Tetrachalcogenafulvalenes with Four Additional Heteroatoms

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in "TTF CHEMISTRY: Fundamentals and Applications of Tetrathiafulvalene"
edited by Jun-ichi Yamada and Toyonari Sugimoto,
Kodansha and Springer, Chap. 2 (2004), p.p. 35-58.

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2.1 Introduction

Most organic conductors and superconductors are based on tetrachalcogenafulvalenes (TCFs) and metal 1,2-dichalcogenolenes.[1] TCFs serve as π-electron donors, and tetrathiafulvalene (TTF, Chart 2.1) is the first member of this series and one of the simplest symmetrical TCFs. TTF was synthesized for the first time in 1964,[2,3] although prior to this synthesis, DB-TTF (Chart 2.1) had already been reported.[4] Following the synthesis of TTF, selenium and tellurium analogues of TTF, *i.e.*, tetraselenafulvalene (TSF, Chart 2.1)[5] and tetratellurafulvalene (TTeF, Chart 2.1),[6] which are the two other simplest symmetrical TCFs, were synthesized. The discovery of electrical conductibility in charge-transfer (CT) complexes of some polycyclic aromatic compounds acting as π-donors with bromine or iodine, followed by the prediction that the CT complexes of sulfur-containing aromatic systems could exhibit good electrical conductivity[7] have led to the synthesis and study of a variety of TCFs. In fact, the CT complexes of TTF with bromine, chlorine, *etc.* were found to be good conductors.[8] It was also found that TTF with organic π-acceptors such as TCNQ (Chart 2.1)[9] or with metal 1,2-dichalcogenolenes such as $Ni(dmit)_2$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate, Chart 2.1)[10] forms CT complexes exhibiting good room-tempera-

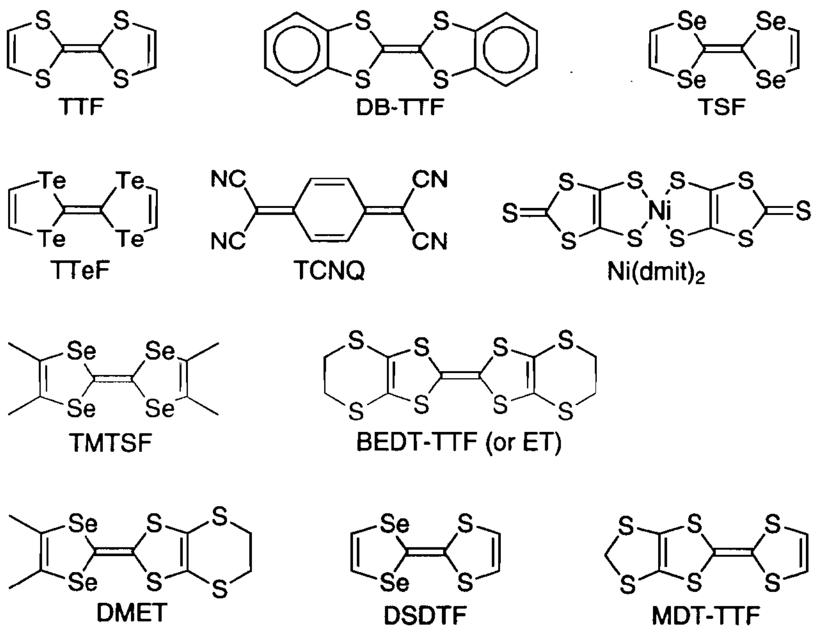
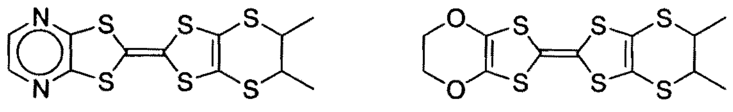


Chart 2.1

ture conductivity. Some of these CT complexes were metallic and underwent metal-to-insulator (MI) transition at low temperatures. In addition, the symmetrical π-donors TMTSF (Chart 2.1) and BEDT-TTF (or ET, Chart 2.1)[3b,11] have been found to give a number of conducting CT complexes and radical-cation (RC) salts (also called cation-radical salts), several of which underwent metal-to-superconductor transition at very low temperatures.[12,13] The first organic superconductor $(TMTSF)_2PF_6$, with a critical superconducting transition temperature (T_c) of 1.4 K under a pressure of 6.5 kbar, and the first ET-based organic superconductor $(ET)_2ReO_4$, with T_c = 2 K under a pressure of 4 kbar, were discovered in 1980[12] and 1982,[13] respectively. The superconducting salts based on TMTSF (the so-called Bechgaard salts) are quasi one-dimensional (1D) conductors, while the ET-based superconductors are regarded as quasi two-dimensional (2D) conductors. Furthermore, unsymmetrical donors, such as DMET (Chart 2.1),[14] which is a derivative of diselenadithiafulvalene (DSDTF, Chart 2.1), and MDT-TTF (Chart 2.1),[15] were found to give superconducting salts.

During the last two decades, a large number of conducting and superconducting materials based on symmetrical and unsymmetrical TCFs as well as $M(dmit)_2$ (M = metal) have been prepared and studied.[1,16–83] These systems are usually divided into the two categories labeled CT complexes and radical-ion (RI) salts.[1,76–78] In the case of CT complexes, a donor molecule (D) and an acceptor molecule (A) associate to form a stable complex through partial CT from D to A: $D^0 + A^0 \rightarrow D^{+\rho}A^{-\rho}$, where ρ denotes the amount of CT in a DA complex, and its value depends mainly on the ionization potential of D and the electron affinity of A, which can be estimated by the redox potentials of D and A in solutions.[76–78] In RI salts, a donor or an acceptor is first transformed into the corresponding RI *via* a chemical oxidation or reduction process, and then the resulting RI is spatially organized when molecular association with a counterion is feasible. A compound with $0 < \rho < 1$, leading to a mixed valence system, is a conducting material and obtained by the reaction of a donor having a moderate oxidation potential with an acceptor having a moderate reduction potential or by the reaction of a strong donor (or acceptor) and a weak acceptor (or donor). The combination of a strong donor and a strong acceptor leads to an ionic or a single valence complex ($\rho = 1$), whereas the combination of a weak donor and a weak acceptor gives rise to a neutral or a molecular complex in which no CT occurs. TCFs with organic π-acceptors, such as TCNQ, form CT complexes, whereas TCFs with inorganic anions, such as Cl^-, ClO_4^-, PF_6^- and $AuBr_2^-$, give RC salts. There is another type of salt composed of TCFs and metal 1,2-dichalcogenolenes, which has not yet been well defined.[1,19] RC salts crystallize in many different phases, such as the so-called α, β, γ, δ, ε, ζ, η, θ, κ, λ, τ, α′, β′, γ′ and β″ phases, which belong, for example, to the triclinic (α, β, γ, ζ, λ, β′, γ′ and β″), monoclinic (δ, ε, ζ, η, κ and α′), orthorhombic (γ, δ, θ and κ) and tetragonal (θ and τ) crystallographic systems. RC salts have interesting electronic structures and exhibit remarkable physical properties, such as optical properties (*e.g.*, vibronic mode), transport properties (*e.g.*, superconductivity) and magnetotransport properties (*e.g.*, magnetoresistance oscillation and quantum Hall effect), which arise from the low dimensionality of their electronic states.

A small number of RC salts were found to crystallize in the τ-phase.[21–36] Organic conductors or, more precisely speaking, organic-inorganic hybrid conductors of τ-phase have been obtained by electrocrystallization of some unsymmetrical TTFs, such as P-DMEDT-TTF (Chart 2.2) and EDO-DMEDT-TTF (Chart 2.2), with linear counteranions, such as $AuBr_2^-$, AuI_2^- and I_3^-, in stoichiometries ranging from 2:1.75 to 1:~1. The structural and physical characteristics of τ-phase conductors are as follows: (i) they crystallize in the tetragonal system simpler than the orthorhombic, monoclinic and triclinic systems; (ii) their structures predict star-like Fermi surfaces; (iii) with decreasing temperature, they exhibit metallic behavior and a change to semiconducting



P-DMEDT-TTF EDO-DMEDT-TTF

Chart 2.2

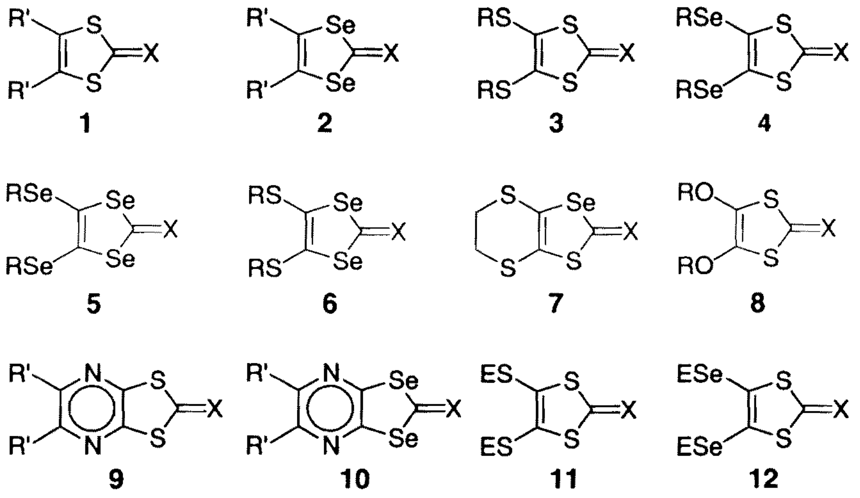
or insulating behavior at low temperatures; (iv) they exhibit broad ESR bands even at low temperatures; (v) they show negative Hall coefficients, indicating negative carriers (*i.e.*, electrons), negative magnetoresistances and positive magnetoreflectances at low fields; (vi) at higher field, they exhibit giant magnetoresistance oscillations and quantum Hall Plateaus.[21–36]

In this chapter, in addition to the synthesis and properties of TCFs with heteroatom-containing substituents, the formation and properties of their charged species, including their RCs, are reviewed. Special emphasis is placed on the unsymmetrical TCFs incorporating four additional heteroatoms and their charged species, which are components of τ-phase conductors. For the naming of derivatives of TCF, empirical or nonsystematic abbreviations rather than *Chemical Abstracts* or IUPAC nomenclature are used. Definitions of the abbreviations used herein have frequently appeared in the original papers and review articles.[1–83]

2.2 Preparation of Building Blocks

A variety of reactants and building blocks have been used for constructing TCFs. Elemental S, Se and Te, as well as many simple oxygen-, sulfur-, selenium- and nitrogen-containing compounds, such as CS_2, CSe_2, H_2Se, $HSCH_2CH_2SH$, $Me_2NC(=S)SNa$, 1,4-dioxane, $(Me_2N)_2C=S$ and 2,3-dichloropyrazine, have been used as reactants. Most of these reactants are commercially available. In contrast, most building blocks used for the synthesis of TCFs, *i.e.*, 2-oxo-1,3-dithioles (or 1,3-dithiol-2-ones), 2-oxo-1,3-diselenoles (or 1,3-diselenol-2-ones) and related compounds, were prepared by several methods.[1,2,5,14,15,28,30,37–75,82] Here, the preparation of 1,3-dichalcogenole-2-chalcogenones with more than one additional heteroatoms (O, S, Se and N) is mainly described. These compounds are listed in Chart 2.3, although most of them have been reported in the literature.[1,47,48,50,51,55]

