

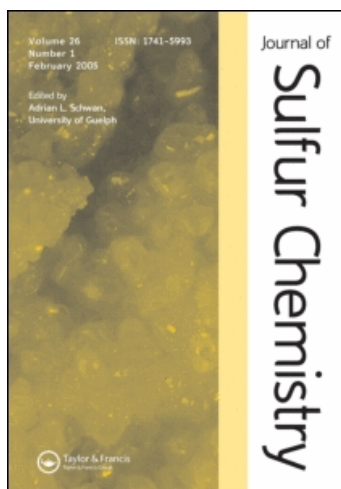
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Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

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To cite this Article Ogura, Fumio , Otsubo, Tetsuo and Aso, Yoshio(1992) 'Design of Novel Chalcogen-Containing Organic Metals: Extensively Conjugated Electron Donors and Acceptors With Reduced On-Site Coulomb Repulsion', *Journal of Sulfur Chemistry*, 11: 3, 439 – 464

To link to this Article: DOI: 10.1080/01961779208048774

URL: <http://dx.doi.org/10.1080/01961779208048774>

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DESIGN OF NOVEL CHALCOGEN-CONTAINING ORGANIC METALS: EXTENSIVELY CONJUGATED ELECTRON DONORS AND ACCEPTORS WITH REDUCED ON-SITE COULOMB REPULSION

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(Received October 7, 1991)

This review describes the design of extensively conjugated electron donors and acceptors based on structural modifications of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ), respectively. These molecules have the advantage of reduced on-site Coulomb repulsion which is one of the prerequisites for components of organic metals. The construction of such large compounds is currently accomplished by insertion of an extensively π -conjugated system between two 1,3-dithiolyldiene or dicyanomethylene groups. The usefulness of a heteroquinoid system as such a building block is demonstrated by examples of heteroatom-incorporating TCNQ acceptors (hetero-TCNQs), which form a variety of highly conductive charge-transfer complexes. In addition, recent advances concerning quino-2,2'-bis(1,3-dithioles) and TTF vinyls as novel electron donors are introduced.

Key words: Conductive charge-transfer complexes, conjugated electron donors and acceptors, design of organic metals, effect of heteroatoms, hetero-TCNQ, reduced on-site Coulomb repulsion.

INTRODUCTION

Ever since the discovery of the charge-transfer complex of tetrathiafulvalene **1** (TTF) and 7,7,8,8-tetracyanoquinodimethane **2** (TCNQ) as a new synthetic metal¹⁻⁷ the development of novel electron donors and acceptors has been of great current interest.⁸ Highly conductive complexes generally consist of segregated columns of the donors and acceptors with incomplete charge transfer. Such components have been proposed to satisfy a number of requirements: ready oxidation or reduction, a high degree of planarity, high symmetry, high polarizability, strong heteroatomic interaction, reduced on-site Coulomb repulsion etc.⁹⁻¹² Reduced on-site Coulomb repulsion contributes to the minimization of the band gap and the enhancement of charge mobility in an

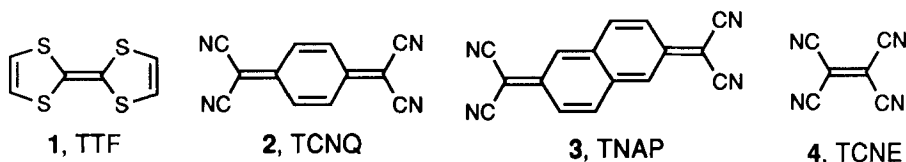
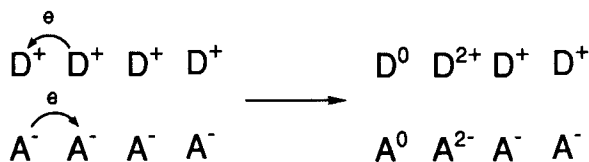


Figure 1.

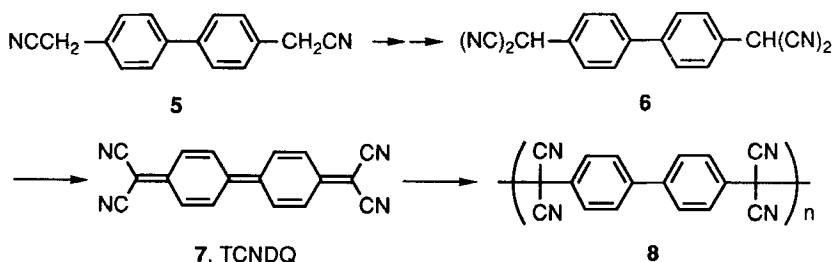


Scheme 1.

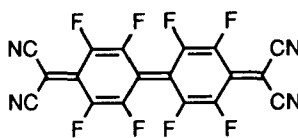
open-shell molecular assembly (Scheme 1). Garito and Heeger first noted the importance of reduced on-site Coulomb repulsion when comparing the reduction potentials of three electron acceptors: TCNQ, $E_{1/2}(1) + 0.13$ and $E_{1/2}(2) - 0.29$ V; tetracyanonaphthoquinodimethane **3** (TNAP), $+ 0.21$ and $- 0.17$ V; tetracyanoethylene **4** (TCNE), $+ 0.15$ and $- 0.57$ V vs. SCE.¹³ The large acceptors TCNQ and TNAP are capable of reducing the intramolecular Coulombic repulsion in the dianionic states as indicated by a decrease in the difference between the two half-wave reduction potentials, forming a variety of metallic complexes including TTF complexes. On the other hand, the small acceptor TCNE possesses a first reduction potential comparable to that of TCNQ or TNAP, but requires much more energy to form the dianion, forming no electrically conductive complexes. The reduced on-site Coulomb repulsion of TCNQ and TNAP is unambiguously responsible for the high conductivities of their complexes. Such large electron acceptors can be formally designed by inserting an extensively conjugated quinoid system between two electron-withdrawing dicyanomethylene groups. In this context the insertion of a heteroquinoid system as a building block is of current interest. The same idea also holds for the modification of the prototypical donor TTF, and consequently *p*-quinodimethane analogs of TTF have been actively studied. In addition, related TTF vinyls are also under current study.

1. EXTENSIVELY CONJUGATED TCNQ AND HETERO-TCNQ HOMOLOGS

Since the successful appearance of TCNQ as a superior electron acceptor, 13,13,14,14-tetracyanodiphenylquinodimethane **7** (TCNDQ) has aroused considerable interest as a promising electron acceptor for superior charge-transfer complexes with large metallic band widths as a result of better overlap of extended π -systems, and smaller on-site Coulomb repulsion due to charge dispersal.¹⁴⁻¹⁸ Its synthesis was attempted in a similar manner as successfully used for TNAP,^{15,19} but the final dehydrogenation in the effort to prepare neutral TCNDQ from the precursor 4,4'-biphenyl- α,α' -dicyanodiacetonitrile **5** failed (Scheme 2). As a result, TCNDQ turned out to be very unstable in the neutral



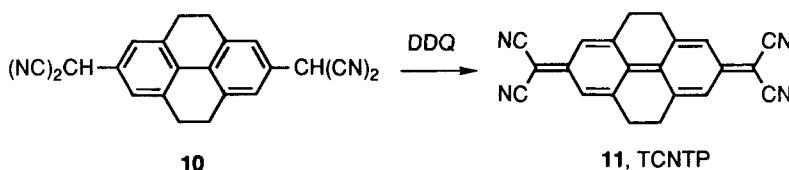
Scheme 2.



