Synthesis of materials for molecular electronic applications

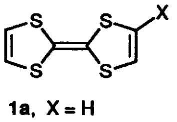
MARTIN C. GROSSEL* and SIMON C. WESTON

Department of Chemistry, University of Southampton, Highfield, Southampton, SO9 5NH, UK

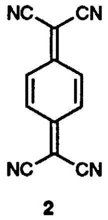
Reviewing the literature published between mid-1992 and December 1993

1 Introduction

The discovery of the high electronic conductivity of salts of the electron-donor tetrathiafulvalene (TTF, **1**) and the electron-acceptor 7,7′,8,8′-tetracyano-*p*-quinodimethane (TCNQ, **2**) provided a key stimulus for the development of electronically active materials. More recently there has been an explosion of interest in the behaviour of TTF derivatives since the discovery that its salts can behave as organic metals and superconductors[1] and this has stimulated a wealth of activity from synthetic chemists keen to improve synthetic routes to and investigate structural modification of the TTF skeleton. Key points of attention include variation of the heteroatoms and peripheral substituents, modification of the bridge between the dithiolium rings, and the properties of unsymmetrical structures.



1a, X = H
b, X = Li
c, X = C(S)NHMe
d, X = S⁻
e, X = Se⁻
f, X = SCH$_2$CH$_2$OH



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Whilst the properties of TCNQ salts played a key role in the development of organic metals, more recent work has focused on their use as components for organic devices (ferromagnetic, non-linear optical, and molecular rectification). However, the TCNQ skeleton has until recently proved less amenable to structural modification, but the development of cyano-imino derivatives has greatly increased the repertoire of structural variation available.

Incorporation of donor and acceptor moieties into one molecule provides an important approach to optical and electronic devices and there is increasing interest in the construction of such structures. Another important area involves the design of molecular optical and electronic switching systems and important developments are underway in this area.

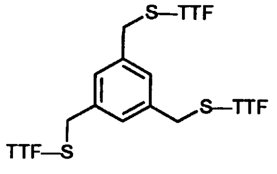
2 Electron-donor systems

2.1 Tetrathiafulvalene, its derivatives and analogues

Within the period covered by this review (mid- 1992 to the end of 1993) there has been considerable activity in the synthesis of new donors and acceptors and, though there has been comparatively little innovative synthetic work, important strides have been made in the control of, for example, unsymmetrical TTF analogues. The application of TTF moieties as structural building blocks in supramolecular chemistry has been reviewed.[2]

2.1.1 Peripheral substitution of the TTF skeleton

Several new reactions of the mono-lithiated TTF **1b** have been reported. That with methyl thiocyanate affords the thioamide which forms a highly conducting 1 : 1 stoichiometry TCNQ complex,[3] whilst addition to Eschenmoser salts (CH$_2$=N$^+$R$_2$) affords tertiary aminomethyltetrathiafulvalenes which give semiconducting paramagnetic TCNQ charge-transfer complexes.[4] TTF-Li is readily converted into the thiolate **1d** and selenolate **1e**. The former has been used as an intermediate in the preparation of bis- and tris-(TTF) derivatives such as **3** [by reaction with tris(bromomethyl)benzene] and **1f**, formed when TTF-S$^-$ is treated with 2-bromoethanol, has proved a particularly versatile building block for the formation of a range of esters, ethers, urethanes, and vinylthio derivatives.[5] Reaction of the mono-anions **1d,e** with bromoethane provides a one-pot route to the known unsymmetrical donors EDT-TTF (**4**, X = S) and EDS-TTF (**4**, X = Se).[6]



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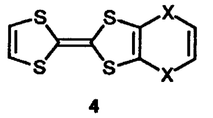

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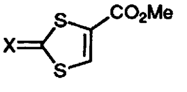
DIBAL-H reduction of the methyl ester moiety in **5** affords the corresponding alcohols which are readily converted into their corresponding phosphonium salts. The latter provide useful Wittig reagents for the preparation of sulfur-rich and space-extended TTF derivatives such as **6**.[7]



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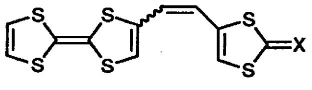
X = S, O



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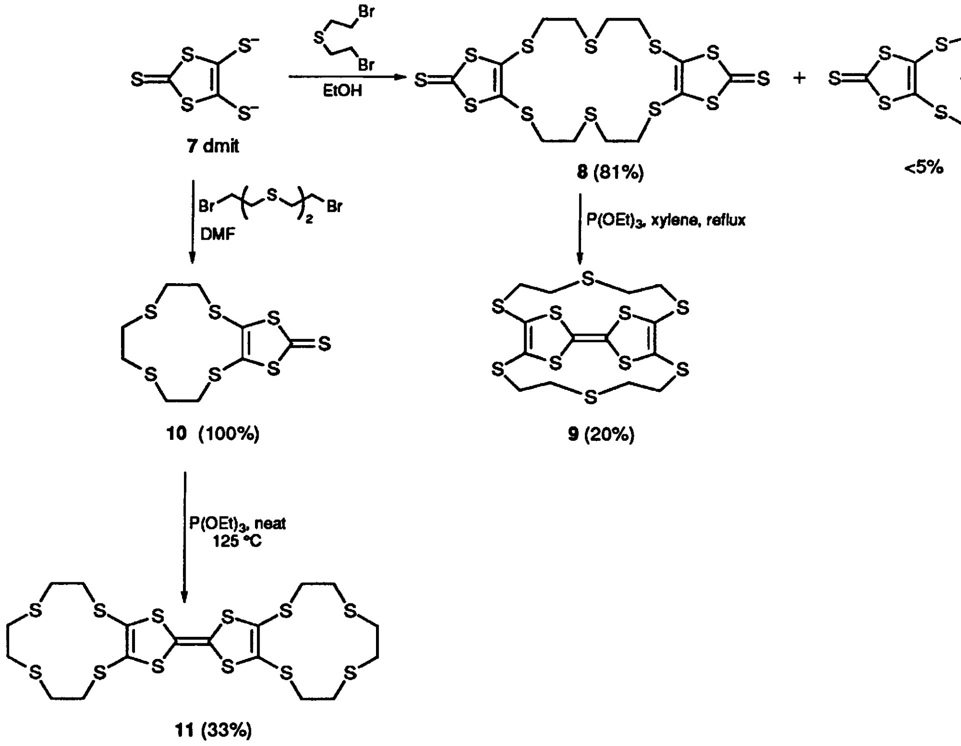
Whilst reaction of dithiolate **7** with 1,5-dibromo-3-thiapentane gives as major product the macrocyclic dimer **8** which has been converted into the novel TTF-bridged cryptand **9**, that with the homologous dibromodithianonane gives exclusively the macrocyclic monomer **10**, a precursor to the bis-macrocylic TTF derivative **11** (**Scheme 1**). This latter shows a marked cyclic voltamometric response in the presence of AgClO$_4$ but is unaffected by alkali metal perchlorates.[8]

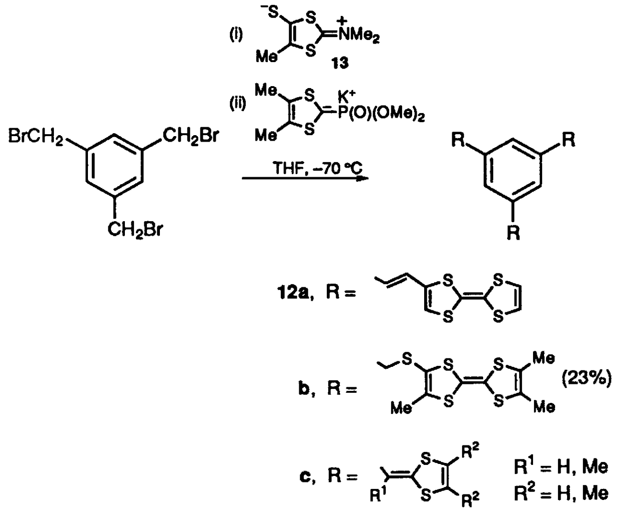
A series of bis(aryl)-substituted tetrathiafulvalenes (aryl = 2,3,4,5-tetramethylbenzyl, 1,4-benzodithian-6-yl, 2-naphthyl, and biphenyl-4-yl), all showing good donor behaviour, have been prepared by reaction of the chloroacetylarene with sodium t-butylthiocarbonate, followed by acid-catalysed cyclization to the 4-aryl-1,3-dithiole-2-thione and phosphite-mediated coupling, though neither the 3,4-dialkoxyphenyl nor the indol-3-yl thione could be converted into the corresponding TTF derivative.[9]

Novel π-donors **12** having three-fold symmetry have been constructed[10] by attaching TTF units to a 1,3,5-trisubstituted benzene core using Wittig and Horner–Wittig techniques (**Scheme 2**).

Yields from the Wittig route to **12a** were poor, the product being very insoluble, and significant improvements were achieved through the use of a more flexible spacer between the TTF units and the core. Introduction of the iminium unit **13** and subsequent reaction with a phosphonate ylid gave the unsymmetrical tris(TTF) structure **12b** in 23% yield. Similar yields [50% for (**12c**, R^1 = Me, R^2 = H)] were achieved by reaction of phosphonate ylids with 1,3,5-triformyl- and 1,3,5-triacetyl-benzene. Of particular interest is **12b** which can be reversibly oxidized electrochemically to its tri- and hexa-cation and forms a paramagnetic mixed valence salt ($\mathbf{12b}^{2+}$)·($Mo_6Cl_{14}^{2-}$).



Scheme 1

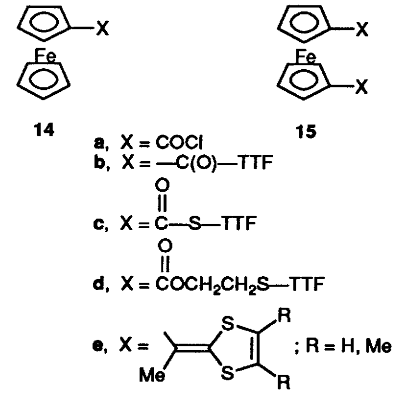


Scheme 2

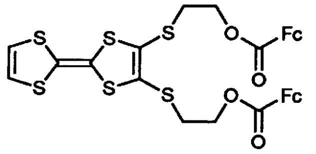
Covalent attachment of ferrocene to the TTF skeleton has also been investigated, systems so far prepared having the two separated by one, two, or five spacer atoms.[11] Mono- and di-substituted ferrocenyl esters (**14b–d**, **15b**, and **16**) are readily obtained by reaction of the appropriate alcohols with the acid chlorides **14a** and **15a** in variable (12–80%) yields. The *trans*-linked ferrocenylvinyl-TTF (**17**) is obtained in good yield (58% after isomer separation) by Wittig reaction of ferrocene–CH=PPh$_3$ with TTF–CHO. Electrochemical studies of these materials suggest three independent reversible single-electron oxidation processes ($TTF^0 \rightarrow TTF^+$, $TTF^+ \rightarrow TTF^{2+}$, and $Fc^0 \rightarrow Fc^+$). In addition, ferrocene has been inserted into the central alkenyl bridge of the TTF skeleton. For example, the derivatives **15e** have been prepared in 60–70% yield from 1,1′-diacetylferrocene using the appropriate 1,3-dithiole Horner–Wittig reagents. These compounds form charge-transfer salts with TCNQ (1 donor : 2 TCNQ) which have high room-temperature conductivities [σ_{RT} (compressed powder) = *ca.* 0.1 S cm^{-1}].