Some building blocks, such as vinylenetrithiocarbonate (or 1,3-dithiole-2-thione, **1a'**, X = S) for TTF and 4,5-dimethyl-1,3-diselenole-2-selenone (**2b'**, X = Se) for TMTSF (Chart 2.1), are commercially available. Compounds **1** and **2** have been prepared by several cyclization procedures.[1–3,49,74] Vinylenetrithiocarbonate (**1a'**, X = S) was obtained in good yield by treating potassium trithiocarbonate [KS-C(=S)-SK] with 1,2-dichloroethyl ethyl ether [$ClCH_2CHCl(OEt)$], followed by elimination of ethanol promoted by *p*-toluenesulfonic acid. In addition, compound **1a'** and its selenium analogue **2a'** (X = Se) were prepared by thermolysis of 1,2,3-thiadiazole and 1,2,3-selenathiazole in the presence of CS_2 and CSe_2, respectively. Substituted derivatives of **1a'** and **2a'** were obtained from the corresponding β-keto-*N*,*N*-dialkylthiocarbonates, β-keto-*S*-alkylthiocarbonates and their Se-containing analogues by different cyclization procedures depending on the types of R' group, heteroatom, *etc.* Compounds **1d'** and **2d'**, containing electron-withdrawing groups (R' = CN, COOMe, CHO, *etc.*), were prepared by the reaction of the corresponding acetylenes with ethylenetrithiocarbonate and ethylenetriselenocarbonate, respectively.[1,41,43,46,50,51] Some compounds of types **1d'** and **2d'**, as well as compounds **11** and **12**, have functional groups which can be transformed into other functional groups. For example, (i) transformation of the CN group into the COOH group,[47,51] (ii) transformation of the ES group [E =



X = O, S, Se

a': R' = H, **b'**: R' = CH_3, **c'**: R'–R' = $CH_2CH_2CH_2$ *etc.*,

d': R' = CN, COOMe, CHO, *etc.*

a: R = CH_3, **b**: R–R = CH_2, **c**: R–R = CH_2CH_2, **d**: R–R = $CH_2CH_2CH_2$,

e:R–R = $CH(CH_3)CH_2$, **f**: R–R = $CH(CH_3)CH(CH_3)$, **g**: R–R = CH=CH *etc.*

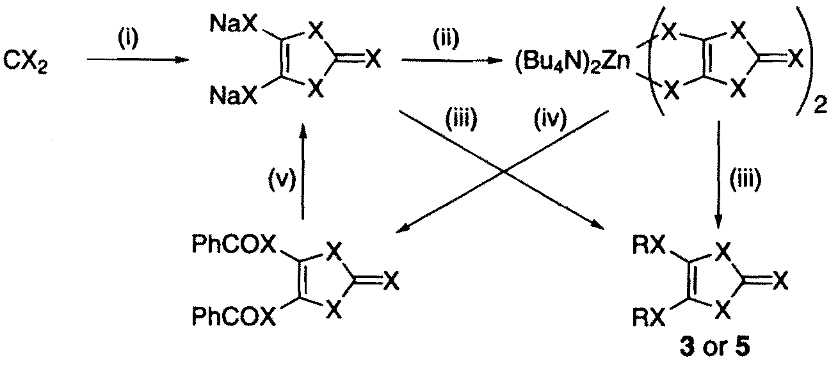
a: E = $CH_2O(CH_2)_2SiMe_3$, **b**: E = $CH_2C_6H_4Ac$-*p*,

c: E = CH_2CH_2CN, **e**: E = COPh *etc.*

Chart 2.3

$CH_2O(CH_2)_2SiMe_3$, $CH_2C_6H_4Ac$-*p*, CH_2CH_2CN, COPh, *etc.*] into the RS group *via* the corresponding thiolate (S^-),[48,53,62,70] *etc.*[74] have been reported. Also, compounds containing the vinylenedithio end group have been transformed into further extended compounds (see Schemes 2.2 and 2.13 for details).[46,51,60,61,74]

Compounds **3**–**5** have been prepared by treating the corresponding metal 1,2-dichalcogenolates such as $(Bu_4N)_2Zn(dmit)_2$ with alkyl halides such as CH_3I or with dibromoalkanes such as $BrCH_2Br$ and $BrCH_2CH_2Br$.[39,40,42,45–48,50,51,59,69] Although $(R_4N)_2Zn(dmit)_2$ (R = Bu and Et) are commercially available, they can be obtained by chemical reduction of CS_2 with Na in DMF followed by addition of $ZnCl_2$ and R_4NBr (R = Bu and Et).[40,47,51] Their selenium analogues can also be obtained by a similar method using CSe_2 instead of CS_2.[47,51] An analogous compound



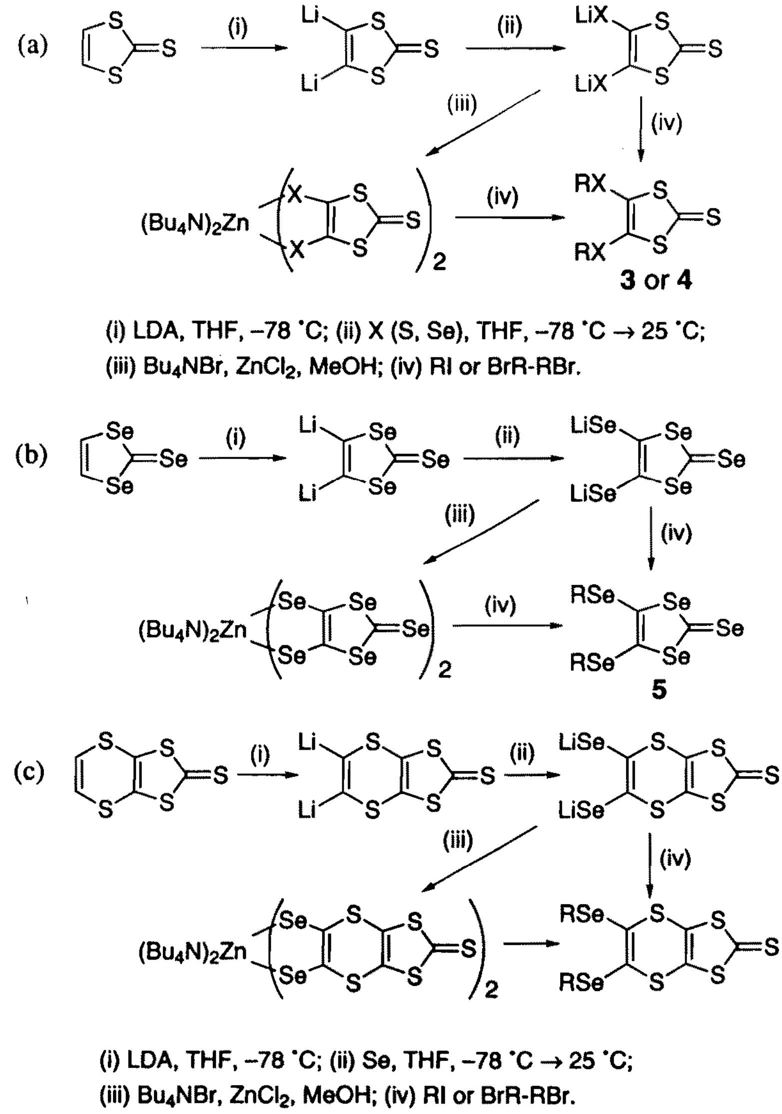
X = S, Se; (i) Na, DMF, 0 °C; (ii) Bu_4NBr, $ZnCl_2$, MeOH; (iii) RI or BrR-RBr *etc.*; (iv) PhCOCl; (v) EtONa.

Scheme 2.1

$(Bu_4N)_2Hg(dmit)_2$ has been obtained by electrochemical reduction of CS_2 with Hg electrodes in DMF containing Bu_4NI.[10,37] Scheme 2.1 outlines the procedures for the preparation of **3** or **5**. Procedures (i), (ii) and (iii) for the preparation of **3a–f**, procedures (i), (ii), (iv), (v) and (iii) for the preparation of **3g**, *etc.* have been utilized.[1,39,40,42,45–47,51,52,60]

Vinylenetrithiocarbonate (**1a'**, X = S) and its selenium analogue **2a'** (X = Se) have been used for the preparation of the corresponding zinc 1,2-dichalcogenolenes. Dilithiation of compounds with the vinylenedichalcogeno end group, in which each of two acidic hydrogen atoms bonded directly to the C=C bond is replaced by lithium, was achieved by using lithium diisopropylamide (LDA) as a metalation reagent at low temperature (–78 °C). To the resulting dilithiated product, elemental S or Se was added and the reaction mixture was allowed to warm up to 25 °C. Subsequent reaction with $ZnCl_2$ and Bu_4NBr led to a solid zinc 1,2-dichalcogenolate.[46,51,60,61] The procedures for preparations of **3–5** and further extended compounds are outlined in Schemes 2.2a–c. Starting from 2,3-dihydro-1,4-dithiin and its analogues, similar procedures were applied to the preparation of compounds of type **6**.[35,36,75]

An alternative method has been developed to prepare compounds of types **3** and **4**. The use of cyclic sulfates instead of the corresponding dibromoalkanes allowed the preparation of **3e,f**, as

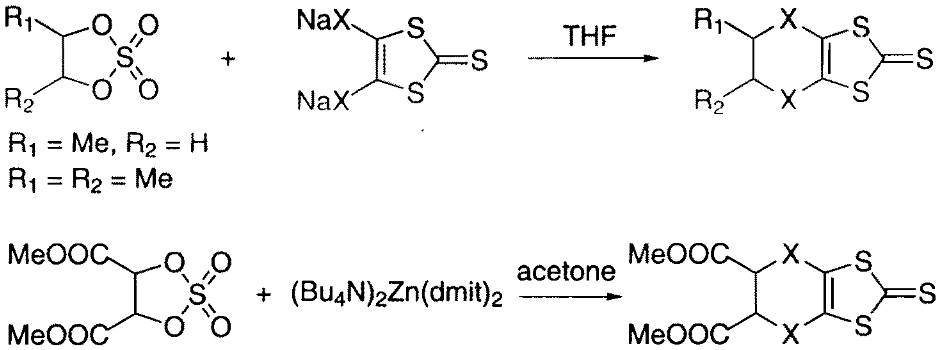


(i) LDA, THF, –78 °C; (ii) X (S, Se), THF, –78 °C → 25 °C;
(iii) Bu_4NBr, $ZnCl_2$, MeOH; (iv) RI or BrR-RBr.