9

Figure 2.

state because of its ready polymerization, though its small on-site Coulomb repulsion was evaluated by cyclic voltammetry of its anion salt ($E_{1/2} - 0.16$ and -0.31 V vs. Ag/AgClO_4).¹⁶ This is also the case for the octafluoro derivative **9** ($E_{1/2} + 0.75$ and $+ 0.57$ V vs. SCE).²⁰ The instability of **7** and **9** is attributable to steric interaction between the biphenylic ortho hydrogens or fluorines. This assumption was verified by the isolation of a stable ethano-bridged derivative, tetracyano-4,5,9,10-tetrahydropyrenoquinodimethane **11** (TCNTP) (Scheme 3).^{17,21,22} As expected TCNTP exhibits a highly



Scheme 3.

decreased Coulomb repulsion ($E_{1/2} - 0.15$ and -0.45 V vs. Ag/AgNO_3), but the lower reduction potentials compared to TCNQ or TNAP pose a problem with regard to its complexation.²² Later on the synthesis of pyrenoquinoid compound **12** (TCNP) and its dianion was claimed by Maxfield *et al.* ($E_{1/2} - 0.03$ and -0.34 V vs. Ag/AgNO_3),²³ but the isolation of the neutral molecule was later disproved.^{22,24} As a related heterocyclic compound, Wudl *et al.* reported tetracyanoquinazolinoquinazoline **13** (TCQQ) as a dianion which, however, exhibits uninteresting solid state properties.²⁵ Recently, tetracyanobianthraquinodimethane **16** (TBAQ) was synthesized in high yield by treatment of bianthrone **14** with malononitrile **15** in pyridine (Scheme 4).²⁶ TBAQ is very

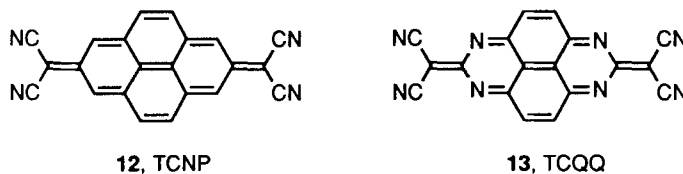
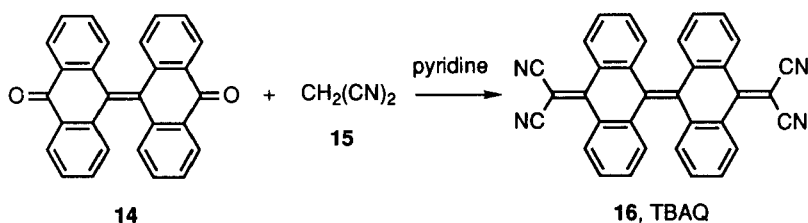


Figure 3.

stable in contrast to TCNDQ, and its cyclic voltammetry exhibits a two-electron redox wave ($E_{1/2} - 0.70$ V vs. SCE). This apparent minimization of on-site Coulomb repulsion, however, is rather ascribable to steric causes than to the extensive conjugation, since even the lower homolog tetracyanoanthraquinodimethane **17** (TCNAQ) shows the same electrochemical behavior.²⁷⁻³² As shown by X-ray analyses both TBAQ and TCNAQ are butterfly-shaped with the central quinoid ring strongly distorted into a boat form



Scheme 4.

because of steric hindrance between the cyano function and the *peri*-hydrogen.^{26,33} Accordingly both compounds, despite their highly reduced Coulomb repulsion, do not form conductive complexes.

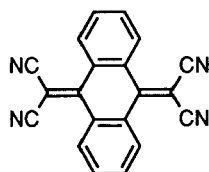
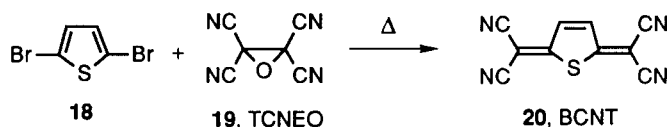
**17, TCNAQ**

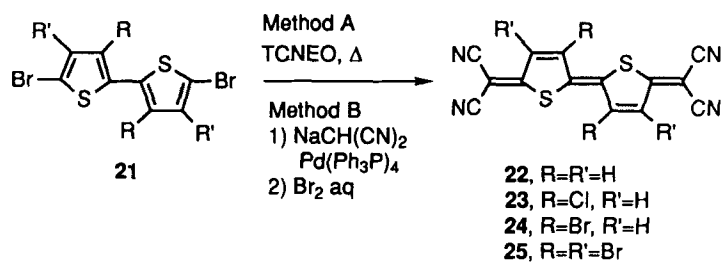
Figure 4.

Gronowitz and Uppström encountered the unusual formation of 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene **20** (BCNT) in the pyrolytic reaction of 2,5-dibromothiophene **18** with tetracyanoethylene oxide **19** (TCNEO) in 1,2-dibromoethane at reflux (Scheme 5).³⁴ The reaction mechanism has not been elucidated yet, but is presumed to involve addition of dicyanocarbene, followed by liberation of halogen. The structure of BCNT was characterized by X-ray crystallography to formally correspond to a heteroquinoid analog of TCNQ (hetero-TCNQ).³⁵ However, it has attracted little attention as an electron acceptor.³⁶ In contrast to the above homoquinoid system, such a heteroquinoid system is suitable for establishing extensive polyconjugation, because it can avoid the steric interaction of the biaryl ortho hydrogens by assuming a *trans*-configuration. In addition, such a hetero-TCNQ acceptor has the advantage of increasing intermolecular interactions due to the heteroatoms embedded in the quinoid system.

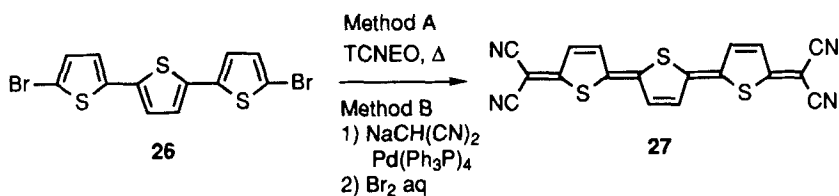


Scheme 5.

The Gronowitz-Uppström reaction was successfully applied to the synthesis of the bi-heteroquinoid compound **22** from 5,5'-dibromo-2,2'-bithiophene **21** (Scheme 6, Method A) and the ter-heteroquinoid compound **27** from 5,5'-dibromo-2,2':5',2''-terthiophene **26** (Scheme 7, Method A).³⁷ The yields are reasonable, but tend to decrease with extension of the conjugation chain (Table 1). The improved syntheses of **22** and **27** were carried out by treatment of **21** and **26**, respectively, with sodium dicyanomethanide



Scheme 6.



Scheme 7.