The attachment of four short oligo(ethyleneglycol) chains to the TTF skeleton affords a room-temperature melt which freely dissolves electrolytes like LiClO$_4$ to give an ionically conductive liquid.[12]

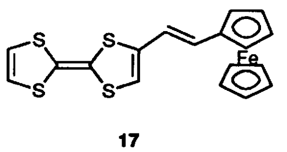
The introduction of peripheral sulfur substituents provides the most important precursors to superconducting salts. bis-(Ethylenedithio)-Tetrathiafulvalene (BEDT-TTF or ET, **18**) is perhaps the most important of these and a novel and facile two-step synthesis of this material has recently been reported[13] which has the additional merits of using exclusively commerically available starting materials, requiring short reaction times, reliably giving good yields of high purity products, and avoiding hazardous procedures. Contrary to previous reports the key intermediate 4,5-dimercapto-1,3-dithiol-2-one **20** is readily generated by base-catalysed cleavage of the bicyclic lactone **19** (**Scheme 3**). It is then bis-alkylated using dibromoethane to give the dithiolone which is converted into ET (**18**) most efficiently using triethyl phosphite. The authors have further demonstrated that the controlled cleavage of **19** provides a good general route to tetrakis(alkylthio)-TTF derivatives such as **21**.



14 **15**



16 Fc = ferrocenyl



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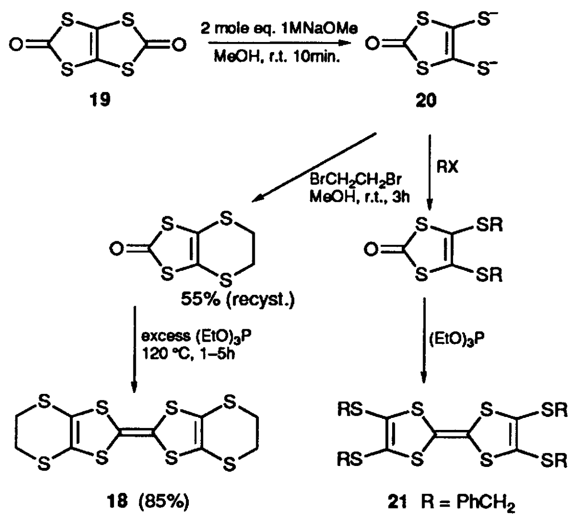
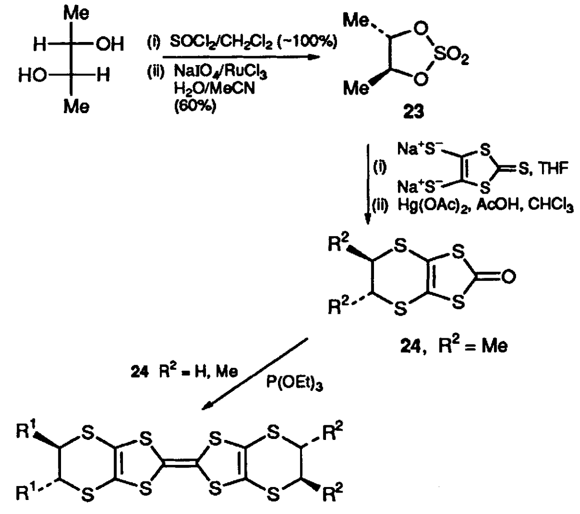


Scheme 3

The stereoselective synthesis of the methylated ET derivatives **22** has been achieved from optically pure (2*S*,3*S*)-2,3-butanediol (obtained by reduction of L-threitol-1,4-ditosylate) (**Scheme 4**).[14] Reaction with thionyl chloride and subsequent oxidation gives the cyclic sulfate **23** which is then converted into the bicyclic dithiolone **24** in moderate yield. This is homocoupled to give **22b**$_{RR}$ (74%). Cross-coupling with **24** (R = H) gave the expected but separable (1 : 2 : 1) mixture of **18** : **22a**$_{R}$: **22b**$_{RR}$.

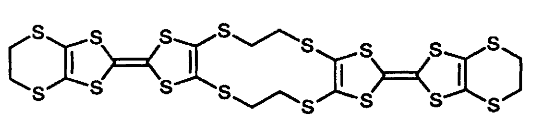


18, $R^1 = R^2 = H$
22a, $R^1 = H$, $R^2 = Me$
b, $R^1 = R^2 = Me$

Scheme 4

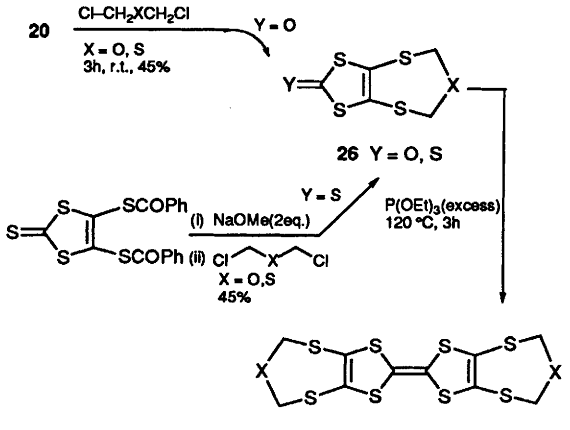
The electrochemical behaviour of these materials is similar to that of ET itself, but intermolecular steric interference arising from the presence of four methyl substituents changes the molecular packing behaviour in the solid-state. **22b**$_{RR}$ has a conformational preference for di-equatorial location of the methyl groups within each dihydrodithiin ring whereas the substituents prefer a diaxial geometry in **22a**$_{R}$.

Linking of two ET units has been achieved through the synthesis of the twin donor **25** which forms a crystalline charge-transfer salt with DDQ in which columns of 'U'-conformation donor pairs sandwich DDQ – units.[15] Such materials are of particular interest as potentially ferromagnetic organic metals.



25

Until recently, little information has been available on the effect of the introduction of additional heteroatoms (O or S) into the peripheral alkyl chains of the ET skeleton. Reports have now appeared of the synthesis of several such structures. Introduction of both an oxygen and a sulfur link to give **27a,b** was readily achieved[16] by alkylation of the intermediate **20** generated as described above[13] with bis(chloromethyl) ether or the corresponding sulfide. Coupling with triethyl phosphite gave BOBMT-TTF (**27a**) and its thio-analogue BTBMT-TTF (**27b**) in *ca.* 80% yield whereas the more common approach involving phosphite coupling of the 1,3-dithiole-2-thione **26** (X = Y = S) gives much more modest yields (≤30%) (**Scheme 5**).

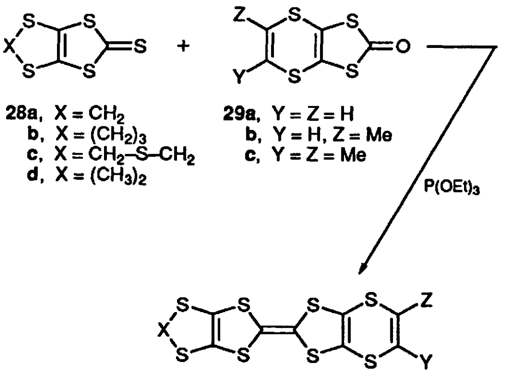


27a, X = O; BOBMT-TTF
b, X = S; BTBMT-TTF

Scheme 5

The relatively high oxidation potentials of BOBMT-TTF, **27a**, (relative to **18** and **27b**) restrict the choice of anions suitable for electrocrystallization experiments but it forms a black crystalline (1 : 1) charge-transfer complex, when reacted with TCNQ in chlorobenzene, which has a very high room-temperature conductivity ($\sigma_{powder} = 10$ S cm^{-1}) making it an attractive candidate for further investigation. In contrast, the insolubility of the thio-analogue **27b** would appear to limit its use.

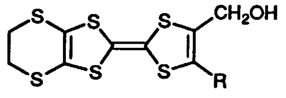
In a related study a series of unsymmetrical derivatives **30** have been prepared by coupling of the thiones **28** with ketones **29**.[17] Good yields were obtained in several cases and the cross-coupled products are readily separated from the symmetrical analogues by silica-gel chromatography (**Scheme 6**).



30 + homo-coupled products
a, X = CH_2, Y = Z = H; MVT
b, X = $(CH_2)_3$, Y = Z = H; TMVT 58%
c, X = CH_2–S–CH_2, Y = Z = H; TMTVT 45%
d, X = $(CH_2)_2$, Y = H, Z = Me; EMVT 61%
e, X = $(CH_2)_2$, Y = Z = Me; EDMVT 49%

Scheme 6

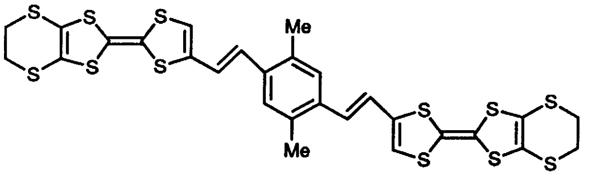
There is considerable interest in unsymmetrical structures in which half of a TTF moeity and half of a BEDT-TTF moiety are linked. The preparation of **31** is of particular interest since it exploits the coupling of two 1,3-dithiole-2-thiones using $Co_2(CO)_8$, and allows



31 R = H, CH$_2$OH

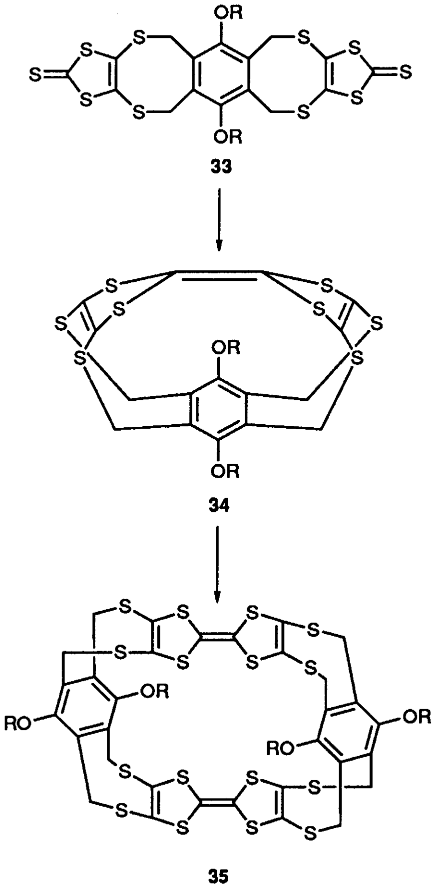
the possibility of hydrogen-bonded structural organization through the presence of the hydroxyl substituent.[18]

The novel donor BETE-DMB (**32**), which has been obtained in high yield by Wittig coupling of 2,3-ethylenedithio-6-formyltetrathiafulvalene with 2,5-dimethyl-*p*-xylylidene-bis-(triphenylphosphonium chloride), forms highly conducting radical cation salts. For example, (**32**-I_2Br) has σ_{RT} (single crystal) = 80 S cm^{-1}.[19]



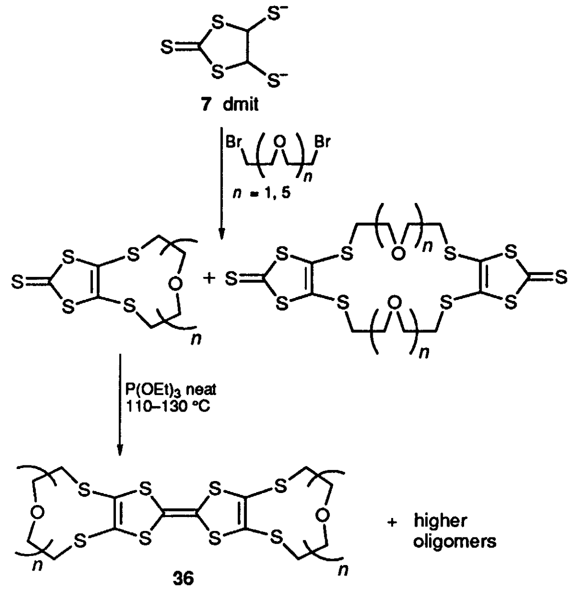
32

The TTF-bridged cyclophane **34**, formed in the trialkyl phosphite mediated coupling of the dithione **33**, undergoes a surprising electrochemically induced metathesis-like dimerization to give the expanded electron-rich cage **35** (**Scheme 7**) which forms charge-transfer complexes with I_2, DDQ, and TCNQ-F_4, but not with TCNE or TCNQ itself.[20]



