Linearly extended π-donors: when tetrathiafulvalene meets conjugated oligomers and polymers

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Molecular or polymeric π-electron donors based on the association of tetrathiafulvalene (TTF) with linear π-conjugated systems are reviewed. Two main classes of materials are considered, namely electrogenerated polymers, either conjugated or not, and linearly extended TTF analogues built by insertion of different π-conjugating spacer groups between the two 1,4-dithiafulvenyl moieties. Particular emphasis is placed on the relationships between structure and electronic properties and on the potential offered by these new classes of π-electron donors.

For more than twenty years, organic materials with metal-like conductivity have been the focus of a considerable and sustained interest, motivated by both the fundamental problems that their electronic properties pose to theoreticians and solid-state physicists and their high technological potential. Apart from the recently emerged doped fullerenes, which form an important new family of organic metals,[1] organic conductors involve basically two main classes of materials that differ in their structure, electronic properties and the scope of their potential industrial applications.

Charge-transfer salts of tetrathiafulvalene (TTF) represent the prototype of molecular conductors.[2] These crystalline materials are composed of segregated stacks of π-donors and counter-anions. The short interplanar distances allow significant interactions between π-molecular orbitals of neighbours, which result in a high anisotropy of conductivity along the direction of stacking through intermolecular intra-stack migration of aromaticity.[3]

The discovery of the superconductivity of cation radical salts of tetramethylselenafulvalene in 1980[4] triggered the development of a rich synthetic chemistry which has as its main goal the raising of the critical temperature for superconductivity through the synthesis of materials likely to exhibit an increase in the dimensionality of the conduction process.[5] As a matter of fact, theoretical works have shown that low dimensional conductors are unstable; the coupling of electrons and phonons with lattice vibrations results in a localization of the charge density wave and thus in the suppression of the metallic state at a certain temperature.[6]

The increase of the dimensionality of the materials has been identified at an early stage as a priority, and to this end various approaches have been defined, such as (i) the replacement of sulfur by chalcogens with more diffuse orbitals (Se, Te), (ii) the increase of the sulfur content in the structure, or (iii) the spatial extension of the donor molecule in order to stabilize multicationic states and to enhance intermolecular and interstack interactions. The most well-known illustration of these approaches is bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), in which the presence of extra sulfur atoms contributes to intra- and inter-stack interactions. Consequently, most metallic BEDT-TTF salts are quasi-two-dimensional materials and some of them remain superconducting up to *ca.* 12 K at ambient pressure.[7]

For more than fifteen years, the synthetic chemistry of TTF has been almost exclusively focused on the search for new π-donor structures prone to produce conductors of higher dimensionality,[5,8] and it was only recently that TTF chemistry has deviated from this rather fundamental aspect to touch on other areas like, for example, macrocyclic chemistry[9] or dendrimers.[10]

Conjugated polymers (CPs) represent the other broad class of organic conductors. The unique electronic properties of these materials originate from the existence of a linear π-conjugated system extending over a large number of recurrent units. Polyacetylene is the archetype of this type of structure,[11] however, owing to its limited stability it has been progressively supplanted by more stable aromatic CPs such as polyphenylene,[12] polypyrrole,[13] polyaniline[14] or polythiophene.[15] During the past decade, polythiophene (PT) has progressively emerged as the prototype of this second generation of CPs due to a unique combination of stability and structural versatility.[16]

Similarly to TTF charge transfer salts, CPs are basically low dimensional conductors. In this case, Peierls instability leads to the localization of single and double bonds, which results in the opening of a gap generally larger than 1.50 eV between the valence and the conduction band. Thus, instead of the metallic conductivity which should result from the delocalization of π-electrons over the whole conjugated backbone, neutral CPs behave as insulators. Consequently, achievement of electrical conductivity requires the injection of holes or electrons by oxidation (p-doping) or reduction (n-doping) of the conjugated chain. Doped CPs exhibit a strong anisotropy of conductivity along the chain direction through the migration of charged defects coupled to a local deformation of the π-conjugated structure (polarons or bipolarons).[17]

Technological applications of CPs have been considered at an early stage. Consequently, soon after their discovery, an important part of the synthetic chemistry devoted to these materials has been focused on the development of a large variety of functional CPs in view of specific applications,[15,18] whereas more basic research aiming at the structural control of their electronic properties has attracted less attention.

The recent and rapid emergence of advanced applications of CPs in electronic devices[19] or light-emitting diodes[20] during the past few years has strongly contributed to drawing the

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problems related to the control of the electronic properties of CPs to the forefront of their chemistry.[21] The growing importance acquired by more basically oriented synthetic chemistry has been accompanied by a considerable intensification of research effort on conjugated oligomers of defined structure and in particular oligothiophenes.[15,19,21–23] From a fundamental viewpoint, these compounds represent almost ideal models for the analysis of the electronic properties of the parent polydisperse polymers.[22] On the other hand, their processibility by vacuum sublimation techniques has considerably renewed the application of linear π-conjugated systems in the field of electronic devices such as diodes or field effect transistors.[19,23]

Thus, whereas the spatial extension of TTF π-donors has become a major trend in modern TTF chemistry,[8] some recent developments in that of CPs have taken the opposite direction, with the synthesis of shorter systems of controlled structure and dimensions more suitable for fundamental research and some technically oriented domains. The crossroad of these two research lines has given birth to new classes of electronic materials combining some structural features and electronic properties of TTF derivatives and linear π-conjugated systems. Such a combination can be envisioned *via* various strategies. The first consists in the covalent attachment of TTF onto a conjugated polymeric backbone. Depending on the context, this approach can be viewed either as a means of improving the processability of TTF charge-transfer salts and of increasing their dimensionality, or as a way to increase the charge-storage capacity of CPs and to control the long-range order in the π-conjugated backbone by taking advantage of the strong propensity of TTF to form ordered stacks.

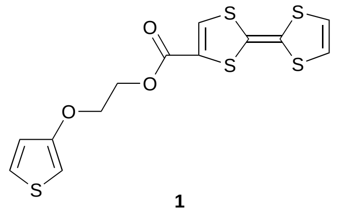
The second type of association involves the connection of two half-TTF moieties to both ends of a linear π-conjugated system. Whereas the seeds of this strategy can be found in the general context of spatially extended TTF π-donors,[8] the insertion of π-conjugated systems of increasing dimensions has modified this view and these compounds appear more and more as a new class of end-capped π-conjugated oligomers.

The aim of this review is to present a brief overview of these emerging classes of electronic materials. Particular emphasis is placed on the relationships between molecular structure and electronic properties and on the possible cross-fertilization offered by such structural combinations, rather than on the synthetic chemistry of these new compounds, for which further details can be found in the literature cited.