Table 1. Yields^a and half-wave reduction potentials^b of hetero-TCNQs

Compounds	Yield/%	$E_{1/2}(1)/\text{V}$	$E_{1/2}(2)/\text{V}$	$\Delta E/\text{V}$
BCNT (20)	70	+0.07	-0.54	0.61
22	42 (68)	-0.03	-0.26	0.23
23	30	+0.18	-0.06	0.24
24	27	+0.20	+0.03	0.17
25	12	+0.28	+0.13	0.15
27	11 (73)		-0.03	0
BCNS (28)	47	+0.03	-0.54	0.57
29	28 (26)	-0.05	-0.25	0.20
30	53	+0.15	-0.08	0.23
31	3 (7)		-0.07	0
32	9	-0.07	-0.30	0.23
33	23	+0.11	-0.10	0.21
BCNF (34)	29	+0.03	-0.55	0.58
35	12	-0.09	-0.31	0.22
36	34	+0.08	-0.12	0.20
37	(12)		-0.09	0
38	(25)		-0.01	0
39	(1.5)		+0.14	0
41	17	+0.21	-0.01	0.22
43	36	+0.06	-0.36	0.42
44	40	+0.25	-0.13	0.38
45	39 (78)	+0.05	-0.23	0.28
46	27	+0.16	-0.11	0.27
47	34	+0.28	-0.05	0.33

^aThe yields of the Gronowitz-Uppström method are given, and values in parenthesis indicate those of the nucleophilic substitution method.

^bvs. Ag/AgCl.

Table 2. Stoichiometries, nitrile stretching vibrations, and electrical conductivities of hetero-TCNQ complexes

Complex ^a	D:A	$\nu_{\text{CN}}/\text{cm}^{-1}$	Conductivity ^b / Scm^{-1}
TTF · 20	1:1	2221	6.8×10^{-9}
HMTTeF · 20	1:1	2221	5.5×10^{-9}
TPBP · 20	1:1	2184	4.9×10^{-1}
TTF · 22	1:1	2217	2.2×10^{-4}
TTT · 22	1:1	2219	3.0×10^{-4}
TTF · 23	1:1	2197	19
TTT · 23	1:1	2190	4.6
HMTTF · 23	1:1	2199	6.3
HMTTeF · 23	1:1	2180	170
TMPDA · 23	1:2	2192	7.3×10^{-1}
TPBP · 23	1:1	2193	8.3×10^{-5}
TTF · 24	1:1	2203	15
TTT · 24	1:1	2203	13
HMTTF · 24	1:1	2194	22
HMTTeF · 24	2:1	2169	57
TMPDA · 24	1:1	2198	2.9×10^{-2}
TPBP · 24	1:1	2196	4.5×10^{-1}
TTF · 25	1:1	2200	31
TTT · 25	1:1	2193	18
HMTTF · 25	1:1	2200	39
HMTTeF · 25	1:1	2182	29
TMPDA · 25	2:3	2192	7.1×10^{-1}
TPBP · 25	1:1	2195	11
TTF · 27	1:5	2215	3.3×10^{-3}
TTT · 27	1:1	2204	7.2×10^{-1}
HMTTeF · 27	1:2	2215	1.1
TPBP · 27	2:5	2209	3.7×10^{-1}
TTF · 28	1:1	2230	1.3×10^{-9}
HMTTeF · 28	1:1	2223	3.9×10^{-9}
TTT · 29	1:1	2222	1.1×10^{-4}
HMTTeF · 29	2:1	2221	6.2×10^{-8}
TTT · 30	1:1	2200	11
HMTTeF · 30	1:1	2190	86
TMPDA · 30	1:1	2195	2.9×10^{-1}
TPBP · 30	1:1	2195	4.6
TTT · 32	3:1	2220	3.1×10^{-4}
TTT · 33	1:1	2196	5.8
TTF · 34	1:1	2242	1.0×10^{-10}
TTF · 35	1:1	2228	3.1×10^{-10}
TTF · 36	1:1	2224	1.6×10^{-8}
TTT · 36	1:1	2203	2.4
TPBP · 36	1:1	2200	1.3×10^{-7}
TTT · 38	3:1	2215	1.9×10^{-6}
TTF · 41	1:1	2236, 2213	4.3×10^{-9}
TTT · 41	3:1	2214, 2206	6.0×10^{-4}
TTF · 43	1:1	2199	13
TTT · 43	1:1	2216	1.9×10^{-7}
HMTTF · 43	1:1	2201	4.7
HMTTeF · 43	1:1	2200	140
TMPDA · 43	1:2	2196	5.0×10^{-3}
TPBP · 43	1:2	2195	2.7
TTF · 44	1:1	2195	11

Table 2. Continued

Complex ^a	D : A	$\nu_{\text{CN}}/\text{cm}^{-1}$	Conductivity ^b /Scm ⁻¹
TTT · 44	2 : 1	2194	3.1
HMTTF · 44	1 : 1	2192	7.5
HMTTeF · 44	2 : 1	2192	170
TMPDA · 44	1 : 1	2193	2.0×10^{-1}
TTF · 45	1 : 1	2198	2.3
TTT · 45	2 : 1	2172	3.0
HMTTeF · 45	1 : 1	2200	20
TPBP · 45	1 : 2	2202	6.2×10^{-1}
TTF · 46	1 : 1	2205	23
TTT · 46	1 : 1	2194	5.8
HMTTF · 46	1 : 2	2205	2.3
HMTTeF · 46	1 : 1	2192	14
TMPDA · 46	1 : 2	2197	2.4
TPBP · 46	1 : 2	2190	4.9
TTF · 47	1 : 1	2192	1.2×10^{-2}
TTT · 47	2 : 1	2193	2.1
HMTTeF · 47	2 : 1	2192	7.7
TPBP · 47	1 : 1	2192	7.7×10^{-6}

^aAbbreviation of the donors; TTF: Tetrathiafulvalene; TTT: Tetrathiotetracene; HMTTF: Hexamethylenetetrathiafulvalene; HMTTeF: Hexamethylenetetratellurafulvalene; TMPDA: Tetramethyl-*p*-phenylenediamine; TPBP: Tetraphenylbipyranlydene.

^bElectrical conductivities were measured on compressed pellets at RT.

in refluxing 1,2-dimethoxyethane containing a catalytic amount of tetrakis(triphenylphosphine)palladium(0), followed by oxidation with aqueous bromine (Method B). The bi-heteroquinoid derivatives **23–25** bearing electron-withdrawing halogens were also synthesized in a similar manner. In contrast to the unstable TCNDQ these extended hetero-TCNQs are extremely stable materials whose decomposition points lie above 300 °C. The electronic spectra of a series of the three hetero-TCNQs **20**, **22**, and **27** fairly resemble one another in shape, but their absorption maxima are largely bathochromically shifted to the visible region with extension of the conjugation system; UV/VIS data of **20**: 330 nm (log ϵ 3.81), 400 (4.26) 421 (4.31); **22**: 343 (3.85), 525 (4.82), 550 (4.86); **27**: 304 (3.67), 358 (3.66), 415 (3.88), 643 (5.03). In cyclic voltammetry, BCNT shows lower first and second reduction potentials than does TCNQ (+0.25 and -0.47 V vs. Ag/AgCl), reflecting less aromaticity of the central heterocyclic ring formed upon reduction. The first half-wave reduction potentials of **22** and **27** are furthermore lower than that of BCNT (Table 1). However, the difference between the first and second waves becomes rather small, demonstrating effective reduction of the on-site Coulomb repulsion in the dianionic states. In particular, the second wave of **27** coalesces into the first one as if the on-site Coulomb repulsion had been minimized. The series of hetero-TCNQs **20**, **22**, and **27** form charge-transfer complexes with some strong electron donors such as TTF, HMTTeF (hexamethylenetetratellurafulvalene), TPBP (tetraphenylbipyranlydene), and TTT (tetrathiotetracene) (Table 2). These complexes, except TPBP · **20**, TTT · **27**, and TPBP · **27**, are essentially nonionic owing to the weak electron affinities of the acceptors, judged by absent or small shifts of the nitrile stretching vibrations in the IR spectra on complexation.³⁸ Their electrical conductivities are generally low, but tend to increase with extensive conjugation of the acceptor, demonstrating the apparent effect of reduced