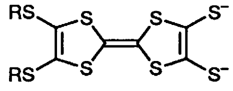
Scheme 7

bis-Alkylation of dmit (**7**) leads to monomer, dimer, and higher oligomeric dithiolone-bridged crown ethers which are readily coupled (30–40%) to give the bis-crown substituted TTF's **36** (**Scheme 8**). The 15-crown-5 and 18-crown-6 analogues **36** ($n = 3$) and **36** ($n = 4$) are readily prepared without resorting to high-dilution techniques and both show significant selective spectroscopic and electrochemical responses towards alkali metal cations.[21]



Scheme 8

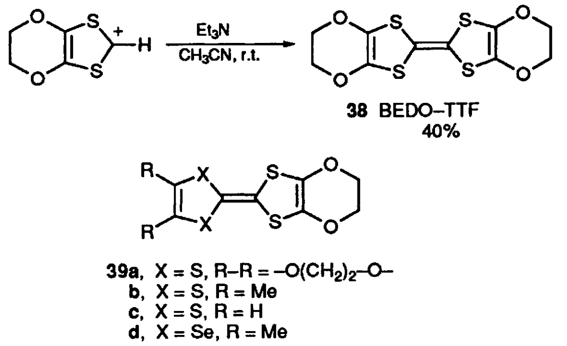
The *p*-acetoxybenzylthio- protecting group is stable to triethyl phosphite-mediated cross-coupling of 4,5-dialkylthio-1,3-dithiol-2-ones thereby providing a convenient source of the dithiolates **37a** and **37b**, both valuable precursors to unsymmetrical tetrathioalkyl-TTF derivatives.[22]



37a, R = Me
b, R = Bu^n

Replacement of the peripheral sulfur atoms by oxygen gives bis-(ethylenedioxo)-tetrathiafulvalene (BEDO-TTF) **38**, two superconducting salts of which are known. Several synthetic routes to **38** have been explored, of which the self-coupling of 4,7-ethylenedioxo-1,3-dithiolium tetrafluoroborate was the most satisfactory (**Scheme 9**), some literature methods having proved to be poorly reproducible.[23]

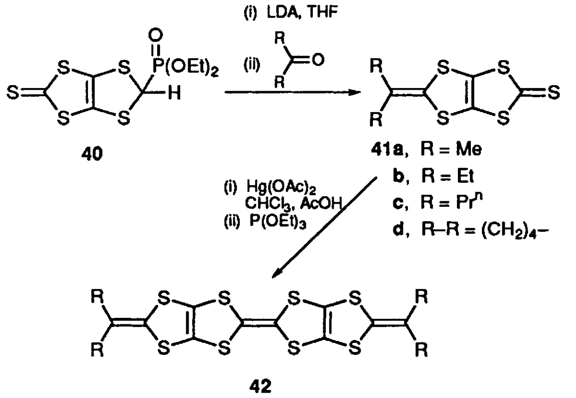
Two new charge-transfer salts were prepared, the most interesting of which is (BEDO-TTF)$_2$.CF$_3$SO$_3$ which is the first κ-phase material obtained from **38** and is metallic at room temperature. However, whilst the crystal structure suggests that it should be a good candidate for superconductive behaviour this is not observed, the material reverting to an insulating state at low temperatures. Wittig and Wittig–Horner coupling reactions give improved yields of unsymmetrical BEDO-TFF analogues, *e.g.* **39a–d**.[24]



Scheme 9

2.1.2 Fused TTF analogues

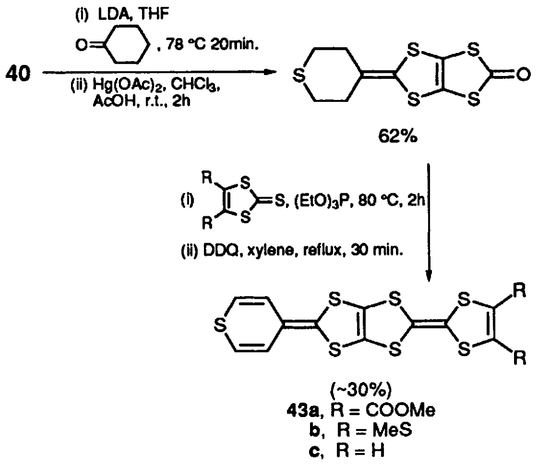
Four alkyl derivatives of bis-(2-methylidene-1,3-dithiolo[4,5-*d*])-tetrathiafulvalene, BDT-TTF, (**42a–d**), have been prepared,[25] a Wittig–Horner reaction being used to introduce the exocyclic alkenyl unit of the dithiolo-dithiol-thione **41** (**Scheme 10**).



Scheme 10

The first oxidation potentials of **42b** and **42c** are similar to that of BEDT-TTF and semiconducting charge-transfer salts are obtained with DDQ and TCNQ-F$_4$, though no reaction has been observed with TCNQ itself. Both **42a** and **42d** proved too insoluble for study.

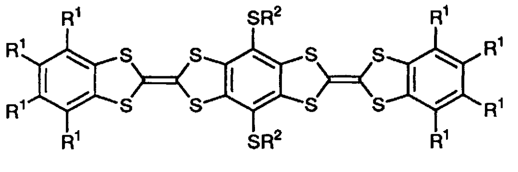
Highly conductive complexes have been obtained from the tetrathiapentalene-cored donor **43** which has been prepared from the phosphonate **40** by Horner–Wittig reaction followed by phosphite-induced cross-coupling (**Scheme 11**).[26]
Whilst the diester **43a** is very insoluble, it has been successfully decarboxylated (LiBr, HMPA, 90°C 1 h; then 130°C, 30 min.; 45%) to the parent donor **43c**. The first oxidation potential observed for the latter is equal to that of TTF but the dication is formed more easily, reflecting reduced Coulombic repulsion in **43c**$^{2+}$.



Scheme 11

A similar approach (but employing a sulfur ylid) has been used to prepare the linear 'fused' dibenzo-TTF dimers **44** and their bent isomers.[27] The linear structures are more readily oxidized and form the more conductive (1 : 2) charge-transfer salts with TCNQ and TCNQF$_4$.

The syntheses of a number of tetrathiapentalene-bridged TTF derivatives have been reported.[28–31]



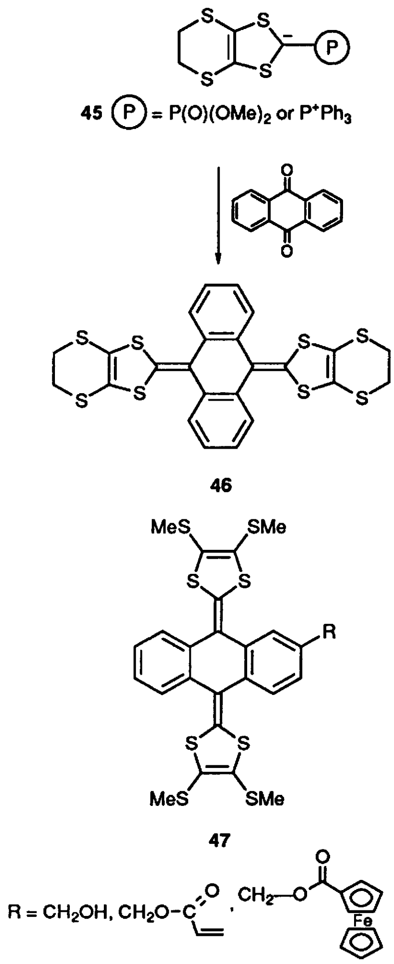
44 R^1 = H, Me, S, EtS
R^2 = OEt, O-hexyl, O-dodecyl, SMe, S-isoamyl

2.1.3 Centrally spacered *i.e.* 'stretched' TTF's

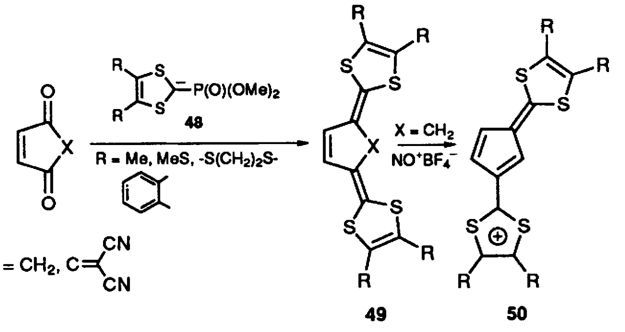
There have been a number of reports describing the incorporation of unsaturated, particularly heterocyclic, spacers into the TTF skeleton. The phosphonate carbanion **45** reacts with anthraquinone to give the anthracene-spacered TTF **46** which is the first *p*-quinodimethane analogue of BEDT-TTF to have been reported (**Scheme 12**).[32] Several substituted derivatives of **47** have now been prepared in a similar fashion.

Reaction of phosphonates **48** with, for example, cyclopenten-1,3-dione has been used to prepare several cyclopentene-bridged derivatives **49** in variable yields (8–46%) (**Scheme 13**).[33] These latter are readily oxidized by NOBF$_4$ to give cations **50** which are very stable and give semiconducting (1 : 1) charge-transfer complexes with TCNQ.

Trimethyl phosphite induced coupling of thiosuccinic anhydride with dithiolethiones has provided an efficient route to BDTT (**51**) and some novel unsymmetrical derivatives *e.g.* EDT-BDTT (**52**).[34] BDTT is one of the most powerful donors of the TTF class and alkylthio-substitution as in **52** leads to a slight reduction in its electron-donor ability though TCNQ salts of the latter show significantly

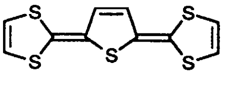


Scheme 12

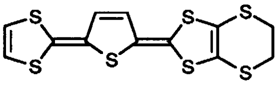


Scheme 13

higher conductivity (by *ca.* 10^2–10^3), reflecting enhancement of intra- and inter-stack interactions produced by the sulfur atoms at the edges of the donor skeleton.

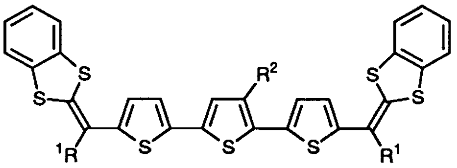


51 BDTT



52 EDT–BDTT

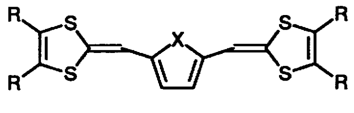
Horner–Wittig coupling provides an efficient route to oligothiophene-bridged dibenzo-TTF analogues such as **53**.[35] The presence of an alkyl substituent in the median thiophene ring significantly increases solubility of such materials, although the introduction of more than one thiophene spacer does not produce any further dramatic changes in the redox behaviour of these systems.



53

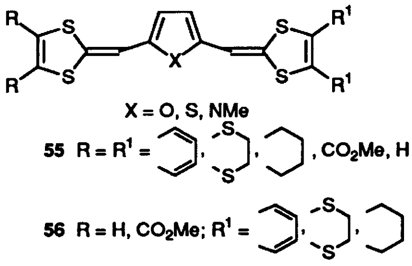
$R^1 = H$; $R^2 = H$, Me, octyl, Me(OCH$_2$CH$_2$)$_2$–
$R^1 = Me$; $R^2 = Me$

Conjugation-extended TTF analogues (**54**) incorporating a central furan or thiophene ring have been prepared by Wittig condensation of the appropriate heterocyclic 2,5-dialdehyde with 1,3-dithiol-2-ylidenetributylphosphorane and its 4,5-bis(methoxycarbonyl) derivative.[36] This approach giving significantly improved yields over the Wittig–Horner route, particularly when BuLi in THF is used to form the ylid.



