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Highly Functionalized Tetrathiafulvalenes: Riding along the Synthetic Trail from Electrophilic Alkynes

Alain Gorgues,* Piétrick Hudhomme, and Marc Sallé

*Laboratoire de Chimie, Ingénierie Moléculaire et Matériaux d'Angers, UMR CNRS 6200, 2 Boulevard Lavoisier, Université d'Angers,
F-49045 Angers, France*

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Contents

1. Introduction

1.1. Background

Since the famous work by Wudl et al. on tetrathiafulvalene (TTF),[1] long after dibenzoTTF was first reported,[2] interest in this exceptional π-donor in the field of materials chemistry has regularly increased. This results from its ability to be reversibly oxidized to cation radical and dication at accessible potentials, these properties being tuned by substitutions or chemical modification of the TTF framework. Crucial landmarks in the story of TTF-based "organic metals" lie in the discoveries of the electroconductive TTF-

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* To whom correspondence should be addressed. Phone: (33) 2 41 73 53 76. Fax: (33) 2 41 73 54 05. E-mail: alain.gorgues@univ-angers.fr.

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Alain Gorgues was born in Bordeaux (France) in 1942. He studied at the Ecole Nationale Supérieure de Chimie de Rennes (ENSCR) and Rennes University, where he obtained his diploma of engineer and his M.Sc. degree in 1965. He completed his Ph.D. degree in 1971 under the supervision of Professor E. Levas in Organic Synthesis. He was appointed as an assistant and maître-assistant in Rennes University from 1965 to 1983, and during this period, he spent two years (1977–1978) in the coordination chemistry group of Professor R. Dabard as a postdoctoral fellow. In 1983, he moved to Angers University as a Professor. There, in 1987, he created a research laboratory on organic materials, which became a unit of CNRS from 1994. Just retired in 2003, he has obtained an *emeritus* Professor position in the new team of CNRS of Angers University founded and directed by his colleague Dr. P. Batail. He has a wide range of research interests in synthetic organic chemistry and organometallic chemistry mainly focused, during last years, on molecular materials of the tetrathiafulvalene series.

Piétrick Hudhomme was born in Nantes (France) in 1963, and he is a graduate of the University of Nantes. He spent one year at the Ecole Polytechnique (Palaiseau) with Dr. H. E. Audier, and then he joined the laboratory of Professor H. Quiniou in the University of Nantes. He received his Ph.D. degree in 1990 under the supervision of Professor G. Duguay working on the total asymmetric synthesis of cephalosporin antibiotics. After a postdoctoral stay at the University of Sussex (U.K.) with Professor D. W. Young developing the synthesis of antithrombotic drugs, he became Maître de Conférences at the University of Nantes in 1991. His research interests moved progressively to the organic synthesis of molecular materials with the chemistry of tetrathiafulvalene and fullerene derivatives. He joined the University of Angers in 1998 as Professor in the laboratory of Professor A. Gorgues. His current research interests concern the organic chemistry of donor–acceptor systems related to molecular electronics and photovoltaic conversion.

Marc Sallé was born in Toulon (France) in 1963. He studied chemistry at the Ecole Nationale Supérieure de Chimie de Rennes (ENSCR) and at the University of Paris VI. He received his Ph.D. degree in Organic Chemistry from the University of Angers in 1991 under the supervision of Professor A. Gorgues. For this work he was awarded the Dina Surdin prize of year 1992. After a postdoctoral stay with Professor M. R. Bryce at the University of Durham (U.K.), he became Maître de Conférences at the University of Angers, where he was promoted to Professor in 1998. He has been a *junior* member of the Institut Universitaire de France (IUF) since Sept 2003. His research interests are in the organic chemistry of molecular materials and supramolecular chemistry associated with electroactive molecular receptors.

TCNQ charge-transfer complex[3] and the first superconducting Bechgaard's salts.[4] Much effort has been devoted to enhancing the critical temperature T_c of these superconducting materials by chemical modification of the π-donor,[5] in particular by enhancing the dimensionality of the corresponding salts.[6] Best results in this field have been obtained with bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).[7] In addition to work on electrical conductivity, applications using TTFs have progressively been extended in varied areas of modern materials.[8,9] Excellent reviews have been published regularly over the years, emphasizing either the incomparable width of possible applications of TTF-based systems (macromolecules,[10−14] supramolecular systems,[15,16] donor−acceptor assemblies[17,18]) or the extraordinary imagination developed by synthetic chemists around TTF[19−25] and 1,3-dithiole[26−30] frameworks.

1.2. Scope of the Review

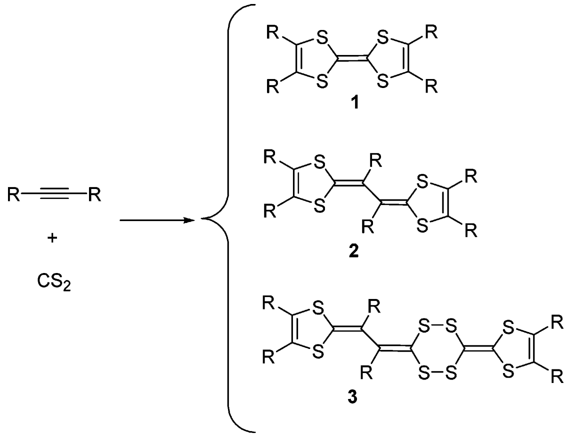
The aim of the present review is to give an updated vision of synthetic aspects in the field of the TTF chemistry with, as a guideline, the central role of electrophilic alkynes in the synthesis of 1,3-dithiole and TTF systems. Of particular interest will be dimethyl acetylenedicarboxylate (DMAD) and acetylenedicarbaldehyde (ADCA) or its monodiethylacetal (ADCA-MA), which can be regarded as prototypical electrophilic alkynes. Their dienophilic (Diels−Alder reactions) and dipolarophilic properties, combined with their electrophilicity, have been widely exploited in the development of highly functionalized TTFs.

The general reactivity of electrophilic alkynes leading to 1,3-dithiole or TTF derivatives is discussed, followed by the discovery of ADCA and its synthetic applications in this field. This review also presents the more recent interest in organic materials, particularly in the use of electrophilic alkynes as starting building blocks for the synthesis of highly extended sulfur-rich and highly functionalized TTF derivatives.

2. 1,3-Dithioles and TTFs from Electrophilic Alkynes: More Usual Reactions

Acetylenic aldehydes will be detailed in section 3 and so are excluded from this section.

Scheme 1



2.1. Reactions of Alkynes with Carbon Disulfide

2.1.1. Electrophilic Alkynes

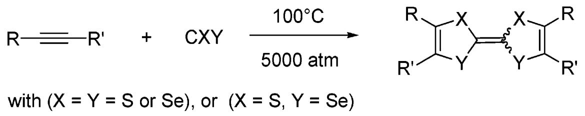
Carrying on the pioneering work of the Du Pont de Nemours Central Research Department,[31] in 1970 Hartzler found that, at 100 °C, it is possible to add carbon disulfide to acetylenes having at least one electron-attracting substituent (in particular with $R = CF_3$) to give the products **1**−**3** (Scheme 1) whose relative yields depend on the experimental conditions.[32] In the presence of a large excess of CS_2, compound **3** is predominant, whereas in the presence of trifluoroacetic acid, the TTF derivative **1** is quantitatively formed.

Detailed investigations of this reaction using various trapping reagents (alcohols, phenols, alkenes, aldehydes, ketones) allowed a mechanism to be suggested.[33] This involves formation of an aromatic 1,3-dithiolium carbene **4** and accounts for the formation of all the products (Scheme 2). Similar mechanistic conclusions were suggested by Coffen[34] in the case of addition of dimethyl acetylenedicarboxylate (DMAD) to CS_2.

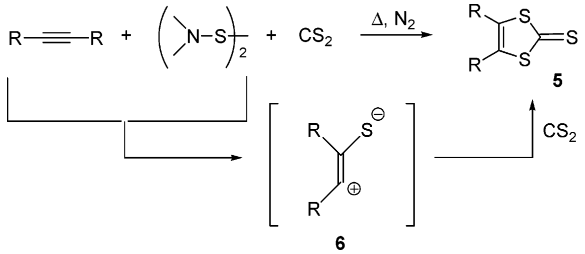
Some years later, a one-step synthesis of TTFs from CS_2 and electrophilic alkynes (DMAD, acetylenedicarboxamide, propiolic acid and its methyl ester) under high pressure (5000 atm) was proposed.[35] Replacing carbon disulfide by CSe_2 and CSSe (Scheme 3)[36] allowed this reaction to be used to access the elementologues of TTF.

2-Thioxo-1,3-dithioles **5**, which are good precursors of TTFs upon dimerization−desulfurization,[19,21−23] can also be obtained from acetylenes, carbon disulfide, and either bis(2,2,6,6-tetramethylpiperidine)-disulfide or bis(morpholino)disulfide at 140 °C under nitrogen.[37] This methodology is not restricted to electrophilic alkynes since it also works with terminal alkynes. A mechanism involving a 1,3-dipolar cycloaddition between CS_2 and a transient thioketocarbene **6** has been proposed (Scheme 4).

Scheme 3



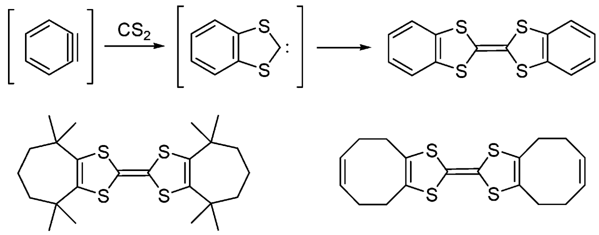
Scheme 4



2.1.2. Strained Cyclic Alkynes

Benzyne[38] and seven- or eight-membered cycloalkynes[39] are known to cycloadd rapidly to CS_2 to afford dibenzoTTF and dicycloalkyl or alkenylTTFs, respectively (Scheme 5).

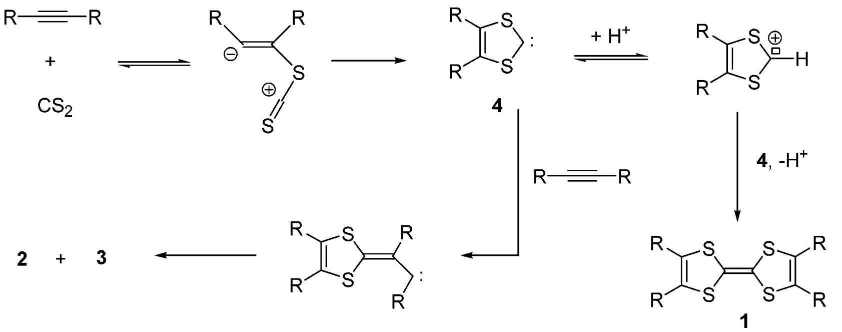
Scheme 5



2.2. Reaction of Electrophilic Alkynes with the Adduct of Bu_3P and CS_2

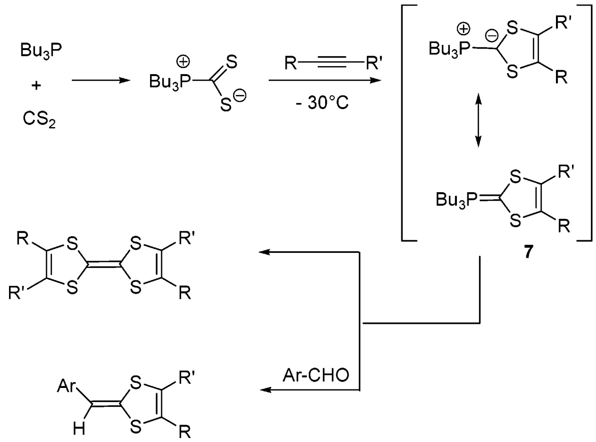
In 1971 Hartzler found that the purple-red adduct Bu_3P-CS_2 reacts very rapidly with acetylenes having at least one electron-withdrawing substituent at temperatures as low as −30 °C as judged by the disappearance of the color. Poor yields of TTFs were obtained, but when aromatic aldehydes were also present, excellent yields of 2-benzylidene-1,3-dithioles were formed.[40] The tremendous rapidity of this Wittig

Scheme 2



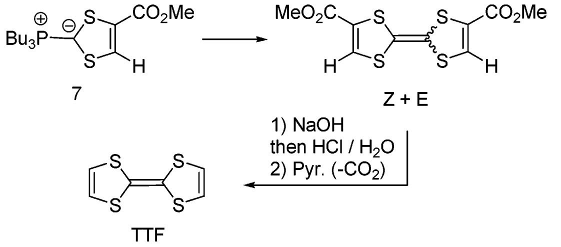
reaction was noted and explained as being due to the antiaromatic character of the ylid **7** (Scheme 6).

Scheme 6



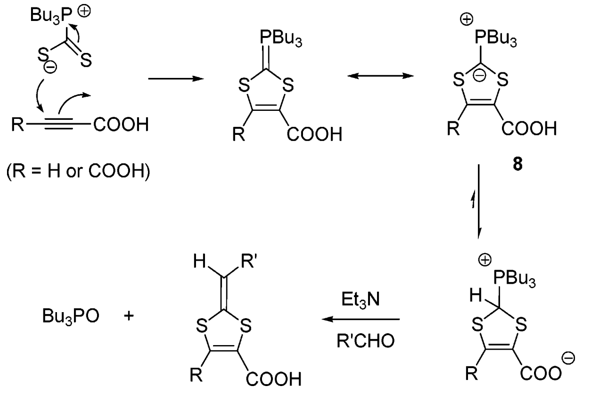
When methyl propiolate was added to a THF$-CS_2$ solution of Bu_3P-CS_2 adduct at −30 °C, *Z*- and *E*-isomers of 4,4′(5′)-bis(methoxycarbonyl)TTFs were formed in 21% yield. Their saponification with sodium hydroxide and further pyridine-induced decarboxylation of the resultant mixture of *Z*- and *E*-diacids afforded the parent TTF in 16% overall yield based on methyl propiolate (Scheme 7).[41,42]

Scheme 7



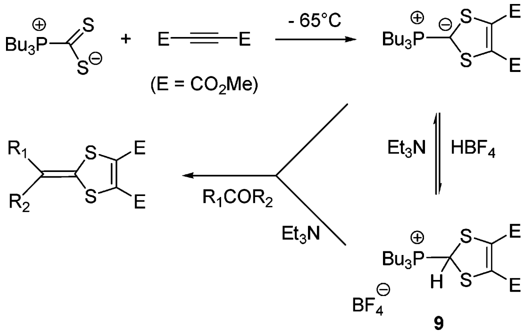
Propiolic (R = H) or acetylenedicarboxylic (R = CO_2H) acids react at low temperature with Bu_3P-CS_2 to give the zwitterionic compounds **8,**[43] which are useful olefinating Wittig reagents of carbonyl compounds (Scheme 8).[44]

Scheme 8



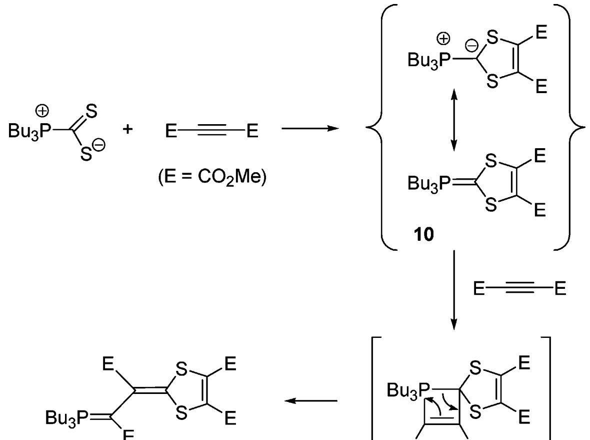
In 1979 Cava suggested a modification of Hartzler's procedure: by adding a *mixture* of DMAD and tetrafluoroboric acid etherate at −65 °C to Bu_3P-CS_2, the intermediate ylid was protonated and then trapped as its phosphonium salt **9,** which was isolated in 72% yield.[45a] This salt proved to be of high synthetic value in 1,3-dithiole and TTF chemistry since it allowed Wittig olefination of carbonyl compounds (see ref 45 and references cited for the extended analogues of TTFs which are discussed in more detail in sections 4.1. and 4.2; Scheme 9). A similar preparation was applied to the 1,3-diselenole series by replacing carbon disulfide with carbon diselenide.[46] In the sulfur series, the preparation of **9** has been generalized to other diesters (E = CO_2R) of acetylenedicarboxylic acid with long alkyl chain alcohols. This gave TTFs with suitable amphiphilic properties for Langmuir−Blodgett film formation.[47]

Scheme 9



When DMAD is reacted with Bu_3P-CS_2 at room temperature without any trapping of the ylid **10** first produced (Scheme 10), a further reaction occurs which gives rise to another ylid **11** whose formation is explained as resulting from a [2+2] cycloaddition of a second molecule of DMAD to the first ylid, followed by electrocyclic ring opening.[48]

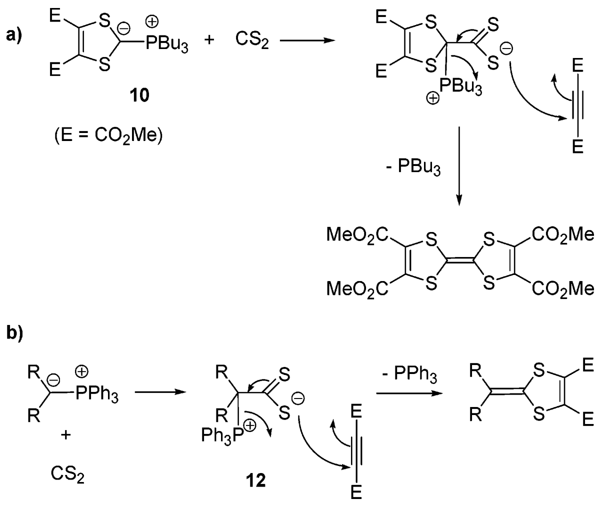
Scheme 10



Carrying on their studies, Aitken et al.[49] suggested a modification of the mechanism initially proposed (Scheme 11a)[41] for the direct formation of the TTF core when DMAD or methyl propiolate is reacted with Bu_3P-CS_2 (Scheme 11b). This reaction is very similar to the known cycloaddition of DMAD to trialkylphosphonodithioacetates **12**.[50]

These workers also found that the cycloadduct of Bu_3P-CS_2 and norbornene, after reversible addition of CS_2, cycloadds to DMAD to afford the norbornane-fused dihydroTTF **13**. The same sequence, starting

Scheme 11



from norbornadiene, affords the norbornane-bisfused dihydroTTF **14**.[51] More recently, it was shown that 600 °C flash vacuum pyrolysis of compounds related to structure **13** allows extrusion of cyclopentadiene moiety, thus offering an unusual indirect synthesis of TTFs (Scheme 12).[52]

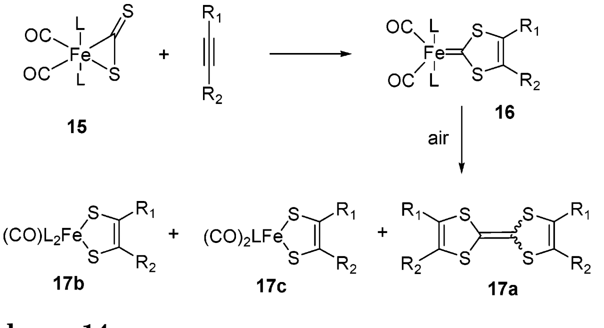
2.3. Reaction of Electrophilic Alkynes with (η^2-CS$_2$)Metal Complexes

2.3.1. Reactions with (η^2-CS$_2$)FeL$_2$(CO)$_2$

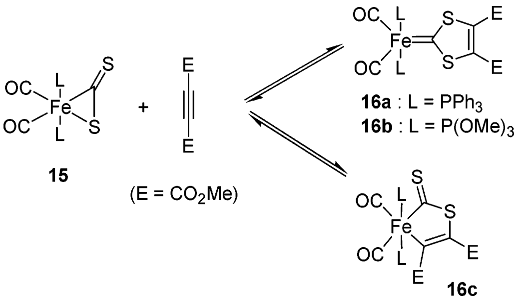
It was found in 1978 that electrophilic alkynes cycloadd readily to the CS$_2$ moiety of the iron complexes **15** (with L = Ph$_3$P or P(OMe)$_3$) to afford the carbene–iron complexes **16**, stable only under an inert atmosphere. In air, these species are decomposed to the 1,2-dithiolene–iron complexes **17b** and **17c** accompanied by ca. 25% yield of the TTF **17a** resulting from dimerization of the 1,3-dithiole-2-ylidene carbene moiety (Scheme 13).[53–56]