Electrogenerated TTF-derivatized polymers

Despite their unique electronic properties, single crystals of TTF charge-transfer salts are unprocessable materials, which represents a major obstacle to practical applications. In order to overcome this problem there have been several attempts to incorporate TTF into processable polymeric matrixes. While several groups have developed the synthesis of polymers such as polyamide,[24] polyurethane,[25] polyphenylene,[26] polystyrene,[27] or polyesters[28] in which TTF moieties were included either in the main chain or as pendant groups, it was only recently that the grafting of TTF on a CP backbone has been considered. The interest in such an approach is based on several points. From the CP viewpoint, the propensity of TTF to form ordered stacks can represent an interesting tool to control the long range order of the conjugated backbone.[29] On the other hand, in the frame of TTF-based conductors, such a combination can contribute to an increase in the dimensionality of the conduction process and might eventually lead to materials presenting hybrid conduction.

As a first step in this direction, Bryce *et al.* reported the synthesis of compounds **1**–**3**.[29]



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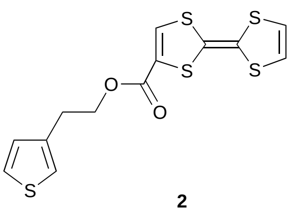

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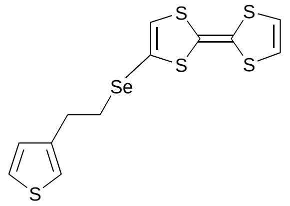

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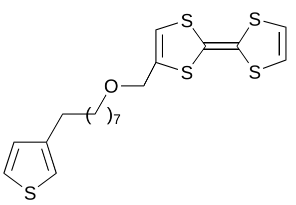

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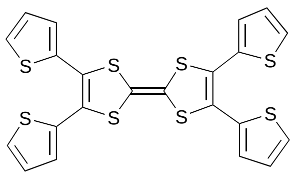

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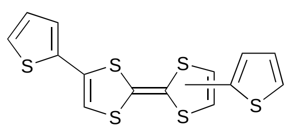

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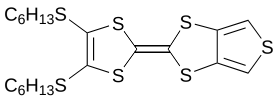

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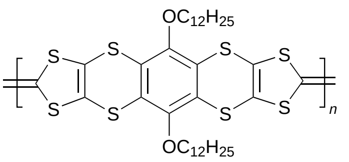

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Attempts to electropolymerize **3** led to a thin orange film. Although detailed characterization was not reported, the colour of the film suggests a rather limited conjugation length which might be related to steric problems. Electropolymerization of **4** in which steric interactions between TTF moieties are reduced by insertion of an oxadecyl spacer has been reported by Thobie-Gautier *et al.*[30] Attempts at electrolymerization in acetonitrile were unsuccessful but application of recurrent potential scans to a nitrobenzene solution led to the formation of a dark blue film. This different behaviour has been attributed to the formation of a charge-transfer complex between TTF and nitrobenzene. The cyclic voltammogram (CV) of the resulting polymer exhibits the typical signature of TTF and PT (Fig. 1), while the splitting of the first reduction wave indicates the presence of a mixed valence dimer $(\mathrm{TTF})_2^{\cdot+}$.

Recently Charlton *et al.* have described the synthesis and X-ray structure of compound **5**.[31] The cyclic voltammogram of this compound shows two reversible oxidation waves at potentials more positive than TTF, a result attributed to the electron-withdrawing effect of the attached four thiophene rings. Attempts to electropolymerize this compound did not provide conclusive evidence for polymerization. The oxidation potentials of TTF in the related compound **6** were also found to be more positive than those for free TTF but its electropolymerization has not yet been attempted. This compound forms a highly conducting complex with TCNQ ($\sigma = 4.6\ \mathrm{S\ cm^{-1}}$).[32] Owing to the presence of the free 2,5-positions in the thiophene ring, the structure of **7** could seem *a priori* more suitable for electropolymerization than that of **5** or **6**. However, attempts to electropolymerize this compound remained unsuccessful.[33] Frenzel *et al.* have attempted to reach a fully conjugated structure by inserting the TTF moiety in the conjugated path **8**. However, due to its insolubility, the obtained material could not be characterized in detail.[34]

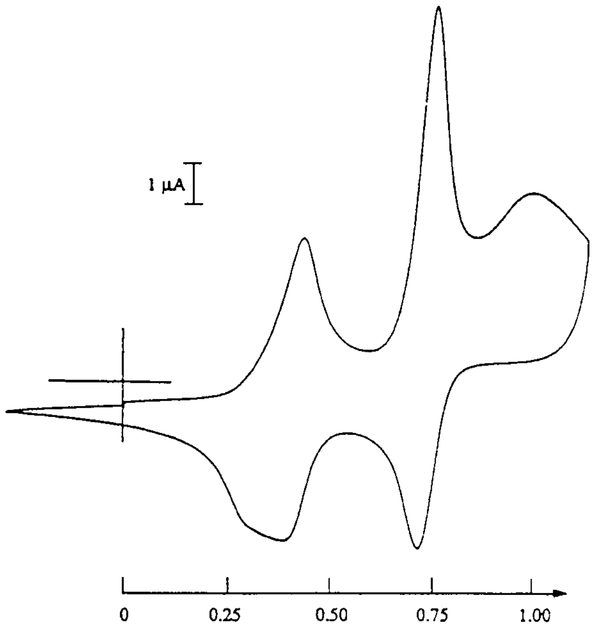
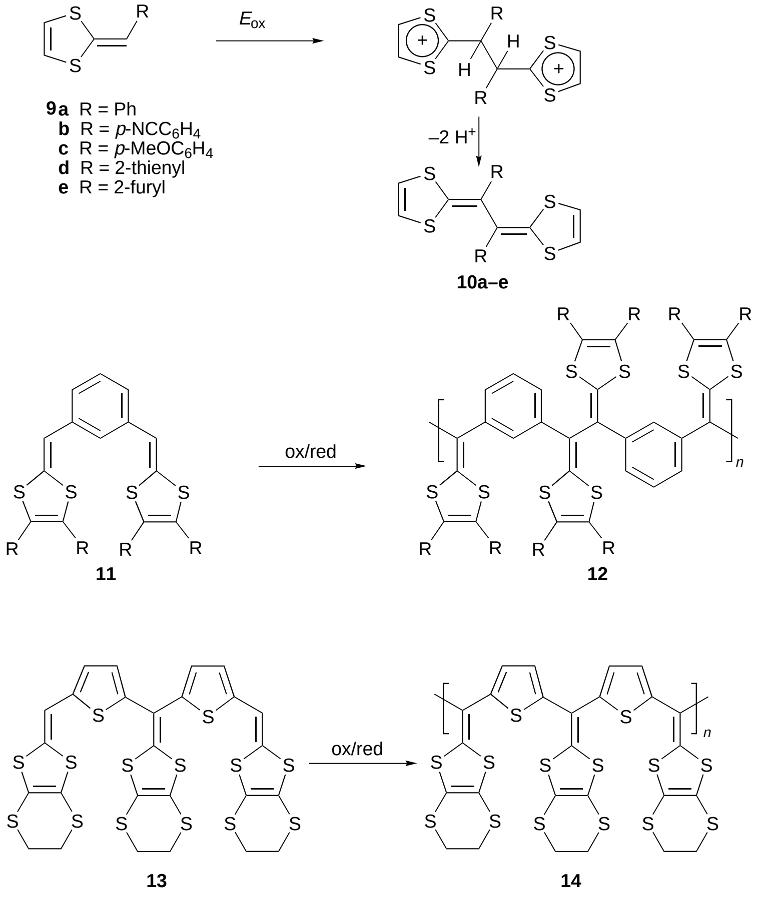