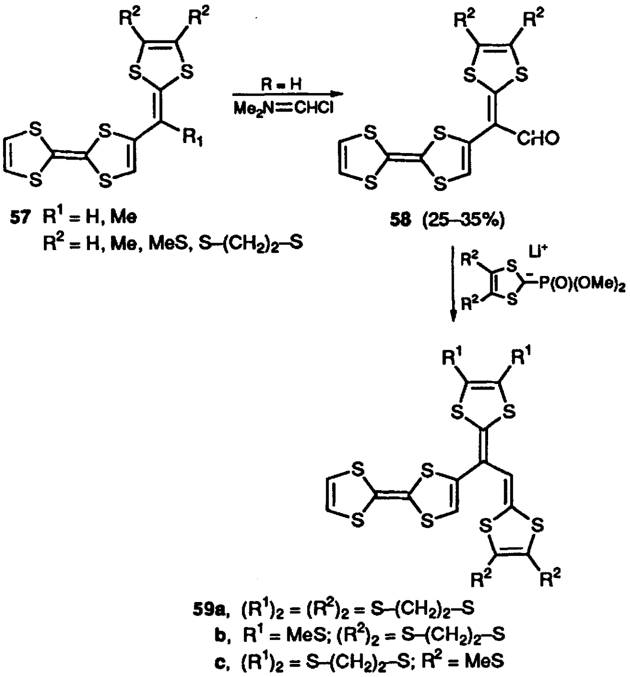
54a, X = O, R = H
b, X = S, R = H
c, X = S, R = CO_2Me

Similar conclusions are drawn from a more detailed study of routes to symmetrical **55** and unsymmetrical **56** derivatives, good yields (*ca.* 70%) of the thiophene and *N*-methylpyrrole-bridged compounds being obtained.[37] Significantly improved yields are gained from the Wittig–Horner route if the base (Bu^{n}Li) is added dropwise to a mixture of phosphonate and ylid at 0–10°C.[38] These materials show ready oxidation to the dication [the mono(radical)cation] not very stable two close or coincident one-electron processes are seen. Charge-transfer complexes of **54b** with I_2 and DDQ have moderately high conductivities $\sigma = ca.$ 10^{-3} S cm^{-1}.



2.1.4 Vinylogous TTF derivatives

Wittig coupling provides a convenient method for the synthesis of the novel TTF derivatives **57** from formyl and acetyl-TTF.[39] Vilsmeier formylation of **57** followed by phosphonate coupling affords the cross-conjugated vinylogous TTF derivatives **58** (the Wittig reaction failing in this case) (**Scheme 14**). Both **59b** and **59c** show remarkably strong and reversible two-electron donor behaviour whereas **59a** is surprisingly unstable to electrochemical oxidation.



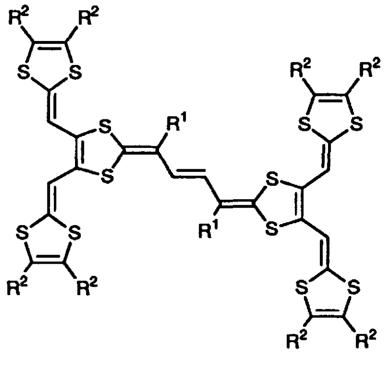
57 R^1 = H, Me
R^2 = H, Me, MeS, S–(CH$_2$)$_2$–S

58 (25–35%)

59a, (R^1)$_2$ = (R^2)$_2$ = S–(CH$_2$)$_2$–S
b, R^1 = MeS; (R^2)$_2$ = S–(CH$_2$)$_2$–S
c, (R^1)$_2$ = S–(CH$_2$)$_2$–S; R^2 = MeS

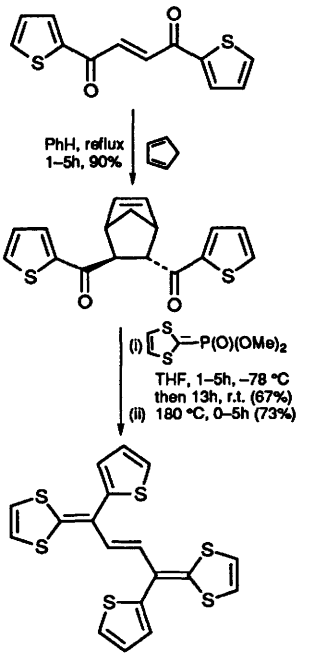
Scheme 14

Several tetra-(1,4-dithia-fulven-6-yl)-substituted TTF-derivatives and vinylogues such as **60** have been reported, the latter being obtained *via* cycloaddition of 3-thioxo-1,2-dithioles onto electrophilic alkynes followed by thermally induced dimerization of the resulting thials and subsequent peripheral Wittig olefination.[40,41] Once again such compounds are very strong 2π-electron donors which readily react with TCNQ to form electroconductive charge-transfer salts.



60 R^1 = H, Ph, *p*-Me–C$_6$H$_4$–
R^2 = H, CO$_2$Me, –(CH=CH)$_2$–

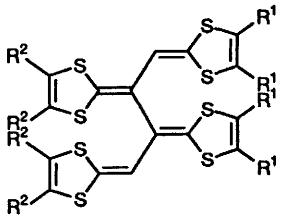
Thienyl-substituted fulvalene and TTF-vinylogues such as **61** which have been prepared using a Diels–Alder/retro-Diels–Alder protection sequence (**Scheme 15**) have even lower, reversible, first oxidation potentials and form stable and well-defined TCNQ salts despite expected non-planarity of the donor skeleton.[42]

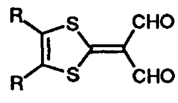


61

Scheme 15

[3]- and [4]-Dendralenes such as **62** have been prepared in good yields by combinations of Horner–Wittig and Vilsmeier elaboration of **63**, this latter deriving from reaction of 2-thiomethyl-1,3-dithiolium salts with malondialdehyde monoanion.[43]



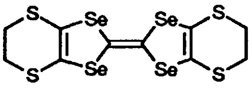


63

62 R^1 = R^2 = MeS
(R^1)$_2$ = –S–(CH$_2$)$_2$–S–; R^2 = Me

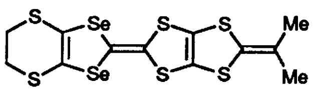
2.2 Tetrachalcogenofulvalenes

An efficient synthesis of BETS (**64**), the tetraseleno analogue of BEDT-TTF is still being sought, though progress had been made through thiabenzylation of tetralithiotetraselenafulvalene.[44] This material is an attractive target since it retains the sulfur periphery which plays a major role in the superconductive behaviour of BEDT-TTF salts but the addition of core selenium atoms should enhance transverse intermolecular interactions.



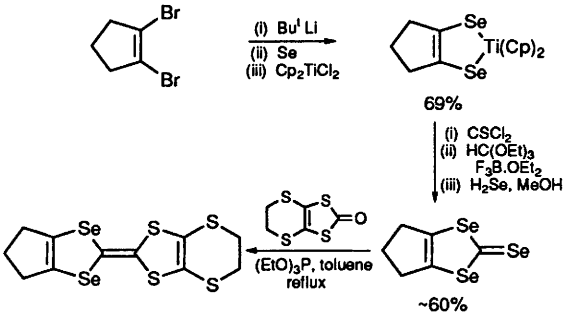
64 BETS

A number of other tetraselenafulvalene derivatives of this type have been prepared using the titanocene route to 1,3-diselenol-2-ones which were then coupled in neat triethyl phosphite.[45] Unsymmetrical donors such as **65** (ETIT) were also prepared by cross-coupling methods though in rather poor yield.



65 ETIT

The titanocene-route has also been successfully exploited in the synthesis of **66** (TMET-STF) (**Scheme 16**).[46] A number of novel unsymmetrically substituted dithiadiselena- and tetraselena-fulvalenes bearing one or two functionalities such as diethylacetal, formyl, or hydroxymethyl substituents have been prepared,[47] and routes to TTF analogues in which one sulfur atom has been replaced by selenium have been described.[48]

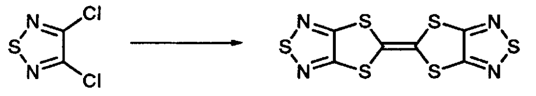


66 TMET—TSF (27%)

Scheme 16

2.3 Other novel donor systems

bis-(thiadiazole)Tetrathiafulvalene (BTDA-TTF) (**67**) which has been prepared in low yield by triethyl phosphite induced coupling (**Scheme 17**), is poorly soluble in common organic solvents and undergoes single-electron irreversible oxidation impeding the formation of charge-transfer salts.[49]



67

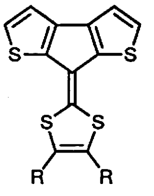
Reagents: (i) Na_2S, H_2O, EtOH; (ii) $CSCl_2$, 20 °C, 30min., N_2; (iii) $(EtO)_3P$, 100–130 °C,15 min.

Scheme 17

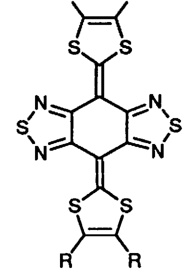
Wittig–Horner coupling has been used to prepare in good yields the bithiopheno-TTF analogues **68** bearing a variety of electron-withdrawing and donating substituents.[50] Electrochemical oxidation of these compounds is also irreversible and leads to the formation of semiconducting polymers.

Routes to other novel TTF analogues such as dithiadiazafulvalenes,[51] diazatetrathiafulvalenes,[52,53] and bis-[1,2,5]-thiadiazolo-*p*-quino-bis-(1,3-dithiole) (BTQBT), **69**,[54] and its selenium analogues have been reported. Single crystals of **69** show unusually high conductivity ($\sigma_{RT} \sim 10^{-4}$–10^{-6} S cm^{-1}) for a single component organic material.[55]

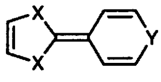
A large number of derivatives of 2-(thiopyran-4-ylidene)-1,3-dithiole (TPDT) **70a** and its selenium analogues **70b–d** have been prepared by phosphite coupling of 2-thioxo-1,3-dithioles with 4-oxo-tetrahydrothianes or selenanes, followed by chloranil-induced dehydrogenation.[56] These are strong electron-donors which in some cases form highly conducting TCNQ complexes.



68

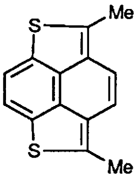


69 R = H, BTQBT



70a, X = Y = S
b, X = S, Y = Se
c, X = Se, Y = S
d, X = Y = Se

Introduction of sulfur atoms into the periphery of polynuclear aromatic systems provides a useful means of lowering the oxidation potentials of such structures. Photocyclization of substituted 1,2-dithienylethenes provides a versatile synthetic route to naphtho[1,8-*bc*; 4,5-*b′c′*]dithiophene **71**.[57] Other interesting donors which have recently been prepared include 1,6-diselena-pyrene[58] and 2,3,8,9-tetrahydro-1,4,7,10-tetrathiachrysene.[59]



71

3 Electron-acceptors

3.1 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) and related systems

The majority of TCNQ derivatives undergo two reversible single-electron reductions, the intermediate radical anion having high thermal stability and the presence of dicyanomethylene groups makes TCNQ a far stronger electron-acceptor than benzoquinone.

Three general synthetic approaches are available for the manipulation of the TCNQ structure, thereby modifying its properties:

(a) Ring substitution, allowing fine tuning of the redox behaviour through careful choice of substituents.

(b) Extension of the π-system which reduces intramolecular Coulomb repulsion in the dianion state.

(c) Incorporation of heteroatoms or heterocyclic rings into the TCNQ skeleton, leading to greater intra- and inter-stack interactions which increase dimensionality, stabilize the conductivity, and enhance the metallic state.

However, the synthesis of the majority of TCNQ derivatives remains difficult and this has restricted the use of these acceptors in the development of new organic materials. Early routes proceeded *via* cyclohexanedione[60] or 1,4-bis(cyano-methyl)benzene derivatives.[61] In the latter, introduction of the cyano substituents was a painstaking, multistep procedure involving the use of highly toxic cyanogen chloride as the electrophilic cyanating reagent, but in recent years the advent of new synthetic methods has made the preparation of TCNQ analogues more viable. Techniques of particular importance are:

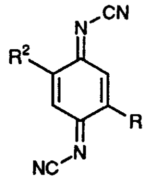
(i) The Lehnert procedure which involves direct bis(dicyanomethylation) of the quinone using malononitrile and $TiCl_4$ in pyridine; this method which works best for tetrasubstituted TCNQ's, *e.g* **2b**.

