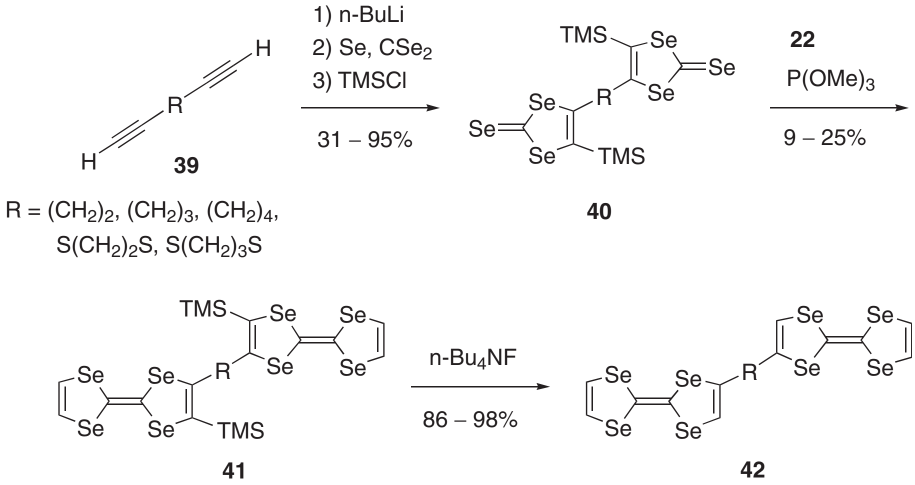
3. Dimeric Tetraselenafulvalenes

As one of the promising modifications of TTF, dimeric TTFs and higher oligomers have attracted much attention; in this modification the TTF units are linked by one or more spacer groups.[49] Such systems might have intramolecular through-bond or through-space interactions between the component TTF units, which would affect the formation, structures, and physical properties of their molecular complexes. In other words, such dimeric and oligomeric TTFs might provide an opportunity to control the stoichiometry, band filling, and molecular assembly of their complexes. Although a number of dimeric TTFs have been developed, there was no dimeric example of TSF until quite recently. Iyoda's group, in corporation with our group, succeeded in the synthesis of bitetraselenafulvalene (**38**, Fig. 6) by the copper(II)- or palladiun(II)-catalyzed homo coupling reaction of trimethylstannyl-TSF directly derived from TSF.[50] The bi-TSF **38** showed a rigid planar structure when subjected to the X-ray structural analysis and formed highly conductive complexes owing to the effect of stoichiometric control.

The one-pot synthetic protocol of 1,3-diselenole-2-selones is very effective in the development of the bridged TSF dimers **42**. As outlined in Scheme 6, the one-pot cyclization reactions of the appropriate α,ω-alkanediynes (**39**) gave the bridged bis(1,3-diselenole-2-selone)s (**40**). These were subjected to cross-coupling with 1,3-selenole-2-selone (**22**) to afford the trimethylsilylated bis-TSF **41** and then desilylated to the desired compounds **42**.[51] The X-ray structural analysis of the bridged dimeric TSF **42** (R = $(CH_2)_3$) revealed that it adopts a completely stretched conformation. However, its voltammetric study suggested that in the oxidized state, it favors an interactive folded conformation owing to the flexible single spacer group. In particular, the two-electron oxidation resulted in the observation of a characteristic transition due to a π-dimer in the UV–vis spectral region.[52] In contrast to the bi-TSF **38**, **42** gave only semiconductive complexes.

In the series of dimeric TTFs, special interests are focused on tetrathiafulvalenophanes (so-called TTF phanes), in which the two TTF units are forced to adopt a sandwich structure so as to interact strongly with each other.[49] In this regard, we previously studied a variety of unique TTF phanes of double-bridged type (**43**),[53] triple-layered type (**44**),[54] quadruple-bridged type (**45**),[55] and crisscross-overlap type (**46**)[56,57] (Fig. 7). These compounds can behave as different electron donors, depending on the individual stacking modes. Among them, the double-bridged TTF phanes (**43**) formed the most conductive complexes with various counter inorganic ions.

Since non-bonded interaction of selenium is generally more effective than that of sulfur, tetraselenafulvalenophanes (TSF phanes) might be more potential electron donors. With this in-



Scheme 6.

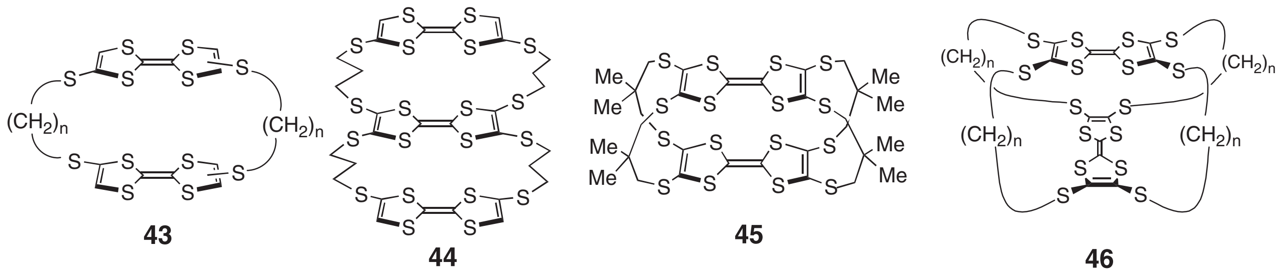
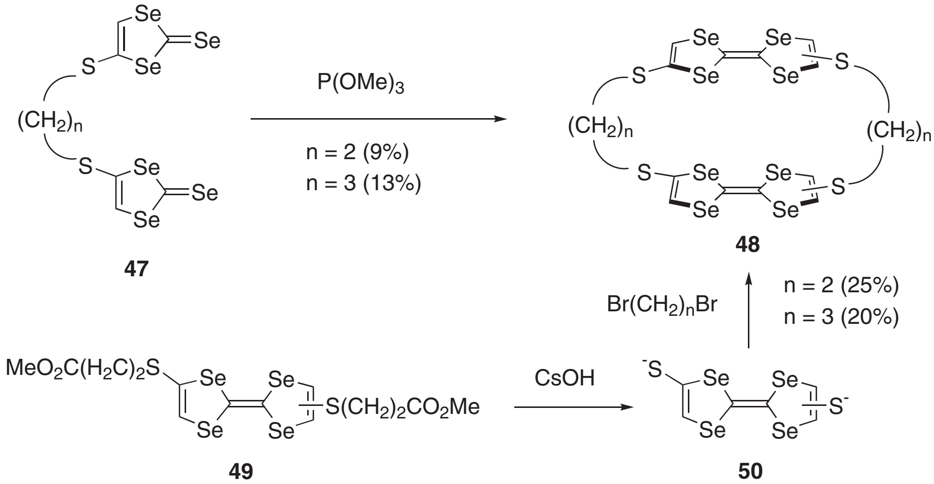


Fig. 7.