The importance of the electron-donating character of the phosphine ligand L on the behavior of the reaction is obvious. By adding DMAD to complex **15** at room temperature, whatever the electron-donating character of the phosphorus ligand L (PPh$_3$, P(OMe)$_3$, PMe$_2$Ph, PMe$_3$), carbenic complexes **16** are always instantaneously formed (kinetic products). These complexes are stable only with poorly donating ligands (L = PPh$_3$ or P(OMe)$_3$), but they are unstable with better donating ligands (L = PMe$_3$ or PMe$_2$Ph) when they isomerize into the metallacyclic complexes **16c** (thermodynamic products). Therefore, for the synthesis of TTFs, PPh$_3$ and to a lesser extent P(OMe)$_3$ are the ligands of choice (Scheme 14).[54,55]

Scheme 13

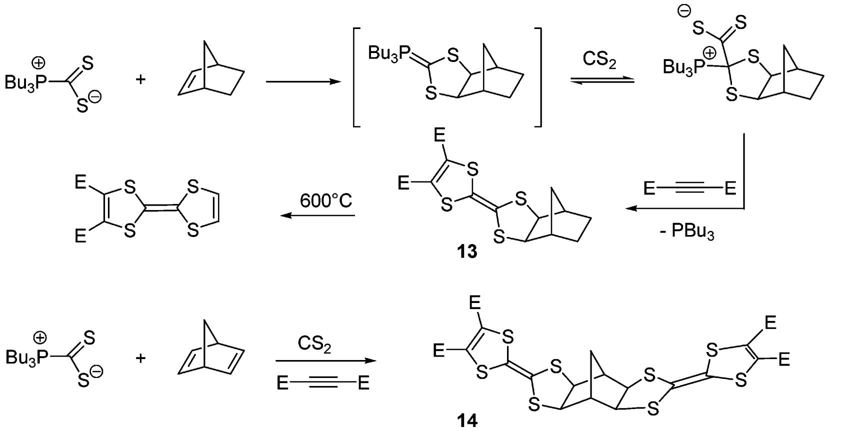


Scheme 14

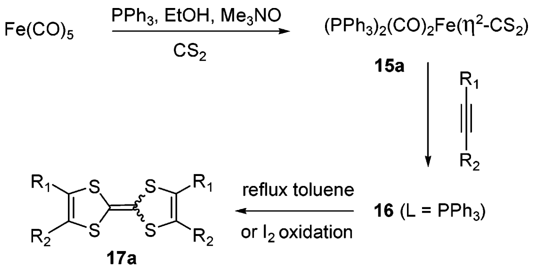


The yields for the conversion of the carbenic complexes **16a** and, to a lesser extent **16b**, into TTFs **17a** can be significantly improved (up to 30–80%) by either iodine oxidation or thermal treatment (reflux in toluene).[57] Optimized access to the starting material (η^2-CS$_2$)Fe(CO)$_2$(PPh$_3$)$_2$ was reported using an ethanolic solution of iron pentacarbonyl in the presence of triphenylphosphine and carbon disulfide with an excess of trimethylamine oxide.[58] This methodology appears to be very useful for the one-pot synthesis of TTFs **17a** substituted with electron-withdrawing groups (Scheme 15). Its main limitation lies in the availability of the required alkyne. Additionally, electrooxidations and other chemical oxidations (with silver triflate or ferricenium hexafluorophosphate) of the carbenic complex **16a** (with R = CO$_2$Me) have also been carried out.[59]

Scheme 12

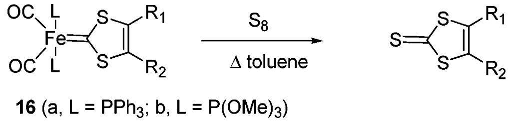


Scheme 15



It should also be noted that on thermal treatment of carbenic complexes **16a** or **16b** in the presence of sulfur, 2-thioxo-1,3-dithioles are formed in moderate yields (Scheme 16).[58]

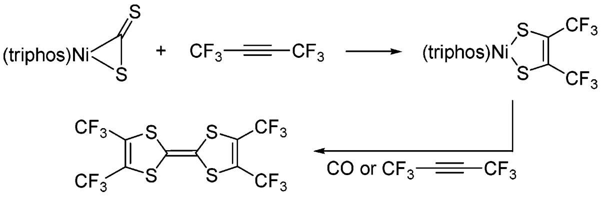
Scheme 16



2.3.2. Reactions with [(triphos)Ni(η^2-CS_2)]

Another metal-assisted synthesis of TTFs from electrophilic alkynes was the use of the (triphos)Ni-(η^2-CS_2) complex in which triphos represents 1,1,1-tris(diphenylphosphinomethyl)ethane, but this method is restricted to the case of perfluorobut-2-yne and requires the use of either carbon monoxide or a very large excess of alkyne (Scheme 17).[60]

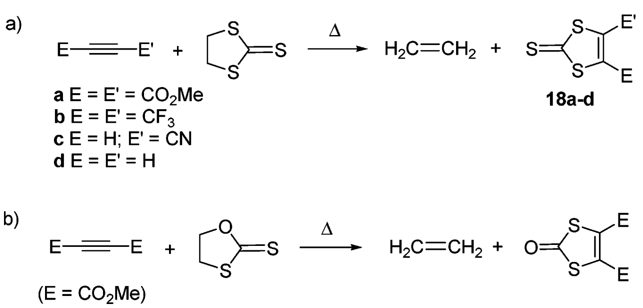
Scheme 17



2.4. Reaction of Electrophilic Alkynes with Ethylene Trithiocarbonates

Easton and Leaver found in 1965 that on heating at 140 °C, DMAD cycloadds to ethylene trithiocarbonate with evolution of ethylene and production of 4,5-bis(methoxycarbonyl)-2-thioxo-1,3-dithiole **18a** in almost quantitative yield (Scheme 18a).[61] The latter compound was further used for the synthesis of the parent TTF[41] and bifunctionalized TTFs.[42] Cycloaddition of DMAD with *O,S*-ethylene dithiocarbonate with evolution of ethylene and production of the corresponding 2-oxo-1,3-dithiole was observed, but no reaction occurred with either *S,S′*-ethylene dithiocarbonate or *O,O′*-ethylene thiocarbonate (Scheme 18b).[62]

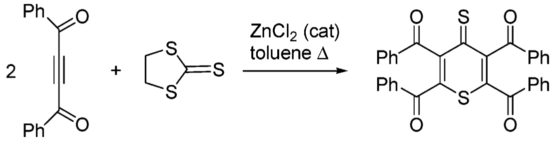
Scheme 18



This reaction has been applied to other dipolarophilic acetylenes such as perfluorobut-2-yne (**18b**, 76% yield), cyanoacetylene (**18c**, 33%), and even acetylene (**18d**, less than 5%) but is fully different in the case of bromocyanoacetylene. It was also found that DMAD reacts in the same way with phenyl- and *cis*-diphenylethylene trithiocarbonates.[62]

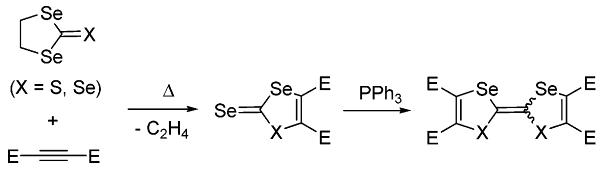
Recently, Becher et al. demonstrated that the reaction of dibenzoylacetylene with ethylene trithiocarbonate in the presence of Zn(II) chloride as a catalyst does not produce the expected 2-thioxo-1,3-dithiole but 2,3,5,6-tetrabenzoylthiopyran-4-thione (Scheme 19).[63]

Scheme 19



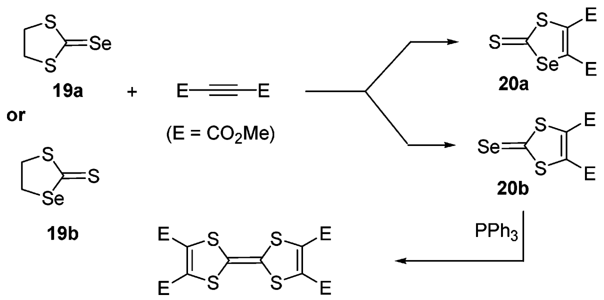
This general scheme was extended to the synthesis of diselenadithiafulvalene, the first step being cycloaddition of DMAD to 2-thioxo-1,3-diselenolane.[64] It was also used for the synthesis of tetraselenafulvalene from ethylene triselenocarbonate (Scheme 20).[65]

Scheme 20



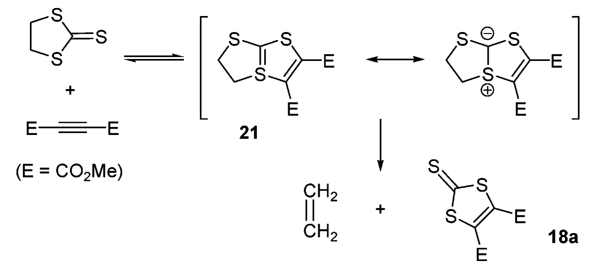
When the isomeric ethylene selenodithiocarbonates either **19a** or **19b** are reacted with DMAD, unexpectedly, a mixture of isomeric thione **20a** and selone **20b** was obtained, the latter compound being possibly dimerized with loss of selenium under Ph_3P treatment (Scheme 21).[66]

Scheme 21



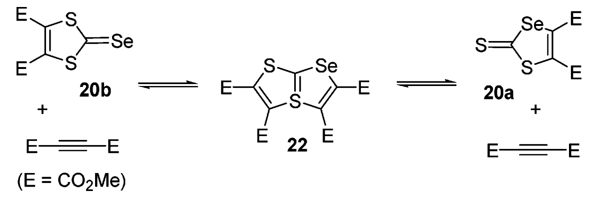
To explain the formation of this mixture (**20a** + **20b**), Cava et al. suggested that 1,3-cycloaddition of DMAD to ethylenetrithiocarbonate was stepwise, with formation of a discrete intermediate corresponding to the bicyclic tetracovalent sulfur heterocycle **21** (Scheme 22).

Scheme 22



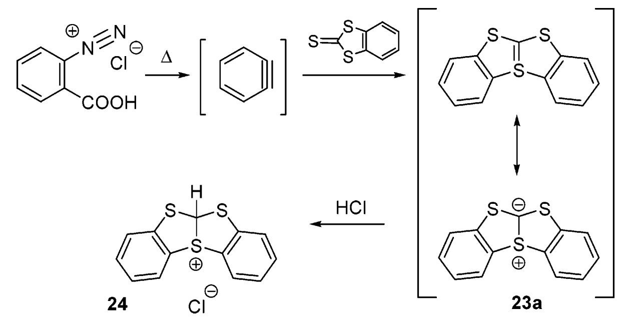
From the reaction of **19a** or **19b** with DMAD, the expected intermediates would have afforded different reaction products, but it was observed that whereas both compounds **20a** and **20b** are quite stable in pure refluxing toluene, they are interconverted under these conditions in the presence of DMAD, thus explaining that, due to the key intermediate **22**, both compounds **20a** and **20b** are formed (Scheme 23).

Scheme 23



On the basis of this mechanism, Nakayama et al.[67] decided to intercept such intermediates and exploit them for synthetic purposes. Thus, HCl-mediated trapping of the intermediate **23a** first produced by interaction between benzyne (generated by thermal decomposition of 2-carboxybenzenediazonium chloride) and 2-thioxo-1,3-benzodithiole allowed them to isolate the chloride salt **24** (Scheme 24).

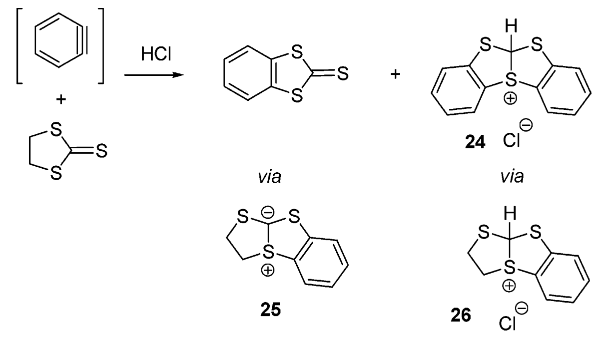
Scheme 24



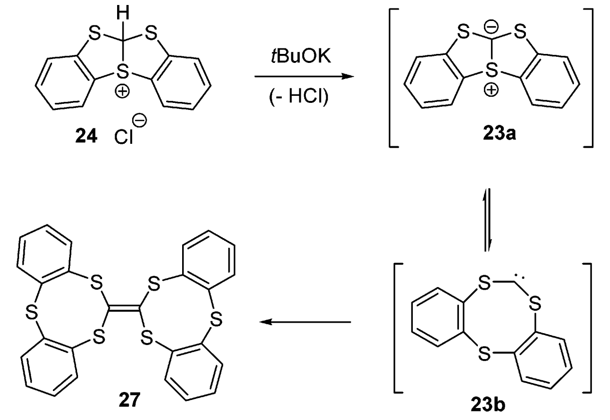
More importantly, by reacting ethylenetrithiocarbonate with benzyne (similarly generated), they obtained a mixture of 2-thioxo-1,3-dithiole (15% yield) and the salt **24** (62% yield), these results being in agreement with the transient formation of intermediates **25** and **26** (Scheme 25).

Deprotonation of the chloride salt **24** with tBuOK gave the dimeric product **27** (84% yield), a “higher analogue” of TTF, probably arising from initial generation of the carbenic intermediate **23b**, a valence isomer of intermediate **23a** (Scheme 26).

Scheme 25



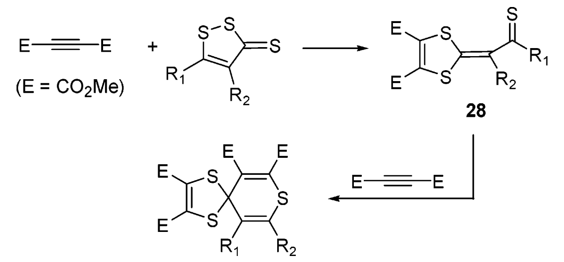
Scheme 26



2.5. Reaction of Electrophilic Alkynes with 3-Thioxo-1,2-dithioles

In 1965, [3+2] cycloaddition using dipolarophilic DMAD was achieved by two research groups. Thus, upon addition of DMAD to 3-thioxo-1,2-dithioles (1,2-trithiones), the 1:1 adducts **28** were first produced[61,68] (similar behavior being observed when benzyne was used instead of DMAD[61]), but using an excess of DMAD, a second cycloaddition took place, finally giving rise to 1:2 adducts (Scheme 27).[61]

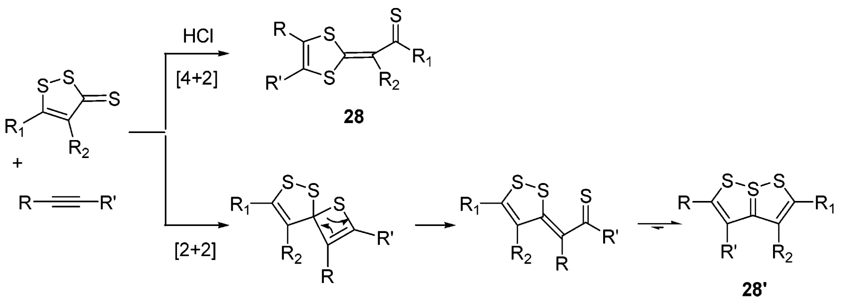
Scheme 27



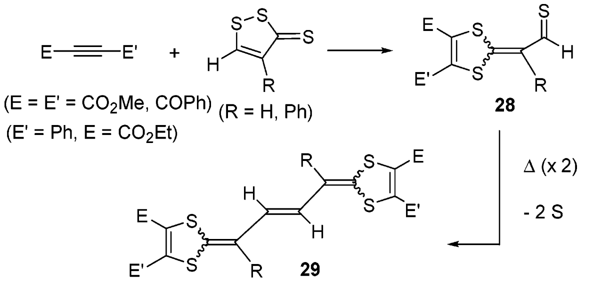
This reaction was applied to other alkynes such as arylacetylenes and tolane, and it was simultaneously observed by several groups that the nature of the adducts **28** or **28′** produced was dependent on the experimental conditions (presence or absence of dry HCl; Scheme 28).[69−73]

The thials **28** (R_1 = H), originating from DMAD, dibenzoylacetylene, and ethyl phenylpropiolate with 1,2-dithiole-3-thione and 4-phenyl-1,2-dithiole-3-thione, have been shown to undergo thermally induced dimerization−desulfurization with production of the trienic TTF analogues **29** (Scheme 29).[74]

Scheme 28



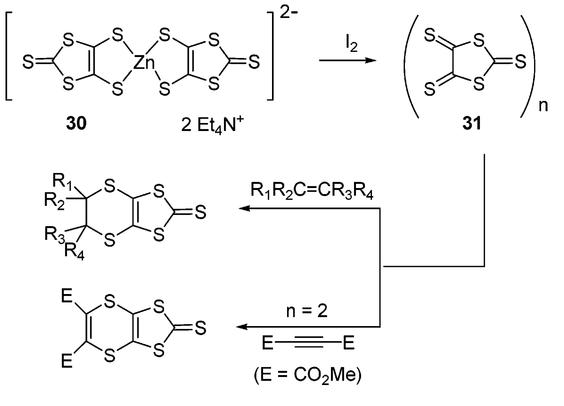
Scheme 29



2.6. Reaction of DMAD with 1,3-Dithiole-2,4,5-trithione

When submitted to iodine oxidation, the zincate complex salt[30,75] is converted into a polymeric insoluble material, $(C_3S_5)_n$, which upon heating presumably depolymerizes to the 1,3-dithiole-2,4,5-trithione **31**.[76] This latter compound may behave as a conjugated heterodiene to afford with dienophiles the corresponding Diels–Alder cycloadducts. After experimental improvements[29] and application to various alkenes[77] including the parent TTF itself[77b] (by its external ethylenic linkage), Rauchfuss et al. showed that this cycloaddition also occurred in the case of dimeric C_3S_5 and DMAD[78] (Scheme 30).

Scheme 30



2.7. Ester Group as a Synthetic Tool for Varied Functionalized TTFs: Scope and Limitations

2.7.1. General Considerations based on the Availability of Starting Alkynes

As previously seen, in addition to DMAD (or the corresponding diethyl ester), other electrophilic alkynes (acetylenedicarboxylic or propiolic acids, cyano and dicyano acetylenes, α-carbonyl alkynes, α-acetylenic esters, etc.) have been used to synthesize various functionalized TTFs. However, due to practical considerations, DMAD has been the most widely used starting material, the ester functionalities of the initially generated TTFs (or of their precursors 2-(thi)oxo-1,3-dithioles) being further modified depending on the final targeted functionality. Therefore, we shall review the main transformations of methoxycarbonyl substituents which allow introduction of given functionalities to TTFs or 1,3-dithioles. The case of acetylenic aldehydes will be developed separately in section 3.

2.7.2. Proto-Decarbomethoxylation of the Methoxycarbonyl Group

Conventional methods based on saponification (NaOH or KOH) or hydrolysis (HCl) of the ester functionality and further decarboxylation of the corresponding acid[41,42,63,79] were used until the discovery of the one-step proto-decarbomethoxylation of the CO_2Me functionality upon thermal treatment with LiBr salt in a dipolar solvent (HMPA or DMF). In addition to the less toxic character of DMF related to HMPA, it has been noted that slightly better yields are obtained for monodecarbomethoxylated products when LiBr is used in DMF instead of HMPA (Scheme 31).[80]

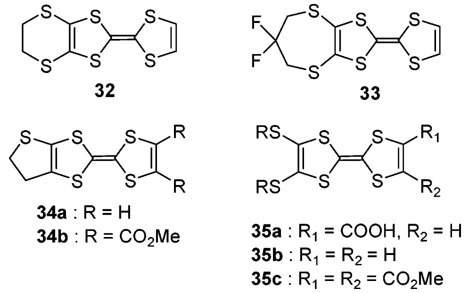
Scheme 31

This methodology,[81] first introduced by Cava during the synthesis of tetraselenafulvalene (TSeF),[64] is now commonly used to prepare more or less sophisticated TTF derivatives or 1,3-dithioles.