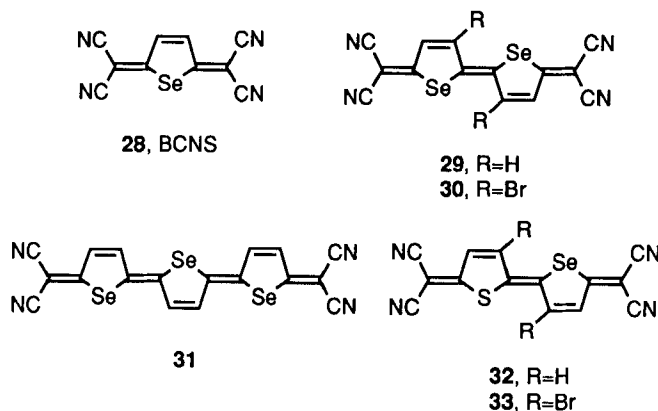


Figure 5.

on-site Coulomb repulsion. On the other hand, the modified halo derivatives **23–25** have high reduction potentials comparable to that of TCNQ, forming a variety of molecular complexes with considerable charge transfer. Most of the complexes are very highly conductive and show a broad electronic absorption in the infrared region, being characteristic of a segregated stacked structure in the mixed valence state.³⁹

Since selenium-containing compounds generally tend to be more conducting than their sulfur-containing counterparts and stay metallic down to lower temperatures, 2,5-bis(dicyanomethylene)-2,5-dihydroselenophene **28** (BCNS) and the conjugated homologs **29–31** attracted interest. They were similarly prepared by the Gronowitz-Uppström reaction and/or nucleophilic substitution with sodium dicyanomethanide.^{34,40} The hybrid compounds **32** and **33** linking both thienoquinoid and selenoquinoid systems were also prepared.⁴¹ These selenium-containing compounds possess almost the same accepting abilities as their sulfur counterparts and form similar complexes (Tables 1 and 2); the solid-state properties of the hetero-TCNQ complexes are little influenced by the intramolecular structural disorder of sulfur and selenium.

In connection with the strong interaction of chalcogen atoms incorporated in organic metals, oxygen-containing organic metals are a current synthetic target.⁴² As novel oxygen-containing electron acceptors, 2,5-bis(dicyanomethylene)-2,5-dihydrofuran **34** (BCNF) and the bi-quinoid homologs **35** and **36** were successfully prepared by the Gronowitz-Uppström reaction. However, the ter-quinoid homologs **37–39** could not be prepared by the same reaction but only by substitution with sodium dicyanomethanide in the presence of tetrakis (triphenylphosphine)palladium(0) as a catalyst, followed by

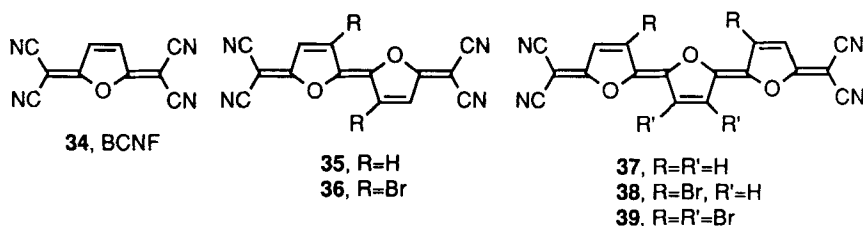
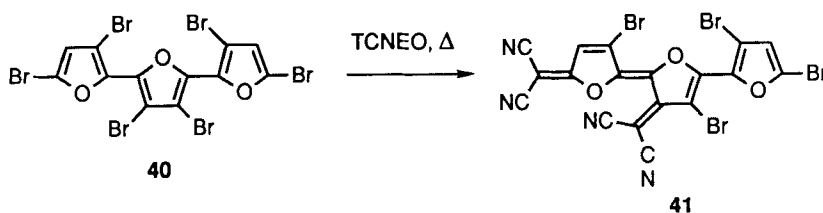


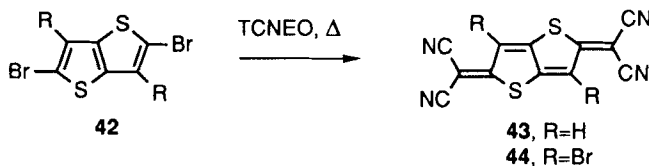
Figure 6.

oxidation with DDQ.⁴³ The reaction of 3,3',3'',4',5,5''-hexabromo-2,2':5',2''-terfuran **40** with TCNEO gave the unusual compound **41** whose structure contains a unique 2,3-furanoquinoid conjugation in the central heterocycle (Scheme 8). BCNF and the conjugated homologs **35–39** are somewhat weaker electron acceptors than their sulfur or selenium counterparts, forming less conductive complexes except for the TTT-**36** complex. In contrast, compound **41** has a relatively strong accepting ability comparable to that of TCNQ, but forms an almost insulating complex with TTF and a semi-conductive complex with TTT. The crystal structure of the TTF-**35** complex reveals that the oxygen embedded in the quinoid conjugation unlike sulfur or selenium does not take part in appreciable nonbonded interactions.



Scheme 8.

Other potential tetracyanoheteroquinodimethanes are of the fused type. 2,5-Bis(dicyanomethylene)-2,5-dihydrothieno[3,2-*b*]thiophene **43** is the first molecule of this type and isoelectronic with TNAP. The reaction of 2,5-dibromothieno[3,2-*b*]thiophenes **42** with TCNEO gave **43** in a reasonable yield (Scheme 9).⁴⁴ The Gronowitz-Uppström reaction was equally well applicable to the syntheses of its derivative **44** and the additional extended homologs **45–47**. Compounds **43** and **45** possess almost the same first reduction potentials as BCNT, but higher second reduction potentials (Table 1). In this regard, it may be concluded that the hetero-TCNQs of the fused type behave as better electron acceptors than those of the above chain type. They thus readily give conductive complexes with strong heteroatomic interactions in their crystal structures.⁴⁵ Furthermore, the dibromo derivatives **44** and **46** form a variety of highly conductive complexes (Table 2). As an exception, the sulfone acceptor **47**, in spite of its very strong accepting ability, can not give so many conductive complexes because of the steric bulk of the sulfone moiety.



Scheme 9.