Scheme 7.

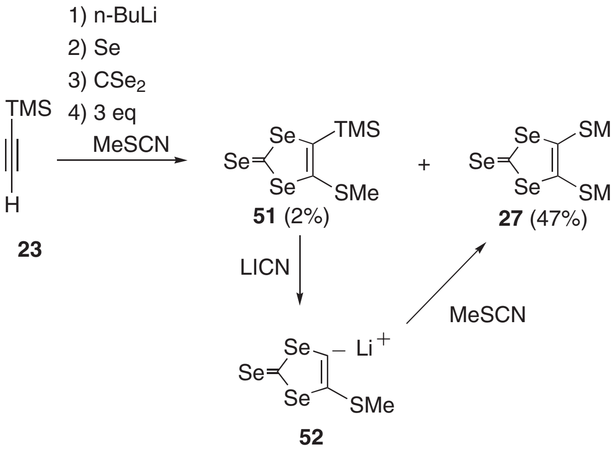
terest, we studied the synthesis of double-bridged TSF phanes (**48**). Initially, the trimethyl phosphite-induced double-coupling reaction of the bis(1,3-diselenole-2-selone)s **47**, similarly obtained from **39**, gave a straightforward access to **48** (Scheme 7).[58] However, this double-coupling reaction bore problems of low yield (9–13%) and poor reproducibility. We then developed an alternative synthetic method based on deprotection/realkylation of the protected TSF dithiolate.[59] Treatment of bis[2-(methoxycarbonyl)ethylthio]TSF (**49**) with cesium hydroxide generated the TSF dithiolate (**50**), which was coupled with 1,2-dibromoethane or 1,3-dibromopropane to give **48**. This coupling is a four molecular reaction, but the yield is reasonable (20–25%) and the reproducibility is quite high.

These TSF phanes are capable of forming more conductive complexes than the corresponding TTF phanes (**43**). More specifically, the trimethylenedithio-bridged TSF phane (**48**, $n = 3$) formed the $Au(CN)_2$ radical cation salt with a high conductivity of 53 $S\,cm^{-1}$. The crystal structure is characterized as the stacked packing of the TSF phanes comprised of many intramolecular and intermolecular Se–Se contacts. The high conductivity is ascribable to the control of the TSF phane over the stoichiometry and dimensionality of the complex.

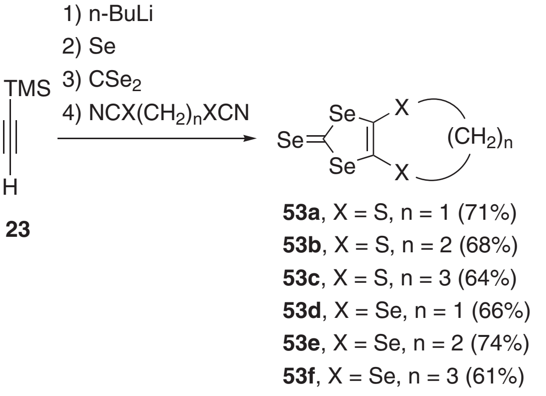
4. Hetrocycle-Fused 1,3-Dichalcogenole-2-chalcogenones

In a one-pot reaction of trimethylsilylacetylene (**23**), we accidentally found that quenching with excess methyl thiocyanate formed the 4,5-bis(methylthio) derivative (**27**) (47% yield), instead of the expected 4-methylthio-5-trimethylsilyl derivative (**51**) (2% yield).[42] The formation of **27** is well explained, as shown in Scheme 8. Here the initial product **51** produced by quenching with methyl thiocyanate further reacts in situ with lithium cyanide concomitantly formed during the quenching to generate another intermediate **52**. This subsequently reacts with an additional methyl thiocyanate, leading to **27**.

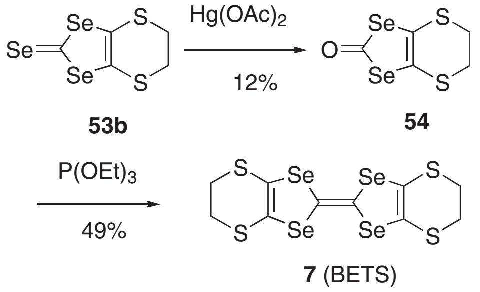
We anticipated that the above reaction path of bis-functionalization might provide a very short access to the heterocycle-fused 1,3-diselenole-2-selones (**53**) if an α,ω-bis(chalcogenocyanato)alkane is used as a quencher. Actually, various 1,3-diselenole-2-selone derivatives **53** with different methylene numbers, $n = 1$–3, and different chalcogen elements, S and Se, in the fused heterocyclic ring were obtained in good yields by quenching the reaction mixture of **23** with one equimolar α,ω-bis(chalcogenocyanato)alkanes (Scheme 9).[42]



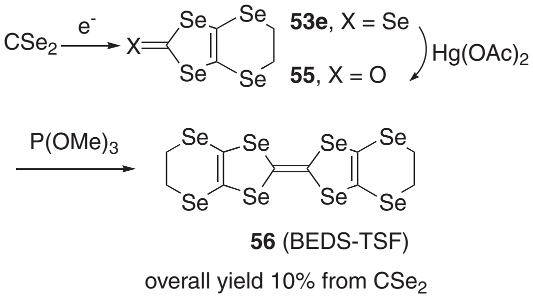
Scheme 8.