Fig. 1 Cyclic voltammogram of poly(**4**) in 0.1 M Bu_4NPF_6/CH_3CN, scan rate 10 mV s^{-1} (Reprinted from ref. 30. Copyright 1993, American Chemical Society)

The synthesis of CPs with TTF pendent groups remains a very attractive goal with, as a long-term objective, the development of materials of increased dimensionality exhibiting mixed-conduction properties. However, the design of an appropriate precursor structure remains a challenging task which requires the simultaneous control of many variables. As a matter of fact, the introduction of the TTF group should not affect the aptitude for electropolymerization, which implies that electronic and steric effects are properly taken into account. Furthermore, only a precise control of the relative position of TTF moieties in the polymer can ensure a proper packing allowing mixed-valence interactions and hence intra-stack conduction. Finally, since the development of hybrid conduction implies that both components become conductive in the same potential range, a precise tuning of the oxidation potential of both the attached TTF group and the conjugated backbone is required. Simultaneous fulfilment of these various conditions poses considerable problems for the synthetic chemistry and this probably explains why most attempts in this direction have so far remained unsuccessful. Some results from our laboratory have shown that one of the key problem lies in the excessive difference between the oxidation potential of TTF and that of the polymerizable moiety. In this context, the recent synthesis of easily electropolymerizable tailor-made precursors can be expected to give new impetus to this research area.[35]

Electrochemical synthesis has been successfully applied to the preparation of non-conjugated polymers involving TTF vinylogues. This approach is based on the initial observation that oxidation of compounds **9** induces an intermolecular dimerization leading to a TTF vinylogue disubstituted at the ethylene linkage (Scheme 1).[36]

More recently, several groups have reported that this process could be achieved *via* electrooxidation of compounds **9**.[37–39] The CVs of the resulting TTF vinylogues show a reversible single oxidation wave at a less positive potential than that of the precursor. In the case of compounds containing phenyl substituents (**9a**–**c**) this single wave has been attributed to a two-electron transfer leading to the direct formation of the dication.[39] This behaviour contrasts with that of the corresponding vinylogues with R = H which present two monoelectronic waves.[40] Furthermore, contrary to the unsubstituted



Scheme 1

vinylogues that adopt a planar geometry, X-ray diffraction data for a crystal of **10c** reveal a highly twisted structure.[39] In the case of thiophene-containing vinylogues, the similarity of the oxidation potential of the precursor **9d** and its dimer **10d** has led to an alternative proposal involving formation of a bis-cation radical in which the two dithiafulvenylthiophene moieties are oxidized independently without through-conjugation Coulombic repulsion.[38]

As suggested by extended Hückel calculations performed on π-donor molecules built on the 1,3,5-substituted benzene core, the occurrence of this electrochemical coupling process is related to a high electronic density at the linking site.[41] Consequently, molecules possessing such a high electronic density at more than one potential coupling site can be expected to give rise to the formation of a polymeric material upon electrooxidation. Thus, in compound **11**, the *meta* linkage of the two 1,4-dithiafulvenyl moieties prevents their conjugation through the benzene ring, thus favouring a high density of unpaired electrons at the vinyl carbon in the cation radical. As appears in Fig. 2, application of repetitive potential scans to a dichloromethane solution of **11** leads to the development of a new redox system at a less positive potential than the oxidation peak of **11**. This behaviour indicates that electrodeposition of a material containing π-donor moieties more conjugated than in the precursor occurs. The CV of the resulting polymer shows two very close reversible oxidation waves assigned to the successive generation of the cation radical and dication of the formed TTF vinylogue.[42]

Ohta and Yamashita have described π-donors of general structure **13**.[43] Here the high electronic density at the ethylene linkage is probably due to a distortion of the molecule caused by steric interactions between the substituted 1,4-dithiafulvenyl moieties. This twisted structure is confirmed by the fact that the resulting electrogenerated polymer **14** oxidizes at more positive potential than its precursor **13**.[43]

To summarize, the electrochemical polymerization of *meta*-disubstituted benzenes **11** represents a potentially interesting, novel approach towards non-conjugated polymers containing TTF vinylogues. However, much further work, with in particular the development of more soluble precursors allowing the synthesis of high molecular weight polymers, is needed before this method becomes of practical interest.

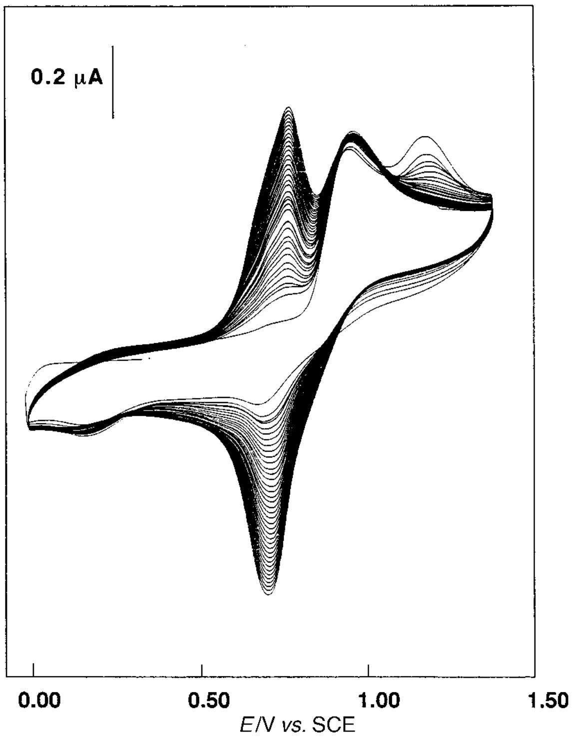


Fig. 2 Repetitive cyclic voltammograms corresponding to the electropolymerization of **11** (2×10^{-3} M) in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, ref. SCE, scan rate 300 mV s^{-1} (Reprinted from ref. 42. Copyright 1995, Société Française de Chimie)