(ii) Reaction of 1,4-di-iodobenzenes with malononitrile anion in the presence of a palladium catalyst, leading to phenylene-dimalononitrile derivatives which are then oxidized to TCNQ's.

(iii) A two-step approach in which terephthaloyl chlorides are reacted with cyanotrimethylsilane-pyridine followed by phosphorus oxychloride-pyridine to give TCNQ's.

(iv) Use of 2-chlorobenzyl thiocyanate **72** as a cyanogen chloride substitute.

(v) The Hünig procedure for making DCNQI **73** derivatives. Direct reaction of quinones with bis(trimethylsilyl)carbodiimide (BTC) in the presence of $TiCl_4$.

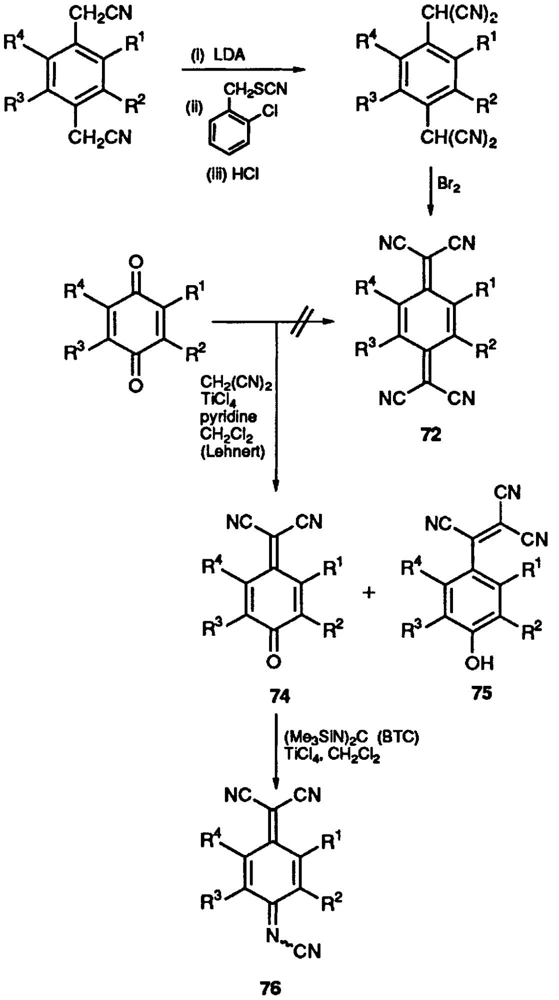


73a, $R^1 = R^2 = H$
b, $R^1 = R^2 = Me$
c, $R^1 = R^2 = Br$
d, $R^1 = Me$, $R^2 = Br$

3.1.1 Ring substitution of TCNQ and its analogues

An example of the difficulties in synthesizing TCNQ derivatives is exemplified by Bryce's[62] largely unsuccessful use of the Lehnert reagent to prepare a series of ring substituted TCNQ derivatives, the notable exception being the known preparation of tetramethyl-TCNQ (TMTCNQ) **2b** (55% reported yield from duroquinone) (**Scheme 18**). Small scale reactions (1–3 mmol) produced no TCNQ products while on a large scale (≥ 6 mmol) a maximum yield of 15% of **2b** was obtained. In all other cases only a monocyanomethylated intermediate (25–40%) **74** and a phenolic side product (15–30%) **75** were isolated. These results contrast with those previously reported for the synthesis of TCNQ and 9,9,10,10-tetracyano-anthraquinodimethane (9,10-TCAQ) **2k**.

The quinomethide intermediates **74** could, however, be reacted with $BTC/TiCl_4$ to afford novel *N*,7,7-tricyano-*p*-quinomethanimine (TCNQI) hybrid acceptor **76(a–d, k–m)** in typical yields of 65–80%.



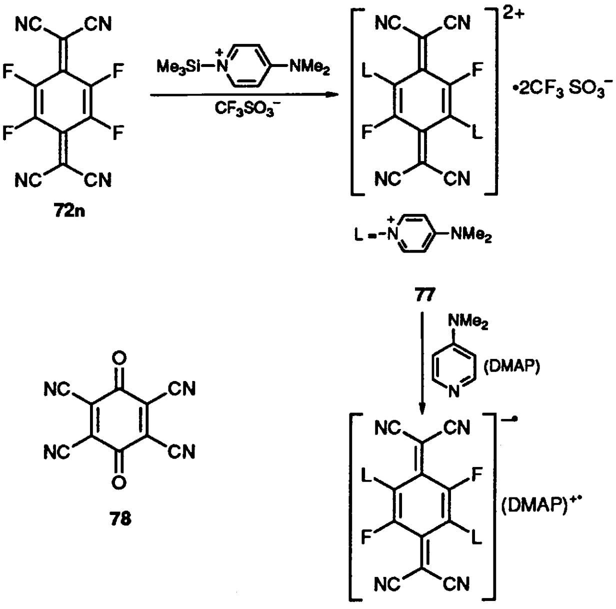
	R^1	R^2	R^3	R^4
a(≡2)	H	H	H	H
b	Me	Me	Me	Me
c	H	Me	Me	Me
d	H	Me	Me	H
e	Cl	H	Cl	H
f	Br	H	Br	H
g	MeO	H	MeO	H
h	CO_2Me	H	H	H
i	Cl	Cl	Cl	Cl
j	H	H	$-(CH{=}CH)_2-$	
k	$-(CH{=}CH)_2-$		$-(CH{=}CH)_2-$	
l	$-S-(CH_2)_2-S-$		$-S-(CH_2)_2-S-$	
m	$-(CH{=}CH)_2-$		$-S-(CH_2)_2-S-$	
n	F	F	F	F

Scheme 18

Electrochemical studies on each of these TCNQ derivatives showed a reversible first reduction wave. As expected TCNQI shows behavioural trends similar to those seen for TCNQ and DCNQI derivatives, progressive methyl substitution reducing the electron affinity.

Use of 2-chlorobenzyl thiocyanate **72** as a source of electrophilic cyanide provides a significantly improved synthetic approach to several TCNQ derivatives,[63] *e.g.* **2e–h** which were previously difficult to prepare, and allows a wide variety of substituents to be incorporated into the TCNQ ring in yields of 35–45%, including for the first time a functionalized carbon group, *i.e.* CO_2Me. However, this new methodology fails to produce the elusive tetrachloro-TCNQ **2i**.

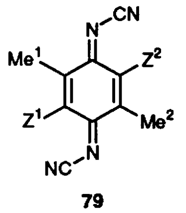
The current holder of the title of *strongest electron-acceptor* is claimed to be the di-positive electron-acceptor ($[TCNQF_2L_2)]^{2+}$ **77**, L = $DMAP^+$), a result of the electron-withdrawing power of the onio functionality.[64] This is prepared from $TCNQF_4$ by onio substitution (**Scheme 19**). Cyclic voltammetry has confirmed the first reduction potential for **77** as 0.96 V (*versus* Ag/AgCl in MeCN). However, $TCNQ(CN)_4$ has a first reduction potential of 1.31 V although this latter compound is not stable in its oxidized form.



Scheme 19

The strongest *uncharged* electron-acceptor based on the TCNQ system remains 2,5,7,7′,8,8′-hexacyano-*p*-quinodimethane [$TCNQ(CN)_2$, $E_1 = 0.67$ V *versus* Ag/AgCl in MeCN]. However, tetracyano-1,4-benzoquinone (cyanil) (**78**) is the strongest known *uncharged* electron-acceptor [three electrochemcially quasi-reversible single-electron reductions at potentials of 0.90, 1.09, and − 1.81 V (*versus* SCE in MeCN)] and can now be easily prepared from various commerically available benzoquinones.[65]

Following the discovery of a metal–insulator–metal transition (re-entrant behaviour) in $(Me_2DCNQI)_2Cu$ [$(\mathbf{73b})_2Cu$] at low pressure, and the subsequent discovery of an ambient pressure giant re-entrant state in the disordered alloys $[(Me_2)_{1-x}(MeBr)_x$-$DCNQI]_2Cu$ {$[(\mathbf{73b})_{1-x}(\mathbf{73d})_x]_2Cu$} and $(Br_2DCNQI)_2Cu_{1-x}Li_x$ [$(\mathbf{73c})_2Cu_{1-x}Li_x$] the search for re-entrant phenomena in a non-alloy at ambient pressure has attracted much interest. Workers have recently found giant re-entrant behaviour in the alloy $[(Me_2DCNQI\text{-}d_0)_{1-x}(Me_2DCNQI\text{-}d_8)_x]_2$-Cu{$[(\mathbf{73b})_{1-x}(\mathbf{79h})_x]_2Cu$} in which the only disorder arises simply from the fact that some hydrogens have been replaced by deuterium.[66] Seven of the possible thirty five deuterated versions of Me_2DCNQI (**73b**) have been synthesized[67] (**79a–h**). Electrical studies on the copper salts of the deuterated DCNQI's $[Me_2DCNQI\text{-}d_n]_2Cu$ (where *n* is the number of deuteriums present) reveal giant re-entrant behaviour for the first time in ordered (non-alloys) at ambient pressure (**79e–g**). The methyl ^2D's are introduced by the reduction of the corresponding α-chlorinated *p*-xylenes by zinc powder in AcOD. Deuterations of the ring protons were performed by applying $^1H/^2D$ exchange reactions in acidic media. It seems that selective deuteration of the methyl groups plays a much greater role than deuteration of the ring protons.



79

	Me¹	Me²	Z¹	Z²
73b	CH_3	CH_3	H	H
a	CH_3	CH_3	D	H
b	CH_3	CH_3	D	D
c	CH_2D	CH_3	H	H
d	CH_2D	CH_3	D/H	
e	CH_2D	CH_2D	H	H
f	CH_2D	CH_2D	D	H
g	CH_2D	CH_2D	D	D
h	CD_3	CD_3	D	D

3.1.2 Extended π-systems

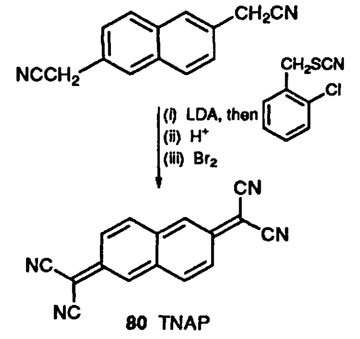
In general the acceptor ability of the benzene-fused TCNQ derivatives is poorer than that of TCNQ itself. Some TCNQ derivatives containing fused aromatic rings afford highly distorted molecular structures arising from steric interference between the cyano groups and the peri-hydrogens of the fused benzene rings. Planarity of donor and acceptor molecules is recognized as being one of the most important prerequisites in the search for organic conductors and it is this non-planarity that is blamed for the decrease in E_1 with the increase in benzannelation in the series benzo > naphtho > anthraquino derivatives. Three approaches are now known in the fight to keep such extended systems planar:

(a) β-substitution as in 9,9,10,10-tetracyano-2,6-naphtho-quinodimethane (TNAP, **80**) and 11,11,12,12-tetracyano-2,6-anthraquinodimethane (TANT, **81**) leads to truly π-extended, as opposed to fused systems, which do not suffer from peri-hydrogen interference.

(b) Replacement of the dicyanomethylene groups with the less sterically demanding imine group.

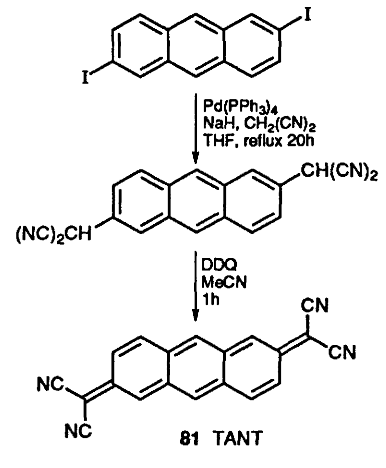
(c) Replacement of the carbon bearing the peri-hydrogen on the fused aromatic ring with a hydrogen-free heteroatom.