Scheme 9.



Scheme 10.



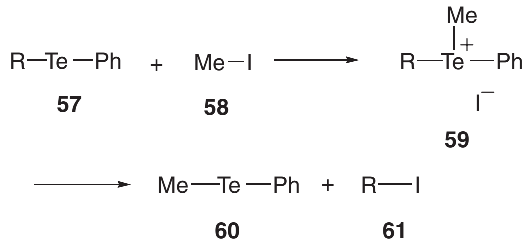
Scheme 11.

These readily available 1,3-diselenole-2-selones (**53**) are expected to be promising precursors of inaccessible heterocycle-fused TSF derivatives. Scheme 10 demonstrates a specific example for the conversion of 4,5-ethylenedithio-1,3-diselenole-2-selone (**53b**) to BETS. The previous synthesis of BETS was accomplished through multi-steps involving 4,5-ethylenedithio-1,3-diselenol-2-one (**54**) from inaccessible dihydro-1,4-dithin.[60] The direct coupling of **53b** to BETS failed, so the conversion was carried out via the ketone **54**. The conversion yield of **53b** to BETS is low due to the thermal lability of **53b**; even so, the present protocol gives a much shorter route to BETS.

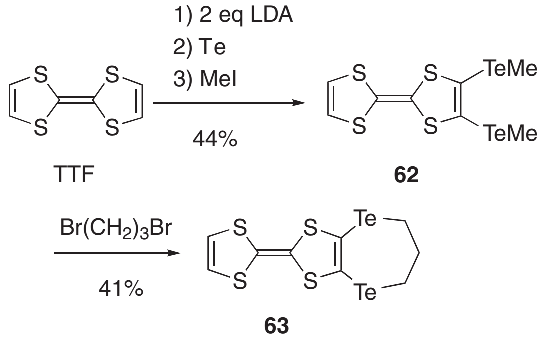
Engler and co-workers synthesized the all-selenium variant of BEDT-TTF, bis(ethylenediseleno)tetraselenafulvalene (**56**, BEDS-TSF), according to the route depicted in Scheme 11.[61] This route involves troublesome electrochemical reduction of carbon diselenide. Because our method readily produces the key intermediate **53e**, it nicely complements the drawback of Engler's method.

5. Selenium Variants of BEDT-TTF

Since the discovery of numerous superconductors based on BEDT-TTF (**6**), extensive efforts have been devoted to its structural modifications, especially replacement of the sulfur atoms with selenium atoms. As already mentioned, however, such selenium-containing compounds are generally hard to access. The preceding section demonstrates that the one-pot preparation of hetrocycle-fused 1,3-diselenole-2-selones gives a straightforward approach to such compounds as BETS and BEDS-TSF, but this route is not suitable for large-scale preparation because of the thermal lability of the intermediates. This forced us to develop a different synthetic method for heterocycle-fused TSF derivatives, which is based on a strategy of constructing the outer heterocyclic rings after the construction of the TSF skeleton. For this purpose, we devised the formation of a heterocyclic ring via transalkylation on a chalcogen atom. This idea came from our discovery of the ready conversion of



Scheme 12.

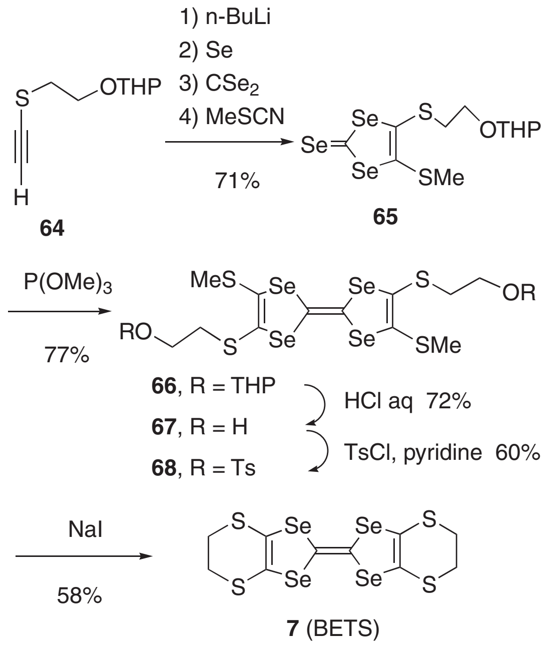


Scheme 13.

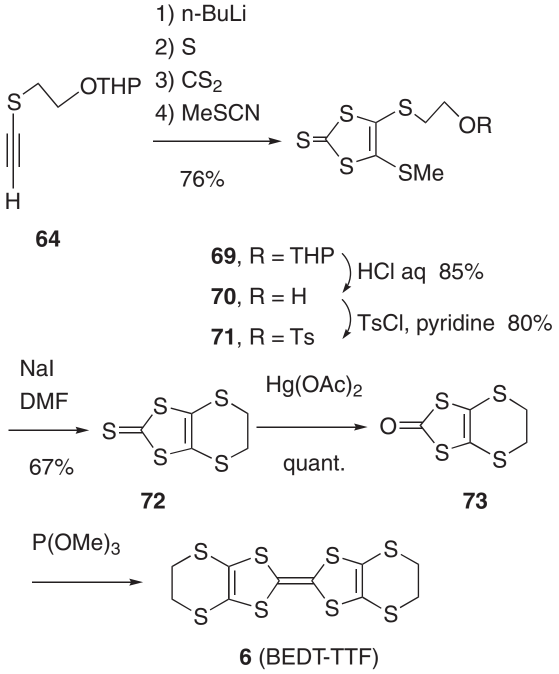
alkyl phenyl telluride (**57**) and methyl iodide (**58**) to methyl phenyl telluride (**60**) and alkyl iodide (**61**), as shown in Scheme 12.[62] This transalkylation reaction is considered to proceed via the telluronium intermediate **59**.