Linearly extended TTF analogues with π-conjugated oligomeric spacers

The design of TTF-based donors with linearly extended π-conjugation has progressively emerged as one of the main synthetic strategies towards TTF charge-transfer salts of higher dimensionality. This approach is based on the following rationale: (i) stabilization of the oxidized states by the increased delocalization of the positive charges, (ii) access to upper multi-charged oxidation states, (iii) reduction of the intra- and inter-molecular Coulombic repulsion between positive charges in the multi-cationic states and (iv) enhanced intermolecular interactions leading to new packing arrangements in the crystal.[8]

However, with the insertion of linear π-conjugated spacers of increasing dimensions between the two 1,4-dithiafulvenyl moieties, these systems appear more and more as a peculiar class of end-capped conjugated oligomers. This different viewpoint has progressively enlarged the scope of this research area, which at present also represents an interesting strategy to control the electronic properties of linearly π-conjugated systems.

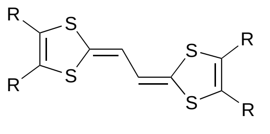
Conjugated oligomers and especially oligothiophenes (*n*Ts) have attracted considerable attention during the past few years. From a technological viewpoint, these compounds have been shown to constitute organic semiconductors usable as the active element in diodes,[23a] field effect transistors,[23b] or light-emitting diodes.[44] At a more fundamental level, because of their simple and unequivocal structure, *n*Ts represent interesting simplified model compounds for the analysis of the electropolymerization mechanism of thiophene,[45,46] or for the study of the electronic and electrochemical properties of the parent polydisperse polymer.[22] More recently, end-substitution has received special attention as an efficient way of improving some of the properties of *n*Ts, such as packing arrangement in the solid state,[47] fluorescence quantum yield,[22b] or stability of the cationic state.[48]

In this context, the grafting of the strongly electron-releasing 1,4-dithiafulvenyl groups on to both ends of a conjugated oligomer offers interesting possibilities to control the solid-state structure and electronic properties of the corresponding material. Furthermore, such compounds can significantly contribute to a better understanding of the charge-transport processes in linear π-conjugated systems. By varying the length of the conjugating spacer it should in principle be possible to tune the conduction process from the intracolumnar migration of aromaticity occurring in TTF charge-transfer salts to the polarons/bipolarons mechanism involved in conjugated polymers.

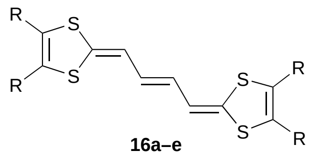
Extended TTF analogues with polyalkenic spacer Groups

Linearly extended TTFs built by insertion of one or several double bonds between the two 1,4-dithiafulvenyl moieties were examined at an early stage. Sugimoto *et al.* first reported the synthesis of vinylogues of TTF (**15**), tetraselenafulvalene and hybrid systems, diversely substituted at the dithiole cycle.[40]

The increase in the number of sp^2 carbons in the spacer group leads to a red shift of the maximum of the absorption

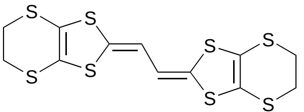


15a–e



16a–e

a R = H
b R = CO_2Me
c R = Me
d R = Ph
e R-R = $(CH{=}CH)_2$–



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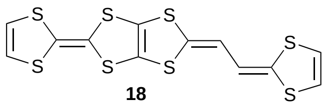

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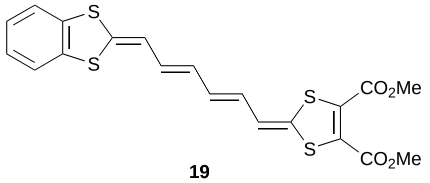

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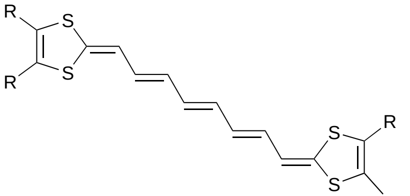
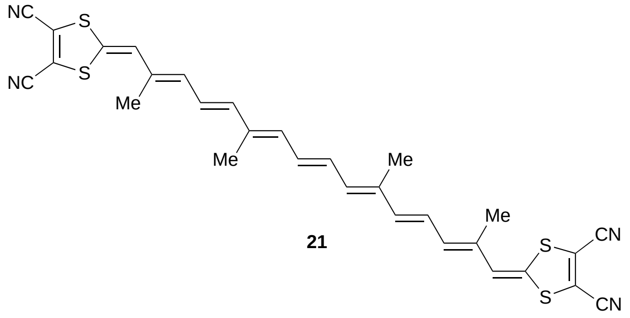


20 a R = CO_2Me
b R = Me



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band of lowest energy from 368 nm for TTF to 404 and 432 nm for **15a** and **16a**, respectively, and to a decrease of the HOMO–LUMO gap.[40] Partial or complete replacement of sulfur by selenium in the structure of **15a** produces a slight blue shift of λ_{max} with a loss of resolution of the vibronic fine structure. With the insertion of two sp^2 carbons in the spacer the two oxidation potentials $E_{ox}1$ and $E_{ox}2$ corresponding to the successive formation of the cation radical and dication shift negatively from 0.34 and 0.71 V *vs.* Ag/AgCl for TTF, to 0.20 and 0.36 V for **15a**, while the difference $E_{ox}2-E_{ox}1$ decreases. Introduction of an additional double bond in the spacer has almost no influence on $E_{ox}1$ but produces a further decrease of $E_{ox}2$, while $E_{ox}2-E_{ox}1$ becomes very small (6 mV), indicating a stabilization of the dication state.

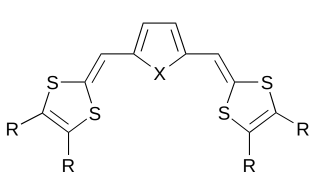
The synthesis of the vinylogue of BEDT-TTF **17** was reported almost simultaneously by three groups.[49] As for the parent TTF-based compounds **15**, insertion of the two sp^2 carbons spacer induces a negative shift of $E_{ox}1$ and $E_{ox}2$ from 0.59 and 0.99 V *vs.* Ag/AgCl to 0.48 and 0.71 V, respectively, while $E_{ox}2-E_{ox}1$ decreases from 0.41 to 0.23 V.[49b] Recently Misaki *et al.* have reported the synthesis of a fused π-donor containing a vinylogue of TTF (**18**).[50] The cation radical salt containing $Au(CN)_2^-$ salt as counter ion was shown to exhibit superconductivity below 4 K at ambient pressure. This first example of a superconductor derived from a linearly extended TTF analogue provides strong support to the validity of this approach and will with no doubt stimulate further work in this direction.