Hünig *et al.* recently reported 2,5-bis(cyanoimino)-2,5-dihydrothieno[3,2-*b*]thiophene **49** (DCNTT) and its derivatives **50–57**, which are accessible from a mixture of the corresponding quinone **48**, bis(trimethylsilyl)carbodiimide, and TiCl_4 in 1,2-dichlorobenzene at 60 °C (Scheme 10).⁴⁶ These compounds are regarded as the extended heteroquinoid analogs of *N,N'*-dicyanoquinone diimine **58** (DCNQI),⁴⁷ which is a new electron

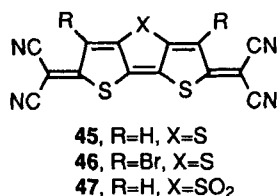
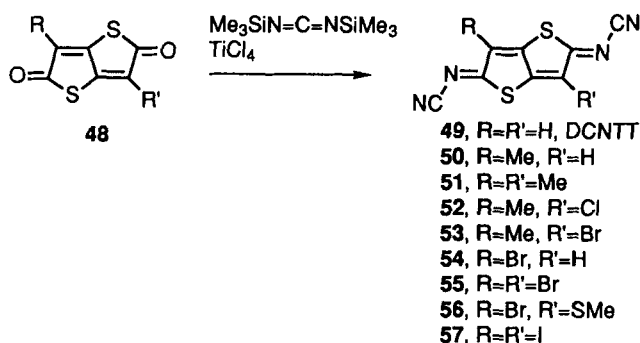


Figure 7.

acceptor comparable to TCNQ. They also behave as good electron acceptors with small on-site Coulomb repulsion and react with TTF and related donors, forming complexes with high powder conductivities: TMTTF-**52**, 0.01 Scm⁻¹; TMTTF-**53**, 2.0 Scm⁻¹; TTF-**55**, 0.07 Scm⁻¹; TMTTF-**55**, 1.2 Scm⁻¹; TTT-**55**, 0.05 Scm⁻¹; TTF-**56**, 0.40 Scm⁻¹; TTF-**57**, 0.06 Scm⁻¹; TMTTF-**57**, 0.15 Scm⁻¹; TTT-**57**, 0.20 Scm⁻¹. In particular, single crystals of the TMTSeF-**55** complex show an unusually high conductivity (120–200 Scm⁻¹) with metallic behavior down to 120 K.



Scheme 10.

2. EXTENSIVELY CONJUGATED TTF HOMOLOGS

An attempt to design novel electron donors with extensive conjugation has been recently made in the TTF series. *p*-Quino-2,2'-bis(1,3-dithiole) **59** (QBD) is the first representative of this class noted, without details, in an early patent.⁴⁸ However, compounds of this quinoid type turned out to be rather air sensitive and to rapidly decompose in solvents. Therefore, the diphenyl derivative **65**⁴⁹ and the tetramethyl derivative **66**⁵⁰ were isolated only as the corresponding dication salts **63** and **64** (Scheme 11), which were used to form some complexes of **65** and **66** by methathesis (Table 3). A number of compounds

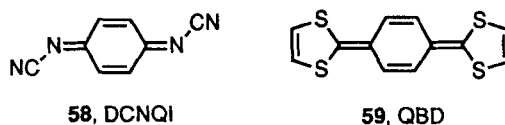
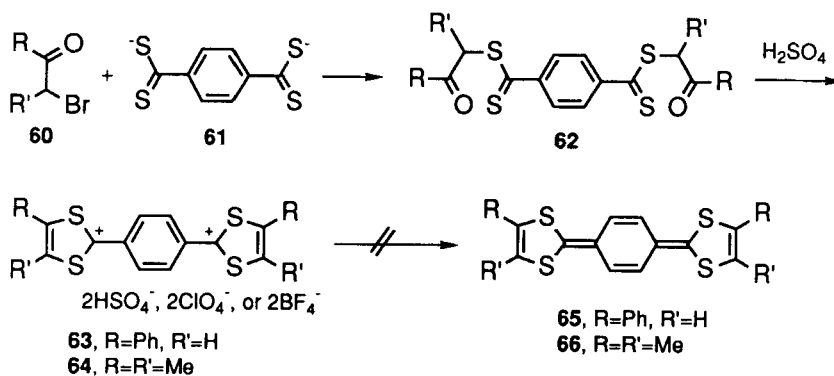


Figure 8.



Scheme 11.

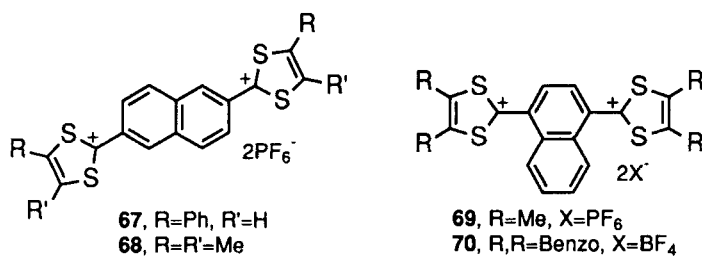
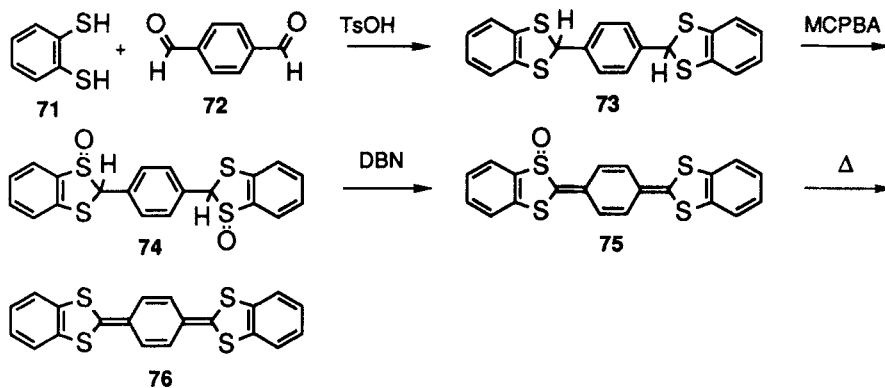


Figure 9.



Scheme 12.

consisting of naphthoquinoid systems were also synthesized as their dications **67–68**,^{51,52} **69**,⁵³ and **70**.⁵⁴ The reported examples of the isolated neutral donors are limited to the dibenzo-annelated derivatives **76**⁵⁵ (Scheme 12) and **79**⁵⁶ (Scheme 13). However, Yamashita *et al.* recently reported the ready synthesis of the parent QBD compound **59** using a Wittig-Horner reaction between 2,3-dimethylphosphono-1,3-dithiole **80** (R = H)⁵⁷ and the cyclopentadiene adduct of *p*-benzoquinone **81**, followed by a retro-

Table 3. Half-wave oxidation potentials of quino-bis(1,3-dithioles) and electrical conductivities of their complexes