We first examined the effectiveness of this reaction in the synthesis of a tellurocycle-fused TTF from TTF.[63] As shown in Scheme 13, successive treatments of TTF with 2 eq LDA, tellurium, and methyl iodide gave the bis(methyltelluro) TTF (**62**). This was then heated with 1,3-dibromopropane to afford 2,3-trimethyleneditelluro-tetrathiafulvalene (**63**) in a reasonable yield. The conversion of **62** to **63** proceeds via two consecutive transalkylation reactions: the first occurs intermolecularly and the second intramolecularly. The transalkylation reactions are promoted by liberation of the resulting volatile methyl bromide from the reaction system. A great advantage of this protocol using transalkylation on a chalcogen atom is that it will be conducted in neutral and mild conditions. Thus it will be very suitable for the formation of a heterocyclic ring on an acid-sensitive and thermally labile TTF skeleton.

A combination of this ring cyclization with the one-pot preparation protocol of 1,3-dichalcogenole-2-chalcogenones paves the way to the selenium variants of BEDT-TTF.[64] Thus, successive treatments of the THP-protected 2-(ethynylthio)ethanol (**64**) with butyllithium, selenium, carbon diselenide, and methyl thiocyanate gave the 1,3-diselenole-2-selone derivative **65** as a key intermediate (Scheme 14). This was self-coupled to the TSF derivative **66**. After **66** was converted via the alcohol **67** to the tosylate **68**, heating **68** with NaI in DMF smoothly gave BETS. Considering that all the sequential reactions proceed in good to high yields and all the intermediates are thermally stable, the present method is the best for large-scale preparation of BETS.



Scheme 14.



Scheme 15.

A similar approach is also effective for the synthesis of BEDT-TTF, as demonstrated in Scheme 15. In contrast to the case of BETS, the formation of the fused ring on the 1,3-dithiole-2-thione derivative **69** is accomplished prior to the conversion to the TTF skeleton, because 1,3-dithiole-2-thione **72** and the ketone **73** unlike the selenium counterparts, are thermally stable. Since the first synthesis of BEDT-TTF by Cava's group[14] and the findings of a numerous amount of superconductors based on BEDT-TTF, several improved methods for the synthesis of BEDT-TTF have been developed.[65] Under the circumstances, this approach may be meaningless. We would rather emphasize that the intermediate **69** is of special use as a partner for cross-coupling directed toward the production of unsymmetrical compounds with the half structure of BEDT-

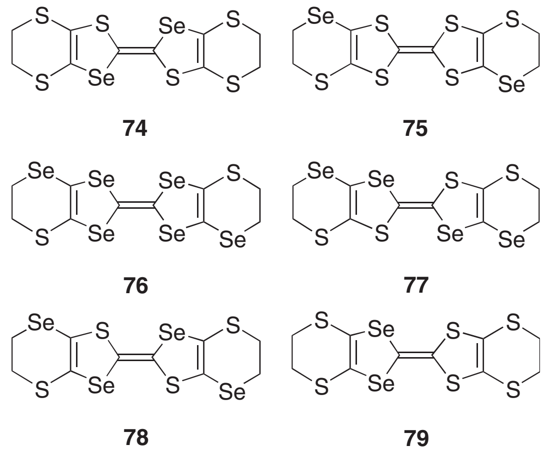
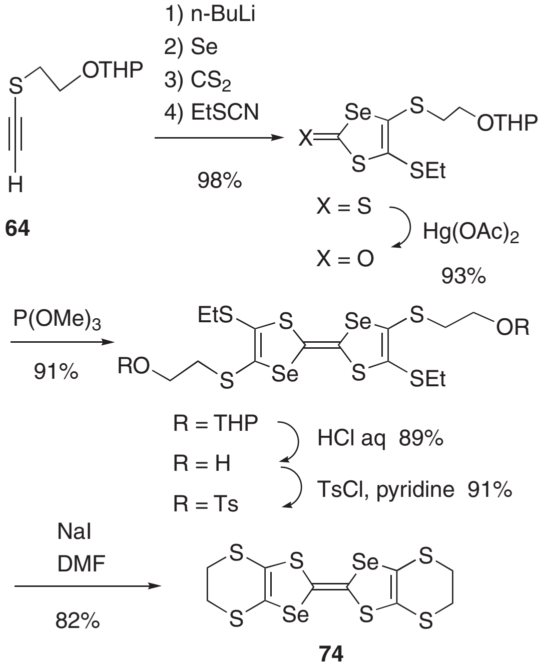


Fig. 8.

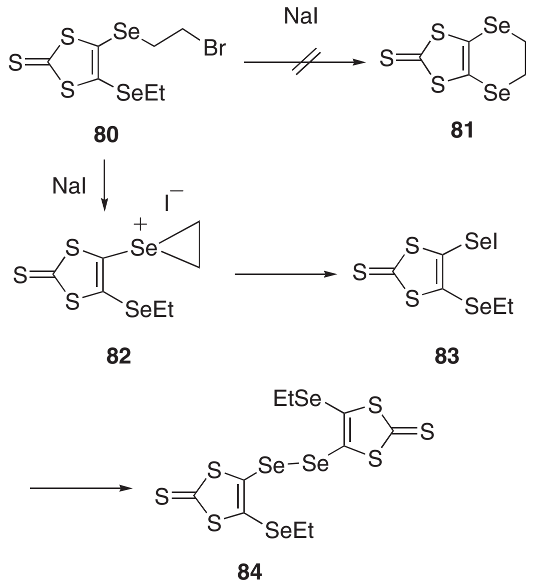


Scheme 16.

TTF.

This synthetic approach is very versatile and is also widely applicable to a number of complicated sulfur/selenium hybrid compounds **74**–**79** that are inaccessible by usual synthetic methods (Fig. 8). Scheme 16 represents the successful synthetic routes to the hybrid compound **74** from the common starting material **64**. The compound **74** was previously synthesized by Papavassilou's group using more than ten steps with only less than 0.5% overall yield.[66] On the other hand, the present method gave **74** in six steps with 67% overall yield from **64**.