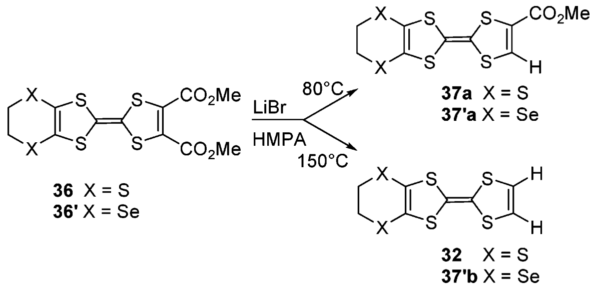
Although nonexhaustive, the following examples illustrate this efficient methodology. The reaction was successfully applied to synthesize unsymmetrically substituted donors such as benzo-TTF,[82] EDT-TTFs **32**,[83,84] and **33**[85] as mono- (**34a** from **34b**)[86,87] or bis-alkylthioTTFs (**35a**, or **35b** from **35c**).[80,88,89] Nevertheless, in the case of the parent TTF, better yields were obtained by decarboxylation of the tetraacid compared to the treatment of the tetramethyl ester with $LiBr{\cdot}H_2O$/HMPA, Chart 1.[79]

The control of the mono or di proto-decarbomethoxylation could be achieved in the ethylenedichalcogenoTTF series (X = S or Se) by operating from the diesters **36** and **36′** at 80 and 150 °C, respectively, thus allowing selective preparation of partially **37a** and **37′a** or fully **32** and **37′b** decarboxylated compounds (Scheme 32).[89–91]

Chart 1



Scheme 32



This methodology has also been applied to extended analogues of TTF or TSeF by the group of Yoshida[92a] (the dienic **38**[92b,c,93b] or trienic **39**[93a,b] vinylogues, dendralenes,[93c] and radialenes,[93d]) or to fused-TTF derivatives by Misaki et al. (BDT-TTP **40**,[94] DT-TTFs **41**,[95] DTEDT **42**,[96] its selenium analogue **43**[97]) or by Yamada et al. (DTH-TTP **44**,[98]) but also by Frère et al. to hybrid TTF analogues **45** using oligo furan or thiophene-2,5-diylvinylenes as π-conjugated spacers, Chart 2.[99]

2.7.3. Conversion of Methyl Esters to Carboxylic Acids, Acid Chlorides, Anhydrides, and Amides

4,5-Bis(methoxycarbonyl)-2-thioxo-1,3-dithiole **18a**[41] can be transformed by hydrolysis with hydrochloric acid into the corresponding dicarboxylic acid **46**, which can be decarboxylated to the corresponding monocarboxylic acid when heated for a longer time.[42] Compound **46** can be easily converted into the corresponding anhydride **47**, a very reactive substance easily hydrolyzed by atmospheric moisture, using acetic or trifluoroacetic anhydride. The ammonium salt is obtained when ammonia is bubbled through a solution of this anhydride. Acidic treatment using an aqueous solution of sulfuric acid affords the amidocarboxylic acid **48** (Scheme 33).[100]

The diamide **49** is easily obtained from the corresponding diester **18a** by reaction of an aqueous solution of ammonia. After transchalcogenation[19,21−23,101] to increase the resistance of the diamide to oxidants, oxidative rearrangement−cyclization takes place smoothly with phenyliodosyl(hydroxy)-tosylate and the pyrimido heterocyclic compound **50** is obtained (Scheme 33).[100] This methodology was applied to the selone derivative **51** to prepare symmetrical or dissymmetrical bis[2,4-dioxo(1*H*,3*H*)-pyrimido]TTFs that are capable of forming specific intermolecular hydrogen bonds.[102] The formation of such bonds may have a specific influence on the solid-state properties of the corresponding cation radical salts by generation of closer packing of molecules and increased dimensionality (Scheme 33).

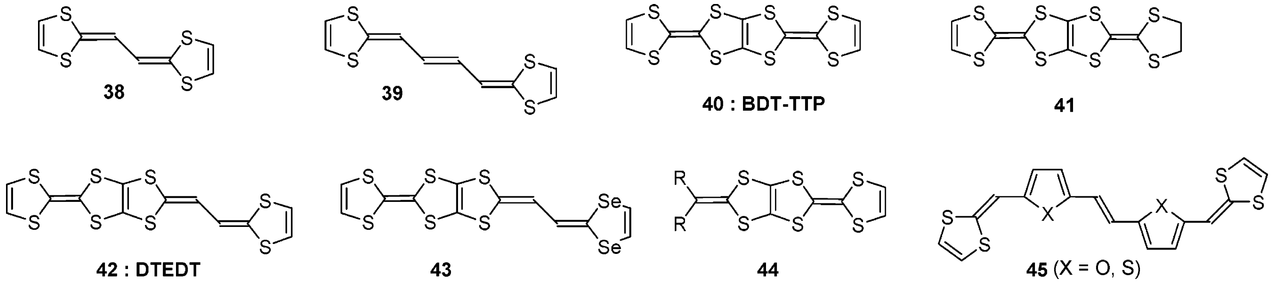
As indicated above (section 2.7.2), methyl esters can be easily saponified with sodium or potassium hydroxides followed by acidic hydrolysis. Nevertheless, lithium hydroxide often gives better results.[80] Subsequent dicyclohexylcarbodiimide (DCC) coupling of the resulting acid was used to prepare amide derivatives. Thus, the monoamide TTF **52** was prepared by reaction with *N*-trityldiaminopropane followed by deprotection of the second amino functionality. The bis-TTF **53** was assembled by coupling the diamine with a suitable monoacid and synthesis, of the tris-TTF **54** was carried out by condensation of the monoamide TTF **52** with the corresponding TTF diacids in basic medium. These new amphiphilic TTFs were subsequently deposited to give Langmuir−Blodgett (LB) films, Chart 3.[80]

Another example in the EDT-TTF series is given by the synthetic sequence methyl ester, carboxylic acid, acid chloride, primary amide as shown in Scheme 34.[103] It has been shown that the carboxylic acid can be converted first into the acid chloride using oxalyl chloride in the presence of catalytic pyridine[104] and then into different alkyl esters.[105] Corresponding primary, secondary, and tertiary amides as well as hydrazides have been similarly obtained upon treatment of the EDT-TTF acyl chloride with ammonia, methylamine, dimethylamine, and hydrazine, respectively (Scheme 34).[106,107]

We should note that 2,3-diamidoTTFs have also been prepared by reaction of the corresponding diesters with an aqueous solution of ammonia or methylamine (Scheme 35).[108,109]

An original supramolecular hydrogen-bond pattern was demonstrated in the solid state of cation radical salts obtained by electrocrystallization from these different donors. The solid-state architecture appears to be a compromise between the hydrogen-bond requirements of the (OH, NH_2, CH) and (C=O) groups, which act as hydrogen-bond donors and

Chart 2



Scheme 33

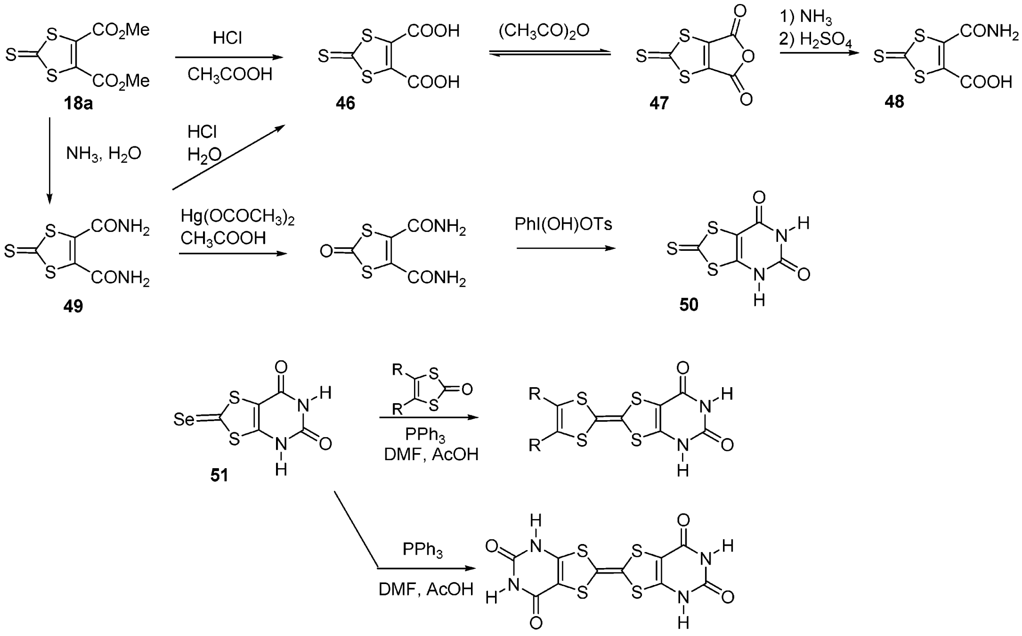
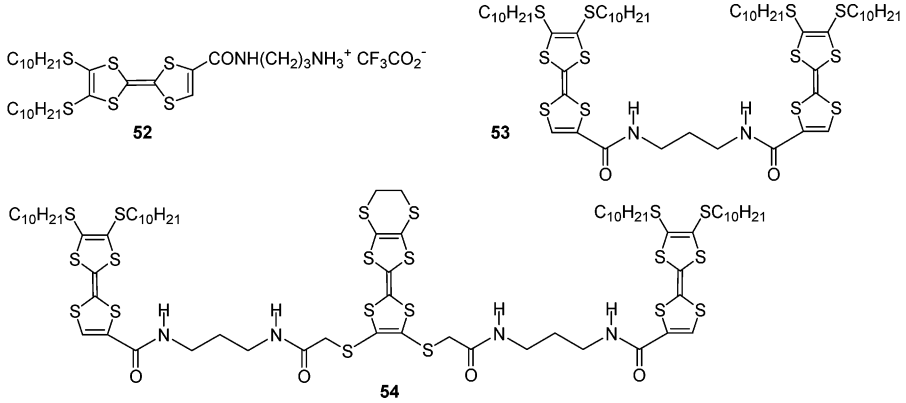
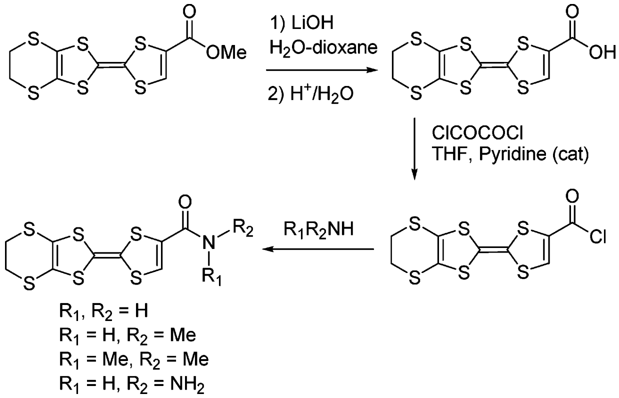


Chart 3



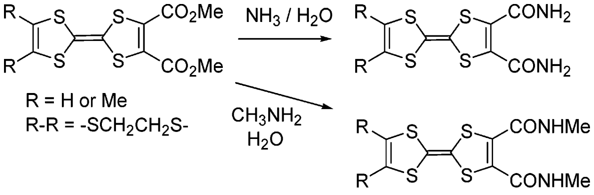
Scheme 34



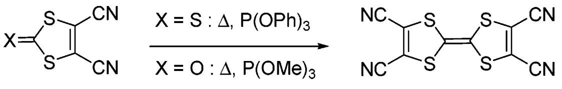
acceptor respectively, and S···S van der Waals interactions of the EDT-TTF moiety.[103,106,107,109]

The conventional route to cyano-substituted derivatives from an ester via saponification, amidation by ammonia, and dehydration of the bisamide with $POCl_3$ has been successfully achieved in the 2-thioxo-1,3-dithiole series.[110] Introduction of the cyano group has also been made at the level of the starting material, either using dicyanoacetylene itself as the electrophilic alkyne[111] or using 4,5-dicyano-2-(thi)oxo-1,3-dithioles,[112] which were further submitted to a dimerization−dechalcogenation procedure with either with $P(OPh)_3$ in the case of thioxo derivative[113] or $P(OMe)_3$ in the case of the oxo compound[114] (Scheme 36).

Scheme 35



Scheme 36

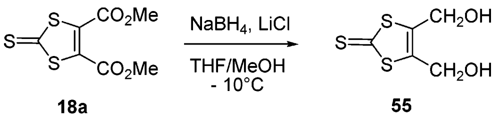


2.7.4. Conversion of Methoxycarbonyl Groups to Alcohols

2.7.4.1. In the Dithiole Series.

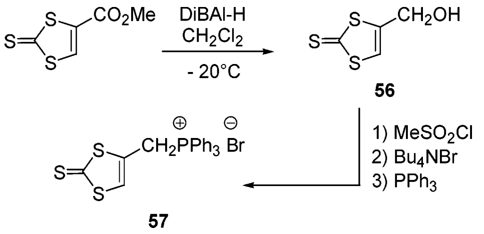
Starting from 4,5-bis(methoxycarbonyl)-2-thioxo-1,3-dithiole **18a**,[41] it proved possible to reduce the ester functionalities by controlling the reaction temperature at −10 °C using sodium borohydride and lithium chloride. The desired diol **55** was produced in reasonable yield (70%), and reduction of the conjugated double bond was thus avoided (Scheme 37).[115] An improved yield (85%) was very recently reported by replacing lithium chloride by lithium bromide.[116]

Scheme 37



In the monoester series, reduction of ester functionality to an alcohol was achieved using DiBAl-H in dichloromethane at controlled temperature. The 4-hydroxymethyl-2-thioxo-1,3-dithiole **56** was converted into the corresponding phosphonium salt **57** as an interesting intermediate for the synthesis of extended-TTFs through Wittig-type reactions (Scheme 38).[117]

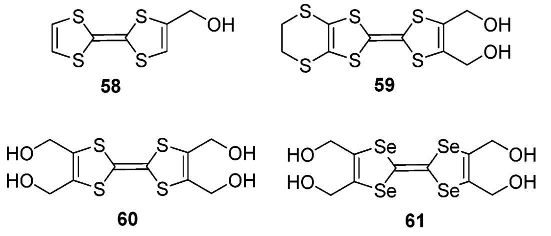
Scheme 38



2.7.4.2. In the TTF Series.

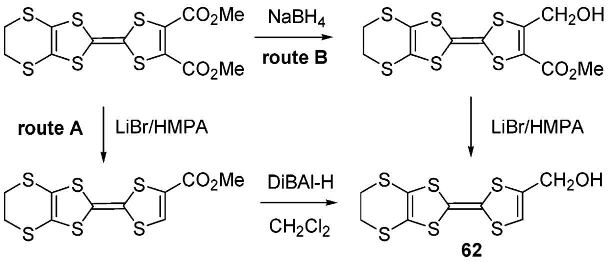
Although not, strictly speaking, a synthesis involving electrophilic alkynes, one should mention that in the TTF series the first method used to prepare the alcohol functionality was introduction of the aldehyde group by successive lithiation−formylation steps.[118] This functionality is one of the most synthetically useful groups in TTF chemistry since it opens the way to many standard transformations, and its reactivity in the case of TTFs and TSeFs has been reviewed by Garín.[25] Thus, monoformylTTF,[118,119] 2,3-diformylEDT-TTF,[89] and tetraformylTTF[120a,c] can be reduced by sodium borohydride to give the corresponding mono-, 2,3-di-, and tetraalcohols, (**58**, **59**, and **60**, respectively) in excellent yields (92%, 93%, and 80%). The analogous tetrakis(hydroxymethyl)-TSeF **61**[120b,c] was also prepared by simple sodium borohydride reduction in 53% yield, Chart 4.

Chart 4



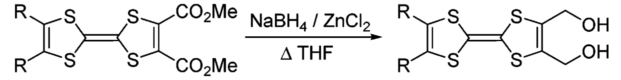
A second method for preparing hydroxymethyl groups is the reduction of ester groups from the readily synthesized mono or bis(methoxycarbonyl)-TTFs. The mono(hydroxymethyl)TTF derivative **62** is obtained in good yield using the LiBr/HMPA monodecarbomethoxylation procedure (route A, cf section 2.7.2) followed by reduction of the remaining ester function using DiBAl-H in dichloromethane. It should be noted that reduction of the diester with $NaBH_4$ and then decarboxymethylation (route B) leads to the same derivative **62** but in lower yields (Scheme 39).[89]

Scheme 39



New difunctionalized TTF derivatives were readily prepared by reduction in mild conditions using sodium borohydride in the presence of zinc chloride to afford the corresponding dialcohols in excellent yields (Scheme 40).[121] This reduction procedure has been extended to the synthesis of the bis(hydroxymethyl)ethylenediselenoTTF (R−R = $-SeCH_2CH_2$-Se−).[90,91] Reduction using DiBAl−H was also reported to produce the bis(hydroxymethyl)TTF derivative in 70% yield.[122]

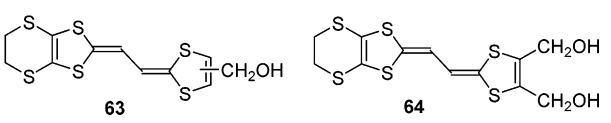
Scheme 40



Functionalized TTF π-electron donors incorporating hydroxy group(s) have attracted considerable interest with the aim of increasing the dimensionality of cation radical salts or charge-transfer complexes by establishment of intermolecular hydrogen bonds.[6] These expectations were confirmed by preparation of the corresponding cation radical salts which associate EDT-TTF−CH_2OH **62** with the closed-shell tetrahedral perchlorate and perrhenate anions and whose X-ray structures demonstrate the presence of hydrogen bonding involving the hydroxyl group and one oxygen atom of the anion, leading to a κ-phase 2D network.[123] Analogously, electrocrystallization of **59** or **60** in the presence of $[n\text{-}Bu_4^+]_2[Mo_6O_{19}]^{2-}$ afforded 2:1 cation radical salts whose crystal structures show hydrogen-bond interactions.[124]

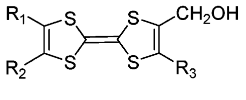
This method of reduction was also applied to the synthesis of the 2-mono- and 2,3-bis(hydroxymethyl)-6,7-ethylenedithioTTF vinylogues **63** and **64,** respectively. For the monoalcohol **63**, stereochemical features were deduced using ^1H NMR spectroscopy due to the presence of a favorable zigzag arrangement, allowing $^5J_{H-C=C-S-C-H}$ coupling in one of the isomers, Chart 5.[125]

Chart 5



Reduction of the ester groups of the readily synthesized tetrakis(methoxycarbonyl)TTF has also been investigated. The first approach to the corresponding tetraalcohol was to consider reduction with DiBAl-H followed by $LiAlH_4$. Problems were encountered due to the presence of some complicated insoluble byproducts.[126] This reduction was more recently reinvestigated for the preparation of new hydroxymethylTTF derivatives using a mixture of $NaBH_4$/LiCl, the proportion of each compound in the mixture being dependent on the relative amounts of reagents and temperature. Consequently, mono-, di-, tri-, or tetra-alcoholTTF derivatives were isolated, Chart 6.[127]

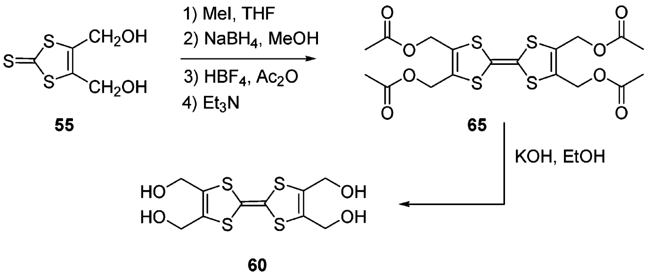
Chart 6



R_1, R_2, R_3 = CO_2Me
R_1 = CO_2Me; R_2, R_3 = CH_2OH
R_1, R_2 = CO_2Me; R_3 = CH_2OH
R_1 = CH_2OH; R_2, R_3 = CO_2Me
R_1, R_2, R_3 = CH_2OH (**60**)

An efficient alternative method for the preparation of compound **60** was developed by Fox.[115] The TTF core was formed by self-coupling of the corresponding 1,3-dithiolium salt prepared in several steps from 4,5-bis(hydroxymethyl)-2-thioxo-1,3-dithiole **55**. Thus, 2,3,6,7-tetrakis(acetoxymethyl)TTF **65** was prepared in 68% overall yield, and subsequent basic hydrolysis led to 2,3,6,7-tetrakis(hydroxymethyl)TTF **60** in 92% yield (Scheme 41).

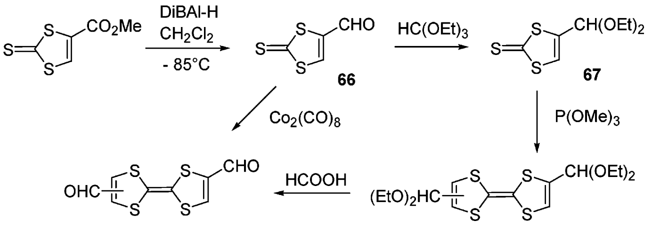
Scheme 41



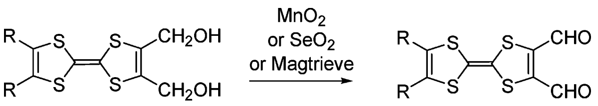
2.7.5. Conversion of Methoxycarbonyl Groups to Aldehydes

Because of its instability (danger of explosion), the reactivity of propiolaldehyde as starting electrophilic alkyne has not been extensively studied, and this was also the case for acetylenedicarbaldehyde until its discovery at the beginning of the 1980s (vide infra). Besides direct formylation of lithiated derivatives of TTF with *N*,*N*-dimethylformamide[118] or related reagents,[25,119,128,129] introduction of the aldehyde group in the 1,3-dithiole or TTF series consisted of reducing the methyl ester either directly to formyl with DiBAl−H at low temperature[129,130] (Scheme 42) or to the alcohol, which was then reoxidized with MnO_2[90] or SeO_2 (Scheme 43).[128,129] 4-Formyl-2-thioxo-1,3-dithiole **66** and its corresponding acetal **67** have also been prepared using two alternative routes.[131]

Scheme 42



Scheme 43



Transformation of the hydroxymethyl group to the formyl group was recently achieved in improved yields using the Magtrieve (CrO_2) reagent (Scheme 43).[132]

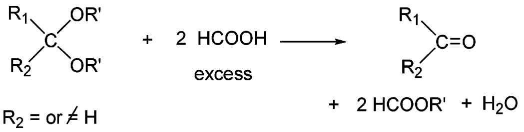
Originally, simultaneous introduction of aldehyde groups together with a vicinal trivalent functional group to TTFs appeared very difficult and the yields in these time-consuming multistep syntheses were often low. This situation has been significantly improved thanks to the efforts devoted to the synthesis of new α-acetylenic carbonylated compounds depicted below.