Compound	$E_{1/2}/V^a$	Conductivity/ Scm^{-1} (Acceptor) ^h	Reference
59	-0.11, -0.04	5.3×10^{-4} (TCNQ)	58
65		1.2×10^{-6} (I)	49
66		1×10^{-3} (TCNQ), 5×10^3 (ClO_4) ⁱ , 10 (BF_4)	50
67		$< 1 \times 10^{-5}$ (I)	51
69	+0.03 ^{b,c}	6×10^{-2} (TCNQ), 2×10^{-8} (DDQ), 1×10^{-12} (I)	53, 62
76		4.1×10^{-3} (TCNQ)	58
79		3.6×10^{-6} (DDQ)	56
85	0.00	2.9×10^{-2} (TCNQ)	58
86	-0.04	1.9×10^{-2} (TCNQ)	58
87	+0.18	1.9×10^{-2} (TCNQ)	58
88	+0.15	2.2×10^{-2} (TCNQ)	58
89	+0.24		58
90	+0.55 ^{d,f}		59
91	+0.52 ^f		59
92	+0.54 ^f		59
93	+0.23, +0.43 ^e		60
94	+0.17, +0.35 ^e	5×10^{-1} (TCNQ), 2×10^{-1} (ClO_4) ⁱ	60
95	+0.33, +0.49 ^e		60
96	+0.37, +0.61 ^f	6.3×10^{-1} (TCNQ), 1.1×10^{-3} (I)	61
97	+0.31, +0.56 ^f	4.8×10^{-2} (TCNQ), 5×10^{-3} (I)	61
98	+0.44, +0.67 ^f	1×10^{-2} (I)	61
100	+0.25 ^d	4×10^{-3} (TCNQ)	58, 62
101	+0.42 ^{b,c}	60 (TCNQ) ⁱ	62
103	+0.39	$< 10^{-8}$ (I), 1.1×10^{-8} (DDQ)	64
116	+0.78 ^{d,f}	2.9×10^{-2} (I)	64
117	+0.65	1.2×10^{-2} (I), 7.1×10^{-3} (DDQ), 1.4×10^{-3} (ClO_4)	64
118	+0.70	5.6×10^{-3} (I), 2.1×10^{-3} (DDQ), 1.4×10^{-3} (ClO_4)	64
119	+0.66 ^f		61
120	+0.61 ^f		61
121	+0.04, +0.31 ^f	1.3×10^{-2} (TCNQ), 1.3×10^{-7} (DDQ), 1.2×10^{-1} (I)	67
122	+0.09, +0.40 ^f	1.4×10^{-7} (DDQ), 3.3×10^{-3} (I)	67
123	+0.34, +0.58 ^g	8.3×10^{-3} (TCNQ), 1.6×10^{-4} (DDQ), 3.7×10^{-7} (I)	68
124	+0.30, +0.54 ^g	2.0×10^{-2} (TCNQ), 1.8×10^{-3} (DDQ), 3.3×10^{-5} (I)	68
125	+0.28, +0.52 ^g	1.6×10^{-3} (DDQ), 2.1×10^{-3} (I)	68

^aCyclic voltammetry was carried out in acetonitrile with SCE as the standard electrode unless otherwise stated;

^bvs. Ag/AgCl;

^cOxidation peak potential;

^dIrreversible;

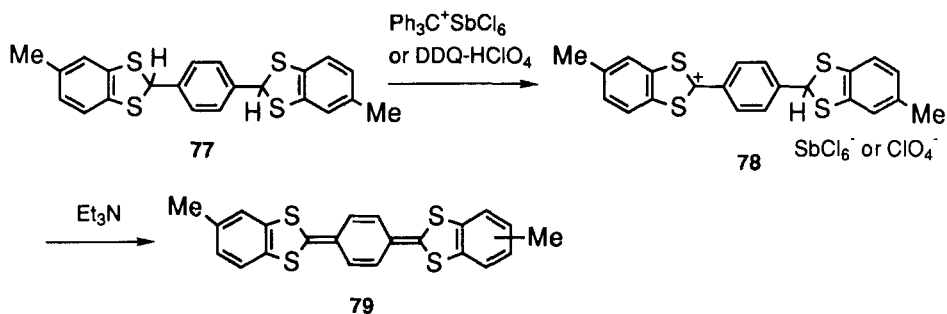
^eIn benzonitrile;

^fIn dichloromethane;

^gIn propionitrile;

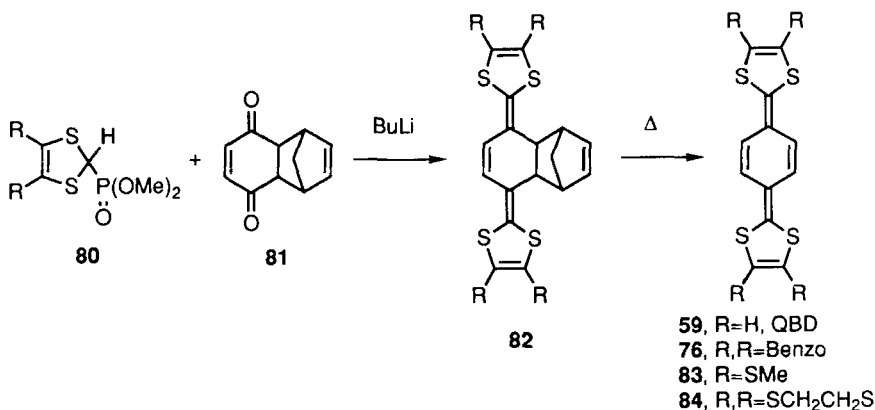
^hOn a compressed pellet;

ⁱOn a single crystal.



Scheme 13.

Diels-Alder reaction under high vacuum (Scheme 14).^{58,59} This method was applied to the syntheses of not only the dibenzo-QBD derivative **76**⁵⁸ and the tetrathio-QBD derivatives **83** and **84**,⁵⁹ but also of a number of monoannulated quinoid derivatives **85–89**.^{58,59} In addition, the thiadiazolo- and selenadiazolo-quinoid derivatives **90–92**⁵⁹ and



Scheme 14.

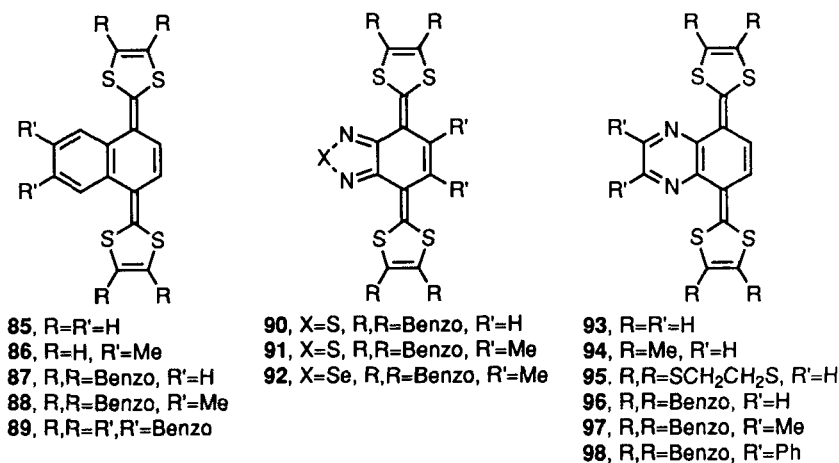
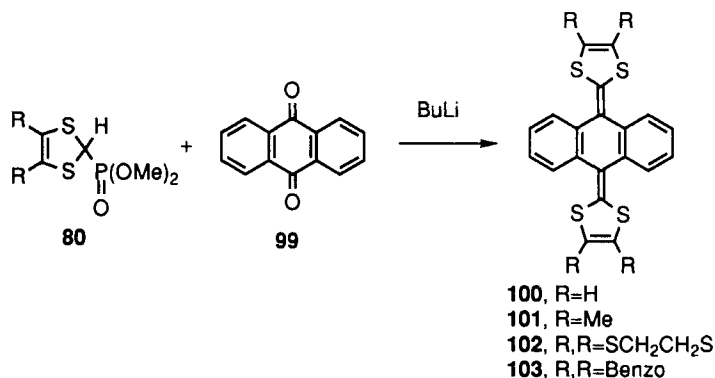


Figure 10.