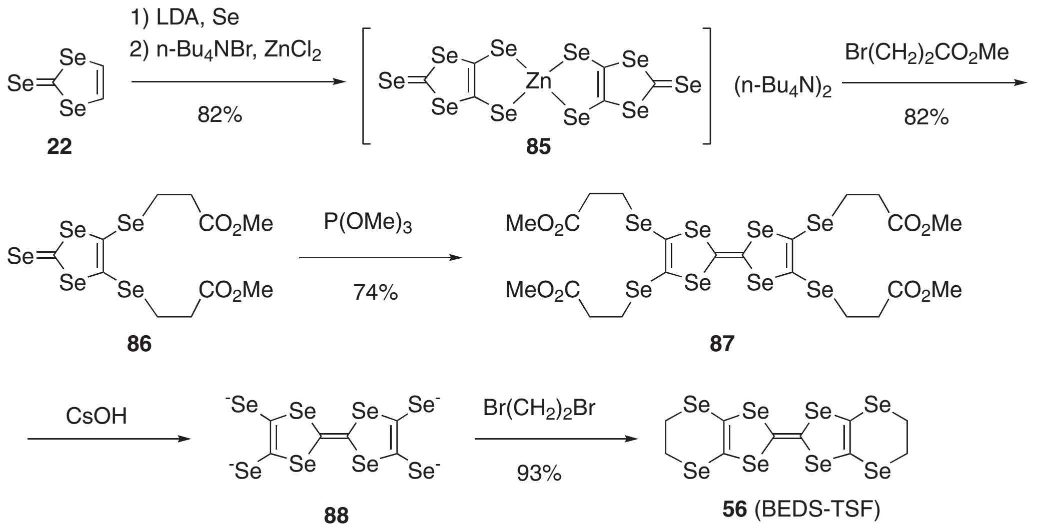
Although the protocol via transalkylation on a chalcogen atom turned out to be very effective for the annelation of heterocyclic rings on the TTF skeleton, we recognized that this reaction suffers from a limitation on the formation of the outer diselenacycloalkane rings of BEDS-TTF (**8**) and BEDS-TSF (**56**). Nigrey and Morosin reported the synthesis of BEDS-TTF (**8**) via 4,5-ethylenediseleno-1,3-dithiole-2-thione (**81**), starting with less available $(n\text{-Bu}_4\text{N})_2[\text{Ni(dsit)}_2]$.[67] When we attempted a more simple preparation of the intermediate **81** by treatment of the *β*-selenoethyl bromide **80** with sodium iodide, we encountered difficulty in the formation of the additional dihydrodiselenin ring (Scheme 17). The main product is the diselenide **84**, which probably forms as follows: **80** is converted via an episelenonium iodide **82** to the selenenyl iodide **83**, which undergoes disproportionation to the diselenide **84**.



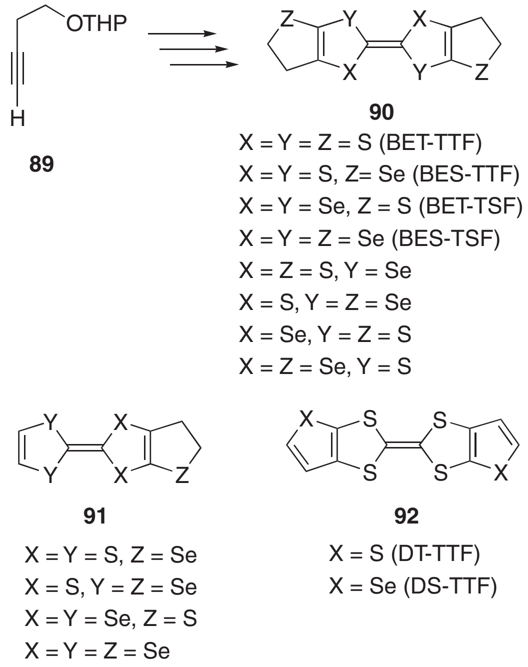
Scheme 17.

In addition to Nigrey's method, there is a more convenient synthetic method of BEDS-TTF, which involves the generation of the TTF tetraselenate ion by tetralithiation of TTF with butyllithium, followed by treatment with selenium, and its capping with 1,2-dibromoethane to give BEDS-TTF.[68] No similar approaches to obtain the all-sellenium variant, BEDS-TSF (**56**) or BETS (**7**) directly from the tetralithio TSF had been reported.[69] We recently developed a successful route to generate the TSF tetraselenate ion **88** from the protected TSF tetraselenolate **87**, as demonstrated in Scheme 18.[70] The $\text{Zn(dsis)}_2\cdot(n\text{-Bu}_4\text{N})_2$ salt **85** was first prepared through the dilithiation of 1,3-deselenole-2-selone (**22**)[71] and then converted to 4,5-bis[2-(methoxycarbonyl)ethylseleno]-1,3-diselenole-2-selone (**86**), which was self-coupled to 2,3,6,7-tetrakis[2-(methoxycarbonyl)ethylseleno]tetraselenafulvalene (**87**). Its deprotection with cesium hydroxide produced the TSF tetraselenate ion **88**, which was capped with 1,2-dibromoethane to give BEDS-TSF.

The methodology using the deprotection/realkylation of the protected tetraselenolates nicely complements a drawback of the above protocol of the heterocycle formation via transalkylation on a chalcogen atom. It is thus now possible to prepare all the selenium variants of BEDT-TTF in practical amounts by using the newly developed methods. Surprisingly, the number of all the selenium variants including the hybrid systems amounts to forty-nine, even if readily interconvertible *trans* and *cis* structural isomers are regarded as a single compound. In addition to symmetrical BETS, BEDS-TTF, and BEDS-TSF as good electron donors, the appearance of versatile hybrid selenium-variants further enriches the chemistry of BEDT-TTF; actually **74** and **79** were revealed to form conductive molecular



Scheme 18.



Scheme 19.

complexes.[72]

6. Ethylenechalcogeno- and Trimethylenechalcogeno-Substituted TTF Systems

The compounds **90**–**92** represent another interesting TTF family of heterocycle-fused type materials classified by the involvement of only one chalcogen atom in the fused five-membered ring. The parent bis(ethylenethio)-tetrathiafulvalene (**90**, X = Y = Z = S; BET-TTF) was first developed by Engler's group in 1978,[73] but it was unrecognized as a superior electron donor until Rovira's group in 1994 reevaluated the data and found that it can form many highly conductive radical salts.[74] Our synthetic method for heterocycle-fused TTF-type compounds can be also applied to the synthesis of this system. The possible selenium variants of BET-TTF (**90**) as well as unsymmetrical ones (**91**) were obtained from the common starting material **89** (Scheme 19).[75] In addition, the dehydrogenation of the fused five-membered rings of **90** offered an access to thiophene- or selenophene-fused TTF derivatives (**92**).