An improved synthesis of the established π-extended systems TNAP (**80**, **Scheme 20**) and benzo-TCNQ **2j** has recently been reported by Bryce[63] using the less arduous method (iv) above in improved overall yields of 20 and 45% respectively.



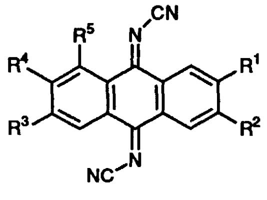
Scheme 20

TANT (**81**) has been prepared for the first time, using method (ii) in four steps from commercially available 2,6-diaminoanthraquinone in a 12% overall yield (**Scheme 21**).[68] Cyclic voltammetry studies on TANT show two reversible single-electron reductions at 0.20 and −0.12 V (*versus* Ag/AgCl in benzonitrile). Although the first reduction potential is equivalent to that of TCNQ **2a** (0.20 V) and TNAP (0.23 V) under identical conditions the second reduction is higher, demonstrating the extensive conjugated nature of the structure. Deep-purple 1 : 1 complexes are formed with tetrathiatetracene (TTT) and hexamethylene-tetratellurafulvalene (HMTTeF) both of which are highly conductive (σ = 7.0 and 11.5 S cm^{-1} respectively).

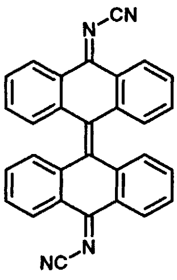


Scheme 21

Four fused-aromatic DCNQI derivatives **82a–c**, and **83** which have been prepared in order to study the effects of benzannulation on the DCNQI moiety[69] were obtained in the usual way by treating the appropriate quinone with BTC [bis(trimethylsilyl)-carbodiimide]/TiCl$_4$. In each case cyclic voltammetry measurements showed two reversible single-electron reductions (whereas similarly annulated TCNQ derivatives, *e.g.* TCAQ, exhibit only a single two-electron reduction) and, as expected, the acceptor ability decreases as the fused aromatic groups become larger (reflecting non-planarity, even for cyanoimine substituents).



82a, $R^1/R^2 = R^3/R^4 = -(CH{=}CH)_2-$, $R^5 = H$
b, $R^1 = R^2 = H$, $R^3{-}R^4 = -(CH{=}CH_2-$, $R^5 = H$
c, $R^1 = R^2 = R^3 = H$, $R^4{-}R^5 = -(CH{=}CH)_2-$



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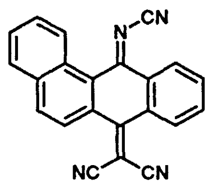
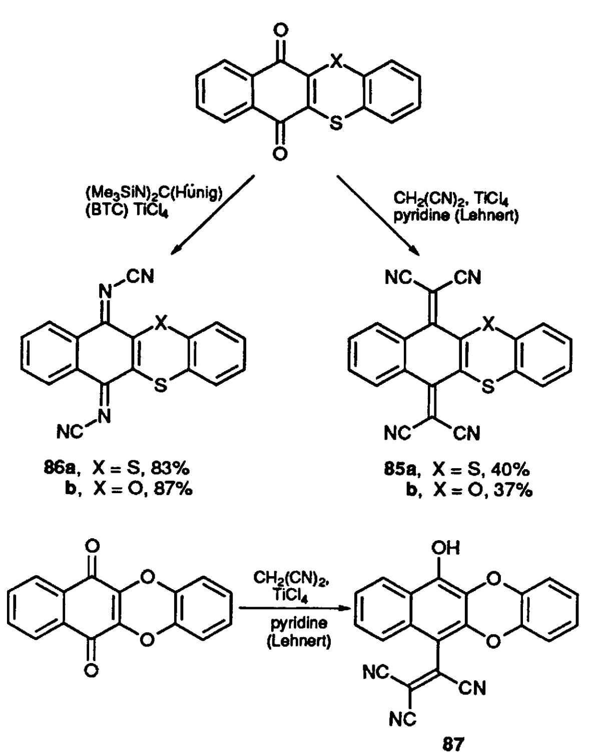


84

The same workers[69] have also prepared the polycyclic TCNQI derivative **84** from benz[*a*]anthraquinonone by Lehnert condensation of malononitrile with the less hindered carbonyl group followed by reaction with BTC/TiCl$_4$. In this case cyclic voltammetry shows a single two-electron reduction in keeping with the increased steric hindrance.

In an attempt to reduce steric interference in tetracyanoanthraquinodimethane (TANT) analogues, a series of TCNQ- (**85a,b**) and DCNQI-based (**86a,b**) structures incorporating dioxan and dithian spacers have been prepared[70] from the corresponding quinones using either the Lehnert procedure (yields of *ca.* 40%) or standard Hünig conditions (yields of *ca.* 80%) (**Scheme 22**). However, attempts to prepare the oxygen–oxygen bridged TCNQ derivative yielded only the phenolic side product **87**. Electrochemical studies on the TCNQ analogues reveal a single two-electron reduction potential (similar to TCAQ), whereas the DCNQI materials show two single-electron reduction potentials (similar to **82** and **83**). These materials are being investigated as potential one-component donor–σ-linked-acceptor (D–σ–A) systems.

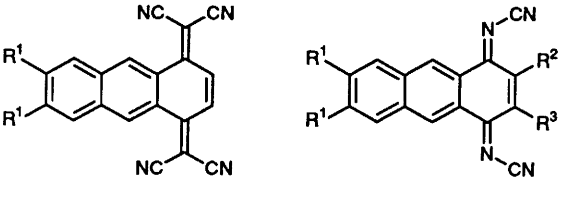
Several pyrazino-TCNQs, **88a–i**, have also been prepared from 1,2-phenylene-diamine in nine steps with widely varying yields (**Scheme 23**). The pyridyl-substituted derivatives were converted into stable neutral radicals (**89d–f**) by treatment with methyl triflate followed by Bu$^n_4$Ni with a view to obtaining single-component organic conductors, conduction electrons being provided by internal charge-transfer within the conjugated D–A system.[71] Attachment of the donor moiety to the pyrazino ring rather than the TCNQ ring minimizes steric interference and the associated non-planarity of similar fused systems.



Scheme 22

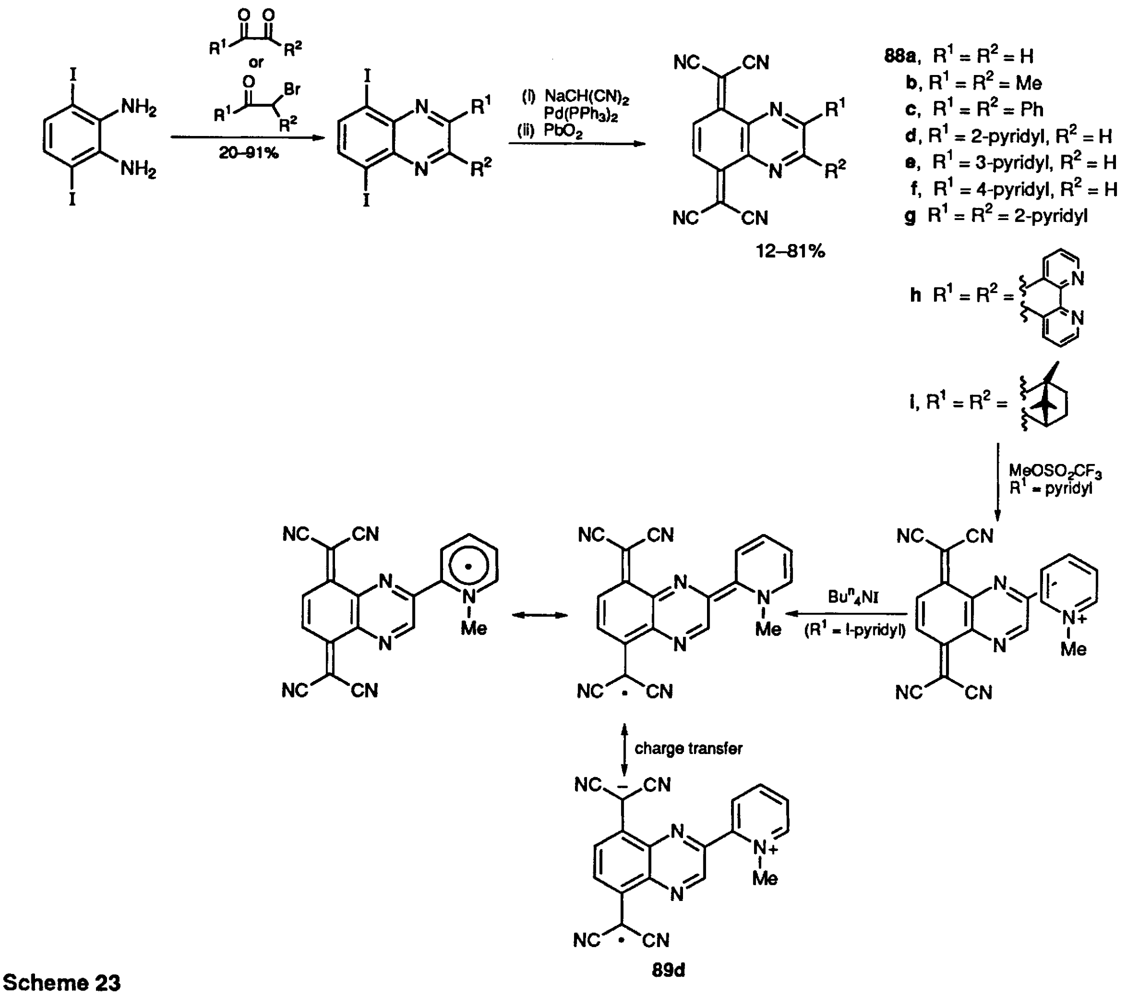
Pyrazino TCNQ **88a** forms highly conductive 1 : 1 charge-transfer salts with TTF and TMTSeF, with powder electrical conductivities of 1.4 and 0.91 S cm^{-1} respectively. Similar studies on the substituted materials (**88b–c**) afforded low conductivity salts as did other donors with **88a**. The powder conductivities of the neutral radicals are much higher ($\sigma = 10^{-5}$–10^{-9} S cm^{-1}) than is normal for a single component organic solid.

Several 1,4-anthraquinone-derived TCNQ (**90**) and DCNQI (**91**) derivatives bearing quinoidal ring substituents have been prepared[72] by standard Lehnert and Hünig procedures. These 2,3-fused structures are stronger acceptors than other similar 2,3,5,6-fused materials.



90 **91**

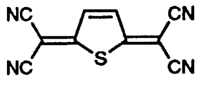
R^1 = H, OMe
R^2 = Me, OMe, Br
R^3 = H, Br, Me



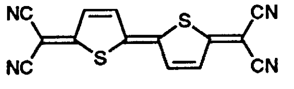
Scheme 23

3.1.3 TCNQ systems containing heterocyclic rings

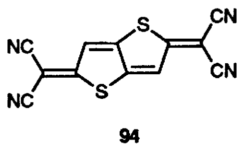
In the late 1980's[73] multiple-ring TCNQ heterocycles were made, both fused **94** and quinoidal **93**, based on thiophene-TCNQ **92**. Such conjugated hetero-TCNQ derivatives should have reduced on-site Coulomb repulsion and strong intermolecular interactions which favour greater dimensionality and thus greater conductivity.