3. Acetylenedicarbaldehyde (ADCA) and Related Acetylenic Derivatives in 1,3-Dithiole and TTF Chemistry

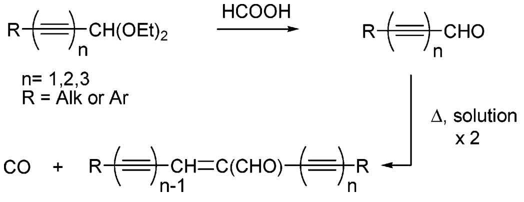
3.1. Advent of Acetylenedicarbaldehyde (ADCA) and Related Compounds

The group of Levas discovered the very efficient acidolysis of acetals using pure formic acid (Scheme 44),[133] and iodo and bromopropynals were first obtained.[133a] This reaction was applied to other α-acetylenic aldehydes, such as phenylpropiolaldehyde,[133,134] and acetals usually known as highly resistant to hydrolysis. In particular, conjugated polyacetylenic aldehydes were isolated and their thermal instability was demonstrated (Scheme 45).[135]

Scheme 44

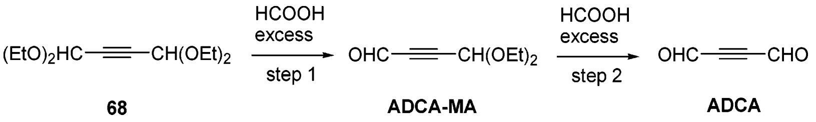


Scheme 45

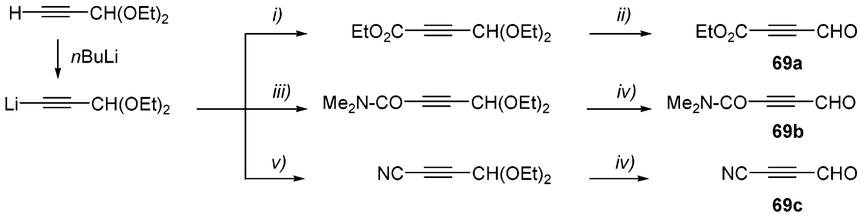


After the development of new preparations of alkynes including α-acetylenic acetals, aldehydes, and ketones by dehydrohalogenation of the corresponding haloalkenes by Triton B[136] or Bu_4NOH[137] (in particular the preparation of propargylic diethyl acetal by ion pair extraction dehydrohalogenation with Bu_4NHSO_4−NaOH[138]), the still unknown acetylenedicarbaldehyde ADCA was studied. It was found that when 1,1,4,4-tetraethoxybut-2-yne **68** was dissolved in pure formic acid at room temperature, formolyses of both acetal functionalities occurred

Scheme 46

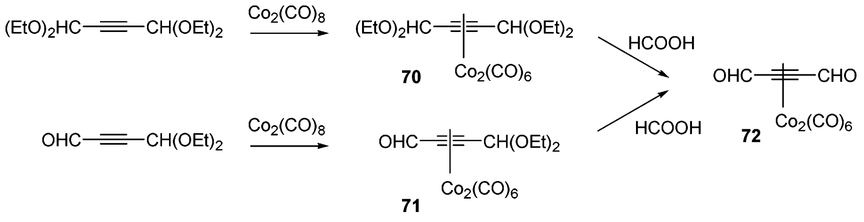


Scheme 47



i) $ClCO_2Et$; *ii)* HCOOH; *iii)* $ClCONMe_2$; *iv)* CF_3COOH; *v)* PhOCN

Scheme 48



(Scheme 46) so that a solution of this highly electrophilic alkyne could be obtained in formic acid in high yield.[139] Thanks to the kinetic difference between steps 1 and 2 in Scheme 46, by using a solvent such as CH_2Cl_2 or $CHCl_3$, it was possible to isolate the monoacetal of acetylenedicarbaldehyde (ADCA-MA) in fairly good yield.[140] Very recently an improved synthesis of 1,1,4,4-tetramethoxybut-2-yne and corresponding ADCA-MA has been described starting from 2,5-dimethoxy-2,5-dihydrofuran.[141]

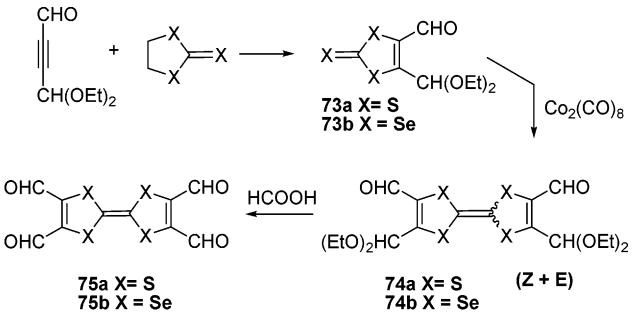
Given the dienophilic and dipolarophilic properties of these compounds, in addition to the electrophilicity of their aldehyde functionalities, the synthetic utility of formic acid solutions of ADCA[139,142,143] and pure ADCA-MA[140,142−145] was revealed (since 1986, compounds **68** and ADCA-MA have been marketed by Janssen Chimica[145j] [now Acros Co.]). This study has been extended to the synthesis of other acetals of but-2-ynal such as the ester **69a**,[142,143] the amide **69b**,[143] and the nitrile **69c**[143] from propargyl diethylacetal (Scheme 47).

Further studies devoted to the isolation of ADCA in the pure state revealed its thermodynamic instability (mp at −10 °C with explosion) and showed differences in its strong electrophilic reactivity between neutral and acidic conditions.[146] ADCA was stabilized by complexation using dicobalt octacarbonyl, affording the much more stable solid compound **72** by formolysis of complex **70** or of the cobalt complex of ADCA-MA **71** (Scheme 48).[147]

3.2. Aldehydic TTFs or 1,3-Dithioles from Acetylenedicarbaldehyde Monoacetal (ADCA-MA)

Although ADCA-MA is far less electrophilic than the free dialdehyde ADCA, given the difficulties of isolation of ADCA and the versatility of the reactivity of ADCA-MA in formic acid solution, ADCA-MA has always been preferred as the starting electrophilic alkyne, and we now discuss its uses in TTF and 1,3-dithiole chemistry below.

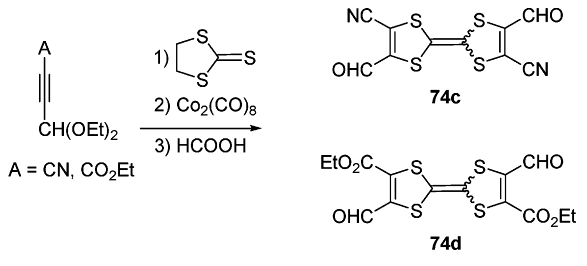
Scheme 49



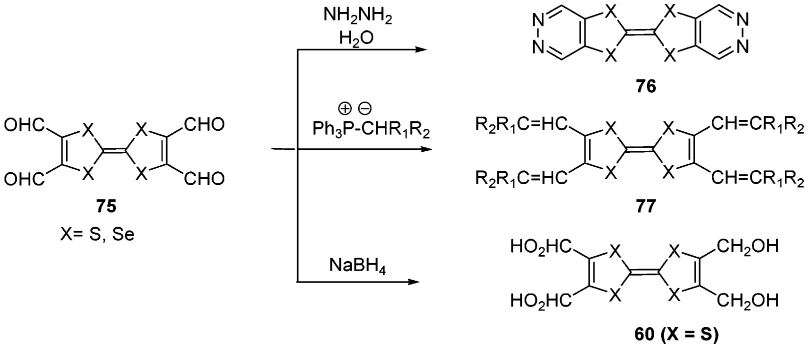
3.2.1. Reaction of ADCA-MA with Ethylenetrithio (or Triseleno) Carbonates

As indicated in Scheme 49, ethylene trithiocarbonate and ADCA-MA give rise to the aldehyde−acetal **73a**, which was dimerized with loss of sulfur to yield a mixture of the [*Z*]- and [*E*]-geometric isomers of the TTF **74a**. The coupling step involves dicobaltoctacarbonyl[148,149] rather than the more classical trialkyl phosphite or phosphine coupling reagents which are incompatible with the highly electrophile aldehyde functionality. Formolysis of **74a** gives tetraformylTTF **75a** almost quantitatively.[120a,150] Similar reactions

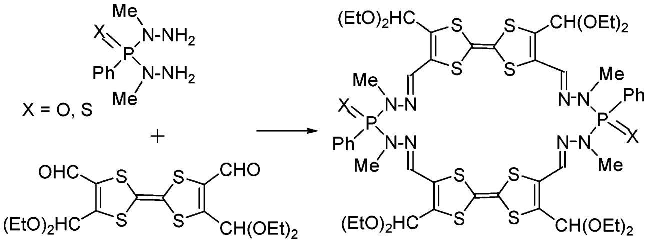
Scheme 50



Scheme 51



Scheme 52



have also been applied to the selenium series starting from ethylene triselenocarbonate to afford **75b** (Scheme 49).[120b,c] This methodology has been successfully applied to the related α,α′-cyanoacetal or α,α′-ester acetal alkyne compounds, thus producing the diformyl dicyano or diformyl dicarboethoxy TTF derivatives **74c** and **74d** (Scheme 50).[151]

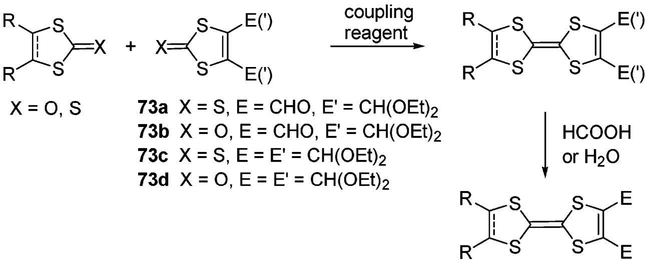
Classical chemical modifications in the 1,3-dithiole or TTF series (and Se analogues) have been achieved, showing the high versatility and utility afforded by the aldehyde functionalities (interaction with hydrazine, Wittig reaction, NaBH$_4$ reduction; Scheme 51).

An illustration of the wide range of applications of the TTF **74a** is the [2+2] cyclocondensation of the *Z*-isomer in the presence of phosphodihydrazides to produce phosphorus-containing TTF macrocycles in yields of up to 60−80%[152] (Scheme 52).

The 5-diethoxymethyl-4-formyl-2-thioxo-1,3-dithiole **73a** was reduced by sodium borohydride and converted into the fused furano-2-thioxo-1,3-dithiole **78**. Compounds **74a** and **79** were also synthesized by symmetrical or dissymmetrical coupling and separated. Further identical reduction and cyclization reactions afforded the corresponding mono- and di-[3,4]furanoTTFs **F-TTF** and **DF-TTF,** respectively (Scheme 53).[153] Coupling reaction using trialkyl phosphite from compound **78** led to **DF-TTF** but in low yield.[153]

Various vic-diformyl TTFs have also been prepared by dissymmetrical coupling of **73a** (or its oxo analogue **73b**) or the corresponding vic-diacetals (**73c** or **73d**) with a variety of 2-(thi)oxo-1,3-dithioles or ethylene trithiocarbonate, as shown in Scheme 54.[121a,c,154]

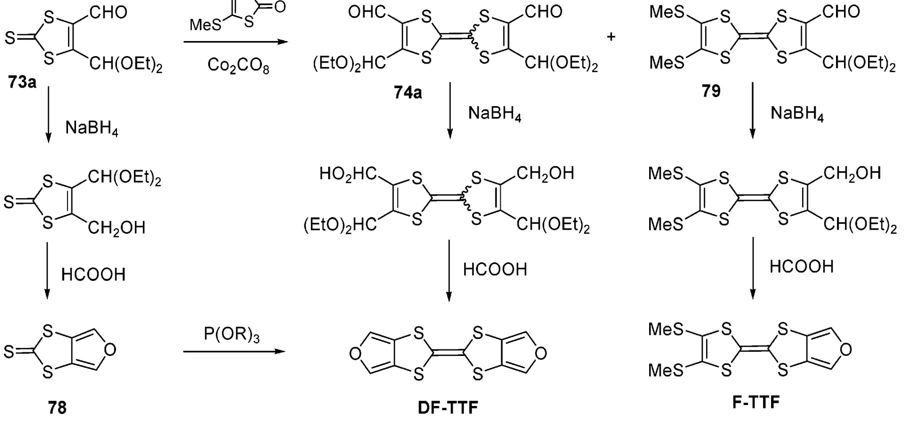
Scheme 54



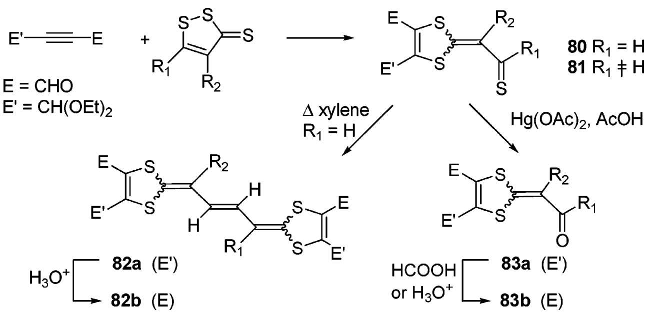
3.2.2. Reaction of ADCA-MA with 3-Thioxo-1,2-dithioles

As expected, given its dipolarophilic properties, ADCA-MA readily cycloadds at 20 °C to 3-thioxo-1,2-dithioles to give rise to the thials **80** ($R^1 = H$)[155−157] or the thiones **81**[156,157] ($R^1 \neq H$; Scheme 55). The thials **80** were dimerized to **82a** with loss of sulfur on refluxing in xylene, both remaining acetal functionalities being further conveniently hydrolyzed in the presence of Amberlyst-15 with production of the tetraaldehydes **82b**. Additionally, when treated with

Scheme 53



Scheme 55

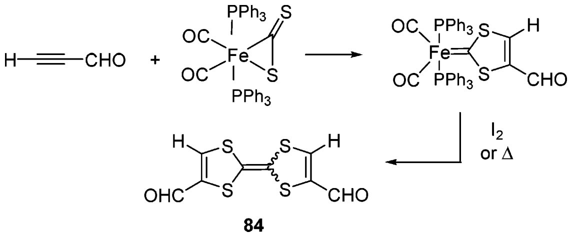


mercuric diacetate in the presence of acetic acid, the thial and thione functionalities of **80** and **81** were readily converted into aldehydes or ketones, the final deketalization of the monoacetals **83a** being achieved with generation of tricarbonylated compounds **83b**, either by formic acid acidolysis or Amberlyst-15 hydrolysis. Because of its more electrophilic properties, ADCA (neutral solutions) also cycloadded to 3-thioxo-1,2-dithioles in the same way but at lower temperatures (less than 0 °C; Scheme 55).

3.2.3. Reaction of ADCA-MA with (η^2-CS$_2$)Fe(PPh$_3$)$_2$(CO)$_2$ Iron Complexes

Production of 1,3-dithiolium carbenic iron complex was achieved at an early date,[144] and the reaction was successfully applied to the preparation of 4,4′-(5′)-diformyl TTF **84** starting from propiolaldehyde obtained by formolysis of its diethylacetal (Scheme 56).[151]

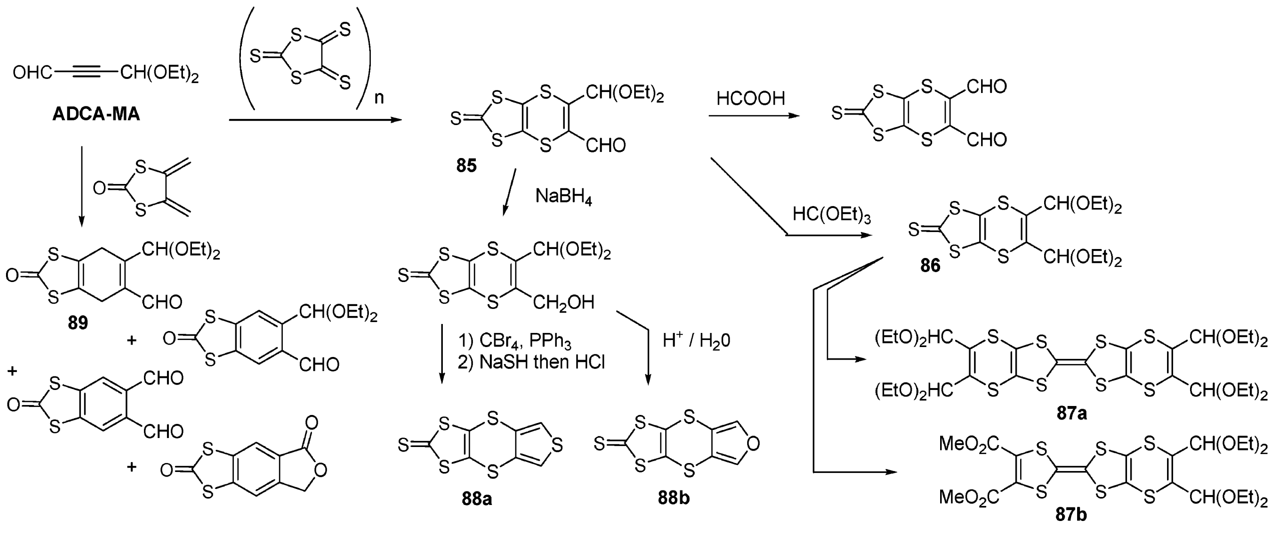
Scheme 56



3.2.4. ADCA-MA as Dienophile in Diels–Alder Cycloaddition with Heterodienes

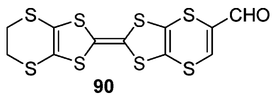
The [4+2] cycloaddition of the electron-rich bisheterodiene, oligo(1,3-dithiole-2,4,5-trithione),[76,77] with ADCA-MA afforded the dithiin-fused 1,3-dithiole-2-thione **85** in satisfactory yields.[158] The latter compound could be transformed into the dicarboxaldehyde by deprotection of the acetal group or it could be submitted to a complete acetalization to give compound **86**. Functionalized TTFs **87a** and **87b** were synthesized using self- or cross-coupling via the phosphite-mediated desulfurization method. Introduction of the thiophene ring was reported to afford compound **88a** as the key intermediate in the synthesis of a polythiophene bearing the strong electron-accepting fluorene unit.[159a] The furano analogue **88b** was reached by acidic treatment using the same intermediate.[159b] Finally, the Diels–Alder reaction with 4,5-dimethylidene-2-oxo-1,3-dithiole, generated by thermal rearrangement of *S*-propargyl xanthate,[160] afforded the cycloadduct **89,** which was converted on silica gel to a mixture of compounds resulting from (i) aromatization, (ii) deprotection of the acetal, and (iii) Cannizzaro-type reaction followed by intramolecular lactonization (Scheme 57).[161]

Scheme 57



A similar Diels–Alder strategy has been used starting from propargyl aldehyde diethyl acetal and oligo(1,3-dithiole-2,4,5-trithione) to prepare the TTF derivative **90** in several steps, Chart 7.[162]

Chart 7



3.3. General Considerations on the Comparative Reactivity of Electrophilic Alkynes, Including α-Acetylenic Aldehydes

As previously seen in the preceding sections (sections 2.1–2.7 and 3.1–3.2), several syntheses of 1,3-dithioles and TTFs using the interaction of electrophilic alkynes and CS$_2$ derivatives are available. Of course, the choice of the method to be employed to reach a given target is fully dependent on the nature of both antagonistic reagents (availability, stability, reactivity). In the absence of kinetic data and systematic study, it is impossible to establish serious comparative scale of reactivity. Nevertheless, some general trends can be extracted from the literature.

Considering electrophilic alkynes substituted with the electron-withdrawing group E (e.g., CN, CHO, COR, CO_2R, $CONR_2$), a general feature is that di-E-substituted alkynes are more reactive than those substituted with only one E group. Among the latter derivatives, terminal alkynes are more reactive, and finally, nonelectrophilic alkynes are mostly unreactive toward CS_2 derivatives, Chart 8.