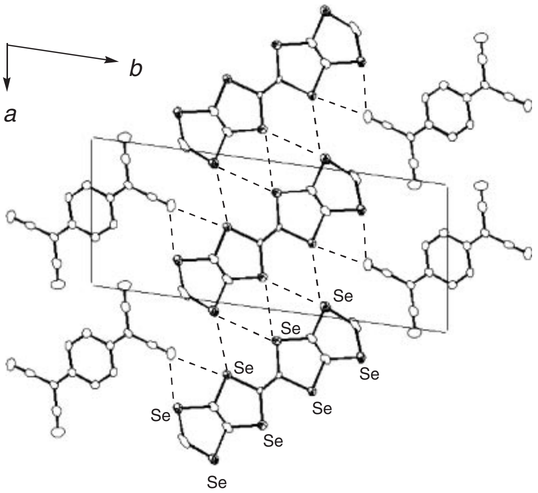
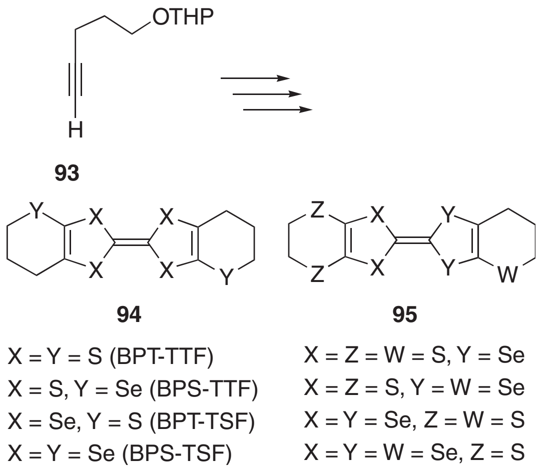


Fig. 9. Crystal structure of the TCNQ complex of BES-TSF (**90**) projected along the stacking direction.

Among the bis-heterocycle-fused donors **90**, BET-TTF, BES-TTF, BET-TSF, and BES-TSF are characterized by giving highly conductive molecular complexes with metallic behavior at room temperature. In particular, one should note that the TCNQ complexes of BET-TSF and BES-TSF show extraordinarily high room-temperature conductivities of 2600 and 2700 $\mathrm{S\,cm^{-1}}$, respectively; such values are of the highest class for molecular complexes.[75b] The crystal structure of the BES-TSF•TCNQ complex was confirmed to adopt conventional segregated stacking columns, as depicted in Fig. 9. An important feature of this structure is that the donor molecules interact not only with the stacked donor molecules but also with both donor molecules and TCNQ molecules in the neighboring columns. It is thus understandable that the high conductivity of BES-TSF•TCNQ is induced by strong heteroatomic interactions not only along the stacking direction but also along the transverse direction. Such interactions are enhanced by the additional outer selenium atoms of BES-TSF. On the other hand, the thiophene- and selenophene-fused TTF derivatives (**92**) form only semiconductive complexes with TCNQ and ClO_4^-. The room temperature conductivity of the DS-TTF•TCNQ complex is lower by three orders of magnitude than that of the BES-TTF•TCNQ complex. The crystal structure is characterized by an unfavorable mixed stacking arrangement of donors and acceptors.

A similar synthetic protocol using THP-protected 4-pentyn-1-ol (**93**) as starting material also allowed us to synthesize another heterocycle-fused TTF family **94**.[76] This was classified by the involvement of only one chalcogen atom in the fused six-membered ring and by unsymmetrical homologues **95**[77] (Scheme 20). A voltammetric study revealed that all of the four donors **94** also have good electron donating properties. However, their complexes with the same counter ions PF_6^- and AsF_6^- showed quite different properties: the complexes of BPT-TSF are metallic; those of BPS-TSF are semiconductive; those of the two TTF donors, BPT-TTF and BPS-TTF are insulating. The crystal structures of the metallic complexes of BPT-TSF are packed with stacking columns of face-to-face dimeric pairs. Among the columns, there are many side-by-side selenium interactions, and the two-dimensional Se–Se contact network gives a conduction path.



Scheme 20.

7. Methylenedichalcogeno-Substituted TTF Systems

Another remarkable family of heterocycle-fused TTF type is the methylenedichalcogeno-substituted compounds **96** and **97** (Fig. 10). These compounds are expected to exert much stronger intermolecular interactions due to the increasing number of chalcogen atoms than the above systems that contain a chalcogen atom in the five-membered ring. For symmetrical compounds **96**, there are four kinds of possible chalcogen-variants: BMDT-TTF,[78] BMDS-TTF,[68a,68c] BMDT-TSF,[79] and BMDS-TSF.[70] These have already been synthesized and are recognized to behave as good electron donors.

The unsymmetrical compounds **97** have attracted much more interest in terms of the formation of superconducting complexes. Three such compounds: MDT-TTF,[80] MDS-TTF,[81] and MDT-TS,[82] were developed by Papavassilou's group. All of their synthetic approaches are based on a conventional trialkyl phosphite-induced cross-coupling between 4,5-methylenedichalcogeno-1,3-dithiole-2-chalcogenone and 4,5-bis(methoxycarbonyl)-1,3-dichalcogenole-2-chalcogenone, followed by pyrolytic decarboxylation with lithium bromide. The remaining selenium-rich compounds: MDT-TSF,[31,79] MDS-TSF,[70] MDT-ST,[30] MDS-TS,[83] and MDS-ST,[83] were recently prepared by our group. Scheme 21 demonstrates the successful synthesis of the methylenedithio-tetraselenafulvalene (MDT-TSF) by a sequence of the one-pot cyclization of methylthioacetylene (**26**) or more conveniently of 1,2-dichloro-1-(methylthio)ethylene (**98**) to the 1,3-diselenole-2-selone deriv-