Compounds **19** and **20** involving longer polyalkenic spacers have been synthesized by Nguyen *et al.*[51] While the extension of the spacer length does not produce significant change in the first oxidation potential, direct formation of the dication state through a two-electron transfer ($E_{ox}2-E_{ox}1=0.00$ V) was observed for **20a**. However, it was reported that replacement of the electron-withdrawing CO_2Me group by a methyl (**20b**) leads to a considerable decrease of stability. This result illustrates one of the major limitations of polyalkenic spacers, namely that the decrease in stability resulting from the lengthening of the spacer must be counterbalanced by the grafting of electron-withdrawing groups on to the 1,4-dithiafulvenyl moiety. Quite recently, Märkl *et al.* reported the synthesis of TTF analogues with polyalkenic spacers containing up to 16 sp^2 carbons (**21**), which are the longest reported to date.[52] For most of the compounds investigated, both 1,3-dithiole rings contained cyano substituents at the 4 and 5 positions, presumably for stability reasons. The analysis of the effect of the spacer length on the optical properties reveals, as expected, a red shift of the absorption maximum of the lowest energy transition with no apparent saturation of effective conjugation. In contrast, the first oxidation potential seems to converge to an asymptotic value of *ca.* 0.60 V *vs.* saturated calomel electrode (SCE).[52]

Extended TTF analogues with heterocyclic spacer groups

While polyalkenic spacers allow optimal π-electron delocalization in the corresponding linearly extended TTF analogues, the limited stability of polyenes appears as a major limitation. The most immediate answer to this problem consists of the use of spacer groups based on the more stable aromatic ring systems. TTF analogues involving benzenic spacers have been considered by several groups.[53–56] Analysis of the effects of the relative placement of the 1,4-dithiafulvenyl moieties has shown that, besides the already discussed dimerization process associated with *meta* linkage,[41,42] *ortho*-disubstituted TTF analogues undergo rapid intramolecular cyclization, either acid-catalysed or electrochemically induced.[55,56] Whereas *para*-substituted compounds represent the only stable members of this series,[53,54] the high oxidation potentials of TTF analogues involving π-benzenic spacers considerably limits the interest of this approach. Since oxidation into the cation radical and dication states implies the dearomatization of the benzene ring into a quinoid form, it is evident that the high oxidation potential of these compounds is related to the localization of π-electron associated with the high resonance energy of benzene.

TTF analogues including five-membered heterocyclic spacers such as furan, thiophene and pyrrole (**22**–**24**), have been reported almost simultaneously by four groups.[37,57–60] As the aromatic resonance energy of these five-membered heterocycles is lower than that of benzene, a better π-electron delocalization over the whole donor molecule can be anticipated.



22 X = O
23 X = S
24 X = NMe

a R = H
b R = SMe
c R = CO_2Me
d R-R = $-(CH{=}CH)_2-$
e R-R = $-(CH_2)_4-$
f R-R = $-S(CH_2)_2S-$

All these compounds show two reversible one-electron oxidation waves *via* cyclic voltammetry. Table 1 lists as representative examples the electrochemical data for the unsubstituted and the dibenzo-substituted compounds together with those of the corresponding TTFs. These data show that introduction of the heterocycle produces a negative shift of the anodic peak potentials corresponding to the successive generation of the cation radical and dication (*E*pa1 and *E*pa2) and to a decrease in their difference. These results reveal both an enhanced delocalization of π-electrons and a reduced Coulombic repulsion between positive charges in the dication. On the other hand, *E*pa1 decreases in the order thiophene > furan > pyrrole. Although the aromatic resonance energy of the heterocycle is likely to play an important role, this is not the only factor since in this case, furan-based compounds should exhibit the lowest *E*pa1 values. The lowest *E*pa1 values found for pyrrole containing donors have been attributed to the ability of pyrrole to stabilize cationic structures with a positive charge localized at the nitrogen atom.[58]

Independently of the nature of the heterocyclic spacer, only introduction of a tetramethylene substituent at the dithiole cycle (**22e**–**24e**) leads to a negative shift of *E*pa1 compared to hydrogen (**22a**–**24a**), whereas all other substituents behave as electron-withdrawing groups and lead to a positive shift of *E*pa1.

Although introduction of the heterocyclic spacer produces in every case a decrease of *E*pa2 − *E*pa1 compared to the corresponding TTF, *E*pa2 − *E*pa1 values for pyrrole-based π-donors are considerably larger than for their thiophene or furan analogues. This unexpected result can be explained by the different geometries of these molecules.

The ORTEP view of **23a** shows that the molecule adopts a *syn* conformation stabilized by intramolecular interactions between the sulfur atom of the thiophene ring (R1) and those of the 1,3-dithiole units R2 and R3 (Fig. 3). The intramolecular S···S contact distances are larger than a covalent bond distance but smaller than twice the van der Waals radius of sulfur. The 5–7° angles between the R1 plane and the R2 and R3 planes show that the molecule adopts a nearly planar conformation. The crystal structure is stabilized by two rather strong intermolecular interactions (S53···S21A) and (S21···S51A).[61]

In contrast, such interactions do not occur in the case of **24a**, for which the X-ray structure shows that steric hindrance caused by the *N*-methyl group produces an important distortion of the molecule.[62]

Compound **23a** forms a 1 : 1 complex with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with a compacted pellet conductivity of 1×10^{-3} S cm^{-1},[59] while conductivities of 1×10^{-2} and 1×10^{-5} S cm^{-1} have been reported for the TCNQ complexes of **22a** and **24c**, respectively.[58] Although compounds **22**–**24** have been known for almost five years, electrocrystallization of the corresponding cation radical salts was reported to be extremely difficult,[58] and it was only quite recently that the first single crystals of **22a** and **23a** were obtained.[63,64] Comparison of the X-ray diffraction data has shown that the cation radical of the furan-containing compound **22a** presents a better delocalization of the positive charge than its thiophenic analogue. Furthermore, the cation radical of **22a** forms uniform stacks, in sharp contrast with that of **23a** which involves weakly interacting dimers. As a consequence of this better charge delocalization and enhanced dimensionality the cation radical salt of **22a** exhibits a two-probe conductivity *ca.* three orders of magnitude larger than that of **23a** (4×10^{-2} and 7×10^{-5} S cm^{-1}, respectively).[63]

Table 1 Cyclic voltammetric data for **22**–**24**

	E/V *vs* SCE		
	*E*pa1	*E*pa2	*E*pa2 − *E*pa1/mV
TTF	0.35	0.71	360
22a[a]	0.23	0.31	100
23a[a]	0.35	0.45	100
24a[a]	0.19	0.40	210
Dibenzo-TTF[b]	0.72	1.06	340
22d[a]	0.41	0.61	200
23d[a]	0.48	0.68	200
24d[a]	0.32	0.56	240

[a]Ref. 60. [b]Ref. 53.