92



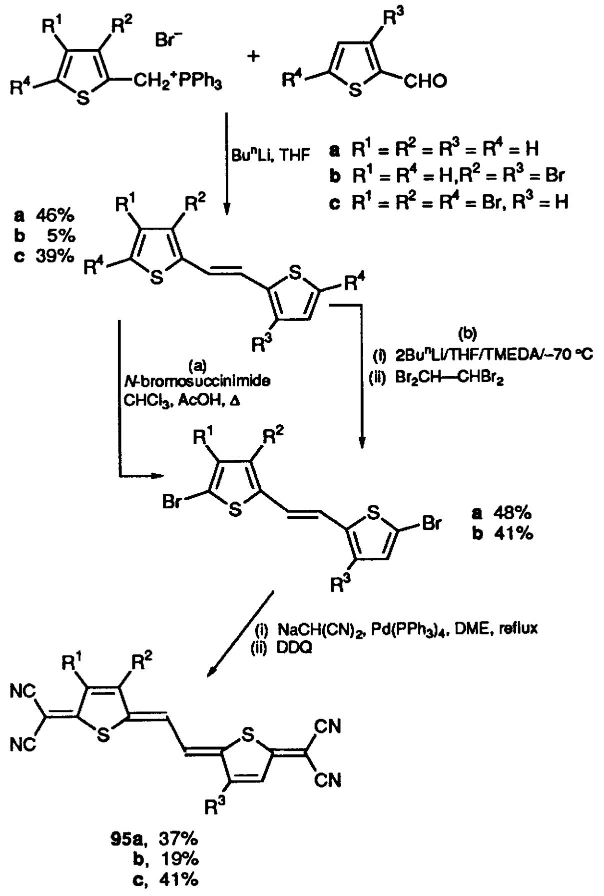
93



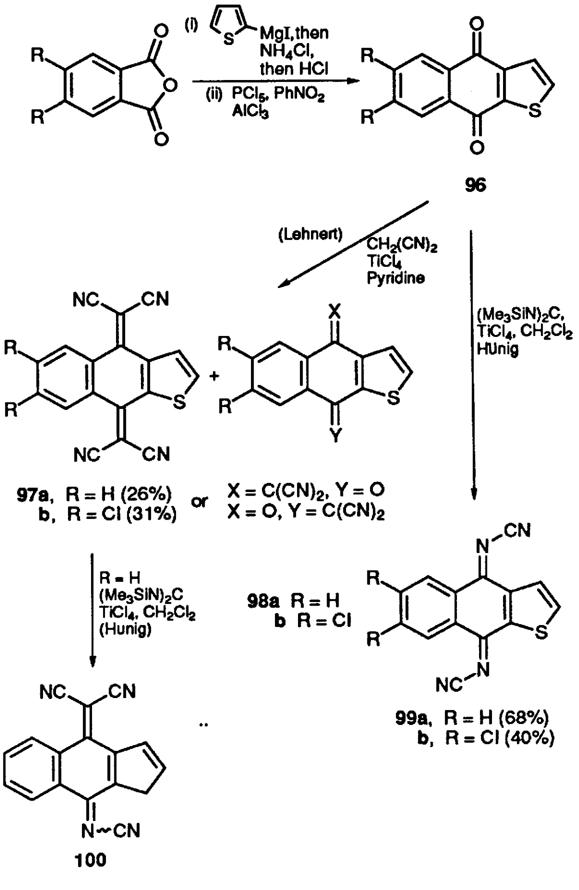
94

Extended vinylogous thiopheno-TCNQ derivatives have now been synthesized in order to further investigate this postulate.[74] Three extended hetero-TCNQ derivatives, **95a–c**, were prepared by the coupling of two thiophene units using Wittig procedures (**Scheme 24**). All three acceptors were obtained as deep violet fine crystals, for **95a, b**, albeit in poor overall yield (4% and < 1% respectively) though that for **95c** was rather better (16% *via* a two-step process). Cyclic voltammetry studies (*versus* Ag/AgCl in DMF) indicate a single reversible two-electron reduction ($E_1 = 0.13$ V) for **95a**, demonstrating the extensive conjugation present here (the first and second reduction potentials coalesce). This electron affinity compares poorly with that for thiophene-TCNQ **94** which exhibits two reversible single-electron reductions (at 0.08 and − 0.50 V). However, the dibromo derivatives **95b,c** show similar behaviour to **94**, the symmetrical isomer being reduced at 0.07 and the unsymmetrical derivative at 0.02 and − 0.18 V, and thus have reduced energy gaps. Both **95a** and **95b** are symmetrical and suffer from poor solubility in organic solvents whereas **95c** is soluble in hot chlorobenzene and forms charge-transfer complexes with TTT and 2,3-dimethyl-1,4,9,10-tetraselenoanthracene each of which show high conductivity, $\sigma = 0.011$ and 0.3 S cm^{-1} respectively. Compound **95c** also forms a poorly conducting charge-transfer complex with tetraphenyl-bipyranylidene ($\sigma = 4.3 \times 10^{-8}$ S cm^{-1}).

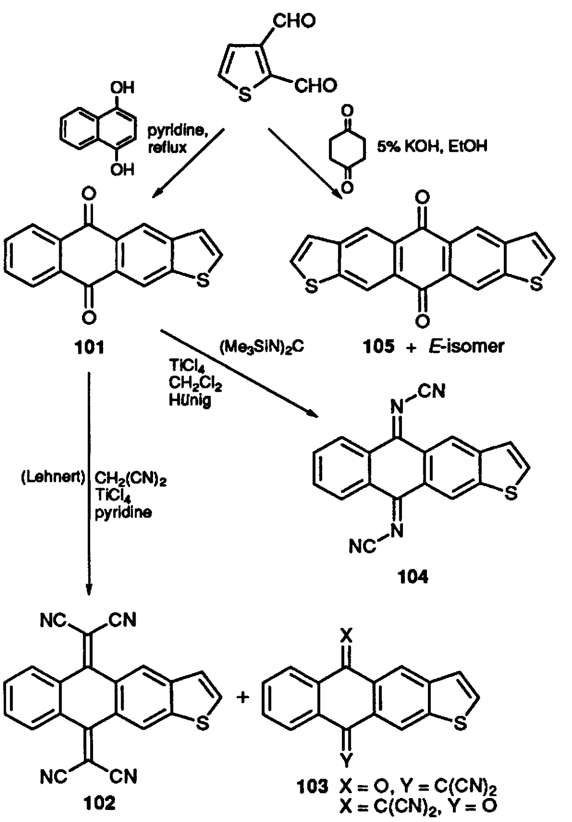
Another approach for increasing dimensionality is to fuse the heterocyclic rings to the main ring of the acceptor. Several TCNQ (**97, 102**), DCNQI (**99, 104**), TCNQI (**100**), and mono-reacted derivatives (**98, 103**) have been prepared[75] from the appropriate thienoquinones (**96, 101, 105**) using combinations of the Lehnert procedure and the Hünig condensation (**Schemes 25 and 26**).



Scheme 24



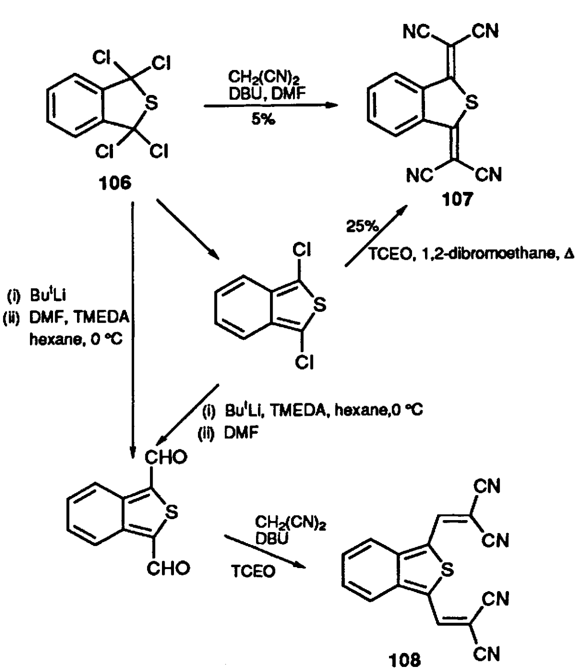
Scheme 25



Scheme 26

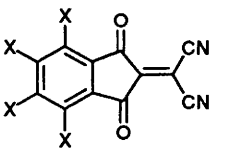
The thieno-quinones were approached by multi-step pathways appropriate to the particular quinone. UV spectroscopy suggests a lack of planarity in the TCNQ derivatives and this is borne out by the electrochemical studies which reveal only single two-electron reductions to the dianions. The DCNQI derivatives, however, exhibit two single-electron reductions consistent with more planar structures. The hybrid TCNQI compound **100** also shows two single-electron reductions and the greatest electron accepting ability.

The isothianaphthene core has also provided a starting point for incorporation of a heterocyclic ring into an electron-acceptor.[76] Two examples have been prepared from tetrachlorothionaphthalene **106** both of which show two reversible one-electron redox potentials (cyclic voltammetry *versus* Ag/AgCl in CH_2Cl_2) (**Scheme 27**). The benzothiophene derivative **107** has $E = 0.31$ and $E = -0.78$ V whereas those for the benzothiophene analogue **108** are -0.25 and -0.62 V respectively, values which are much lower than those found for thiophene-TCNQ **94**.

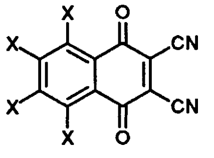


DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene
TCEO = tetracyanoethylene oxide

Scheme 27



109 a, X = H (DCIBD)
b, X = Cl



110 a, X = H (DCNQ)
b, X = Cl

3.2 Electron acceptors DCID and DCNQ

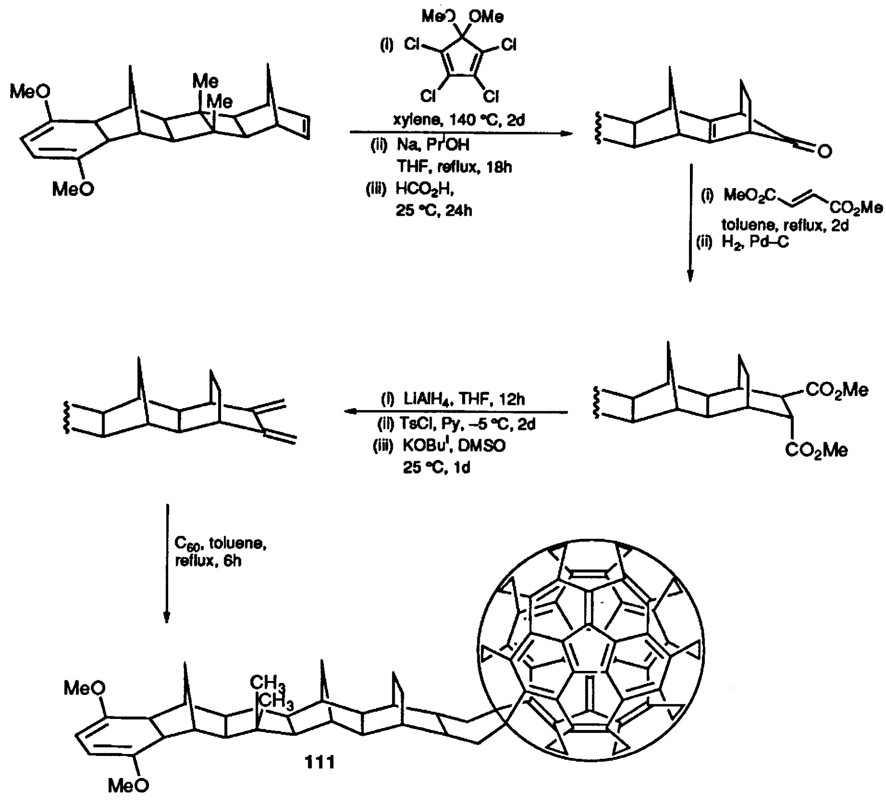
Attempts to prepare charge-transfer salts of the electron acceptor 2-dicyanomethyleneindane-1,3-dione (DCID, **109a**) with TTF or TMTTF were hampered by the rearrangement of the DCID radical anion into the DCNQ (2,3-dicyano-1,4-naphthoquinone) radical anion **110a**.[77] Similar behaviour was observed for tetrachloro-DCID (**109b**), this time giving, however, tetrachloro-DCNQ (**110b**). Other electron-acceptors based on an indane core have been synthesized all of which are weaker acceptors than DCID.