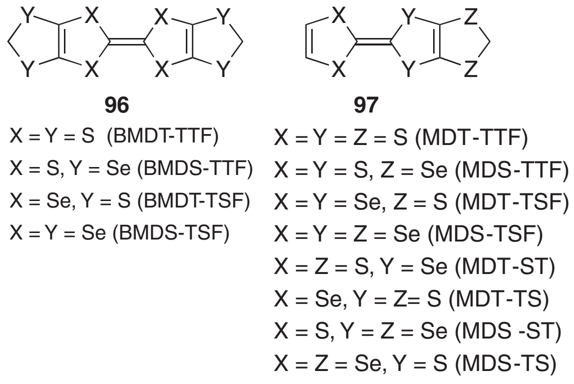
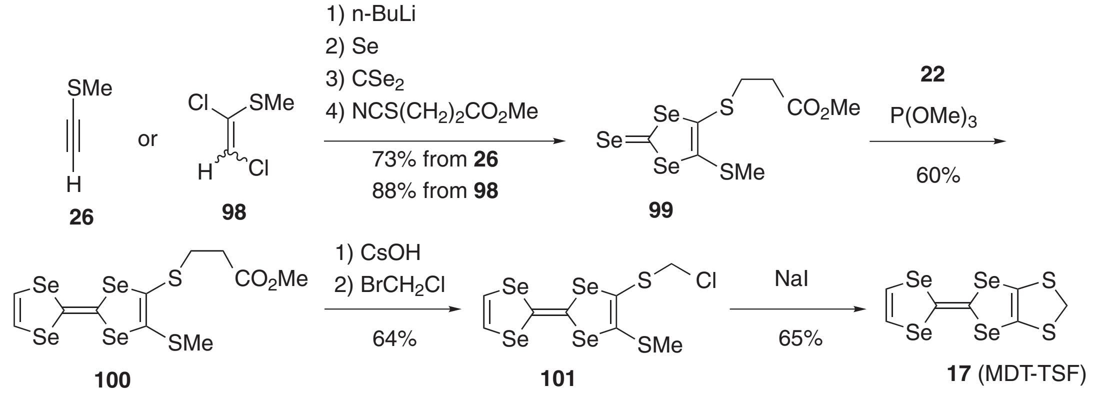
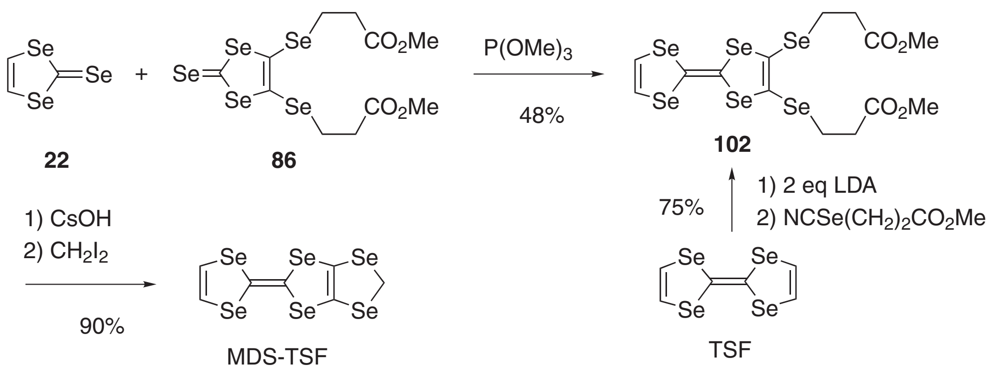


Fig. 10.



Scheme 21.



Scheme 22.

Table 1. Superconducting Complexes of Methylenedithiotetrachalcogenafulvalenes

Donor	Acceptor	$\sigma_{\mathrm{rt}}/\mathrm{S\,cm^{-1}}$	T_c/K	Reference
MDT-TTF (**15**)	AuI_2	20–36	4.1–4.5	29
MDT-ST (**16**)	I_3	1200	3.6	30
MDT-ST (**16**)	I_2Br	390	3.2	30
MDT-ST (**16**)	$I_{2.9}Cl_{0.1}$	300	3.6	30
MDT-TSF (**17**)	AuI_2	2000	4.5	31
MDT-TSF (**17**)	I_3	1500	4.6	85
MDT-TSF (**17**)	I_2Br	1500	5.0	85
MDT-TSF (**17**)	IBr_2	1500	4.0	85
MDT-TSF (**17**)	$I_{2.9}Cl_{0.1}$	1500	5.5	85

ative **99**, the trimethyl phosphite-induced cross-coupling to **100**, and finally the formation of the fused heterocyclic ring via transalkylation on a chalcogen atom. In this reaction sequence, the synthesis of the precursor **101** for the transalkylation was crucial; it was accomplished by a strategy based on deprotection/realkylation of the protected TSF thiolate **100**.

MDS-TSF was derived by capping of the TSF diselenolate ion, which was generated by deprotection of the protected TSF derivative **102** (Scheme 22). The key intermediate **102** was initially obtained by a cross-coupling between the two 1,3-diselenole-2-selones, **22** and **86**, but it was later found to be more easily accessible by dilithiation of TSF with 2 eq LDA followed by treatment with methyl 3-selenocyanatopropionate.[84]

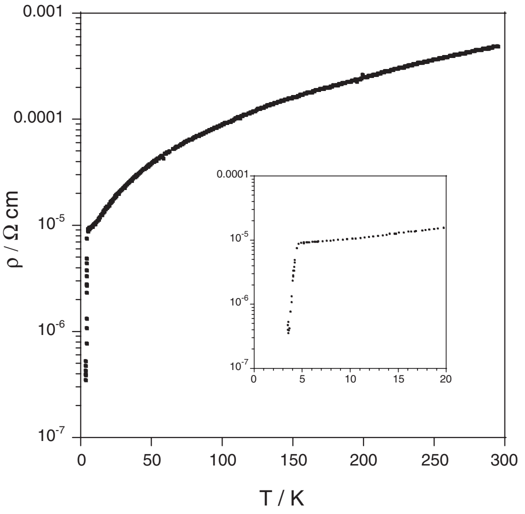


Fig. 11. Temperature-dependent resistivity of the MDT-TSF (**17**)•AuI_2 salt. Inset: the domain 2–16 K, expanded.