(i) LDA, THF, –78 °C; (ii) Se, THF, –78 °C → 25 °C;
(iii) Bu_4NBr, $ZnCl_2$, MeOH; (iv) RI or BrR-RBr.

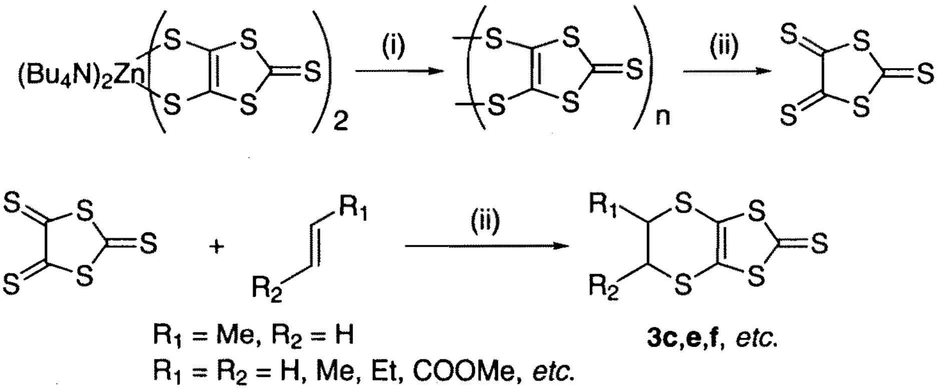
Scheme 2.2

shown in Scheme 2.3.[35,36,63,66,67,71)] Chiral compounds and their racemic mixtures as well as their selenium analogues were also prepared by this method. It has been reported that only the *trans* form of the cyclic sulfate reacts with the disodium dithiolate (X = S) shown in Scheme 2.3.[66)]



Scheme 2.3

Also, Diels-Alder cycloaddition reaction of the *trans*-alkenes with the 1,3-dithiole-2,4,5-trithione oligomer gave thiones **3c,e,f**,[28)] *etc.*,[73,82b)] as shown in Scheme 2.4. 1,3-Dithiole-2,4,5-trithione was obtained from $(Bu_4N)Zn(dmit)_2$ as a mixture of monomeric, dimeric and polymeric forms.[28)] Thermolysis of the polymeric form in benzene at about 82 °C led to the generation of the monomeric form. Compounds **3e,f** were obtained as racemic mixtures of the corresponding enantiomers.



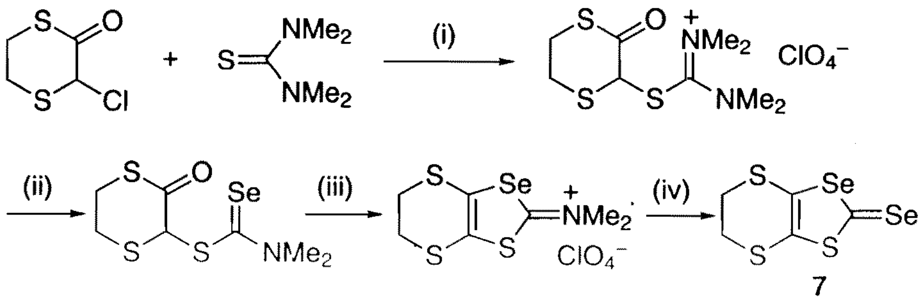
3c,e,f, *etc.*

(i) Br_2, acetone or CH_2Cl_2; (ii) dry benzene, *ca.* 82 °C.

Scheme 2.4

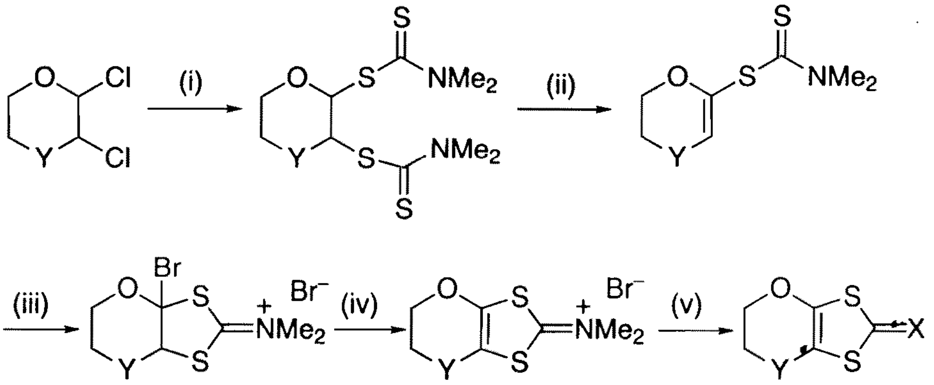
As illustrated in Scheme 2.5, the well-known ring-closure reaction has been applied to the preparation of compound **7** (X = Se) using 3-chloro-2-oxo-1,4-dithiane and tetramethylthiourea as starting materials.[49)] The preparation of **8a** (X = S) and **8c** (X = S) was achieved *via* similar ring-closure reactions using 1,2-dichloro-1,2-dimethoxyethane and 2,3-dichlorodioxane, respectively.[1,38,51)] Scheme 2.6 outlines the preparation of **8c** and its oxathiane analogue 4,5-ethylenoxythio-1,3-dithiole-2-thione.[38a)] In addition, preparation of 4,5-ethylenedioxy-1,3-selenothiole-2-thione,[38b)] 4,5-ethyleneselenothio-1,3-dithiole-2-thione and related compounds[38c)] proceeded *via* analogous ring-closure reactions.

Various short-step methods for the preparation of **9** and **10** have been developed,[54–58)] some of which are outlined in Scheme 2.7. Compound **9a'** (X = S) was directly prepared by the treatment of 2,3-dichloropyrazine with potassium trithiocarbonate in DMF and converted into its



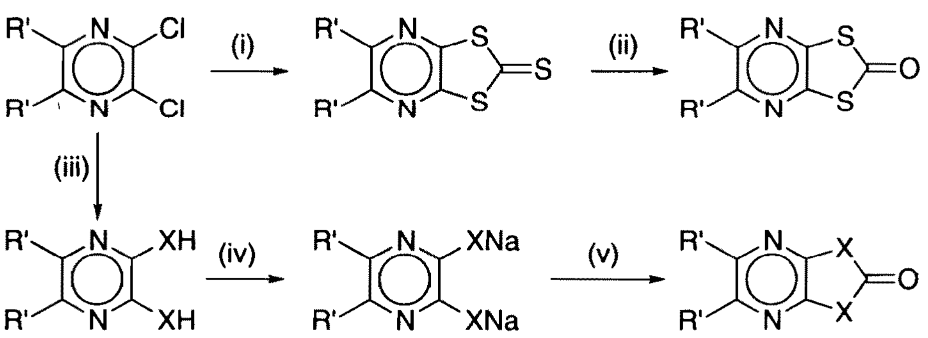
(i) $HClO_4$, EtOH; (ii) H_2Se, H_2O; (iii) H_2SO_4; then $HClO_4$;
(iv) H_2Se, $MeOH$-H_2O.

Scheme 2.5



Y = O, S; (i) $Bu_4N^+\ ^-SC(=S)NMe_2$, MeCN; (ii) DMSO, 110 °C or Et_3N, MeCN, 0 °C; (iii) Br_2, CH_2Cl_2, 0 °C; (iv)110 °C, 25 Torr;
(v) H_2Se, MeOH or NaSH, EtOH-AcOH, 25 °C.

Scheme 2.6



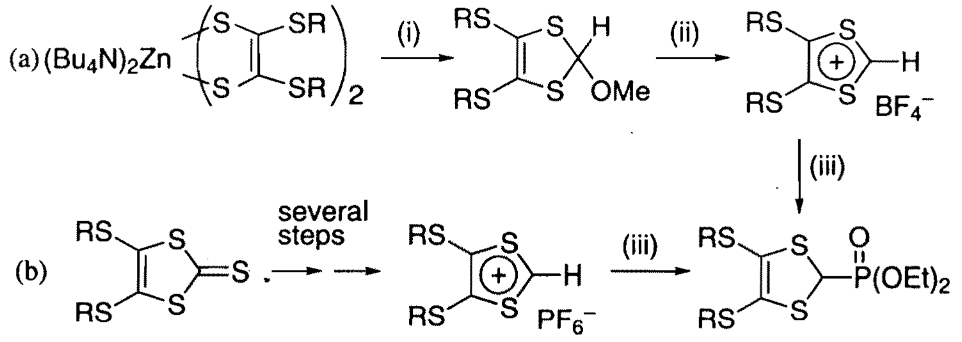
X = S, Se; (i) K_2S, CS_2, DMF; (ii) $Hg(OAc)_2$, CH_2Cl_2-AcOH; (iii) KXH;
(iv) NaOH; (v) $COCl_2$.

Scheme 2.7

oxo-analogue **9a′** (X = O), which was also obtainable by the three-step preparation *via* the reaction of 2,3-dichloropyrazine with KSH. The use of KSeH instead of KSH in this three-step preparation gave the selenium analogue of **9a′** (X = O), *i.e.*, **10a′** (X = O).

According to the procedures shown in Schemes 2.1 and 2.2, compounds **11** and **12** were prepared by treatment of the corresponding zinc 1,2-dichalcogenolenes with $(CH_3)_3Si(CH_2)_2OCH_2Cl$, p-$AcC_6H_4CH_2Cl$, $NCCH_2CH_2Cl$, $PhC(=O)Cl$, *etc.*[1,3b,43,46,47,53,59,62,69b,70,82c]

Compounds **1–10** have been converted into the corresponding 1,3-dithiolium salts, phosphoranes (Wittig reagents) or phosphonate esters (Wittig-Horner reagents). Two synthetic routes to phosphonate esters are shown in Scheme 2.8. The resulting phosphonate esters, as well as organotin and organotitanium compounds, have been used as another building blocks for the synthesis of various TCFs.[1,17,18,40,75]



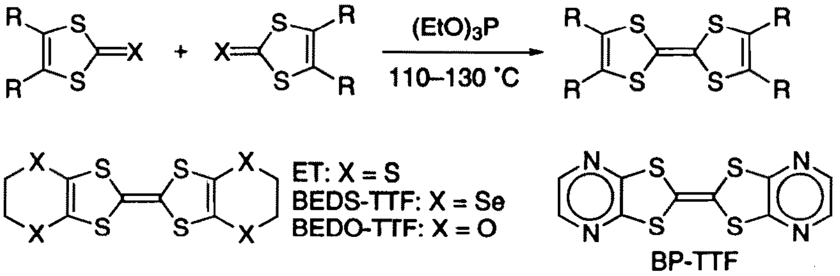
(i) Cl_2CHOMe, acetone; (ii) HBF_4, CH_2Cl_2-Ac_2O;
(iii) $(EtO)_3P$, NaI, acetone or MeCN.