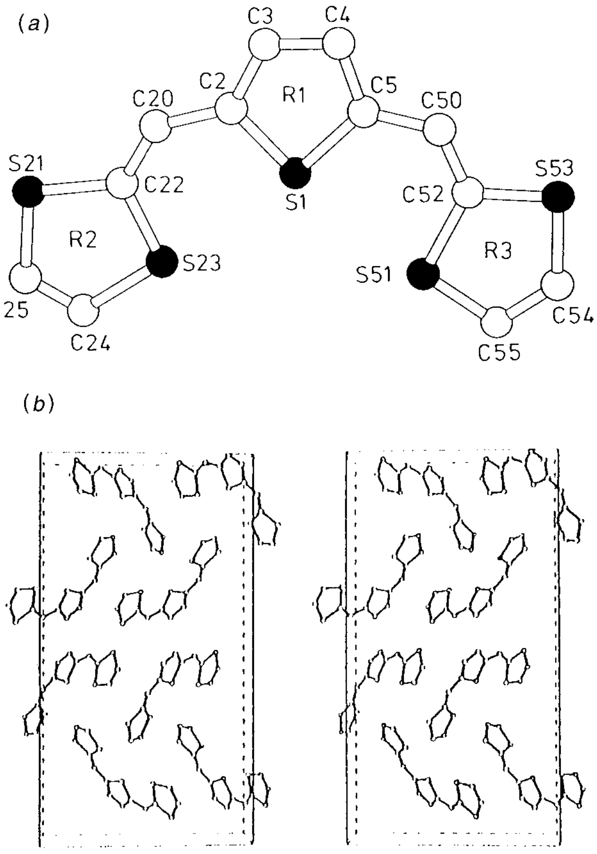
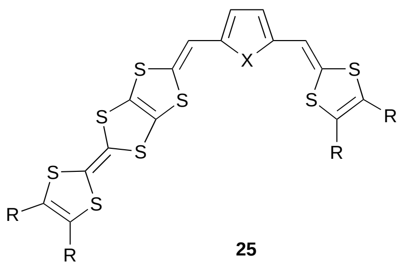


Fig. 3 (*a*) X-Ray structure of **23a**. (*b*) Stereo picture of the packing of **23a** in the crystal. (Reprinted from ref. 61. Copyright 1994, VCH Verlag)

In a recent extension of this approach, Misaki *et al.* have reported the synthesis of bis-fused TTFs (**25**).[64] In contrast to compounds **22**–**24** which adopt a *syn* conformation and a planar structure, X-ray diffraction data of these molecules reveals an *anti* conformation and a small dihedral angle between the planes containing the fused-ring system and the heterocyclic spacer. Although these compounds oxidize at higher potentials than their respective analogues **22** and **23**, cyclic voltammetry shows that they can be oxidized up to the tetracationic state. Compacted pellets of their 1 : 1 TCNQ complexes show conductivities in the range of



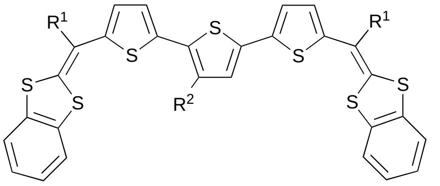
25

X = O, S
R = H, CO_2Me, SMe

10^{-1}–10^{0} S cm^{-1}, significantly higher than those of compounds **22**–**24**.

Extended heterocyclic π-conjugating spacers

A logical extension of this strategy would consist in the use of longer conjugated heterocyclic oligomers as spacer groups in order to achieve a further improvement of π-donor ability and to increase the number of accessible cationic states. Owing to the limited stability of furan and pyrrole oligomers, *n*Ts have been selected as π-conjugating spacer. A first step in this direction involved the synthesis of compounds **26** built around a terthienyl core.[65]

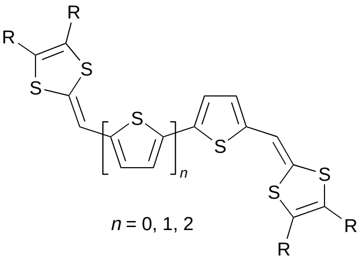


26 a R^1 = H, R^2 = H
b R^1 = H, R^2 = Me
c R^1 = Me, R^2 = Me
d R^1 = H, R^2 = C_8H_{17}
e R^1 = H, R^2 = $(CH_2CH_2O)_2CH_3$

Substitution of the median thiophene ring by alkyl or oxyalkyl chains significantly improves the solubility but produces a *ca.* 30 nm red shift of λ_{max}. These shifts, which largely exceed those observed for terthienyl itself,[45b] suggest that substitution induces considerable changes in the geometry of the terthienyl spacer. On the other hand, introduction of a methyl group at R^1 produces a slight blue shift attributed to a deviation from planarity caused by steric interactions. The insertion of the terthienyl spacer leads to a negative shift of *E*pa1 and *E*pa2 from 0.72 and 1.06 V for dibenzo-TTF[53] to 0.50 and 0.69 V for **26a**, while a third oxidation wave occurs at 0.92 V. The lowest *E*pa1 and *E*pa2 values (0.45 and 0.61 V) are observed for **26c** while **26d** exhibits the smallest *E*pa2 − *E*pa1 difference (120 mV). Compared to dibenzo-TTF, this 220 mV decrease of *E*pa2 − *E*pa1 indicates a significant stabilization of the dication. However, it is worth noting that whereas insertion of a four sp^2 carbon spacer (compound **16**) leads to coalescence of the two successive one-electron oxidation waves into a single-step two-electron transfer,[40] such a phenomenon is not observed for compounds **26**, although the conjugated path of the terthienyl spacer involves twelve sp^2 carbons.

More detailed information on the structure–properties relationships in this series has been gained by analysing the effects of a stepwise increase of the number of thiophene rings (*n*) in the spacer.[61]

Although for each type of R substituent, the increase of *n* leads to a red shift of λ_{max}, this shift is considerably smaller than that observed for the corresponding *n*Ts. Thus, whereas λ_{max} shifts bathochromically by 70 nm between $n = 0$ and $n = 1$ and by 50 nm between $n = 1$ and $n = 2$,[66] these shifts are limited to a few nanometres for the corresponding TTF analogues **23** and **27** while there is almost no further change in λ_{max} between **27** and **28** (Fig. 4). This indicates that the increase of *n* has only a limited influence on the effective conjugation length. Furthermore, the progressive loss of resolution of the vibronic fine structure reveals that chain extension results in a loss of rigidity in the molecule.