Chart 8

$$E-\equiv-E \;>\; H-\equiv-E \;>>\; E-\equiv-R \;>>>\; R-\equiv-R$$

In these series, roughly speaking, the higher the electrophilicity of E, the higher the reactivity of the alkyne.

$$CN \approx CHO > CO_2R > COR$$

Nevertheless, the choice of a methodology for synthesizing a target molecule will also depend on several other data of each antagonistic counterpart: availability, stability, physical properties (boiling point in particular for the alkyne). Thus, for example, for reaching polyaldehydic TTFs, highly reactive ADCA will not be suggested as the starting material because of its instability and its monodiethylacetal will be preferred. For alkynes of low boiling point (propiolaldehyde, alkyl propiolates, cyanoacetylene), CS_2 derivatives cycloadding at room temperature will be preferred to those working at high temperature. Also note that, for practical reasons, commercially available DMAD is often used as the starting alkyne, the ester group being further transformed (section 2.7).

4. Highly Extended Tetrathiafulvalene Derivatives Prepared from Acetylenic Precursors

4.1. Major Principles and Guidelines

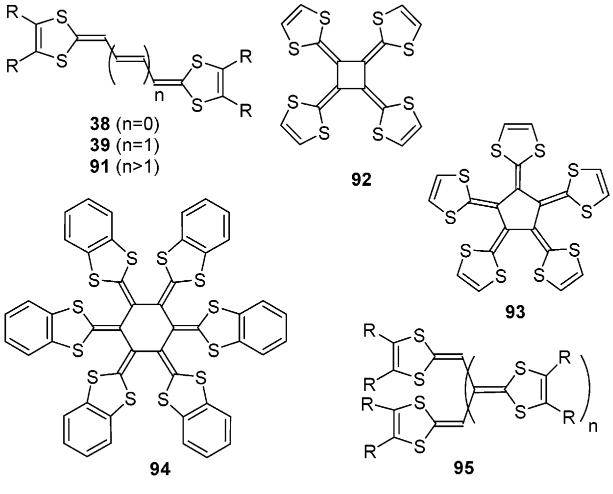
As mentioned in the Introduction, the advent of TTF chemistry was initially closely associated with the discovery in the early 1970s of the solid-state electroconducting properties of the corresponding TTF-TCNQ charge-transfer salts[3] and later with the discovery of a superconducting state at low temperature for the related cation radical salts.[4,5,7] The latter salts were the first superconducting organic materials ever prepared and are obtained by electrooxidation (electrocrystallization) of the corresponding neutral TTF derivatives. Most of the cation radical salts thus obtained undergo breakdown of conductivity when the temperature is decreased, this limitation being associated with their strong monodimensional character in the solid state. It is well established that stabilization of the metallic state of these materials may be reached by increasing their dimensionality,[6] which can be achieved chemically by subtle molecular engineering around the electroactive TTF framework.

Different strategies have been developed in order to increase the intermolecular interactions in the solid state of these cation radical salts, such as (i) replacing of the sulfur atoms of the TTF unit by selenium or tellurium atoms, which possess more diffuse orbitals and therefore allow closer contacts, producing the first superconductors from the tetramethyl tetraselenafulvalene (TMTSF) moiety,[4] or (ii) substituting the TTF framework by *S*-alkyl groups in order to increase the number of S···S intermolecular contacts, as is the case with the superconducting salts of the very prolific bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).[7]

Another actively developed trend is the synthesis of highly extended and S-rich TTF analogues. These compounds are built from a combination of several 1,3-dithiol-2-ylidene heterocycles into a single highly conjugated molecule. The effects which are expected from such extended π-donating molecules are as follows: (a) in the solid state, (i) enhancement of the dimensionality in the related oxidized salts through accumulation of sulfur atoms in the molecular structure, which allows multiple intra- and interchain S···S contacts and therefore a higher conductivity and (ii) strong intermolecular interactions in the stacking mode of related materials due to the lowering of the charge density in the oxidized states; (b) in solution, (i) higher π-donor ability than TTF itself due to the strong electron-donating effect promoted by each 1,3-dithiol-2-ylidene ring and (ii) easy access to unusually high positive charges upon full oxidation, resulting from the lowering of the intramolecular Coulombic repulsions in the oxidized species, which may provide organic salts of unusual stoichiometries.

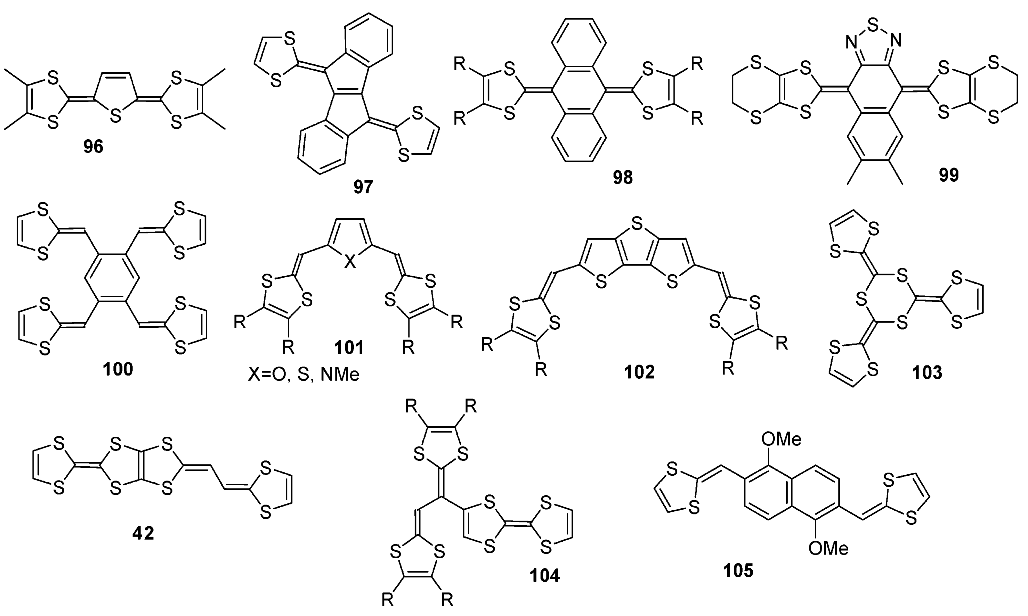
Pioneering work in this area by Yoshida et al.[92a] concerned the synthesis of the vinylog **38** (R = H),[92b,c,93b] ethylenic analogue **39** (R = H) of TTF,[93a,b] [*n*]-radialenes[93d] such as **92**−**94,** and [*n*]-dendralenes **95**.[93c] Several groups have subsequently carried out the synthesis of some analogues of these compounds with different R-substituents or by changing S to Se or Te in the molecular structure of **38**,[125,159b,163] **39**,[45h,164] and **91**[165,166] and of the dendralene-TTF derivatives **95,** Chart 9.[167]

Chart 9



Similar guidelines led to the synthesis of a large number of highly extended π-systems derived from TTF, some representative examples being compounds **96**−**105**, which have been subject to subsequent chemical variations notably on R substituents through different synthetic routes: **96**,[168] **97**,[169] **98**,[170] **99**,[171]

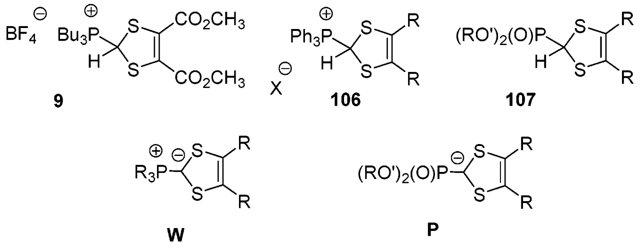
Chart 10



100,[172] **101**,[173] **103**,[174] **104**,[175] **105**,[176] and DTEDT **42**.[96] In the latter case the corresponding cation radical salt (DTEDT)[Au(CN)$_2$]$_{0.4}$ was found to be superconducting below 4 K at ambient pressure, which validates the concept of an increased spatial extension for the π-framework. Frère, Roncali, and coworkers extensively studied the synthesis of various combinations of thiophene-based linear conjugated linkers between both heterocyclic 1,3-dithiol-2-ylidene moieties,[14,99b,159b,177] compound **102** constituting a recent example of such a strategy, Chart 10.[178]

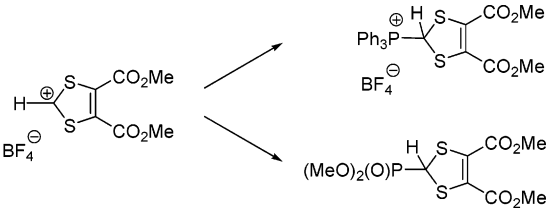
In all of these examples the highly extended system involves two or more 1,3-dithiol-2-ylidene moieties which are generally introduced through Wittig (poly)-olefination under basic conditions using ylides **W** generated from phosphonium salts **9** (described by Cava et al.[45a]) or **106** (first developed by Akiba et al.[179]) The latter group demonstrated that a Horner−Wadsworth−Emmons (HWE) reaction with the phosphonate anions **P**, generated under basic conditions from **107**, can alternatively be used. Extensive developments and mechanistic studies on the synthetic intermediates **106**, **107** were then carried out, notably by Fabre et al.[180] The synthesis of the phosphonium salt **9** in one pot from Bu$_3$P−CS$_2$ and DMAD has been described in section 2.2. The phosphorus compounds **106** and **107** are, respectively, prepared by reacting an aromatic 1,3-dithiolium salt with triphenylphosphine and with trialkyl phosphite in the presence of sodium iodide, a wide variety of R substituents being available for **W** and **P**, Chart 11.

Chart 11



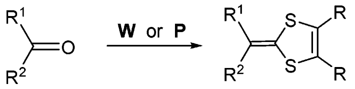
New phosphonium salt[181] and phosphonate[182] (with R = CO$_2$Me) synthetic equivalents of **9** and **107**, respectively, have been prepared recently starting from the key dithiolium salt[183] readily obtained from 4,5-bis(methoxycarbonyl)-2-thioxo-1,3-dithiole **18a**, Chart 12.

Chart 12



Access to the target extended systems has been achieved by reaction between the olefination reagents **W** or **P** and a suitable (poly)ketonic or polyaldehydic derivative (Scheme 58).

Scheme 58



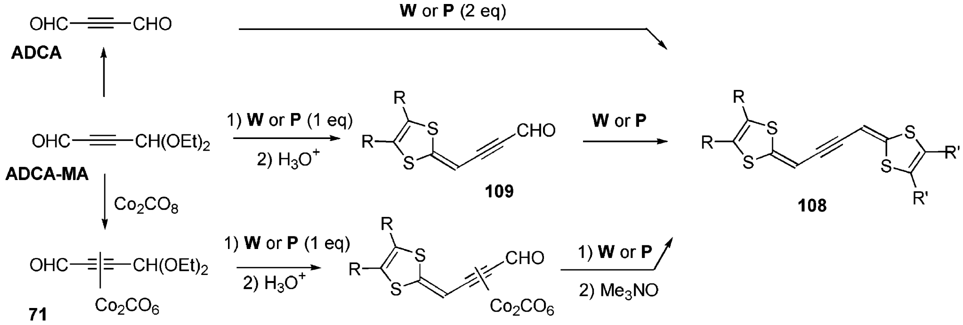
4.2. Highly Extended and Sulfur-rich Tetrathiafulvalene Derivatives Incorporating 1,4-Dithiafulven-6-yl Fragments

4.2.1. Acetylenic Analogs of Tetrathiafulvalene

A huge number of linearly extended analogues of TTF derivatives has been described, incorporating a very large panel of conjugated linkers between both 1,3-dithiole rings (i.e., polyenic (e.g., **39**, **97**), (poly)-aromatic (e.g., **98**, **100**, **105**), (poly)heteroaromatic (e.g., **101**, **102**)), but very few of these incorporate a (poly)acetylenic linker.

Benefiting from our work on ADCA (see section 3), we developed the preparation of acetylenic derivatives of the TTF **108**.[184] Symmetrically substituted derivatives (R = R′) were obtained via a direct 2-fold

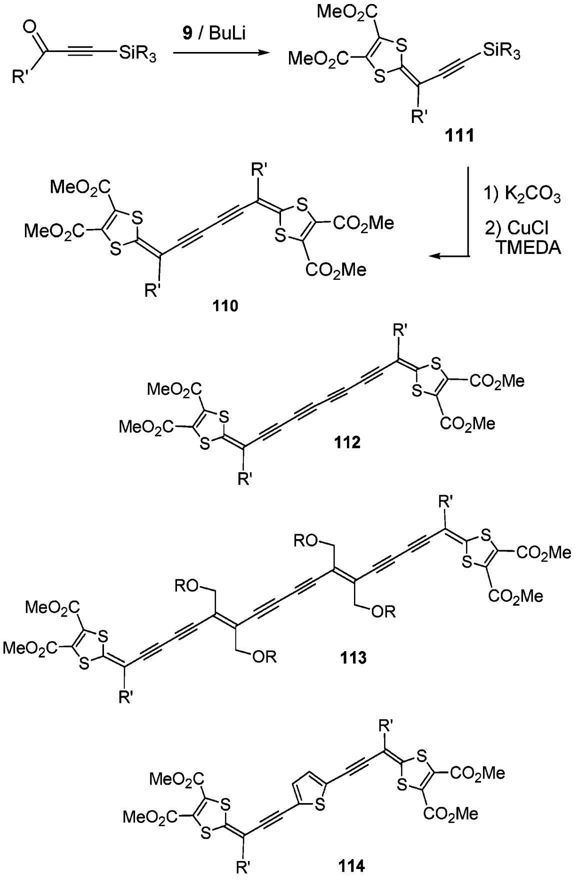
Scheme 59



Wittig or HWE reaction between ADCA and **W** or **P**. Because of hydrolysis problems in freeing the aldehyde intermediate **109** from its corresponding acetal, the two-step strategy, which is required to reach dissymmetrical **108** derivatives (with R ≠ R′), can be significantly improved by prior triple-bond protection of ADCA-MA as a cobalt carbonyl complex, which at the end of the synthesis is oxidatively decomplexed with trimethylamine oxide (Scheme 59). Electrochemical studies by cyclic voltammetry (CV) show that unlike ethylenic analogues of the TTF **39** which exhibit one 2e$^-$ reversible peak, the acetylenic derivative **108** exhibits a moderate π-donating ability associated with poor electrochemical reversibility of the redox processes.

Recently, M. B. Nielsen et al. accessed a new set of acetylenic analogues of the TTF **110**,[185] starting from α-acetylenic ketones, and using Wittig olefination with **9** under basic conditions. The intermediates **111** are then subjected to oxidative coupling after desilylation to produce the diyne analogues of TTF **110**. The same intermediate **111** allows access to a wide variety of extensively conjugated poly-yne TTF analogues such as **112**, **113**, or even **114** incorporating a thienyl ring (Scheme 60). In this case, the electrochemical behavior shows a lowering of the Coulombic repulsions between the two positive charges of the dication compared to **108**, as expected from the longer conjugated linker. These compounds display good third-order nonlinear properties.

Scheme 60



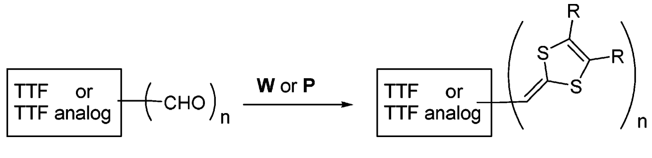
Other molecular assemblies which associate the TTF moiety to an acetylene fragment(s) are ethynyl TTF derivatives,[186] diethynyl TTF,[187] and tetraethynyl TTF.[188] The ability of some of these (poly)ethynyl-TTFs to polymerize and produce polymers with in chain or appended TTF has been studied.[189]

4.2.2. Mono-, Bis-, and Tetrakis(dithiafulvenyl) Tetrathiafulvalene Derivatives

4.2.2.1. Synthesis.

We have shown in section 4.1 that an actively developed trend for the molecular design of TTF derivatives relies on the synthesis of highly extended π-structures based on a Wittig or HWE olefination strategy involving **W** or **P**. Having in our hands the powerful synthetic polyformyl TTF intermediates depicted in section 3.2, we designed highly extended and sulfur-rich TTF derivatives which incorporate one (**115**),[151] two [(**116**)[151] and **117**, **119**[154,190]], three (**120**),[191] or four (**121**[154,190] and **122**[155]) 1,4-dithiafulven-6-yl groups and are therefore obtained by 1-, 2-, 3-, and even 4-fold Wittig or HWE olefinations (Scheme 61).

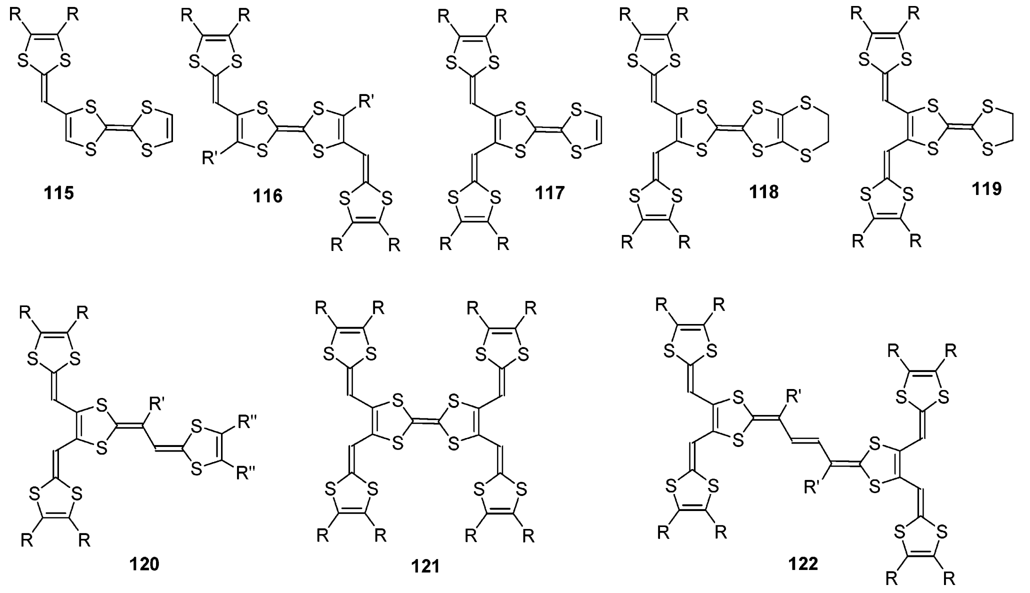
Scheme 61



A wide variety of R substituents are available for **W** and **P**, so that one may easily increase the solubility or the π-donating ability (or both) of the target molecules **115**−**122**. We can even prepare amphiphilic derivatives of **119** designed for LB films from a phosphonium salt **9** bearing long carboalkoxy chains (R = $CO_2C_8H_{17}$), Chart 13.[47]

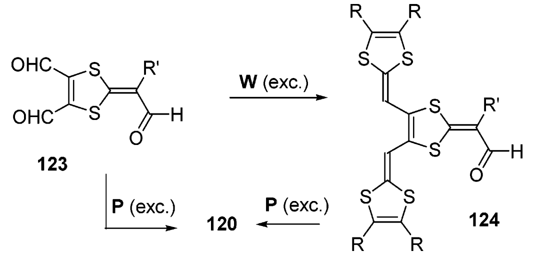
Although the most powerful nucleophilic species are the phosphonate anions **P**, in all cases except for the tris(formyl) derivative **123** the easier to handle

Chart 13



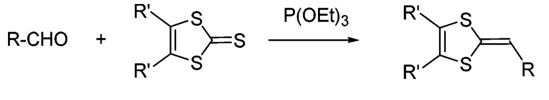
P-ylids **W** are reactive enough to achieve the required polyolefinations of the conjugated aldehydes. These reactions proceed in quite good yields (50−90%) if one considers that up to four olefinations are achieved in one step. In the case of **123**, even the use of a large excess of **W** does not allow the targeted **120** to be prepared since the reaction stops at the stage of the bis-olefinated compound **124**. Nevertheless, the desired tris-olefinated product can be obtained by reacting **124** with **P** or by direct treatment of **123** with an excess of **P** (Scheme 62).[191] This lack of reactivity of the remaining carbonyl group in **124** is attributed to electronic and structural effects, confirmed by an X-ray structural determination of **123**, which shows that the oxygen atom of the carbonyl group concerned is strongly involved in a 1,5- S···O intramolecular interaction.[157b,163h]

Scheme 62



Interestingly, Iijima et al. recently reported an alternative olefination methodology using direct triethyl phosphite-mediated coupling between a conjugated aldehyde and a 2-thioxo-1,3-dithiole derivative. This allows access to TTF vinylogues **38** bearing substituents incompatible with the basic medium necessary for Wittig reactions (Scheme 63).[159b,163m]

Scheme 63



4.2.2.2. Some Key Features of Mono-, Bis-, and Tetrakis(dithiafulvenyl) Derivatives.

The bis and tetrakis(dithiafulvenyl) derivatives **115**−**122** are characterized by an exceptionally strong π-donating ability, illustrated in cyclic voltammetry by a first oxidation potential (E_{pa}^1) markedly lower than that of TTF itself, with E_{pa}^1 values as low as 0.06−0.1 V/SCE (TTF, 0.40V/SCE in DMF) for some compounds of the series. Such low oxidation potential values certainly put this family among the best π-donating molecules of the TTF series. This ability to be easily oxidized is explained by introduction of the strongly donating dithiafulvenyl groups on the periphery of the TTF backbone, which reinforce the π-donating ability. Of course, the E_{pa}^1 values are also strongly dependent on the electronic character of the R-substituent on the dithiafulvenyl groups, electron-donating substituents (R = alkyl) strengthening the π-donating ability (lower Ep_a^1) and electron-withdrawing ones (R = CO_2R') giving rise to higher Ep_a^1. Another singularity of this family lies in their easy access to multicationic states. This remarkable, albeit expected, feature is assigned to the very weak intramolecular Coulombic repulsions in the polyoxidized states of these highly extended systems and is illustrated by the close proximity of the successive redox steps relative to TTF. Such a characteristic gave the opportunity to demonstrate the efficiency of the thin layer cyclic voltammetry technique (TLCV) as a complementary analytical tool in determining the electronic charge involved in each redox process and in the prediction of stoichiometries of subsequent electrogenerated salts.[192]

Also, an unconventional electrochemical behavior has been found for the simplest element of the series, i.e., the mono(1,4-dithiafulven-6-yl) TTF derivatives **115** (Figure 2),[151] for which a strong effect of the electronic character of the R-substituent on the dithiafulvenyl substituent has been found and is attributed, as confirmed by DFT theoretical calculations on both neutral and oxidized states, to the occurrence of an unusual conformation involving a tetravalent sulfur atom.