Scheme 2.8

2.3 Synthesis of TCFs

One can design a wide variety of TCFs by combining two same or different 1,3-dichalcogenole-2-chalcogenones, *i.e.*, building blocks **1-12** shown in Chart 2.3 and their analogues. However, all possible combinations have not actually been attempted, and the number of TCFs giving τ-phase conductors is limited. In this section, some coupling reactions applied to the synthesis of TCFs are described. Some TCFs, such as TTF,[2,3] TMTSF (Chart 2.1)[11a] and ET (Chart 2.1),[11b,c] are commercially available.

Most symmetrical TCFs have been synthesized by the self-coupling reaction of the corresponding 1,3-dichalcogenole-2-chalcogenones in the presence of triethyl phosphite $[(EtO)_3P]$ or other trivalent phosphorus reagents, *e.g.*, Ph_3P (see refs. 19 and 20 for a proposed mechanism for this type of coupling reaction). Scheme 2.9 shows four successful examples of this self-coupling reaction, which led to ET, BEDS-TTF, BEDO-TTF and BP-TTF. The yield depends on the type of 1,3-dichalcogenole-2-chalcogenone and on the reaction conditions (solvent, temperature, *etc.*).

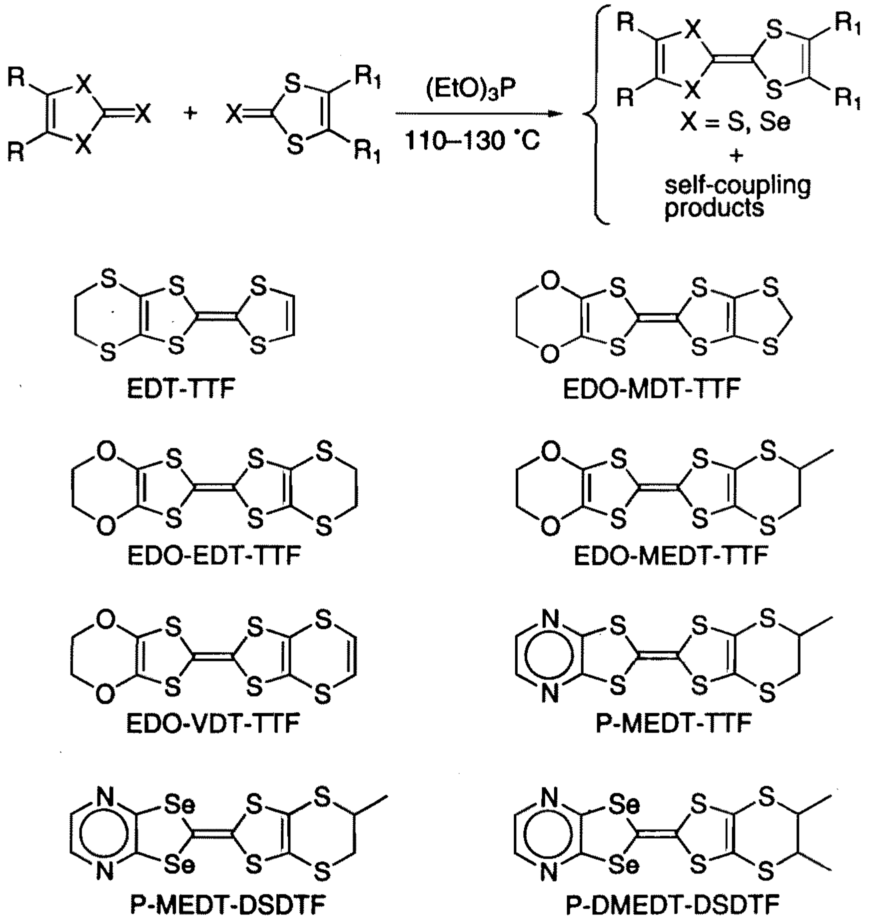


Scheme 2.9

This coupling reaction is usually carried out under an inert atmosphere (N_2 or Ar).[1,39,40,47–57,59,60] In most cases, the best yield of the self-coupling product is obtained by using 2-oxo-1,3-dichalcogenoles (X = O in Chart 2.3) instead of the corresponding 2-thio- or 2-seleno-1,3-dichalcogenoles (X = S or Se in Chart 2.3). Conversion of 2-thio- or 2-seleno-1,3-dichalcogenoles into the corresponding 2-oxo-3-dichalcogenoles can be carried out by using, for example, mercury acetate [$Hg(OAc)_2$] in CH_2Cl_2/AcOH (v/v = 1/1).[42,45,46,49,56,57,71,73,74] Some trial experiments may be required to optimize the yield of the coupling product. Other building blocks, *e.g.*, 1,3-dithiolium salts (see Scheme 2.8) and organotin compounds,[1,18,38,40,74] have been used for different types of coupling reactions with the aid of activating reagents, *e.g.*, Et_3N[23,40] and Me_3Al.[18]

A good number of unsymmetrical TCFs have been synthesized by the cross-coupling reaction between the two different 1,3-dichalcogenole-2-chalcogenones in the presence of $(EtO)_3P$.[1,30,32,33,39,47–57,60] Useful applications of this cross-coupling reaction are found in the synthesis of P-DMEDT-TTF (Chart 2.2) and EDO-DMEDT-TTF (Chart 2.2) as well as the TTFs and DSDTFs shown in Scheme 2.10. The reaction conditions for obtaining these unsymmetrical donors in the best yields have been reported in the literature.[30,32,33,36,51,52,60] Also, the selenium analogues of EDT-TTF and EDO-MDT-TTF, *i.e.*, EDT-DSDTF (Chart 2.4) and EDO-MDS-TTF (Chart 2.4), were synthesized by this kind of cross-coupling reaction.[43,44,51,52,58]

In the cross-coupling reaction, the product is usually accompanied by two self-coupling byproducts, and separation of the cross-coupling product from the mixture with silica gel column chromatography is essential. In the synthetic examples shown in Scheme 2.10, CH_2Cl_2 was used as the eluent solvent for the separation of the pyrazino-substituted TTF and DSDTF derivatives,



Scheme 2.10

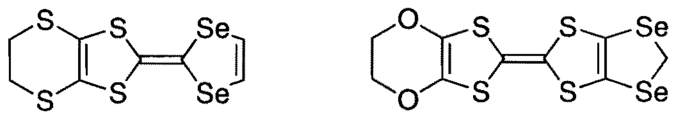

EDT-DSDTF EDO-MDS-TTF

Chart 2.4

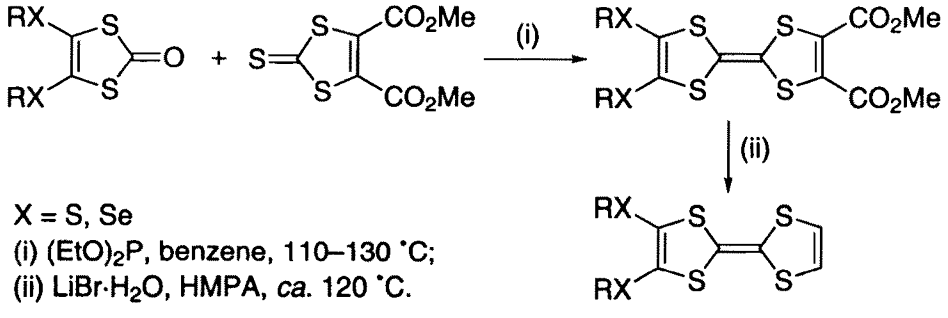
whereas separation of the ethylenedithio- and ethylenedioxy-substituted TTFs required CS_2 as the eluent solvent. It has been reported that the use of silica gel (230–400 mesh) with a mixed solvent hexane-CS_2 (v/v = 1/2) as the eluent solvent results in good separation of an unsymmetrical derivative of ET.[73)] In each case, the value of the retardation factor (R_f) for the cross-coupling product (AB) is approximately given by the following equation:

$$R_f\,(\mathrm{AB}) = \frac{1}{2}\,[R_f\,(\mathrm{AA}) + R_f\,(\mathrm{BB})]. \tag{2.1}$$

where AA and BB are the self-coupling products.[48)] When the polarities between the cross-coupling product and the two self-coupling products differ considerably or moderately, the separation of the cross-coupling product by column chromatography is easily carried out. If this separation poses serious difficulties due to a small difference between the polarities of the cross- and self-coupling products, modification of the cross-coupling reaction is required. For example, as shown in Schemes 2.11 and 2.12a, building blocks with one or two polar functional groups, such as an ester, ether or nitril group, are first used for the cross-coupling reaction. Then, after separation of the desired cross-coupling products, removal of the polar functional group(s) attached is performed by appropriate methods.[1,20,41–43,45–51,53,58,59,61,62,70)] Synthesis of unsymmetrical TCFs which have the ethylenedithio end group ($-SCH_2CH_2S-$) on one side and the deuterated ethylenedithio end group ($-SCD_2CD_2S-$) on the other side was achieved according to the procedures shown in Scheme 2.12b.

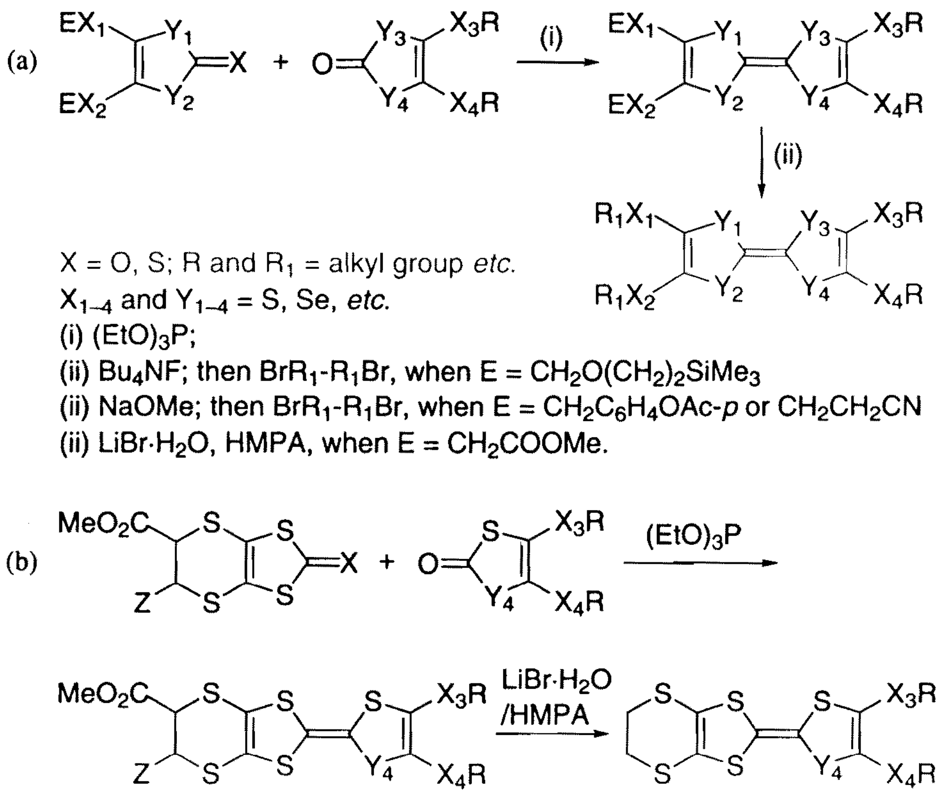
To avoid the formation of the self-coupling products or increase the yield of the cross-coupling product, a Wittig-Horner reaction using a phosphonate ester (see Scheme 2.8) has been utilized in some cases.[1,18)] In addition, for the exclusive formation of unsymmetrical TCFs, the non-phosphite coupling reaction, *i.e.*, the Lewis acid-promoted reaction of organotin dithiolates or diselenolates with esters, has been developed. As a Lewis acid, for example, Me_3Al was used for the synthesis of DMET (Chart 2.1).[18)]

Starting from TCF donors containing at least one vinylenedithio end group, further extended TCFs have been synthesized by the procedures shown in Scheme 2.13.[3b,35,43,48,60,80)] Similar to the procedures shown in Scheme 2.2, (i) dilithiation with LDA, (ii) insertion of S or Se into the C–Li bond, (iii) transformation into zinc 1,2-dichalconolates and (iv) reaction with alkyl halides gave TCFs with extended S- or Se-containing framework.[60)] In these cases, the isolation of zinc 1,2-



X = S, Se
(i) $(EtO)_3P$, benzene, 110–130 °C;
(ii) $LiBr{\cdot}H_2O$, HMPA, *ca.* 120 °C.