27a–c *n* = 1
28a–c *n* = 2

a R = CO_2Me
b R-R = $-(CH{=}CH)_2-$
c R = SMe

As expected, replacement of the electron-withdrawing CO_2Me substituent by benzo or SMe leads to a negative shift of the anodic peak potentials and to a slight decrease of their difference. On the other hand, whereas for $n = 1$ the two oxidation waves are almost coalesced, the lengthening of the spacer to $n = 2$ leads to the opposite of the expected result with an increase in the difference *E*pa2 − *E*pa1 (Fig. 5). Independently of the nature of R, the lowest *E*pa1 value is found for $n = 0$ whereas *E*pa2 − *E*pa1 is minimal for $n = 1$. This evolution of the optical and electrochemical properties with chain length contrasts strikingly with that of *n*Ts for which the chain extension produces a steady bathochromic shift of λ_{max}, a negative shift of *E*pa1 and a decrease of *E*pa2 − *E*pa1.[22] This contrasting behaviour suggests that although the end parts of the donor molecules **27** and **28** are held rigid by strong intramolecular S···S interactions, the extension of the *n*T spacer induces a rotational disorder considerably larger than that occurring in the corresponding isolated *n*Ts chain. Thus, even if the association of *n*Ts and TTF in a π-conjugated hybrid system allows the decrease of the oxidation potential and HOMO–LUMO gap of both constitutive building blocks, interannular rotational disorder in the *n*Ts spacer appears to be major obstacle to extensive π-electron delocalization. Consequently, further extension of the *n*Ts spacer will probably be largely ineffective and the increase of effective conjugation implies the use of more rigid spacer groups.

Oligoheteroarylenevinylene spacers

A first possible answer to this problem consists of the synthesis of extended TTF analogues containing thienylenevinylene oligomers (*n*TVs) as π-conjugating spacer groups. In fact *n*TVs

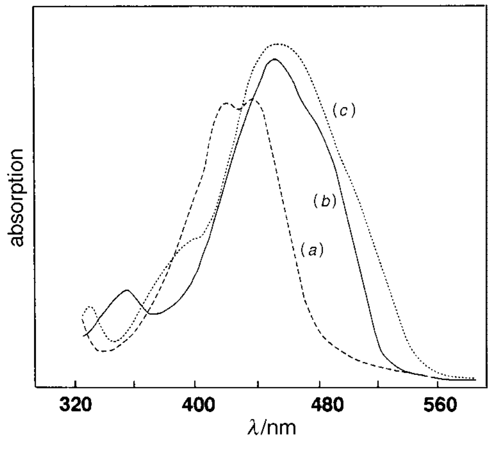


Fig. 4 Electronic absorption spectra of *n*Ts–TTF in CH_2Cl_2; (*a*) $n = 0$ (**23c**), (*b*) $n = 1$ (**27a**) and (*c*) $n = 2$ (**28a**); R = CO_2Me (Reprinted from ref. 61. Copyright 1994, VCH Verlag)

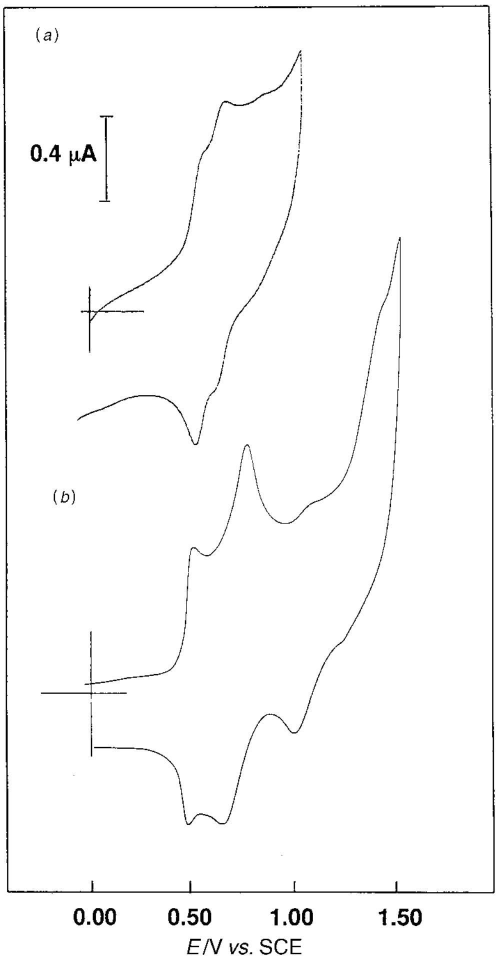
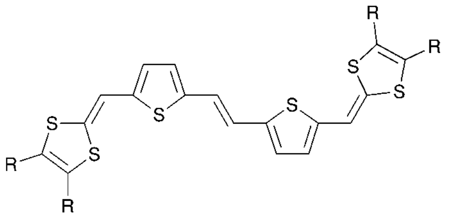


Fig. 5 Cyclic voltammograms of *n*Ts–TTF in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, ref. SCE, scan rate 100 mV s^{-1}; (*a*) *n*=1 (**27b**) and (*b*) *n*=2 (**28b**)

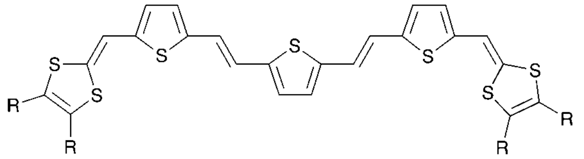
represent an interesting trade-off between the extensive π-electron delocalization associated with polyalkenic systems and the greater stability of the heteroaromatic ones. In addition to a decrease in the overall aromatic character of the spacer compared to *n*Ts, the presence of double bonds of defined conformation can be expected to limit the rotational disorder. The combined effects of these two factors are illustrated by the significantly smaller bandgap of poly(thienylenevinylene) (PTV) compared to PT (1.80 and 2.00–2.20 eV, respectively).[15,21]

The first members of this new series, compounds **29** and **30** have been synthesized using unsubstituted *n*TVs as starting materials.[67] However, due to the rapid decrease of solubility caused by chain extension, access to longer systems required introduction of solubilizing alkyl chains at the 3 and/or 4 positions of the thiophene ring. To this end, new series of soluble *n*TVs containing octyl and dibutyl substituents have been synthesized[68] and used as building blocks for the synthesis of the longer TTF analogues **31** and **32**.