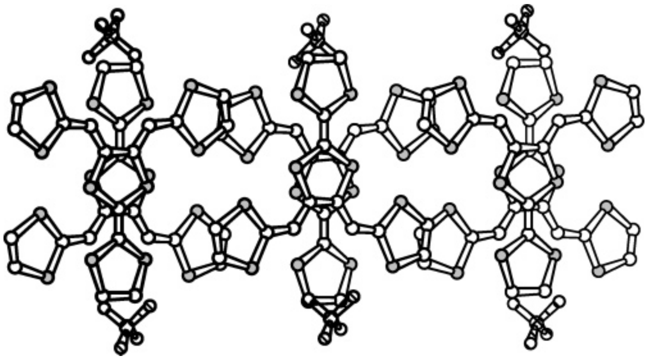


Figure 1. X-ray structure of **119**·ClO_4 showing the overlap mode through the lateral dithiafulvenyl within the organic slab.

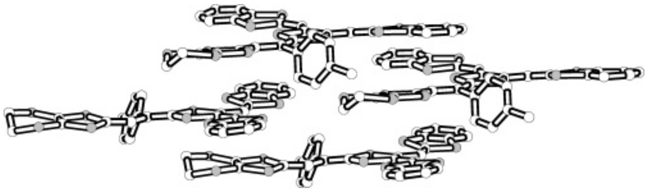


Figure 2. X-ray structure of **120**·PF_6 (anions omitted) showing the overlap mode between π-donors

Electrooxidation[193] of the dithiafulvenyl-TTF derivative (**119**, R = H) produced single crystals of a cation radical salt corresponding to the stoichiometry **119**·ClO_4 as determined by X-ray diffraction (Figure 1) and which shows a remarkably high room temperature conductivity for a 1:1 fully charge-transferred salt (0.4 S·cm^{-1}; E_a = 170 meV).[154,190] This observation is associated with the low Coulombic repulsion in such an extensively conjugated molecule and also with a unique pattern of overlap in the crystal, with multiple S···S intermolecular contacts, notably through the lateral dithiafulvenyl fragments, which confer a novel type of two-dimensional association to this salt.

Electrogenerated single crystals of a 1:1 cation radical salt of **120**·PF_6 could also be obtained, and the X-ray structure shows, as expected, an accumulation of S···S intermolecular contacts within the stacking mode (Figure 2).[191] The powder conductivity is as high as 0.1 S·cm^{-1}, which illustrates again the validity of the concept of designing highly extended and sulfur-rich π-systems to increase the dimensionality of related cation radical salts.

Finally, electrooxidation of **118** (R = H) produced, for the first time in the series of dithiafulvenyl TTF derivatives, a mixed-valence salt ((**118**)$_2$$PF_6$). The quality of the crystals obtained was good enough for a preliminary X-ray structural determination, which demonstrated the expected 2D organization of the donors with multiple S···S intermolecular contacts. Given the 2:1 stoichiometry and the clear bidimensional organization in the solid, such a salt fulfils the requisite criteria for stabilization of the metallic state at low temperature. Unfortunately, the crystals were highly fragile and no conductivity measurement was possible.

From our experience and the intensive efforts we have made to exploit such exciting results in getting new cation radical salts from this family, it appears nevertheless that such π-donors present some difficulties in electrocrystallization.

The explanation for the difficulties in obtaining crystals of high quality was found in the vicinal character of the two 1,4-dithiafulven-6-yl sidearms. Under acidic conditions,[194] these donors undergo an undesirable intramolecular cyclization reaction involving prototropy of the hydrogen at the C-6 position of the substituent (Scheme 64). The cyclization product issued from **119** (R = H) was characterized by an X-ray diffraction study.[194b] On the other hand, upon oxidation, cyclization of the cation radical produces a proton, which acts as catalyst to reproduce the phenomenon observed in acidic conditions.[195] Noteworthy, a bis spiro analogue has been recently described arising through a different process from the thermal transformation of a fluorinated vinylog of TTF.[196]

Since the importance of the purity of π-donors in the electrocrystallization experiments is well established,[193] this internal cyclization during the purification procedure (acid-mediated cyclization) or the electrooxidation process produced the spiro compound in sufficient quantity to have a spoiling effect on the quality of electrogenerated salts.

4.2.3. Giant Analogs of TTF Devoid of Prototropy

To suppress any possible cyclization reaction (see section4.2.2.2), π-donors bearing no hydrogen atom in the 6-position of the 1,4-dithiafulven-6-yl substituent were designed. Different possibilities have been

Scheme 64

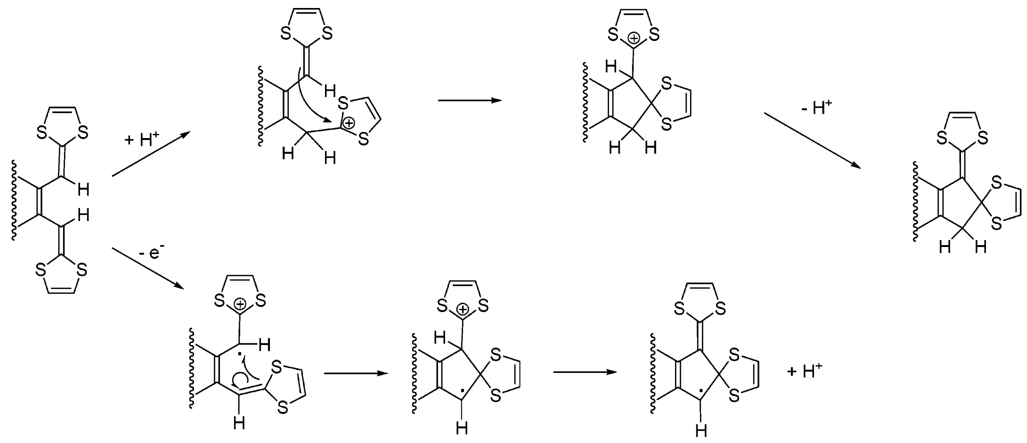
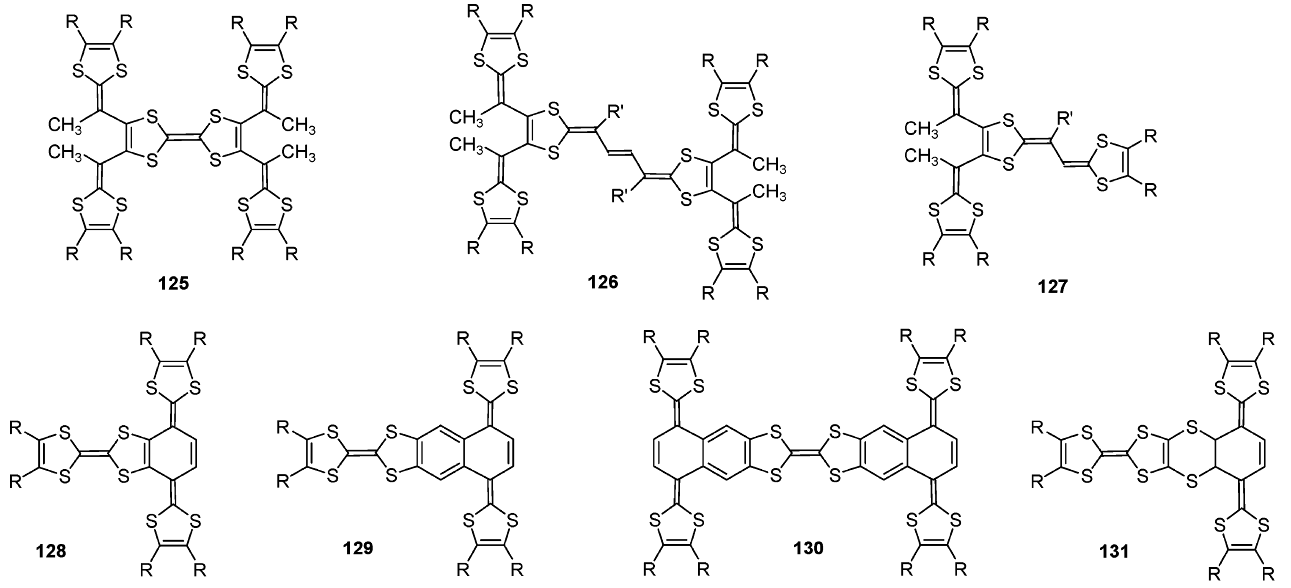
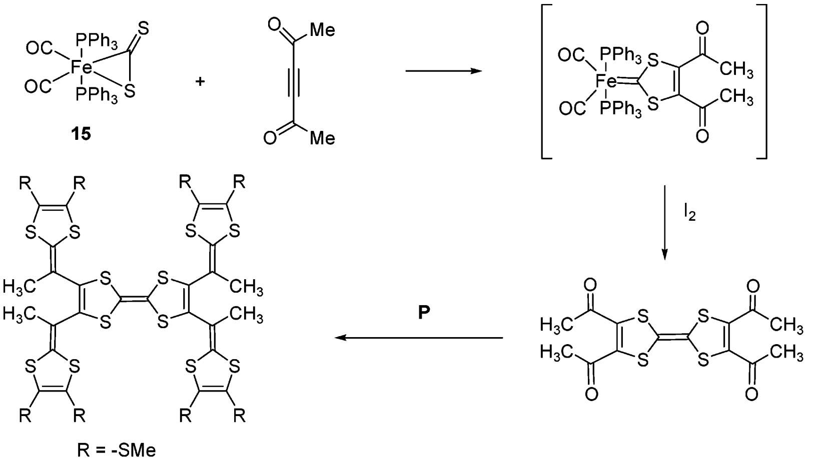


Chart 14



125 126 127 128 129 130 131

Scheme 65



15

125 R = -SMe
R-R = -SCH$_2$CH$_2$S-

considered which consisted of (i) replacing the hydrogen atom by a methyl group (**125**−**127**) and (ii) fusing TTF and extended-TTF, this corresponding to replacement of both hydrogen atoms by a CH=CH linker without (**128**) or by a benzo spacer (**129** and **130**) or by a fused-dithiin fragment (**131**), Chart 14.

4.2.3.1. Synthesis.

The synthetic strategy to prepare **125**[163h,197] (see section 2.3.1) used the reaction of hex-3-yne-2,5-dione with the η^2-CS$_2$ iron complex **15** followed by treatment of the resulting carbenic complex with a stoichiometric amount of iodine. The final HWE polyolefination of the resulting tetracetylTTF was achieved using Akiba's phosphonate anions **P** (see section 4.1) adequately substituted (Scheme 65).

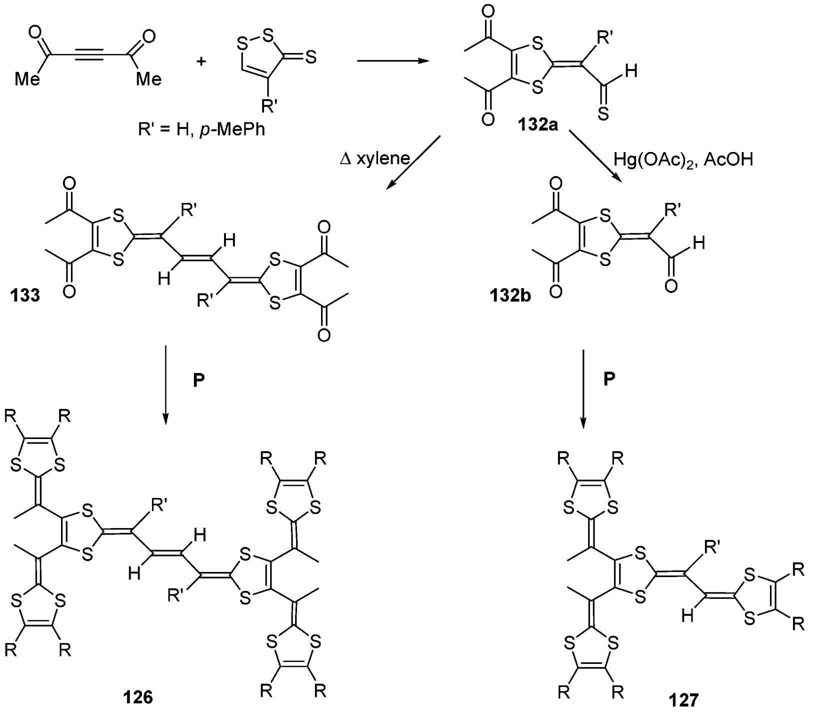
Synthesis of the corresponding symmetrical and dissymmetrical highly extended and sulfur-rich TTF vinylogs **126** and **127** was also developed using tetra- and triolefination reactions. Cycloaddition between hex-3-yne-2,5-dione and 3-thioxo-1,2-dithioles gives rise to the thial **132a**, which was dimerized to **133** or converted into the corresponding aldehyde **132b** (Scheme 66).[163h,197] To bring the successive olefinations to completion, the phosphonate anions **P** were used rather than the less nucleophilic ylids **W** and additionally a very large excess was used.

Synthesis of the fused perpendicular TTF dimers **128** incorporating both a TTF unit and a quinonoid π-extended TTF has been reported but is not detailed in the present review since no electrophilic alkyne was involved as starting material.[198]

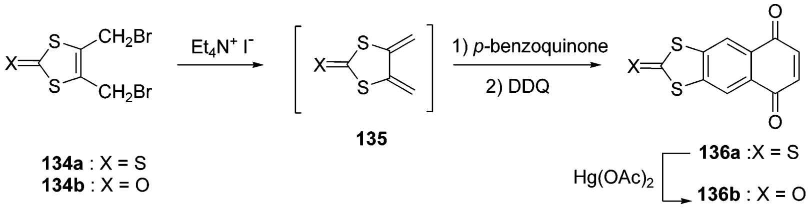
To prepare the dimeric TTF **129** of T-shape morphology in which both TTF and π-extended TTF units are fused but separated by a benzo group, it was necessary to introduce new building blocks such as the bis(bromomethyl) derivative into 1,3-dithiole and TTF chemistry (see section 5.1.1). Thus, 4,5-bis(hydroxymethyl)-2-(thi)oxo-1,3-dithioles (X = S, **55**) were transformed into the corresponding bromide derivatives **134**.[199] After reductive elimination to generate the corresponding dienes **135**, Diels−Alder cycloaddition between these 2-oxo-4,5-bis(methylidene)-1,3-dithioles and quinonic dienophiles was performed followed by aromatization of the [4+2] cycloadduct (Scheme 67).

To perform the required olefinations, it was necessary to suppress the accepting quinonic character of **136,** and the methodology of protection-deprotection

Scheme 66

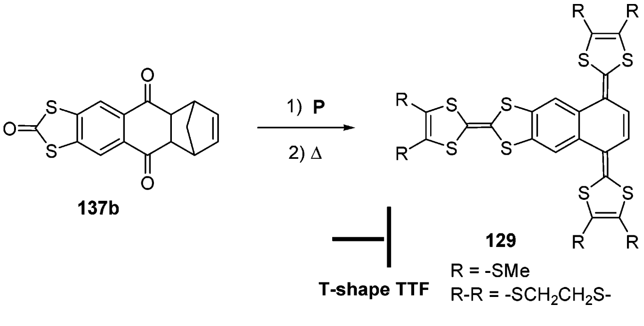


Scheme 67



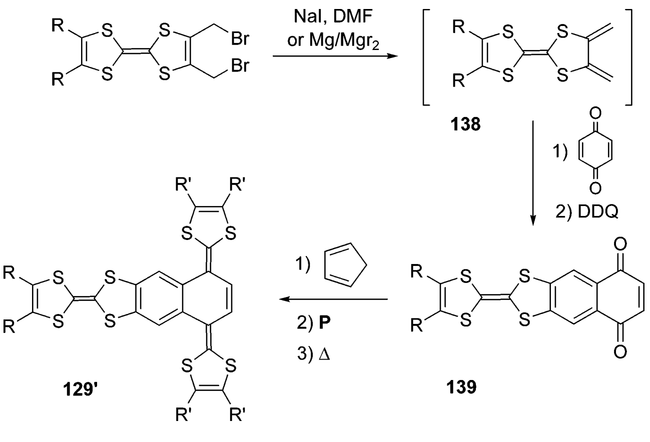
developed by Yamashita using Diels–Alder cycloaddition with cyclopentadiene was applied.[200] After reaction of the cycloadduct **137b** with the phosphonate anion **P**, the bisolefinated compound was accompanied by the trisolefinated compound. Synthesis of the latter compound involved unprecedented TTF core building through HWE olefination of the 2-oxo-1,3-dithiole functionality with Akiba's phosphonate anion **P**.[201] After retro Diels–Alder reaction liberating cyclopentadiene, T-shape π-donors **129** were obtained (Scheme 68).

Scheme 68



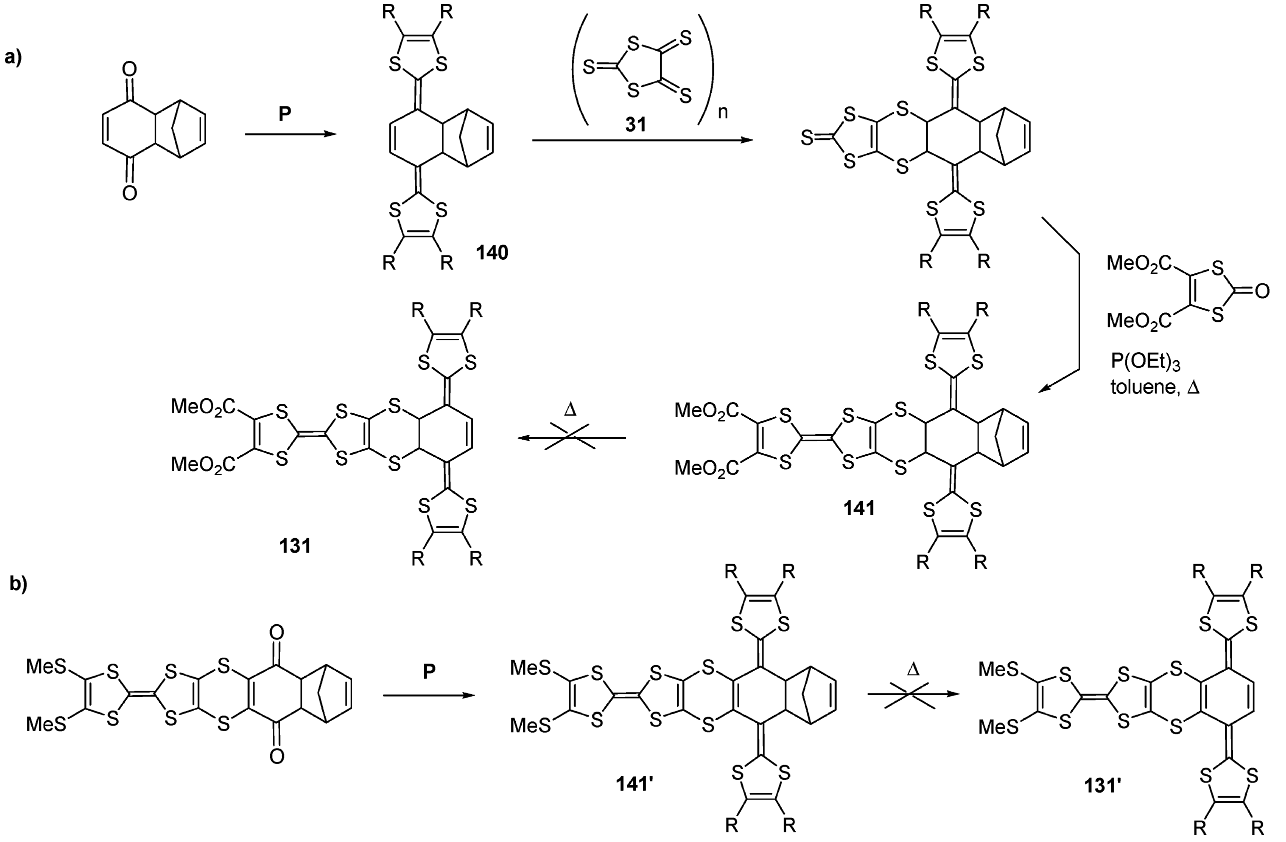
This synthetic strategy suffered from the impossibility of introducing different types of R substituents in the simultaneous trisolefination procedure. Another approach was therefore devised to answer these requirements. This synthesis is based on two main steps: (i) Diels–Alder cycloaddition between the 2,3-dimethylidene-[2*H*]TTFs **138** and quinonic dienophiles with further aromatization of the cycloadduct leading to a conjugated donor–acceptor intermediate **139** and (ii) bis-HWE-olefination of the quinonic carbonyl functionalities with phosphonate anion reagents **P** giving rise to **129′** (Scheme 69).