Scheme 2.11

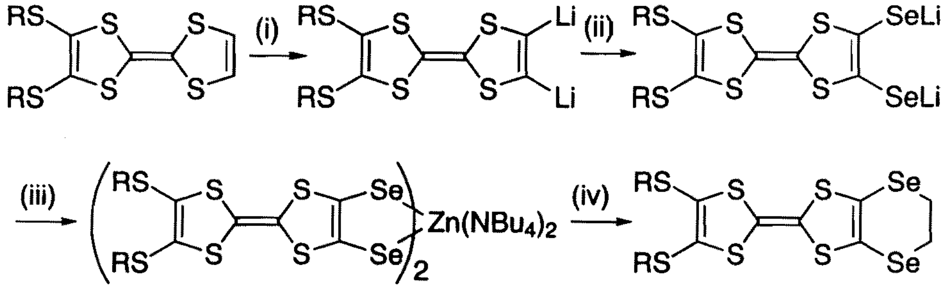


X = O, S; R and R_1 = alkyl group *etc.*
X_{1-4} and Y_{1-4} = S, Se, *etc.*
(i) $(EtO)_3P$;
(ii) Bu_4NF; then BrR_1-R_1Br, when E = $CH_2O(CH_2)_2SiMe_3$
(ii) NaOMe; then BrR_1-R_1Br, when E = $CH_2C_6H_4OAc$-*p* or CH_2CH_2CN
(ii) $LiBr{\cdot}H_2O$, HMPA, when E = CH_2COOMe.

X = O, S; $X_{3,4}$ and Y_4 = S, Se; Z = H or COOMe
R = alkyl group *etc.* (*e.g.*, R–R = CD_2CD_2).

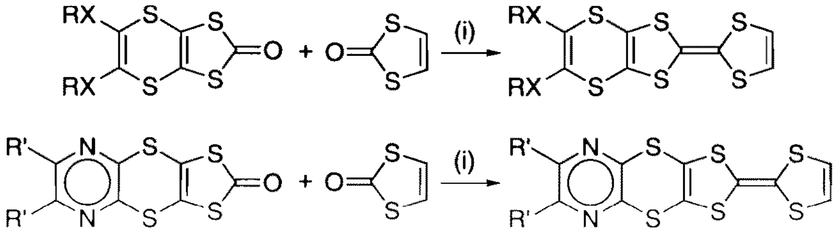
Scheme 2.12

dichalcogenolates was necessary to obtain products of high purity, because direct reaction of dilithium dichalcogenolates, generated *via* insertion of a chalcogen atom into each C–Li bond, with alkyl halides resulted in deterioration in the purity of the products. Synthesis of the TTFs with extended π-conjugation from smaller TTFs with convertible functional groups has also been reported.$^{1)}$ Scheme 2.14 outlines the synthesis of several TTFs containing four additional heteroatoms in only the outer hemisphere of the TTF core.$^{1,18,47,48,56,61)}$ Moreover, the use of building blocks **3**–**8** (Chart 2.3) instead of 2-oxo-1,3-dithiole shown in Scheme 2.14 led to multi-heteroatom-containing TCFs.$^{18,47,48)}$



R–R = CH_2CH_2, $CH(CH_3)CH_2$, $CH(CH_3)CH(CH_3)$
(i) LDA, –72 °C; (ii) Se, –72 °C → 25 °C; (iii) Bu_4NBr, $ZnCl_2$;
(iv) $BrCH_2CH_2Br$.

Scheme 2.13



X = S, Se; R = CH_3; R–R = CH_2CH_2; R' = H, CH_3, *etc.*
(i) $(EtO)_3P$, *ca.* 130 °C.

Scheme 2.14

2.4 Electrochemical Behavior of TCFs

The cyclic voltammetry (CV) measurements of TCFs provide their electrochemical parameters, *i.e.*, the half-wave redox potentials, $E^1_{1/2}$, $E^2_{1/2}$, $E^3_{1/2}$, *etc.*, where $E^i_{1/2} = (E^i_{ox} + E^i_{rd})/2$ (E^i_{ox}: the oxidation potential, E^i_{rd}: the reduction potential), which play an important role in the formation, stability and other properties of CT complexes and RC salts. Fig. 2.1a shows the two reversible redox waves of TTF, in which two anode peaks, corresponding to the first and second oxidation potentials (E^1_{ox} and E^2_{ox}), appear at 470 and 940 mV [*vs.* saturated calomel electrode (SCE)], respectively, whereas there are two cathode peaks, corresponding to the first and second reduction potentials (E^1_{rd} and E^2_{rd}), at 280 and 760 mV, respectively. Fig. 2.1b shows the CV of a derivative of TTF, EDO-VDT-TTF (Scheme 2.10), measured under the same conditions.

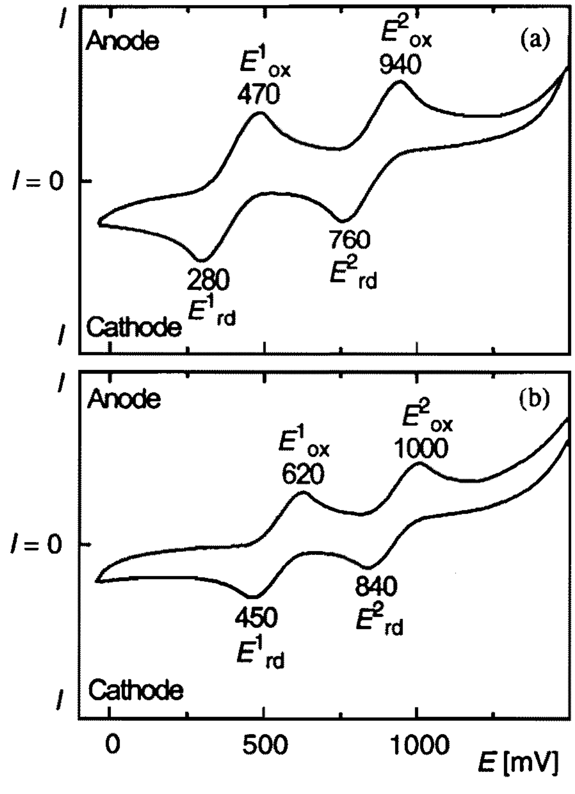


Fig. 2.1 CVs of TTF (a) and EDO-VDT-TTF (b): V *vs.* SCE; 0.025 M Bu_4NPF_6 in C_6H_5CN containing 7 × 10^{-4} M TTF or EDO-VDT-TTF; Pt electrode; at room temperature; scan rate 100 mV s^{-1}.

Although the values of the redox potentials vary under different measurement conditions (temperature, solvent, electrolyte, *etc.*), the value of the first half-wave redox potential ($E^1_{1/2}$) indicates the donor (D) ability to release one electron according to the following equation:

$$D^0 \xrightarrow{-e} D^{\bullet+}.$$

The value of the second half-wave redox potential ($E^2_{1/2}$) represents the generation of a dication, as shown with the following equation:

$$D^{\bullet+} \xrightarrow{-e} D^{2+}.$$

The difference between the first and second half-wave redox potentials ($\Delta E = E^2_{1/2} - E^1_{1/2}$) corresponds to the on-site Coulombic repulsion involved in the formation of a dication.[1,2,76–79)] In general, the value of $E_{1/2}$ of an unsymmetrical donor (AB) can be calculated from those of the two corresponding symmetrical donors (AA and BB) according to the following equation:

Table 2.1 Half-wave Redox, Oxidation and Reduction Potentials (mV) of TCFs[a]

Compound	Conditions[b]	$E^1_{1/2}$	$E^2_{1/2}$	ΔE	E^1_{ox}	E^2_{ox}	E^1_{rd}	E^2_{rd}
TM-TTF[c]	A	290	650	360				
TTF[d]	A	367	748	381				
	B	375	845	470	470	940	280	750
	C	319	701	382				
MDS-TTF[c]	B	405	790	385	490	870	320	710
BEDO-TTF[e]	A	435	699	264				
	B	415	810	395	490	900	340	720
BMDS-TTF[c]	B	(435)	(735)	(300)				
TMTSF[d]	A	440	720	280				
MDT-TTF[d]	B	455	832	377	535	915	375	750
	B	(451)	(829)	(378)	(532)	(910)	(370)	(748)
EDT-TTF[f]	A	(467)	(788)	(321)				
	B	460	885	425	545	970	375	800
	C	390	690	300				
	C	(402)	(720)	(318)				
TSF[d]	A	480	760	280				
EDO-MDT-TTF[f]	B	(466)	(811)	(395)				
EDO-EDT-TTF[f]	A	(501)	(764)	(263)				
	B	(467)	(858)	(391)				
EDO-DMEDT-TTF[g]	A	502	762	260				
	B	(468)	(853)	(388)				
BEDT-TTF[d]	A	567	829	262				
	B	520	907	387	600	980	440	835
	C	486	739	253				
BDMEDT-TTF[c]	B	(521)	(902)	(381)				
EDT-DMEDT-TTF[c]	B	522	897	375	595	970	450	825
BMDT-TTF[c]	B	527	812	285	595	880	460	745
EDO-VDT-TTF[f]	B	535	920	385	620	1000	450	840
P-MDS-TTF[c]	B	(677)	(1049)	(371)				
P-EDT-TTF[c]	B	720	1135	415	790	1220	650	1050
	C	680	1020	340				
	C	(688)	(955)	(267)				
P-DMEDT-TTF[g]	B	(721)	(1130)	(409)				
P-MDT-DSDTF[c]	C	690	960	270				
P-EDT-DSDTF[c]	C	740	1030	290				
BP-TTF[e]	B	(920)	(1363)	(443)				
	C	890	1170	280				
BDMP-TTF[c]	C	990	1280	290				