Scheme 15.

the pyrazino-quinoid derivatives **93–95**⁶⁰ and **96–98**^{59,61} are also available. Here the electron-withdrawing heterocycles serve to stabilize the quinoid structure. On the other hand, the bis-annulated quinoid derivatives **100**,^{58,59,62} **101**,⁶² **102**,⁶³ **103**,⁶⁴ and **104–107**⁶² have been synthesized by direct Wittig–Horner reaction of the corresponding anthraquinone, naphthacenequinone, or bianthrone (Scheme 15). The unsymmetrical derivatives **108** and **109**,⁶⁵ the selenium-containing derivatives **110–112**,^{62,65} and the heteroring-containing derivatives **113–118**^{64,66} and **119–120**⁶¹ are also known. Takahashi *et al.* recently synthesized the tetramethyl and diphenyl derivatives of thienoquinoid-inserted bis(1,3-dithiole) as their dication salts **121** and **122**⁶⁷ and the corresponding dibenzo derivatives as the neutral species **123–125**.⁶⁸

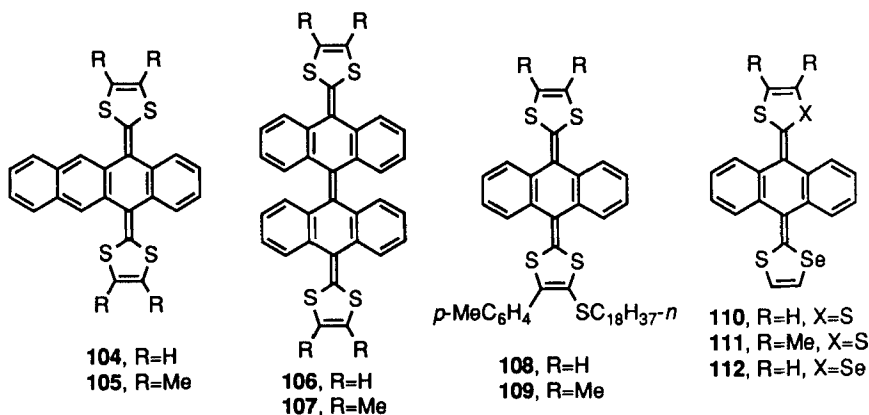


Figure 11.

The quinobis(1,3-dithioles) possess considerably lower oxidation potentials than TTF ($E_{1/2} + 0.28$ and $+0.64$ V vs. SCE), since the central quinonic π -systems form a new aromatic sextet upon oxidation (Table 3). In particular, the parent QBD is an extremely strong donor, and the annelation at both 1,3-dithiole and quinoid rings tends to decrease the donor ability. The thienoquinoid compounds **121–125** do not exhibit as low oxidation potentials as the corresponding homoquinoid analogs, but are still strong donors. In addition, these extended structures reduce the difference between the first and second

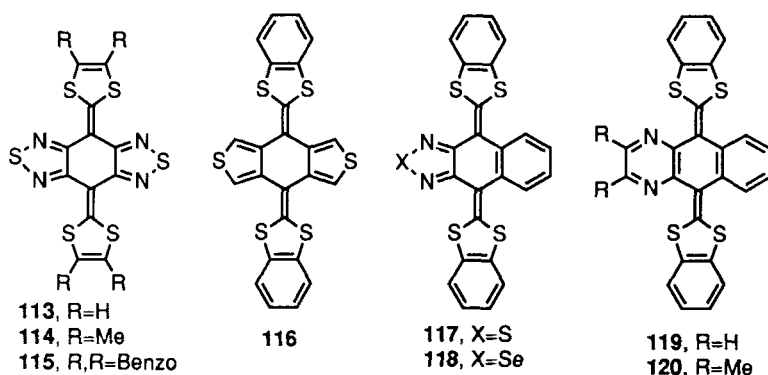


Figure 12.

oxidation potentials which mostly leads to their coalescence. The quinobis(1,3-dithioles) form a few charge-transfer complexes with TCNQ, iodine, or DDQ as well as radical cation salts (Table 3). Their conductivities are generally in a wide range from metallic to insulating, and the effect of reduced Coulomb repulsion is not so much marked as seen in the case of hetero-TCNQ acceptors. Yamashita *et al.* found an unusually high electrical conductivity of bis[1,2,5]thiadiazolo-*p*-quino-2,2'-bis(1,3-dithiole) **113** for a single component (10^{-3} Scm^{-1}). This is considered to be due to a sheet-like network structure of **113** with short S-S contacts.⁶⁶

Another interesting type of extended TTF are TTF vinylogs involving an ethanediylidene or butenediylidene unit in the central conjugation between the two dithiole rings, which were mainly studied in detail by the Kyoto group. The syntheses of ethanediylidene-2,2'-bis(1,3-dithiole) **129**⁶⁹ and its various derivatives **130–134**⁶⁹ and **135–137**⁷⁰ are based on the Wittig reaction of a (1,3-dithiole)phosphonium salt with an appropriate aldehyde (Scheme 16). The selenium counterparts **138** and **139** are also known.^{69,71} By an alternative method, the dibenzo-annelated compounds **132** and **143** were prepared by treatment of 1,2-benzenedithiol **140** with 2,5-dimethoxytetrahydrofuran **141**, followed by hydride abstraction and deprotonation (Scheme 17).^{52,72,73} Furthermore, the 1,4-butenediylidene-2,2'-bis(1,3-dithioles) **145**, **146**, and **151** have been synthesized by either of the following two methods: reductive coupling of aldehyde **144** with $\text{TiCl}_4\text{-LiAlH}_4$ (Scheme 18) and desulfurization coupling of thioaldehyde **149** (Scheme 19).⁷⁴ As expected, these compounds have low reduction potentials as well as small Coulomb repulsion, and form complexes with TCNQ or 2,5-dimethyl-TCNQ.⁶⁹ Although the **129**·TCNQ complex shows the high conductivity of 16 Scm^{-1} with metallic

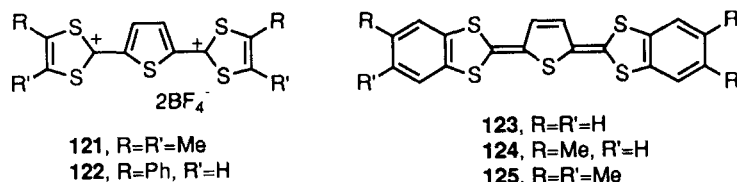
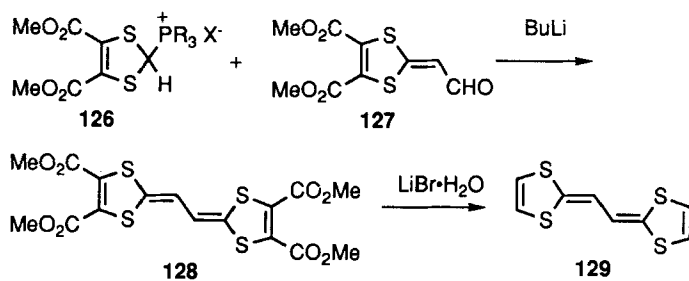


Figure 13.



Scheme 16.