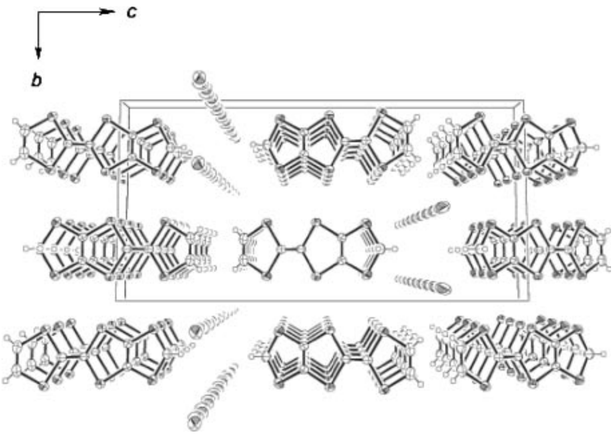


Fig. 12. Crystal structure of the AuI_2 salt of MDT-TSF (**17**) viewed along the stacking direction.

The three unsymmetrical donors, MDT-TTF, MDT-TSF, and MDT-ST formed superconductive complexes, as summarized in Table 1. All the counter ions of these complexes are characterized by linear triatomic ions. MDT-TTF only with the AuI_2 ion gave a superconductor that showed a room temperature conductivity of 20–36 S cm^{-1} and became superconductive at 4.1 K.[29] This crystal structure was characterized as a typical κ-type with the orthogonally packed arrangement of the donor dimers. On the other hand, MDT-TSF gave several superconductors not only with the AuI_2 ion but also with similar triatomic ions.[31,85] Figure 11 demonstrates a superconductive manifestation for MDT-TSF•AuI_2 with a decrease of temperature. The critical temperatures of these superconductors are nearly the same as that of MDT-TTF•AuI_2, but are quite different as regards room temperature conductivity values and crystal structures. In contrast to MDT-TTF•AuI_2, all of these superconductors show much higher room temperature conductivities. In particular, 2000 S cm^{-1} of MDT-TSF•AuI_2 is very remarkable, when one considers that the room temperature conductivities of conventional organic superconductors are generally not so high. The crystal structure of MDT-TSF•AuI_2, unlike that of MDT-TTF•AuI_2, is composed by uniform stacking columns of the donor molecules, as depicted in Fig. 12. This is reminiscent of the crystal structure of the first organic superconductor $(TMTSF)_2ClO_4$ found by Bechgaard.[13] A sharp distinction is that the critical temperature (4.5 K) of the present superconducting salt is much higher than that (1.4 K) of the Bechgaard superconductor. The other superconducting complexes of MDT-TSF show similar critical temperatures and crystal structures. All the organic superconductors based on methylenedithio-diselenadithiafulvalene (MDT-ST) show a little lower room temperature conductivities and critical temperatures, but have nearly the same structural characteristics as the $\text{MDT-TSF}\cdot\text{AuI}_2$ superconductor.[30] The common structural features of these superconductors are: uniform donor stacks, linear chain structures of the anions incommensurate with the donor lattice, and a nonstoichiometric donor/acceptor composition.[86] Finally one may refer to the conducting behavior of the all-selenium variant, methylenediseleno-tetraselenafulvalene (MDS-TSF): it formed a κ-type complex with Br^- ion, which showed a weak but distinct diamagnetic shielding signal below 4 K in the dc magnetization measurement under zero-field-cooled condition, suggesting a sign of superconductivity.[84] These results allow us to say that the methylenedichalcogeno-tetrachalcogenafulvalenes constitute a prototypical class of organic superconductors.

8. Concluding Remarks

This account has given an overview of the recent synthetic chemistry of TTF-based organic conductors. Spectacular advances in preparing new or previously inaccessible TTF-type electron donors have been promoted by the introduction of two key reactions: the one-pot preparation of 1,3-dichalcogenole-2-chalcogenones from terminal alkynes and the formation of an additional heterocyclic ring via transalkylation on a chalcogen atom. The one-pot reaction, in combination with the conventional trialkyl phosphite-induced coupling reaction of the 1,3-dichalcogenole-2-chalcogenones, offers useful synthetic methods of versatile TTF-type compounds, especially selenium variants previously difficult to access. Therefore, a number of functionalized TSF derivatives with trimethylsilyl, phenyl, methylthio, hexyl, THP-protected hydroxymethyl, acetal-protected formyl, and halo groups have been synthesized. In addition, use of different kinds of chalcogen for the two chalcogen reagents used in the one-pot reaction paves the way to the syntheses of the hybrid systems as represented by diselenaditellurafulvalene and triselenatellurafulvalene. Furthermore, this reaction can be successfully extended to the conversion of α,ω-alkanediynes into the bis-(1,3-diselenole-2-selone)s, which are key intermediates of dimeric TSFs including sophisticated TSF phanes. It is remarkable that, when the one-pot reaction is quenched with an α,ω-bis(chalcogenocyanato)alkane, additional cyclofunctionalization occurs to give heterocycle-fused 1,3-diselenole-2-selones. This offers a straightforward approach to inaccessible heterocycle-fused TSF derivatives such as BETS and BEDS-TSF. Furthermore, a more practical and general protocol for the formation of additional heterocyclic ring(s) on the TSF (or TTF) skeleton was found by introducing either the transalkylation reaction on a chalcogen atom or the deprotection/realkylation of the protected diselenolate derivatives. As a result, almost all heterocycle-fused TTF, TSF, and hybrid derivatives, hard or impossible to prepare by the previous synthetic methods, are now accessible. In particular, it should be emphasized that a systematical study of such heterocycle-fused compounds has resulted in the discovery of two new electron donors, MDT-TSF and MDT-ST, that form unique organic superconductors with exceptionally high room temperature conductivities. The authors believe that the synthetic methods described here would be very helpful in developing novel organic (super)conductors in the coming years.

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