[a] The calculated values from equation (2.2) are given in parentheses. [b] A: 0.1 M Bu_4NPF_6 in CH_3CN, V *vs.* Ag/AgCl; B: 0.025 M Bu_4PF_6 in C_6H_5CN, V *vs.* SCE; C: 0.1 M Et_4NClO_4 in CH_3CN, V *vs.* SCE.[1,54,58,59,67,75,77)] [c] See Chart 2.5 for the structural formula. [d] See Chart 2.1 for the structural formula. [e] See Scheme 2.9 for the structural formula. [f] See Scheme 2.10 for the structural formula. [g] See Chart 2.2 for the structural formula.

$$E^1_{1/2}\,(\mathrm{AB}) = \frac{1}{2}\,[E^1_{1/2}\,(\mathrm{AA}) + E^1_{1/2}\,(\mathrm{BB})]. \tag{2.2}$$

This equation is also applicable to the oxidation and reduction potentials (E^1_{ox} and E^1_{rd}). Table 2.1 summarizes the experimental $E^1_{1/2}$, $E^2_{1/2}$, ΔE, E^1_{ox}, E^2_{ox}, E^1_{rd} and E^2_{rd} values for selected TCFs. In several cases, the calculated values from equation (2.2) under various measurement conditions are given.[1,53,57,58,66,71,76] As can be seen from Table 2.1, the $E^1_{1/2}$ values increase on going from TM-TTF to BDMP-TTF. All the unsymmetrical TCFs incorporating four additional heteroatoms, listed in Table 2.1, show higher $E^1_{1/2}$ and $E^2_{1/2}$ values than those of TSF. In the CVs of TCFs with one or two appended heterocycles, more than two redox waves are observed.[1,18,76,80] These waves indicate the appearance of higher oxidized species, and probably arise from the additional heterocycle(s).

2.5 Role of Additional Functional Groups in the Synthesis and Properties of TCFs

There are two ways to obtain extended TCFs: one is the peripheral extension of the TCF core by substitution of the hydrogen atoms of the TCF molecule with other functional groups, while the other is the introduction of a π-linking group as a spacer group between the central C=C bond of TCF. The latter compounds are described elsewhere,[1,74,79] so the substituted TTFs belonging to the former category are described here. For example, substitution of the four hydrogen atoms on both sides of TTF with the CH_3, CH=CH-CH=CH, SCH_2CH_2S and N=CH-CH=N groups leads to the symmetrical donors TM-TTF (Chart 2.5), DB-TTF (Chart 2.1), ET (Chart 2.1) and BP-TTF (Scheme 2.9), respectively, whereas substitution of the two hydrogen atoms on either side of TTF with the same groups gives the unsymmetrical donors DM-TTF (Chart 2.6), B-TTF (Chart 2.6), EDT-TTF (Scheme 2.10) and P-TTF (Chart 2.6), respectively. Additional substituents attached to

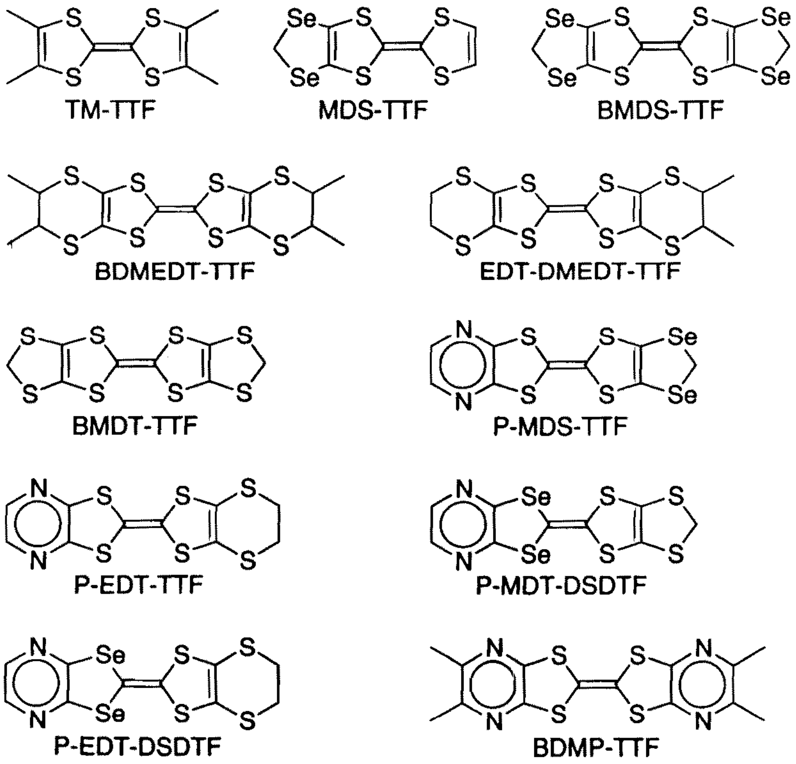


Chart 2.5

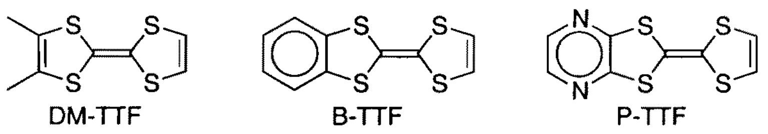
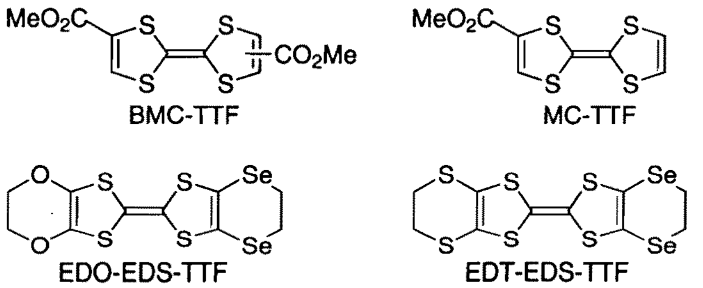

DM-TTF B-TTF P-TTF

Chart 2.6

the TTF core generally affect the polarity, solubility, redox potentials, optical properties and other chemical or physical properties. Some examples are given in the following paragraphs.

As described in Section 2.3, a number of unsymmetrical TCFs have been obtained by the $(EtO)_3P$-promoted cross-coupling reaction of the two corresponding 1,3-dichalcogenol-2-ones followed by separation from the concomitant self-coupling byproducts by column chromatography when the R_f values of unsymmetrical TCFs are considerably or moderately different from those of the self-coupling products. For example, the R_f values of TTF, BMDT-TTF (Chart 2.5), BEDS-TTF (Scheme 2.9), BEDO-TTF (Scheme 2.9), BP-TTF (Scheme 2.9) and BMC-TTF (Chart 2.7) on a silica gel plate using CH_2Cl_2 as an eluent solvent are 0.75, 0.77, 0.55, 0.25, 0.08 and 0.05, respectively; that is, the polarities of the three latter donors are higher than those of the three former donors. This means that the additional substituents, *i.e.*, the OCH_2CH_2O, N=CH-CH=N and CO_2CH_3 groups, affect the R_f values. Consequently, unsymmetrical TTFs, such as MC-TTF (Chart 2.7), P-EDT-TTF (Chart 2.5) and EDO-EDS-TTF (Chart 2.7), were easily separated from the corresponding symmetrical TTFs by column chromatography because of a moderate difference between the R_f values of unsymmetrical and symmetrical TTFs. On the other hand, an easy separation of unsymmetrical TTFs, such as MDT-TTF (Chart 2.1) and EDT-EDS-TTF (Chart 2.7), was unsuccessful, even though the eluent solvent used for a silica gel column chromatography was changed. Therefore, modified cross-coupling reactions were required to obtain these unsymmetrical TTFs.


BMC-TTF MC-TTF

EDO-EDS-TTF EDT-EDS-TTF

Chart 2.7

For the preparation of CT complexes and RC salts in solution, TCFs used as their donor components need to be soluble in organic solvents. For example, TTF and ET (Chart 2.1) are sufficiently soluble in CH_2Cl_2 and C_6H_5CN, while BEDS-TTF (Scheme 2.9) and BP-TTF (Scheme 2.9) are less soluble in these solvents. The solubility is increased by (i) replacement of the hydrogen atoms of TCF by the CH_3, $CH_3(CH_2)_n$, CN, CO_2CH_3 and $CH_2O(CH_2)_2SiMe_3$ groups, (ii) replacement of the XCH_2CH_2X (X = S and Se) groups by their oxygen analogue (X = O) and (iii) replacement of the N=CH-CH=N or SCH=CHS group by the XCH_2CH_2X (X = S or O) group.

It has been reported that TCFs with $E^1_{1/2}$ values close to or lower than that of TTF are oxidized by air in solution.[1,76] On the other hand, symmetrical TCFs derived from the building blocks **9–12** (Chart 2.3) have high $E^1_{1/2}$ values and do not form a stable CT complex or RC salt. For example, the salts based on BP-TTF (Scheme 2.9) are unstable in moist air due to the low electron-donating ability of BP-TTF (see Table 2.1).[56] Accordingly, for the preparation of stable

CT complexes and RC salts, their donor components should have $E^1_{1/2}$ values lower than that of BP-TTF. Substitution of the hydrogen atoms of TTF by electron-donating groups, such as alkyl and cycloalkyl groups, decreases the $E^1_{1/2}$ value, whereas substitution with electron-withdrawing groups, such as the CF_3, CN and CO_2CH_3 groups, increases the $E^1_{1/2}$ value. Introduction of sulfur- and oxygen-containing substituents instead of the hydrogen atoms increases the $E^1_{1/2}$ value, but decreases the ΔE ($E^2_{1/2} - E^1_{1/2}$) value, suggesting a decrease in the on-site Coulombic repulsion.1,76–78) In addition, attachment of sulfur-, selenium-, tellurium- and nitrogen-containing substituents leads to the enhancement of intermolecular interaction in CT complexes and RC salts, but increases the $E^1_{1/2}$ value (see Table 2.1).76,79–82) It should be noted that the extension of TCFs by π-linking spacer groups changes both the $E^1_{1/2}$ and ΔE values,1,74,79) whereas substitution of the sulfur atoms in the TTF core with selenium or tellurium increases the $E^1_{1/2}$ value (see Table 2.1 and ref. 38). The TCFs listed in Table 2.1, except for BP-TTF (Scheme 2.9) and BDMP-TTF (Chart 2.5), were found to be good π-donors for the preparation of CT complexes and RC salts.