Scheme 69



The synthesis of extended-TTFs in which the benzo spacer was replaced by a 1,4-dithiin ring was also considered with the aim of increasing intra- and intermolecular S···S interactions. Compound **140** was obtained by HWE olefinations with phosphonate

Scheme 70



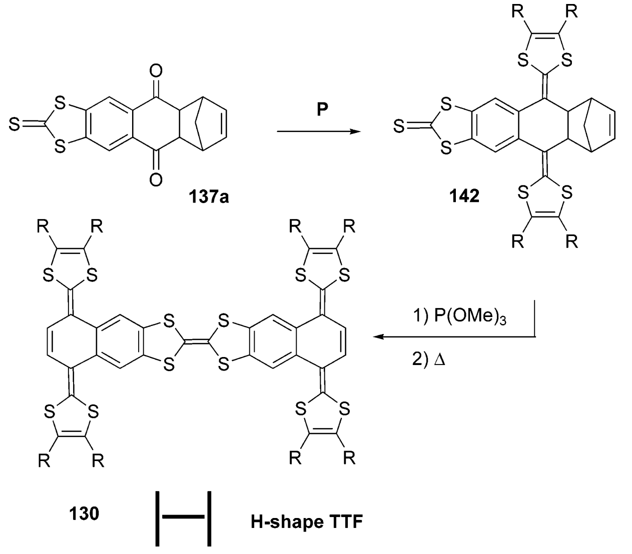
anion **P** on monoprotected benzoquinone. Subsequent Diels−Alder cycloaddition with oligo(1,3-dithiole-2,4,5-trithione)[29,76,77] followed by cross-coupling with 4,5-bis(methoxycarbonyl)-2-oxo-1,3-dithiole produced precursor **141**. Unfortunately, although compound **141** underwent loss of cyclopentadiene in the oxidative step in cyclic voltammetry, preparative synthesis of the corresponding TTF **131** has been so far unsuccessful (Scheme 70a).[202] After this work, a reverse synthetic strategy has been used by Zhang et al., who synthesized the TTF-dithiin-quinone framework and subjected it to bis-olefination with the anion phosphonate **P**. Similarly to **141**, the intermediate **141′** did not undergo the retro Diels−Alder reaction, which would have provided compound **131′** (Scheme 70b).[203]

A straightforward synthesis of the new π-donor **130** which shows the typical *H*-shape design which promises to improve the properties of highly extended and sulfur-rich *T*-shape compounds was reported.[204] The trimethyl phosphite self-coupling reaction of the corresponding thione **142** was followed by retro Diels−Alder loss of the cyclopentadiene protecting group of the quinone unit (Scheme 71).

4.2.3.2. Some Key Electrochemical Features of Giant Analogues of TTF Devoid of Prototropy.

As for the previously depicted dithiafulvenylTTF derivatives **117**−**122** (section 4.2.2.2), TTF derivatives **125**−**130** have electrochemical characteristics typical of highly extended π-donors (lowering of the charge density, lowering of Coulombic repulsions, strong π-donating ability, easy access to multicharged species).

Scheme 71



When comparing the π-donating ability of systems **125**, **126,** and **127** to their nonmethylated analogues (**121**, **122,** and **120,** respectively), it appears that the latter series shows a significantly lower π-donating character, presumably because of lower conjugation induced by distortion between vicinal 6-methyldithiafulvenyl substituents due to steric hindrance between the close methyl groups.[197] Nevertheless, these highly extended systems remain excellent π-donors and give rise to stable polycationic species upon oxidation due to successive reversible redox steps, e.g., **127** can be oxidized to **127**$^{4+}$ via four successive 1e$^-$ processes, whereas a hexacationic state has been characterized for **126**.[197]

The T-shape TTF **129** appears as a strong π-donor and has three reversible oxidation peaks to **129**$^{4+}$,[201] whereas a different behavior is observed for the fused system **128**, which undergoes four sequential 1e$^-$ reversible oxidation processes.[198] Finally, the cyclic voltammogram of the H-shaped TTF **130** (R = SPent) shows three 2e$^-$ oxidation processes to a stable hexacationic species, confirming the tendency of these highly extended systems to allow easy access to unconventional redox states of TTF derivatives.[204]

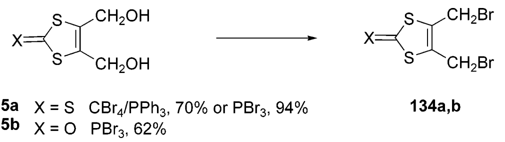
5. Hydroxymethyl Derivatives as Starting Materials for Highly Functionalized TTF

5.1. Conversion of Hydroxymethyl Derivatives to Bromomethyl Derivatives

5.1.1. Preparation

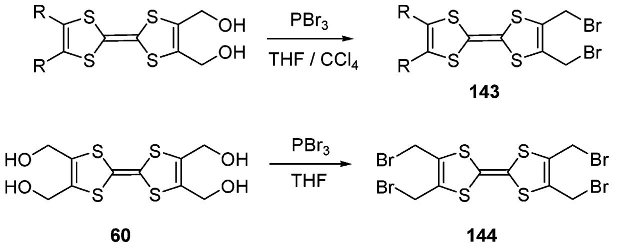
Two strategies were developed in parallel to prepare 4,5-bis(bromomethyl)-2-(thi)oxo-1,3-dithioles by nucleophilic substitution. Thus, diol **55a** was readily converted in the thioxo series to **134a** using CBr_4/PPh_3[205] in 70% yield or using phosphorus tribromide[206] in 94% yield. For the corresponding oxo derivative **55b**, the diol was brominated using PBr_3 in 62% yield (Scheme 72).[199]

Scheme 72



In the TTF series, introduction of the new bis(bromomethyl)TTF derivatives **143** or tetrakis(bromomethyl)TTF **144** proved to be of particular interest for developing organic chemistry on the TTF core requiring the presence of a good leaving group. These versatile building blocks were efficiently obtained on treatment of the corresponding 2,3-bis(hydroxymethyl) or tetrakis(hydroxymethyl)TTFs **60** with phosphorus tribromide in 70% yield (Scheme 73).[207]

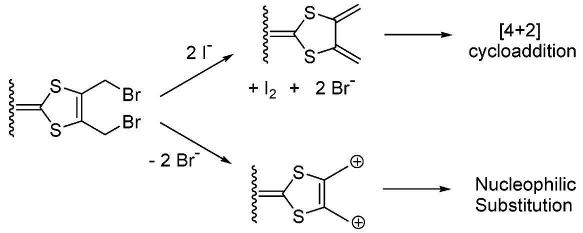
Scheme 73



5.1.2. Applications

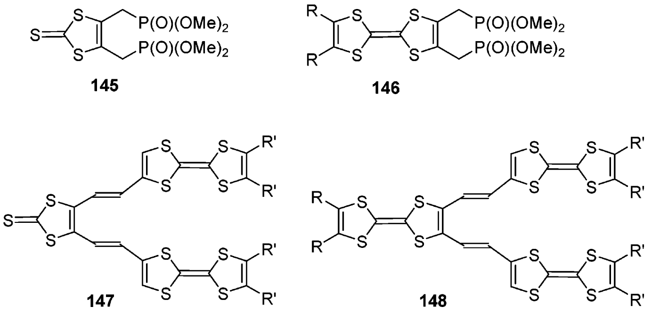
Two synthetic applications were developed starting from these vicinal bis(bromomethyl) groups: (i) generation of the corresponding diene (prone to undergo Diels–Alder cycloaddition) by reductive elimination using naked iodide anion and (ii) the possibility of direct nucleophilic substitution, this group acting as a dication synthetic equivalent (Scheme 74).

Scheme 74



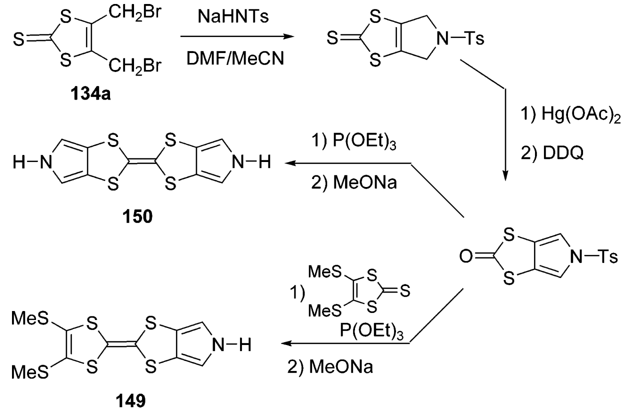
5.1.2.1. Phosphonate Derivatives. The dication synthetic equivalent nature of bis(bromomethyl) derivatives was exploited by preparation of the corresponding phosphonates **145** and **146** by classical Arbuzov reaction using trimethyl phosphite. Subsequent HWE reaction with an appropriately selected monoformylTTF introduced a new area in TTF chemistry by synthesis of the conjugated TTF dimers **147** and trimers **148**, Chart 15.[208]

Chart 15



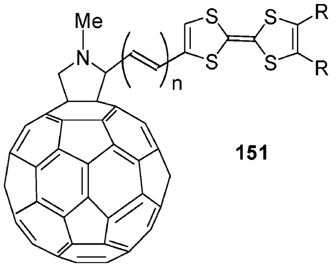
5.1.2.2. Synthesis of Pyrrolo-TTF. New pyrollo-TTFs developed by Becher et al. have turned out to be versatile building blocks for a number of applications in supramolecular chemistry as outlined in examples recently reviewed.[209] The mono(pyrrolo)-TTF **149** and its related bis(pyrrolo)TTF **150** were synthesized as illustrated in Scheme 75.

Scheme 75

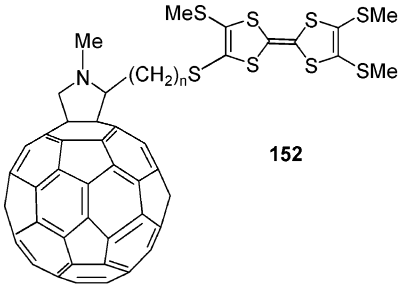


5.1.2.3. Donor–Acceptor Assemblies with C_{60}. Since the discovery of fullerene C_{60}[210] and techniques for its large-scale preparation, development of the molecular chemistry of C_{60} has emerged as a promising field in materials science. Consequently,

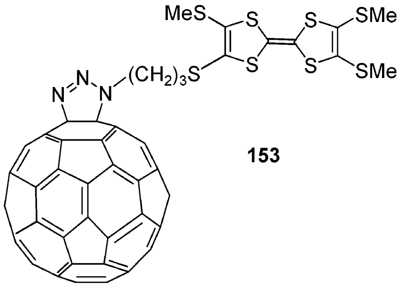
Chart 16



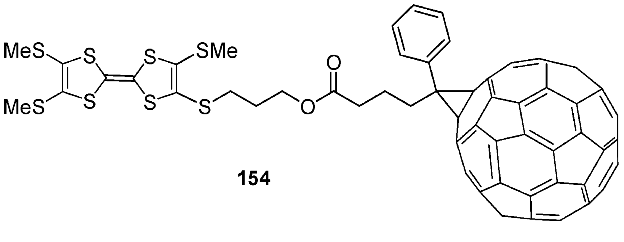
151



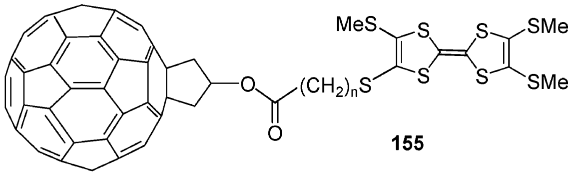
152



153



154



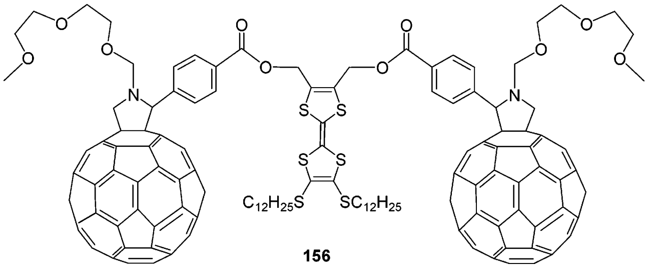
155

the possibility of modifying fullerenes has made C_{60} very exciting to build new molecular assemblies with remarkable physical and chemical properties. The electron-accepting character[211] combined with photophysical properties[212] make C_{60} a very promising starting material for photodriven redox processes. Thus, C_{60} derivatives can interact with π-donor polymers giving rise to long-lived photoexcited species which are useful in the conversion of solar energy.[213] Considerable efforts have been devoted in recent years to the development of systems in which C_{60} is covalently linked to an electron donor.[214] Such molecular assemblies are of particular interest in that they can exhibit characteristic electronic and excited-state properties, which make them promising candidates for investigation of photoinduced electron-transfer processes and long-lived charge-separated states $D^{\bullet+}-C_{60}^{\bullet-}$ [215] with potential applications for molecular electronic devices[216] and photovoltaic cells.[213f,217]

Among the wide variety of donor molecules that have been recently linked to C_{60}, the strong donor tetrathiafulvalene (TTF) has emerged, giving an interesting class of compounds in light of increasing stabilization of the charge-separated state $TTF^{\bullet+}-C_{60}^{\bullet-}$.[218] This peculiarity is due to the gain of aromaticity as a result of the formation of the thermodynamically very stable heteroaromatic 1,3-dithiolium cation(s) upon oxidation(s) of the TTF molecule which is nonaromatic in its ground-state configuration.[219] On this basis, TTF derivatives have been covalently linked to C_{60} through a flexible spacer using several synthetic methodologies,[220] affording more and more sophisticated C_{60}-based molecular assemblies. 1,3-Dipolar cycloaddition following Prato's procedure appeared as one of the most developed strategies,[221] for example, in the synthesis of the dyads **151**[222] and **152**.[223] This methodology was extended to the synthesis of the fullerotriazoline **153** obtained by cycloaddition of an azide derivative to C_{60}.[224] The Bingel cyclopropanation reaction was also used as a powerful tool to prepare C_{60}-based dyads such as **154**,[225] and recently, the chemical reactivity of the C_{60}^{2-} dianion was applied to the preparation of new C_{60}-based assemblies **155**, Chart 16.[226]

Triads were also developed to increase interactions between the chromophores in the ground state and in a long-lived charge-separated radical pair. Such an assembly **156** was prepared using DMAD as starting material. Thus, bis(hydroxymethyl)TTF was reacted with a fullerene derivative in the presence of DCC-DMAP to yield the $C_{60}-TTF-C_{60}$ triad **156** in 43% yield. Although no significant electronic interactions were found between the electroactive species in the ground state, an efficient intramolecular electron transfer occurred in the excited state, resulting in the formation of a long-lived charge-separated state (121 ns in DMF), Chart 17.[122]

Chart 17

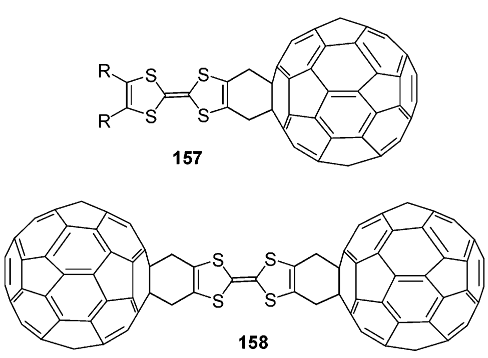


156

In a strategy to control the relative orientation as well as the distance between the TTF and C_{60} counterparts, the $TTF-C_{60}$ **157** and the dumbbell C_{60}-$TTF-C_{60}$ **158** rigidified systems were designed as targets using [4+2] Diels−Alder cycloaddition. This type of cyclohexene bridge had previously proven to be very efficient for mediating electron- and energy-transfer between two electroactive centers by a through-bond coupling mechanism which appeared to be independent of length, Chart 18.[227]

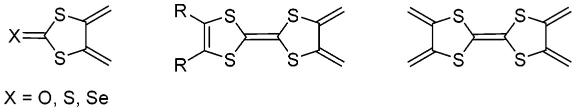
Two different routes were considered for the synthesis of these donor−acceptor systems: (i) formation of the TTF core by a coupling reaction using well-known procedures[19,21−23] from 2-oxo-(or 2-thioxo or 2-selenoxo)-1,3-dithioles or dithiolium salts and (ii) [4+2] Diels−Alder cycloaddition to prepare the cyclohexene ring from a preformed TTF. In these cases,

Chart 18



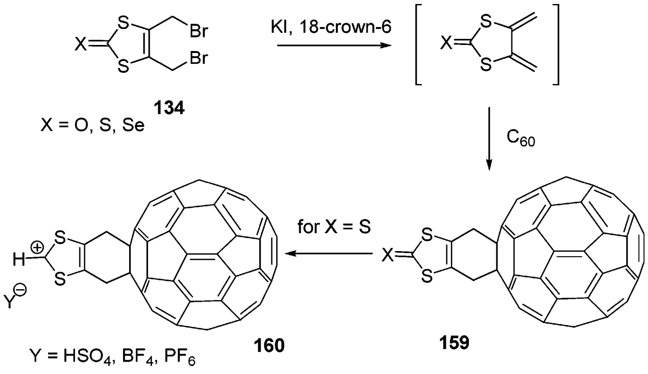
the synthesis used diene intermediates which constitute heteroatomic analogues of *o*-quinodimethane, C_{60} being used as the dienophile, Chart 19.

Chart 19



While the synthesis of new π-electron donors based on the TTF core has been particularly fruitful and varied, the possibility of developing chemistry in this family from a diene group able to react through Diels−Alder cycloaddition was surprisingly missing. Clearly this research area has been restricted by lack of suitable TTF building blocks. The approach developed by our group was based on the synthesis of precursors such as the vicinal bis(bromomethyl) 2-oxo (or 2-thioxo or 2-selenoxo)-1,3-dithioles **134**, which were able to smoothly undergo reductive elimination on treatment with naked iodide to give rise to dienes (Scheme 76).[228] Unfortunately, attempts to complete a symmetrical trialkyl-phosphite-mediated coupling reaction or to use the dicobalt octacarbonyl method from the different 1,3-dithiole-C_{60} systems **159** or 1,3-dithiolium-C_{60} salts **160** to prepare the dumbbell **158** failed. Dissymmetrical coupling involving other 2-(thi)oxo-1,3-dithioles was also unsuccessful in attempts to prepare the dyads **157**.