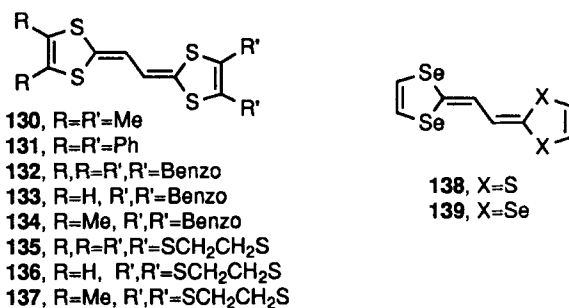
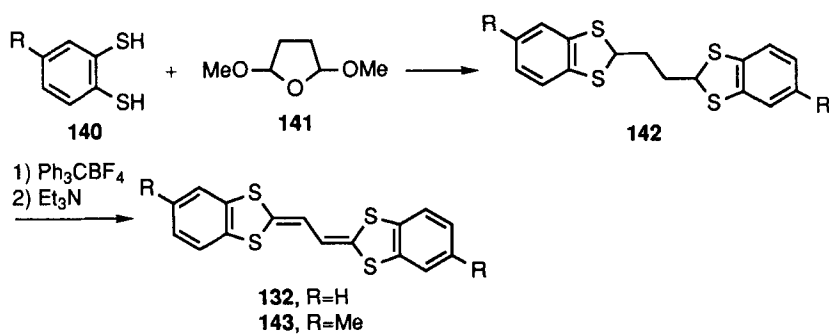
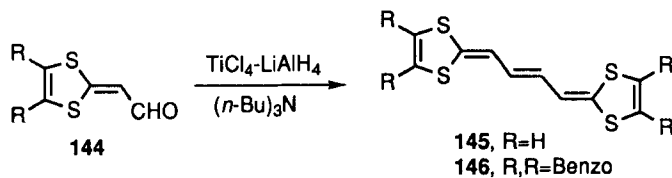


Figure 14.



Scheme 17.



Scheme 18.

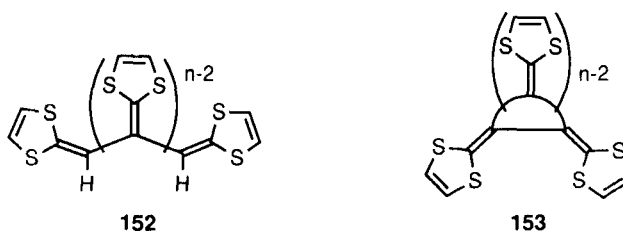
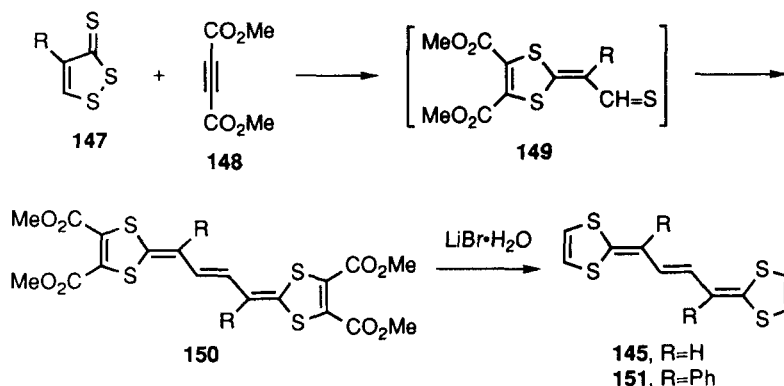


Figure 15.

behavior down to 200 K, most of the compounds are semiconductive. Furthermore, Sugimoto *et al.* extended their research on TTF vinylogs to the novel compounds dendralene **152**⁷⁵ and radialene **153**⁷⁶ with multi-1,3-dithiole rings. The latter compound is of current interest with regard to the elaboration of organic ferromagnets.⁷⁷

The TTF homologs **154** and **155**, inserted with a cumulenenic unit as the extending block, have been also studied, but could not be isolated as the neutral species owing to their instability.⁷⁸ On the other hand, the compounds **156–158** containing an acetylenic unit were recently synthesized, but they do not behave as good electron donors, forming only nonconductive complexes.⁷⁹ The new giant TTF analogs with 1,4-dithiafulven-6-yl substituents **159** and **160**,⁸⁰ their vinylogs **161–164**,⁸¹ and similar giant benzenic donors **165–167**⁸² were recently reported. These compounds react with TCNQ to form black conductive complexes. Also known are extended TTF molecules incorporating a biphenylic framework (**168**⁸³), a pentalene framework (**169**⁸⁴), and a 1,6-methano[10]annulene framework (**170** and **171**⁸⁵). Of them, only **170** was reported to give complexes with DDQ and iodine, both semiconductive.

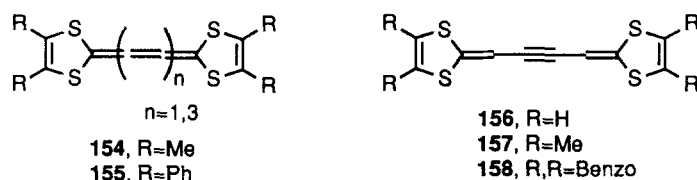


Figure 16.

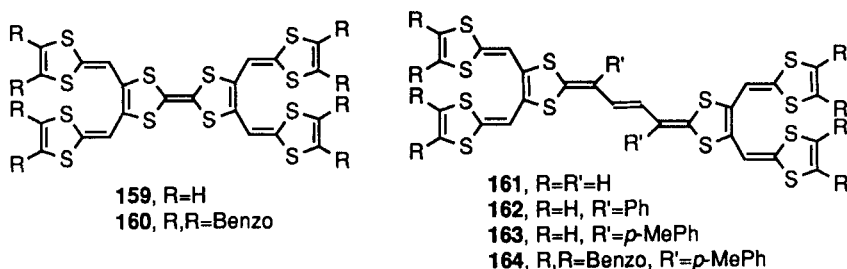


Figure 17.

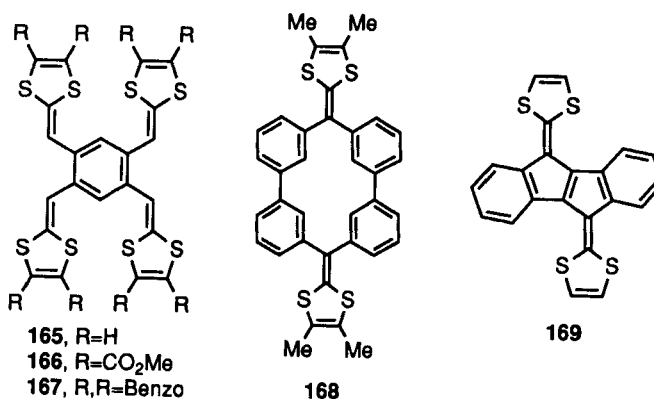


Figure 18.

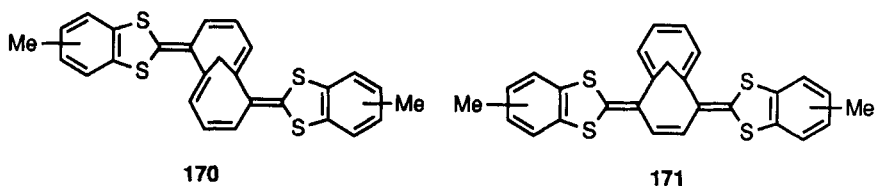


Figure 19.

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