Additionally, the color of the TCF donors depends on the type of chalcogen atom in the TCF core and on the type of heteroatom-containing substituent appended to TCF.20–22,24,38,41–62,74) For example, BP-TTF (Scheme 2.9), P-DMEDT-TTF (Chart 2.2), EDO-DMEDT-TTF (Chart 2.2) and BEDO-TTF (Scheme 2.9) are colored yellow (λ_{max} = 402 nm), brownish-red (λ_{max} = 425 nm),57) red (λ_{max} = *ca.* 480 nm)50–52) and red (λ_{max} = *ca.* 500 nm),50,52) respectively. That is, the optical absorption (OA) spectra of TCFs in the UV-vis spectral region show a variety of absorption bands, and their respective positions, intensities and shapes differ. The absorption bands of unsymmetrical TTFs in solution appear between those of the two corresponding symmetrical ones. For example, Fig. 2.2 shows the OA spectrum of the unsymmetrical P-DMEDT-TTF (Chart 2.2) donor together with those of the symmetrical BDMEDT-TTF (Chart 2.5) and BP-TTF (Scheme 2.9) donors.

Taking into account the above-mentioned and other empirical rules as well as equations (2.1) and (2.2), one can design and synthesize a derivative of TCF with the desired polarity, solubility, electron-donating ability, *etc.* by combining the two same or different building blocks selected from among **1–10** (Chart 2.3) and their analogues.1,47,48,50,51,55,74)

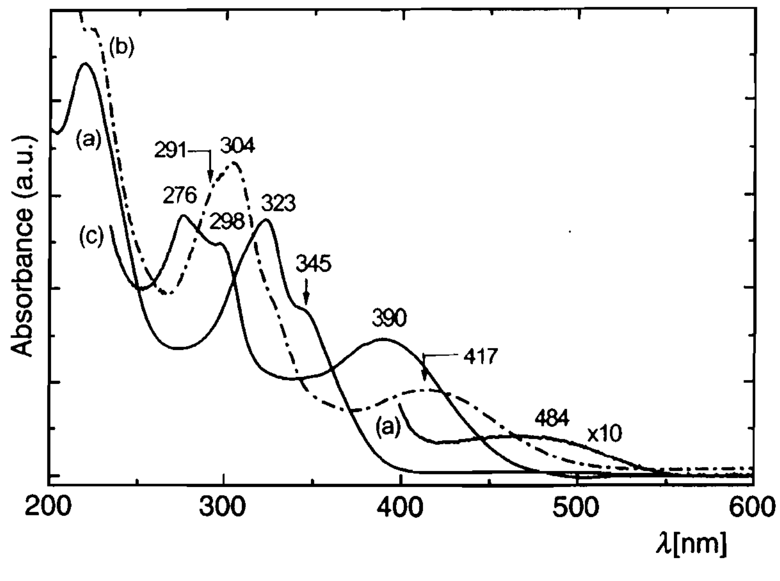


Fig. 2.2 OA spectra of BDMEDT-TTF (a), P-DMEDT-TTF (b) and BP-TTF (c) in CH_3CN at room temperature.

2.6 Formation and Properties of RCs and Other Charged Species

TCFs are easily oxidized by chemical and electrochemical methods to give RCs and other charged species in solution or in the solid state (*e.g.*, crystals and films).[1,19,22,48,76–78] The oxidation conditions affect what kinds of charged species and crystal structure (*i.e.*, α, β, γ, κ, λ, τ, *etc.*) are formed. For example, by chemical oxidation of TTF with chlorine gas in CCl_4 or CH_3CN, the RC of TTF ($TTF^{\bullet +}$) was obtained as a deep-purple crystal, and further oxidation with chlorine gas gave the yellow crystalline dication TTF^{2+}.[2,83] In general, RC ($D^{\bullet +}$) is paramagnetic, whereas neutral (D^0) and dicationic species (D^{2+}) are diamagnetic.[1,2,21,24,32,62,76,83] Charged species can also be obtained by oxidation with an organic acceptor, *e.g.*, TCNQ, or by electrochemical oxidation in the presence of an inorganic anion. Single crystals of CT complexes and RC salts are obtained mainly by the following two methods.

(i) Chemical methods: In the direct reaction method, donor and acceptor components are dissolved in a minimum amount of solvent. Then, to achieve crystallization, the resulting (saturated) solution is either cooled to a lower temperature to lower the solubility of the two components or warmed up to a higher temperature to evaporate the solvent. If this cooling or warming process is performed slowly, large single crystals of good quality could be obtained. When either or both components are not sufficiently dissolved in a solvent, they are mixed with a small portion of solvent in a stopped flask, and the mixture is allowed to stand until the reaction is completed.[48] If the reaction is promoted by heating or ultrasonic irradiation, the yield in this reaction can be improved in a shorter reaction time. In the diffusion method, a cell with two separated tubes connected by a common tube is employed. Donor and acceptor components are placed in two separate tubes, respectively, and the cell is filled with a solvent. When one component is volatile (*e.g.*, iodine vapor), only one tube containing the other component is filled with a solvent.

(ii) Electrochemical (galvanostatic and potentiostatic) methods: An H-shaped cell with a porosity frit and two platinum wire electrodes is usually used. A solution containing both a donor and a supporting electrolyte is added to the anode compartment of the cell, whereas, to the cathode compartment, only a solution of the same electrolyte is added.[1,19,33,77] In the galvanostatic method, crystals begin growing up on applying a constant current with low density (0.2–1.0 $\mu A\ cm^{-2}$). The growth period varies from several days to some months, depending on the nature and purity of the materials, the concentration, the kind of solvent, the current density and the temperature. In most cases, stoichiometries of the resulting salts [D:A or D:anion] are 2:1 ($\rho = 0.5$, see Section 2.1) and 3:2.[1,14,15,19–21,43,44,57–59,62] Other stoichiometries, 1:~1,[20,22,39,44,51] 2:~1.75,[23–36] 3:1,[54,58] *etc.*,[1,10,19,43,48,51,58,59,73,77] are sometimes obtained. A salt with a 1:1 ($\rho = 1$) stoichiometry is obtained by applying a constant voltage (the potentiostatic method), while a salt with a 1:2 stoichiometry ($\rho = 2$) is formed under galvanostatic conditions in a solution containing an oxidizing agent. That is, the divergent formation of RC ($D^{\bullet +}$) and dication (D^{2+}) in the solid state can be attained by changing the electrochemical conditions.[77,83]

RCs are also formed by intermolecular CT from a neutral species to a dicationic species as follows:

$$D^{2+} + D^0 \rightarrow 2D^{\bullet +} \text{ (in solution and in the solid state)}$$

$D_1^{2+} + 2D_2^0 \rightarrow D_1^0 2D_2^{\cdot+}$ (in the solid state).

Treatment of RC and dicationic species with a reducing agent, *e.g.*, sodium hydrogen sulfite ($NaHSO_3$), generates the corresponding neutral species. It is considered that τ-phase conductors with a 2:~1.75 stoichiometry contain several charged species.[32)] For example, it has been suggested by crystallographic and spectroscopic data that the τ-phase conductor based on EDO-DMEDT-TTF (Chart 2.2), τ-$(EDO\text{-}DMEDT\text{-}TTF)_2AuBr_2(AuBr_2)_y$, should consist of a mixture of charged species, expressed by the following formula: $[2D^{2+} + 3D^{\cdot+} + 3D^0][4X^- + 4yX^-]$ or $[1D^{2+} + 5D^{\cdot+} + 2D^0][4X^- + 4yX^-]$ *etc.*, where D = EDO-DMEDT-TTF, X = $AuBr_2$ and y = *ca.* 0.75. Similar formulas have been proposed for τ-phase conductors with other stoichiometries. Table 2.2 summarizes the peak positions in the OA spectra of charged species based on TTF, EDT-TTF (Scheme 2.10), ET (Chart 2.1), BDMEDT-TTF (Chart 2.5), EDO-DMEDT-TTF (Chart 2.2), BEDO-TTF (Scheme 2.9), EDO-VDT-TTF (Scheme 2.10) and P-DMEDT-TTF (Chart 2.2).[83)] It was found that the OA spectral peak positions of charged species derived from unsymmetrical TTFs appear between those derived from the two corresponding symmetrical ones, as is observed for the neutral species. Fig. 2.3 shows, for example, the OA spectra of neutral and charged species of EDO-

Table 2.2 Peak Positions (nm) in the OA Spectra of Neutral and Charged Species[a]

Species	Experimental Value[83c)] (Intensity[b])	Calculated Value[83a,b)] (Oscillator Strength × 10^4)
TTF^0	305–316 (s), 361 (sh), 445 (w, b)	312 (561), 382(180), 452 (2)
TTF$^{\cdot+}$	336 (m), 400 (sh), 435 (s) 500 (sh), 579 (m, b)	365 (3086), 381 (42), 451 (1) 523 (677) or > 362 (317)
TTF^{2+}	350 (?)	362 (3217)
EDT-TTF^0	309 (s)–330, 368 (sh), 440 (w, b)	
EDT-TTF$^{\cdot+}$	403 (s)–441–472, 543 (w) 788 (s, b)	
EDT-TTF^{2+}	600 (s, b)	
ET^0	321 (s)–345, 465–496 (w)	323 (364), 329 (1), 342 (881) 358 (342), 451 (0)
ET$^{\cdot+}$	420 (w, sh), 456 (s)–482 580 (w), 952 (s, b)	416 (2401), 430 (96), 579 (1) 1000 (1816) or 956 (1850)
ET^{2+}	710 (s, b)	
BDMEDT-TTF^0	323 (s)–345, 470 (w)	
BDMEDT-TTF$^{\cdot+}$	420 (sh), 457 (s)–481, 575 (w) 960 (s, b)	
BDMEDT-TTF^{2+}	707 (s, b)	
EDO-DMEDT-TTF^0	312–324 (s), 458–488 (w)	
EDO-DMEDT-TTF$^{\cdot+}$	425 (sh), 457 (s)–485, 596 (w) 937 (s, b)	
EDO-DMEDT-TTF^{2+}	649 (s, b)	
BEDO-TTF^0	316 (s)–337, 479–523 (w)	302 (3319), 324 (170), 331 (15) 378 (1), 517 (0)
BEDO-TTF$^{\cdot+}$	435 (w, sh), 463 (s)–493 604 (w, b), 934 (m, b)	415 (2299), 436 (0), 596 (0) 873 (1513)
BEDO-TTF^{2+}	568 (s, b)	
EDO-VDT-TTF^0	308 (sh)–323 (s)–350 (sh) 480 (w)	
EDO-VDT-TTF$^{\cdot+}$	455 (s)–481 (sh), 584 (w) 858 (s, b)	
EDO-VDT-TTF^{2+}	600 (s, b)	
P-DMEDT-TTF^0	291 (sh), 304 (s), 330 (sh) 417 (m)	
P-DMEDT-TTF$^{\cdot+}$	428 (s), 536 (sh), 890 (s, b)	
P-DMEDT-TTF^{2+}	712 (?)	

[a]In CH_3CN, at room temperature. [b]s = strong, sh = shoulder, m = medium, w = weak, b = broad, ? = poorly defined.