4 Approaches to devices

4.1 Donor–acceptor complexes

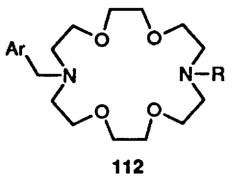
Perhaps one of the most imaginative uses of C_{60} to date has been its incorporation into the 'ball-and-chain' type donor-acceptor array **111**,[78] attachment to the fullerene being achieved through a Diels–Alder process (**Scheme 28**). The rigid spacer is itself prepared in several steps from the Diels–Alder adduct of *p*-benzoquinone and cyclopentadiene and has also been used to construct other arrays in which the acceptor is a 1,2-dicyanoethene or dialkyl maleate unit.[79]

Another novel approach to donor–acceptor systems has involved the use of a diaza-18-crown-6 'active spacer' through which inclusion of metal ions should modulate the donor–acceptor interaction.[80] A number of unsymmetrical structures (**112**) have been prepared; unsymmetrical alkylation of the diaza-crown being achieved through efficient chromatographic separation of the mixture of mono- and bis-alkylation products

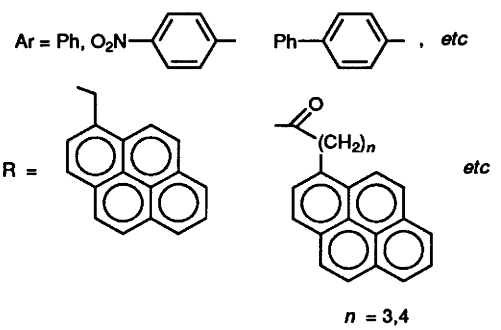


Scheme 28

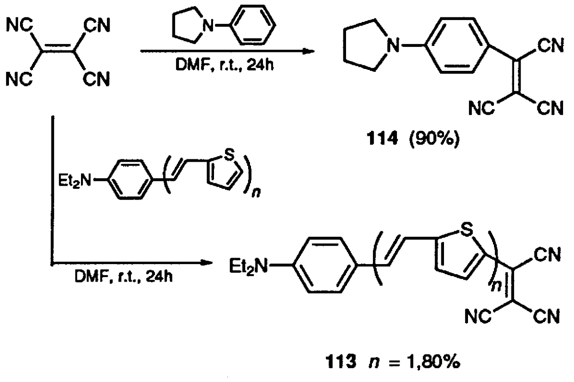
obtained when molar equivalents of diaza-crown ether and alkylating agent are reacted. Such structures offer an interesting approach to ion-selective molecular switching devices.



112



Fully conjugated polyene-linked donor–acceptor systems have large molecular non-linearities, a property of potential importance in molecular electronic devices. A number of syntheses of materials of this type have been reported. These include tricyanovinyl thiophene derivatives such as **113** which have dramatically enhanced molecular non-linearities ($\beta\mu \sim 6000-7000$) in comparison with simple aromtic analogues such as **114** ($\beta\mu \sim 700$) (**Scheme 29**).[81]



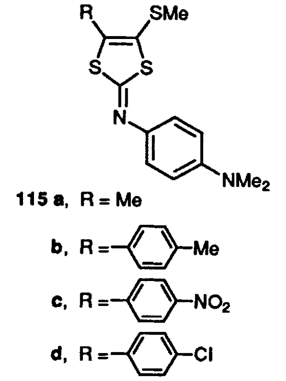
Scheme 29

The imino-dithioles **115**, which are readily prepared by reaction of various amines with 2-amino-1,3-dithiolium cations,[82] are also potentially interesting push–pull polarized systems.

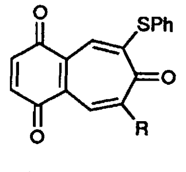
6-Phenylthio- and 6,8-bis(phenylthio)-benzo-cycloheptene-1,4,7-triones **116** have been synthesized.[83] In the solid state the bis(phenylthio) derivative **116b** adopts a segregated column structure with considerable overlap of the π-acceptor systems and seems to be a potential candidate for a new type of organic conductor containing a donor–acceptor–donor molecular unit.

4.2 Molecular switches and rectifiers

The syntheses of two structurally related photochromic switching devices have been

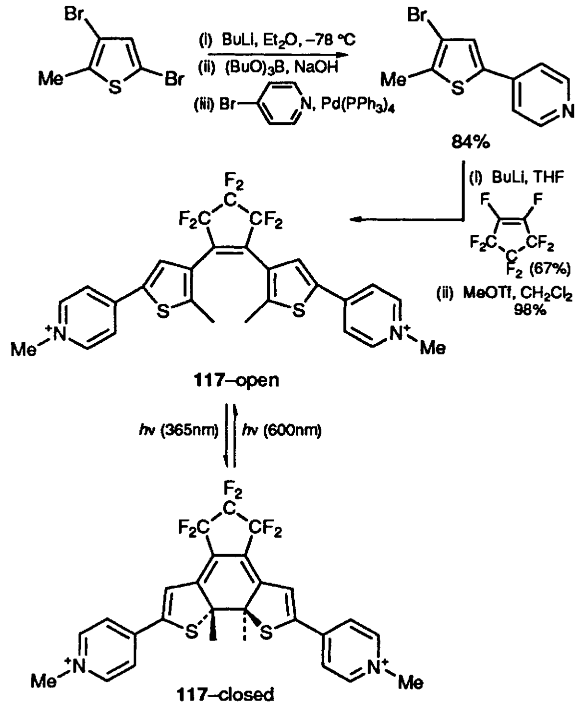


115 a, R = Me
b, R =
c, R =
d, R =



116 a, R = H
b, R = SPh

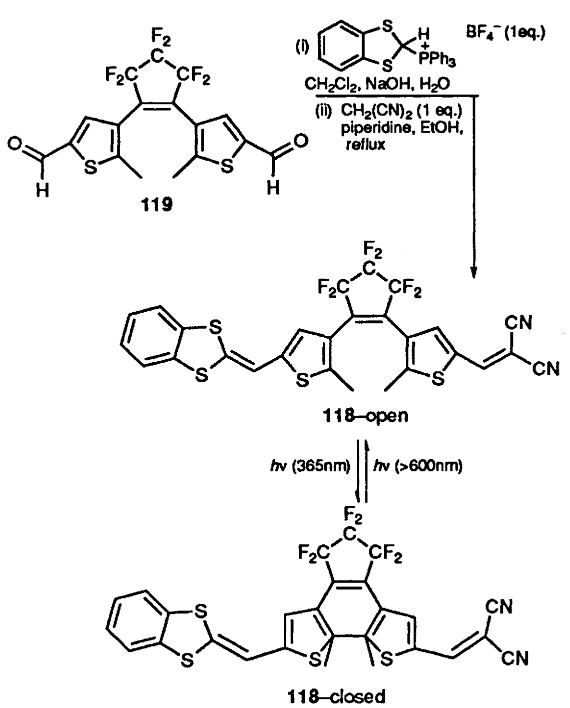
described.[84] Compound **117** (**Scheme 30**) is the prototype of a photo-switchable molecular wire displaying light-triggered reversible changes in optical and electrical properties. In the open form cyclic voltammetry shows no electrochemical process in the region ± 0.6 volts, whereas the closed structure has a reversible one-electron reduction for which $E_{1/2} = -0.23$ volts. **118** (and its symmetrical analogues) are readily prepared from the dialdehyde **119** by Wittig reaction and/or base-catalyzed condensation with malononitrile (**Scheme 31**).



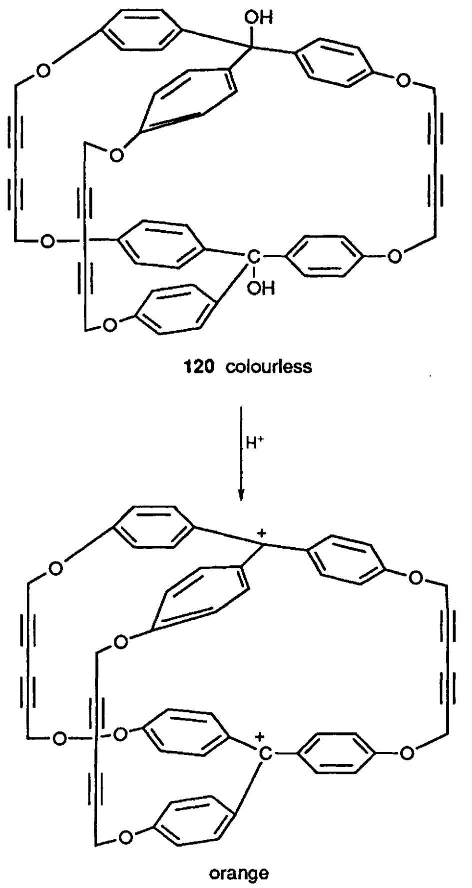
Scheme 30

Irradiation of **118-open** results in effectively complete ring closure (> 98%) to give the conjugated donor–acceptor structure **118-closed** which has λ_{max} 828 nm with a very high ε_{max}. Such systems are of interest for possible use as non-linear optical materials.

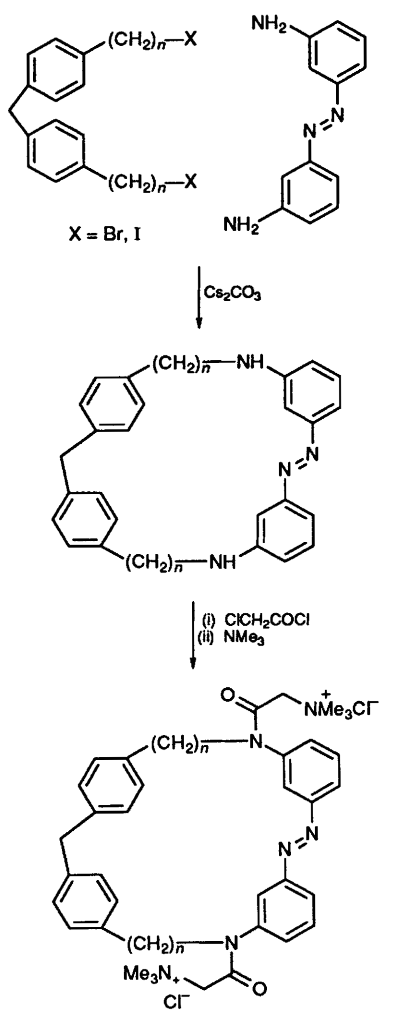
Multiply-bridged dyes such as **120**, which are readily prepared from the corresponding triaryl methanes by Eglinton coupling, act as pH-sensitive optical switches (**Scheme 32**).[85] The water-soluble azo-benzenoid macrocycles **121** are photochemically switched molecular hosts for small molecules such as benzene and naphthalene derivatives (**Scheme 33**).[86]



Scheme 31



Scheme 32



121 n = 1,3–6

Scheme 33

5 Conclusions

The development of improved and more versatile synthetic routes to symmetrical and unsymmetrical tetrathiafulvalene derivatives and analogues remains a major objective for the production of highly conducting organic materials. Of particular interest are structures incorporating heterocyclic (particularly sulfur-containing) units as central spacers and novel systems such as the dendralenes. However, TTF-based moieties are also beginning to find wider application as electron-acceptors in more complex molecular electronic devices for which a versatile repertoire of synthetic techniques is essential. Considerable advances have also been made in the preparation of electron-acceptors related to the TCNQ skeleton and the combination of Lehnert and Hünig procedures has provided simple (if somewhat unreliable) routes to mixed bis(cyanomethine)/*N*-cyano-imino structures. Nonetheless the need remains for new, readily prepared electron-acceptor systems. However, perhaps the most exciting challenges lie in the field of molecular switching devices and we can look forward to important developments in this area.

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