Scheme 76



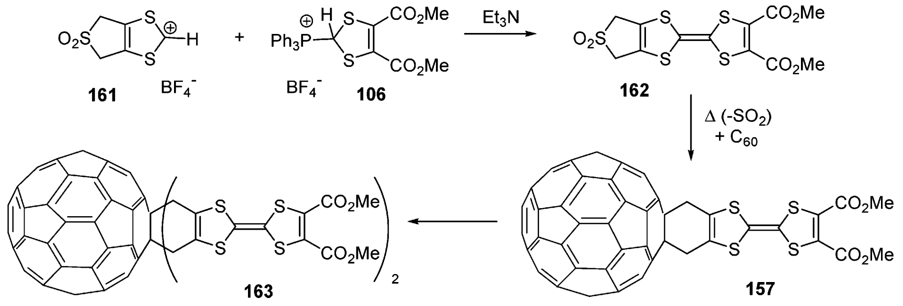
Simultaneously, the group of Rovira et al. developed the synthesis of 2,3-dimethylidene[2*H*]-TTF by in situ thermal extrusion of sulfur dioxide from a sulfone group and our group achieved reductive elimination of the diene precursors bis(bromomethyl)-TTF derivatives. Coupling of the phosphonium salt **106** (with R = CO_2Me) with the appropriate 1,3-dithiolium salt **161** promoted formation of the expected dissymmetrical TTF derivative **162**.[181] Diels−Alder functionalization of C_{60} was achieved using a thermolabile sulfone as the diene precursor to prepare the dyad **157** in which the TTF core was substituted with methoxycarbonyl substituents (Scheme 77).[229] A second identical TTF derivative could be condensed on C_{60} to yield the C_{60}−$(TTF)_2$ triad **163**. The first isolation and characterization of two and four regioisomers of this triad was achieved by a combination of HPLC, UV−Vis spectroscopy, and HMBC NMR.[230]

Treatment of the bis(bromomethyl)TTF derivatives **143** with potassium iodide in the presence of 18-crown-6 generates the transient 2,3-bis(methylidene)-TTF **138,** and final [4+2] cycloaddition can readily be achieved with C_{60}. The reaction proceeds to give the monoadduct **157** as the major product (30−50% yield). New diadducts and unprecedented tri- and tetraadducts **164** were selectively synthesized. Starting from the monoadduct **157**, cycloaddition with the 2,3-bis(methylidene)-TTF **138** afforded diadducts. When this methodology was applied to the triad C_{60}-$(TTF)_2$, the desired triadducts and tetraadducts were isolated in acceptable yields (Scheme 78).[231] Various substituents were introduced to the TTF unit (e.g., polyalkyloxysulfanyl groups) with the aim of increasing the solubility properties of the dyads for physical studies and possible applications.[232]

This strategy was also used to introduce a crown ether-TTF assembly in the preparation of dyad **165**; the influence of C_{60} on the complexation of metal cations into the crown[233] was determined, and the quinonoid π-extended TTF−C_{60} derivative **166** was prepared, Chart 20.[234]

The dumbbell **158** has been prepared from the tetrakis(bromomethyl)TTF **144**. This was converted into tetramethylidene[4*H*]TTF **167** by reductive elimination with naked iodide in the presence of C_{60}

Scheme 77



Scheme 78

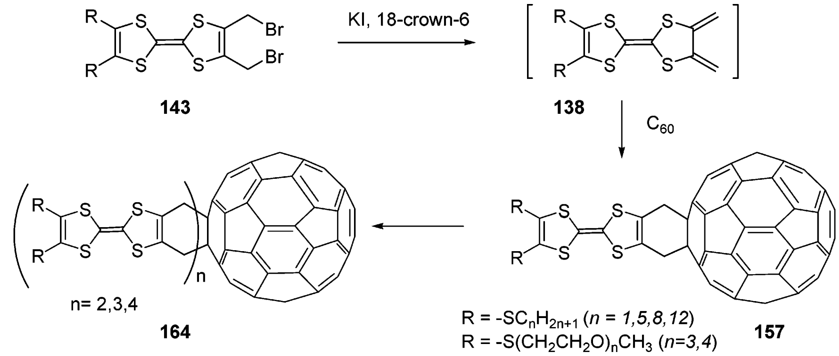
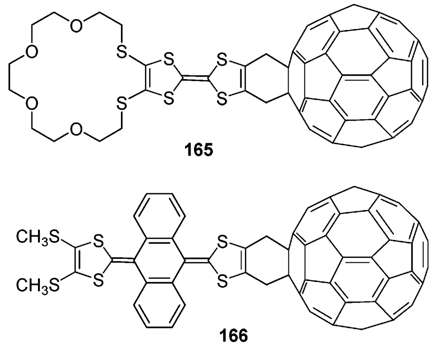


Chart 20



(Scheme 79).[235] To perform further photophysical studies of such assemblies and due to problems resulting from the poor solubility of the dumbbell **158**, an original synthesis of different dumbbells showing interesting solubility properties in various organic solvents was later developed by replacing C_{60} by methanofullerene derivatives.[220]

Electrochemical and optical properties were determined on the neutral and oxidized dyads **157**, the polyads **164,** and the triad **158,** and it was shown that cation radicals and anion radicals display outstanding persistence. Although no significant electronic interaction was found between the electroactive species in the ground state, an efficient intramolecular electron transfer occurred in the excited state, resulting in the formation of a significant long-lived charge-separated state in the case of the soluble dumbbell (20 ns in benzonitrile).[236] These findings suggest that TTF−C_{60} or C_{60}−TTF−C_{60} systems may be promising candidates for the preparation of photovoltaic devices.

5.2. Conversion of Hydroxymethyl Derivatives to Mercaptomethyl Derivatives and the Corresponding Disulfides

The well-known sulfur-rich π-donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) is the basis of two-dimensional conductors and a large number of superconducting cation radical salts endowed with the highest T_c of this type of compound. In the solid-state structure of these compounds, strong sulfur−sulfur intermolecular interactions play an essential role in their well-defined 2D character.[7] The presence of sulfur atoms external to the tetrathiafulvalene core promotes intermolecular interactions that enhance the electronic dimensionality of the salts, avoiding the structural changes that promote metal-to-insulator transitions in 1D conductors and hence allow the transition of the superconducting state.

Efforts in this area have been concentrated in modifying the position of the peripheral sulfur atoms with the aim of establishing specific S···S contacts in the molecular arrangement of related materials. Using this approach in the preparation of new organic conductors, many tetrathiafulvalene derivatives with peripheral sulfur atoms have been synthesized. Such intermolecular interactions have also been described for π-donors that contain peripheral sulfur atoms,[87,237] such as **34a**.[86]

The prominent role of peripheral chalcogen atoms branched on the TTF core was also recognized in the case of bis(ethylenedioxy)TTF, called BEDO-TTF, for which oxygen atoms are responsible for additional intermolecular contacts in the related salts.[238] Thus, bis(oxydimethylene)TTF, called BODM-TTF,[239] obtained by treatment of the tetrakis(hydroxymethyl)-TTF **60** with thionyl chloride, as well as mono- and bis(furano)TTF, F-TTF, and DF-TTF [153] were investigated with the aim of examining the role of peripheral oxygen atoms on the solid-state organization of the resulting cation radical salts, Chart 21.

The bis(bromomethyl)-1,3-dithiole **134** was transformed into sulfide **168** via nucleophilic substitution with sodium sulfide, and aromatization with DDQ afforded the 3,4-substituted thiophene **169**. This methodology has been extended to the incorporation of TTF in the π-extended thiophene monomer **170** with the aim of preparing low-band-gap thiophene polymers. The presence of fused TTF units is expected to be beneficial due to the electronic behavior

Scheme 79

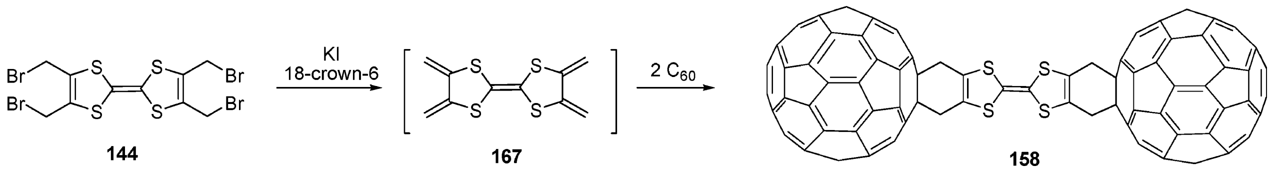
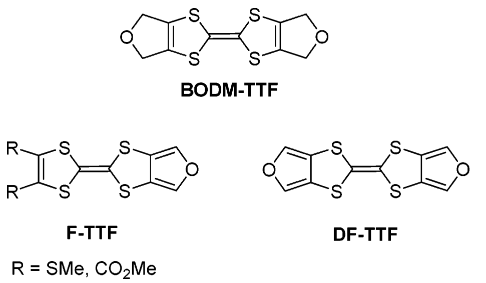
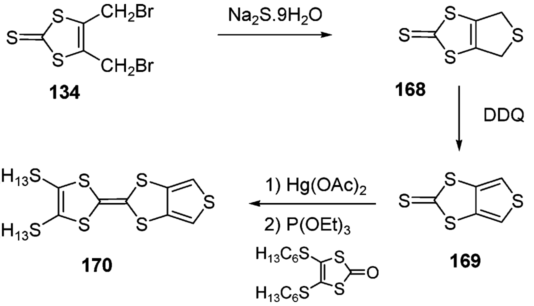


Chart 21



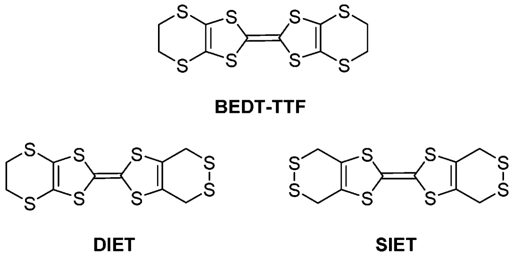
of the polymer and the stabilization of the polymeric quinoid state through the rearomatization of the TTF unit (Scheme 80). [205,240]

Scheme 80



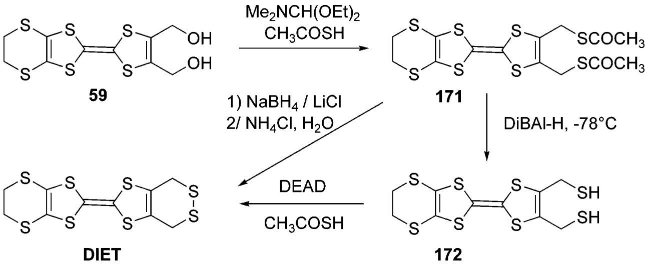
With the aim of understanding the nature of intermolecular interactions in the crystal engineering of molecular materials of the BEDT-TTF (also called ET) family, synthesis of dissymmetrical and symmetrical outer S-positional isomers of BEDT-TTF called **DIET** (dissymmetrical isomer of ET)[241] and **SIET** (symmetrical isomer of ET),[206] respectively, was undertaken, Chart 22.

Chart 22



Using the 2,3-bis(hydroxymethyl)TTF derivative **59** as starting material, generation of a good leaving group was investigated in order to activate nucleophilic substitution and convert the alcohol function into a thioester. Originally activation of the hydroxymethyl group involving *N*,*N*-dimethylformamide diethylacetal reagent was applied, and in the presence of thiolacetic acid, this successfully afforded the corresponding bis(thioester) **171**. The dithiol compound **172** was obtained in excellent yield by reduction using DiBAl-H. Further dehydrogenation with DEAD afforded DIET. It was shown that yields could be improved by using a one-pot reaction after reduction with sodium borohydride in the presence of lithium chloride and subsequent treatment with an aqueous solution of ammonium chloride (Scheme 81).[241]

Scheme 81



For the synthesis of SIET,[206] the first route to provide the key intermediate tetrakis(methylthioester)TTF **173** involved symmetrical coupling of the corresponding 1,3-dithiolium salt **174**. It was demonstrated that an efficient nucleophilic substitution on the 4,5-bis(bromomethyl)-2-(thi)oxo-1,3-dithioles **134** was applicable to reach compound **175** on a large scale. The 1,3-dithiolium salt **174** was produced in excellent yield by methylation followed by reduction then dethiomethylation. The classical carbenoid coupling reaction afforded compound **173,** which was treated with a methoxide solution to cleanly provide the symmetrical S-position isomer of BEDT-TTF. Alternatively, despite its very low solubility, tetrakis(hydroxymethyl)TTF reacted progressively with an excess of *N*,*N*-dimethylformamide diethylacetal and thiolacetic acid to efficiently afford the intermediate **173** (Scheme 82).

This methodology has been extended to the development of S-positional isomers of DMTEDT-TTF[241] **176** and EDT-TTF **177**.[199] For the synthesis of these compounds, the Mitsunobu reaction using DEAD/PPh$_3$ proved to be an efficient method of activation of the hydroxymethyl functionality, and in the presence of thiolacetic acid, the substitution occurred in good yield to give the precursor dithioester TTF, Chart 23.

In addition to discussing the role of peripheral sulfur atoms for TTF materials, one should mention that the dithiol intermediate **173** and targeted disulfides are potentially interesting for developing self-assembled monolayers (SAMs) on a gold substrate. Starting from a 2,3-bis(hydroxymethyl)TTF derivative, Echegoyen et al. reported the preparation of SAMs involving a crown-TTF derivative.[242]

5.3. Cation Radical Salts from S-Positional Isomers of BEDT-TTF

The role of the terminal disulfide bridge(s) in the association mode of the network was evidenced by preparation of cation radical salts by electrocrystallization.[199] Despite the poor contribution of outer sulfur atoms of the disulfide bridge to the HOMO, most of the electrogenerated cation radical salts exhibited interesting structural features with evidence of S···S contacts which are responsible for the crystallographic organization of donors. This was particularly the case for the cation radical salt (**SIET**)$_3$(ClO_4)$_2$, which shows semiconducting properties ($\sigma_{rt} = 10^{-2}$ S·cm^{-1}) and a characteristic "windmill" organization (Figure 3a) which is similarly found in the (**176**)$_2$·$CuCl_4$ salt (Figure 3b).[243]

Scheme 82

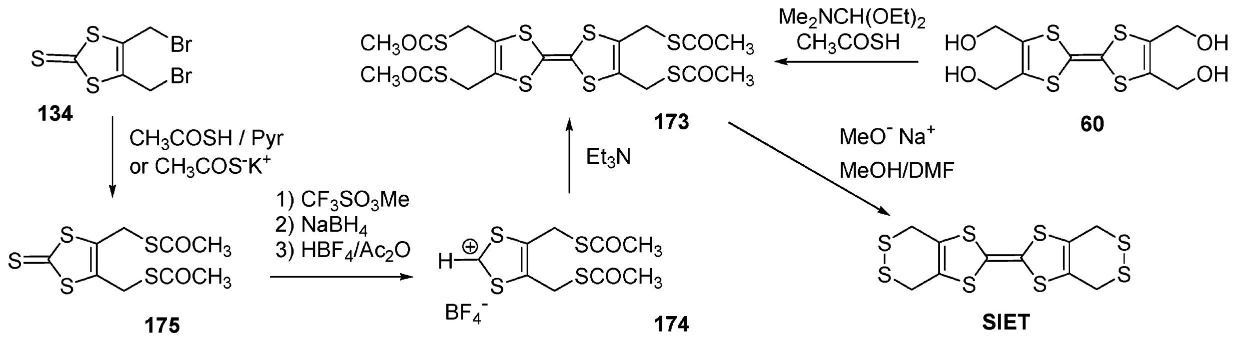
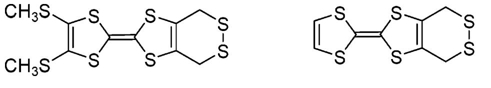


Chart 23



176 S-position isomer of DMTEDT-TTF

177 S-position isomer of EDT-TTF

The prominent role of the outer sulfur atoms in the structural organization of the semiconducting ($\sigma_{rt} = 10^{-4}$ S·cm^{-1}) [1:1] cation radical salt of **SIET** with the polymeric anion Cu(SCN)$_2^-$ has also been demonstrated (Figure 4).[244]

6. Conclusion

It is apparent from the studies discussed in this review that the use of electrophilic alkynes has never stopped occupying a central position in the story of TTF chemistry. Not only do they constitute an efficient entry to basic synthons such as 1,3-dithiole rings or TTF derivatives, but they also allow the introduction of synthetically useful functionalities on the periphery of the TTF framework.

What makes the tetrathiafulvalene unit so fascinating is the fact that it is involved in incredibly varied topics.[8,9] Indeed, applications range from organic electroconducting materials,[5,7] field-effect transistors as very recently demonstrated,[245] magnetic properties,[246] electrooptical properties,[170f,247,248] etc., but concern also its use as a building block in supramolecular chemistry,[16] as a redox sensor in redox-switchable ligands,[249] and even as a catalyst in synthetic radical chemistry.[250] The list of applications above is nonexhaustive and involves the use of different physical forms of TTF (crystalline state or incorporated in LB films, liquid crystals, polymers, gels). Such versatility in the applicability of a single active molecule requires introduction of specific groups on its periphery, and therefore, there is a need to have easy synthetic access to suitably functionalized TTF framework. Though not unique, a very general response to this prerequisite has been given in the last 30 years by using electrophilic alkynes as a common denominator.

The electrophilic character of the starting triple bond, which is generally promoted by the presence of ester(s) or aldehyde(s), is used for incorporation of a C=C fragment in building the TTF core. Different methodologies can be used involving reaction of an electrophilic alkyne with the Bu$_3$P−CS$_2$ complex, with organometallic species, or with a preformed five-membered 1,3-dithiole ring. The classical synthetic transformations of the ester group have also been applied to the TTF series, providing useful access to TTF derivatives functionalized with other trivalent functions (carboxylic acid, acid chloride, acid anhydride, amide). Also, ester reduction gives efficient access to the alcohol function and its derivatives, allowing entry to a wide range of monovalent func-

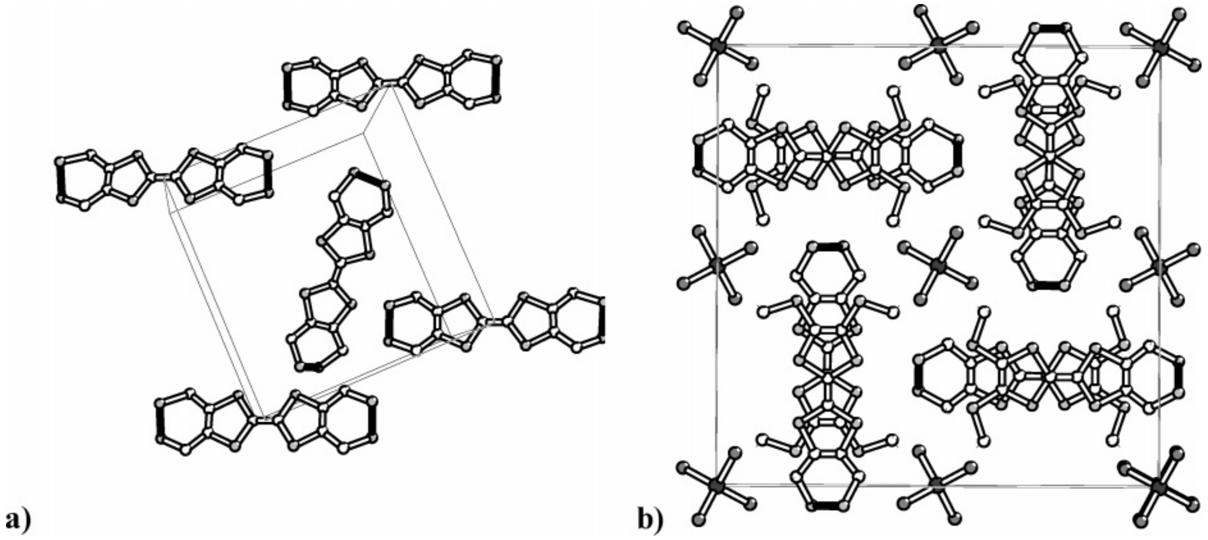


Figure 3. (a) Projection onto the (*bc*) plane of the crystal structure of (**SIET**)$_3$·(ClO$_4$)$_2$ characterizing the "windmill" array (disulfide bond in black line, anions omitted). (b) Crystal structure of (**176**)$_2$·CuCl$_4$ (view along the *c* axis; disulfide bond in black line).

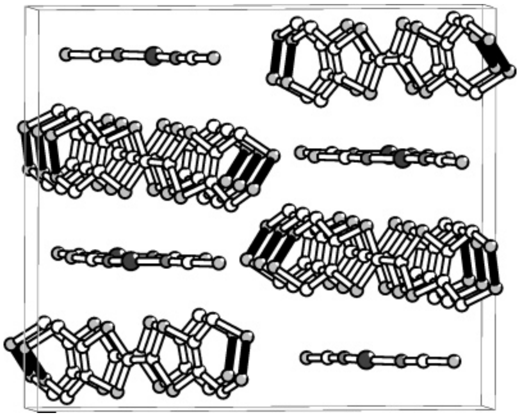


Figure 4. Columnar organization of the cation radical salt (**SIET**)·Cu(SCN)$_2^-$ (disulfide bond in black line, anions omitted).

tions on the periphery of the TTF framework. The preparation of the more synthetically powerful aldehyde by ester reduction remains a puzzling problem in the TTF series, and best results have been obtained by direct introduction of the formyl group using acetylene dicarbaldehyde ADCA or its monoacetal ADCA-MA as the starting electrophilic alkyne. Current interest in these derivatives has been very recently demonstrated by optimization of their syntheses.[141] A detailed illustration of the usefulness of this powerful synthon in the TTF series has been given as well as its efficiency in providing access to highly extended TTF derivatives.

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