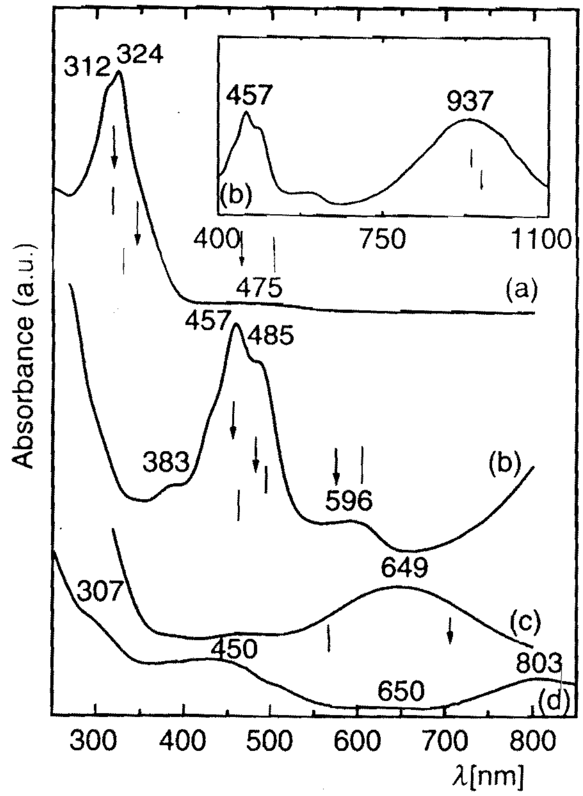


Fig. 2.3 OA spectra of (EDO-DMEDT-TTF)^0 (a), (EDO-DMEDT-TTF)$^{\bullet+}$ (b) and (EDO-DMEDT-TTF)$^{2+}$ (c) in CH_3CN at room temperature and OA spectrum of a thin film based on τ-(EDO-DMEDT-TTF)$_2$AuBr$_2$(AuBr$_2$)$_{0.75}$ (d) at room temperature. Vertical bars indicate the peak positions in the OA spectra of the neutral, RC and dication of BEDO-TTF, whereas arrows indicate those of BDMEDT-TTF.

DMEDT-TTF (Chart 2.2) in solution and in the solid state.[24,32,83] The RC and dication, (EDO-DMEDT-TTF)$^{\bullet+}$ and (EDO-DMEDT-TTF)$^{2+}$, were generated by oxidation of (EDO-DMEDT-TTF)^0 with bromine (or chlorine) in CH_3CN. The resulting charged species can be stabilized in the presence of ClO_4^- or BF_4^- anion in solution. The OA spectrum of a thin film of τ-(EDO-DMEDT-TTF)$_2$AuBr$_2$(AuBr$_2$)$_{0.75}$ on a quartz plate indicated the presence of a mixture of neutral and charged species. It has been reported that, in a concentrated solution containing RCs of TTF or tetrakis(methylthio)-TTF at low temperature,[83] as well as in quasi-1D conductors, 2D κ-phase conductors[1,11,12,15,16,19,22] and others,[75,76] the RCs form π-dimers (D_2^{2+}). The OA spectra in the spectral region from UV-vis to near IR give information on the intermolecular electronic behavior, and the spectrum of an oxidized donor molecule does not depend on the type of counteranion (Cl^-, Br^-, ClO_4^-, BF_4^-, *etc.*). There are, however, several cases where the electronic spectra ranging from far IR to near IR for RC salts in the solid state vary by a phase transition (*e.g.*, an MI transition) accompanying the formation of a different kind of intermolecular interaction;[1,25,29,77a] the same can be said for other physical properties of RC salts and CT complexes.[1,16,17,19]

2.7 Design of New Materials

ET (Chart 2.1) is considered to be the most important derivative of TCF with four additional heteroatoms, because this donor produces the largest number of superconducting salts. The ET-based salts are divided into several phases (α, β, γ, κ, λ, *etc.*), but none of them crystallizes in the τ-phase. In addition to BEDO-TTF (Scheme 2.9),[53] BEDS-TTF (Scheme 2.9)[3b,38e,60,80a] and

EDT-EDS-TTF (Chart 2.7),[48,73,70c,80b] variations of the ET molecule by replacement of the sulfur atom(s) with oxygen and/or selenium are reported (Chart 2.8).[49,62,75] Similar to ET, these analogous donors gave conducting or superconducting salts. On the other hand, the chalcogeno-analogues of ET shown in Chart 2.9 have not yet been synthesized, but they are expected to provide conducting salts comparable to the ET-based salts.

X = S: BEDT-StTF
X = O: EDT-EDO-StTF

X = S, Y = S: BEDT-DSDTF
X = S, Y = O: EDT-EDO-DSDTF
X = Se, Y = S: BEDT-TSF

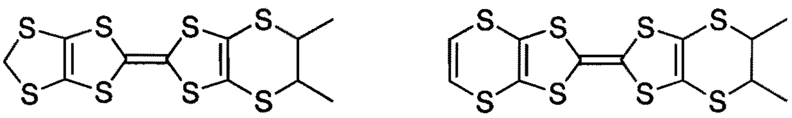
Chart 2.8

X = S: EDO-EDT-DSDTF
X = Se: EDO-EDS-DSDTF

X = S, Y = Se: EDT-EDS-DSDTF
X = Se, Y = O: EDT-EDO-TSF

Chart 2.9

Besides EDO-MDT-TTF,[20,21,53] EDO-EDT-TTF[20,21,53] and EDO-VDT-TTF,[20,22,23,53] which are shown in Scheme 2.10, the racemic and chiral forms of EDO-MEDT-TTF (Scheme 2.10),[20,36] EDO-DMEDT-TTF (Chart 2.2),[23–32,36] EDT-DMEDT-TTF (Chart 2.5),[35,68b] P-MEDT-TTF (Scheme 2.10),[33,36] P-DMEDT-TTF (Chart 2.2)[23,25,26–28,31,34] and P-DMEDT-DSDTF (Scheme 2.10)[34] were found to form at least one τ-phase salt with a linear anion. All these donors are red and reddish-brown in color. Among them, EDO-MDT-TTF (Scheme 2.10) shows the lowest $E^1_{1/2}$ values, while the $E^1_{1/2}$ values of P-DMEDT-TTF (Chart 2.2) are highest (see Table 2.1). However, MDT-DMEDT-TTF (Chart 2.10) and VDT-DMEDT-TTF (Chart 2.10), which exhibit $E^1_{1/2}$ values between those of EDO-MDT-TTF (Scheme 2.10) and P-DMEDT-TTF (Chart 2.2), did not give the τ-phase salt.[60] It should be noted that, although EDO-VDT-TTF (Scheme 2.10) has $E^1_{1/2}$ values close to those of ET (see Table 2.1), this donor, unlike ET, did not produce a superconducting salt. As shown in Chart 2.11, analogues of the TCFs providing τ-phase salts have been synthesized,[35,36,51,52,59,60] but it is not clear whether these donors give the τ-phase conductor. Other analogues, several of which are, for example, shown in Chart 2.12, could be designed and synthesized. Generally speaking, it is possible that new TCF donors are obtained by the coupling reaction of building blocks of types **1–10** (Chart 2.3), but it is not sure that their RC salts will exhibit more interesting physical properties than those obtained from the well-known donors, ET (Chart 2.1), TMTSF (Chart 2.1), MDT-TTF (Chart 2.1), EDT-TTF (Scheme 2.10), P-DMEDT-TTF (Chart 2.2), *etc.*



MDT-DMEDT-TTF

VDT-DMEDT-TTF

Chart 2.10

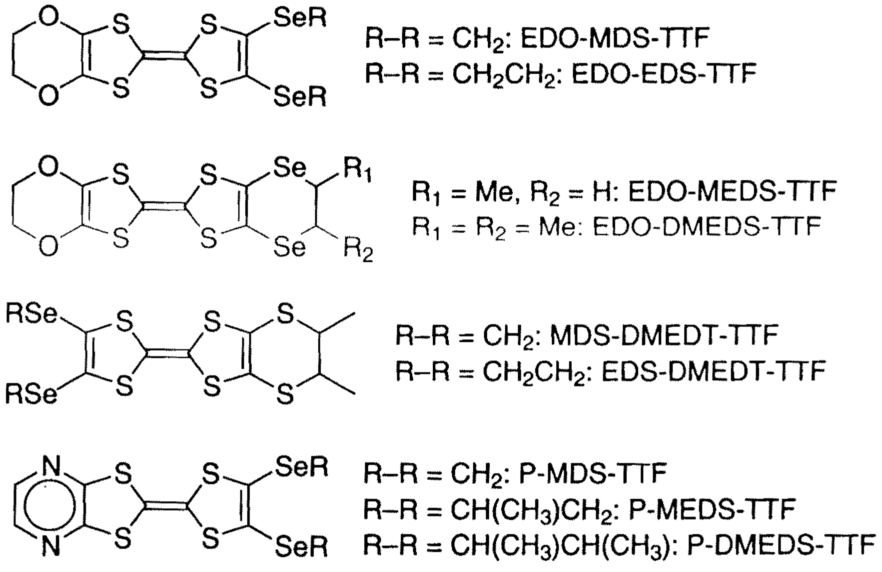


Chart 2.11

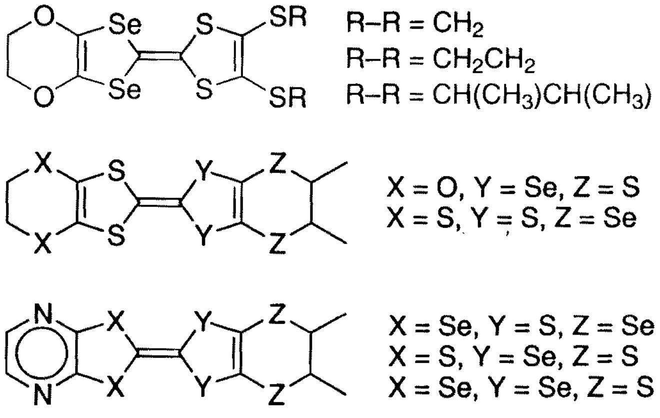


Chart 2.12

2.8 Summary

A number of TCFs with four additional heteroatoms have been synthesized by coupling reactions using mainly 1,3-dithiol-2-ones and their selenium analogues. Unsymmetrical TCFs (AB) exhibit R_f and $E^1_{1/2}$ values as well as OA spectral peaks midway between those of the two corresponding symmetrical ones (AA and BB). Successive oxidation of TCFs generates RCs, dications and other charged species in both solution and the solid state, and the OA spectral peaks of charged species of AB also appear between those of AA and BB. The RC salts based on TCFs crystallize in several phases (α, β, γ, *etc.*), but the τ-phase conductors are formed by the use of a limited number of TCFs. It is possible to undertake further studies of new TCFs as well as their CT complexes and RC salts by applying various building blocks, coupling reactions and empirical rules, which are described herein and elsewhere.

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