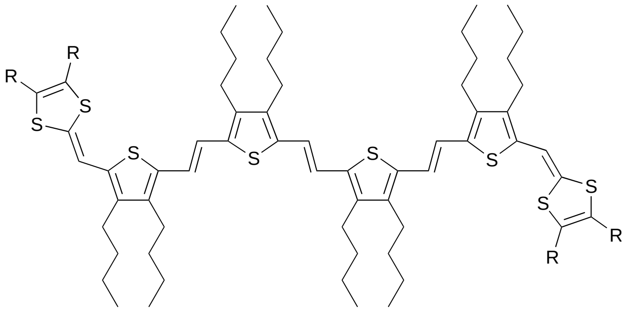
As shown by electronic absorption spectra, the lengthening of the *n*TV spacer leads to a steady bathochromic shift of λ_{max} and the low energy absorption edge, indicating a concomitant reduction of the HOMO–LUMO gap (Δ*E*). The spectra of the longest systems **31** and **32** exhibit λ_{max} in the 550–565 nm region (Fig. 6) and gap values in the range of 1.80 eV, comparable to the bandgap of PTV.[21] Thus, contrary to what has been observed for TTF analogues containing *n*Ts spacers, the lengthening of the *n*TV spacer does not lead to any apparent saturation of the effective conjugation up to the longest spacers



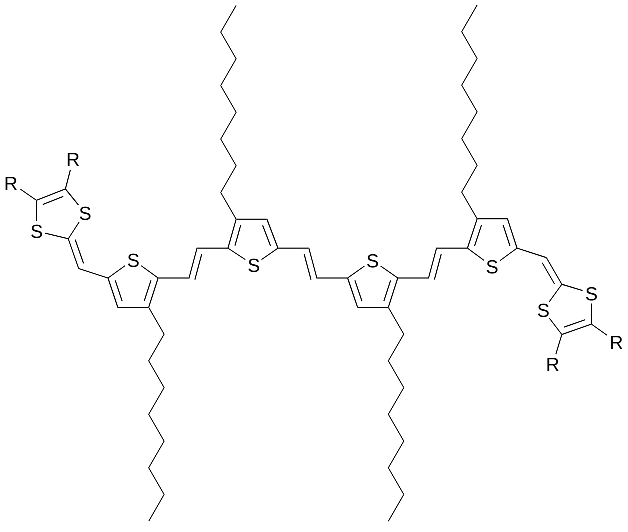
29a–d



30b,c
a R = CO_2Me
b R = SMe
c R = Pr
d R = H



31a R = SMe
b R = Pr



32 a R = SMe
b R = Pr

analysed so far, which contains 22 sp^2 carbons. Furthermore, the persistence of the vibronic fine structure in the optical spectra of **31** and **32** indicates that *n*TV-based systems have a more planar and more rigid geometry than their *n*T counterpart.

As observed for the previous series, the substituent R attached to the 1,3-dithiafulvenyl moiety strongly affects *E*pa1, which decreases from 0.59 V for R = CO_2Me to 0.43 and 0.29 V for R = SMe and propyl, respectively (**29a–c**). The most salient effect of the introduction of an *n*TV spacer is that the two

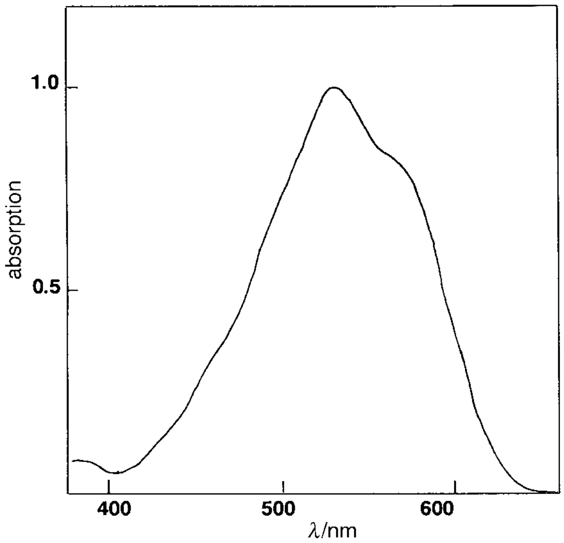


Fig. 6 Electronic absorption spectrum of **32b** in CH_2Cl_2 (Reprinted from ref. 69. Copyright 1996, Elsevier)

successive one-electron waves observed for compounds **23** with a single thiophene spacer coalesce into a single step two-electron transfer, indicating direct formation of the dication. For a given R substituent, the first oxidation potential is practically independent of the length of the spacer, *e.g.* *E*pa1 = 0.30 V for R = propyl. With the lengthening of the *n*TV spacer, second and third reversible one-electron oxidation waves occur. Contrary to *E*pa1, the potentials of these upper oxidation stages show a strong dependence on chain length. For compounds **29b**, **c**, a second peak corresponding to the formation of the trication radical occurs around 1.40 V. This peak shifts negatively by *ca.* 0.40 V for compound **30** while a third peak corresponding to the tetracation is observed around 1.40 V. These trends are confirmed by the CVs of compounds **31** and **32**, for which formation of the tetracationic state occurs around 1.00 V (Fig. 7). These optical and electrochemical results confirm that *n*TV spacers are considerably more effective than *n*Ts for the synthesis of extensively π-conjugated TTF analogues.

The 1 : 1 cation radical salt of **29d** with BF_4^- as counter-anion has been obtained by galvanostatic electrocrystallisation. X-Ray diffraction data show that the donor molecule adopts a planar *trans*-configuration with 1,5-intramolecular S···S interactions between the thiophene and dithiole rings. This salt crystallizes with a molecule of solvent (dichloromethane) per donor molecule. The structure involves donor dimers stacking along the *c* axis. However, intercalation of the anion between the dimers does not allow intra-stack electron delocalization, which explains the insulating character of this material.[70]

In parallel to the synthesis of longer *n*TV-based systems, an interesting extension of this approach consists in replacing *n*TVs by furan-2,5-diylvinylene oligomers (*n*FVs). The smaller aromatic resonance energy of furan (0.70 eV *vs.* 1.26 for thiophene)[71] should allow a further decrease of the overall aromatic character of the spacer and hence a better π-electron delocalization over the whole conjugated system. Furthermore, as already underlined by Schöberl *et al.*, furan-based commodities such as furaldehyde or furfuryl alcohol are much less expensive than their thiophene analogues and represent possible non-food applications for agricultural products.[37]

Compounds **33** and **34** were obtained as single all-*trans* isomers.[72] The X-ray structure of **33d** (Fig. 8) shows that the molecule is nearly planar, with a small dihedral angle (1.34°) between the plane of the furan ring and that of the 1,3-dithiole cycle. Both end parts of the molecule adopt a planar *syn* conformation stabilized by strong 1,5-intramolecular interactions between the oxygen of the furan and a sulfur atom of

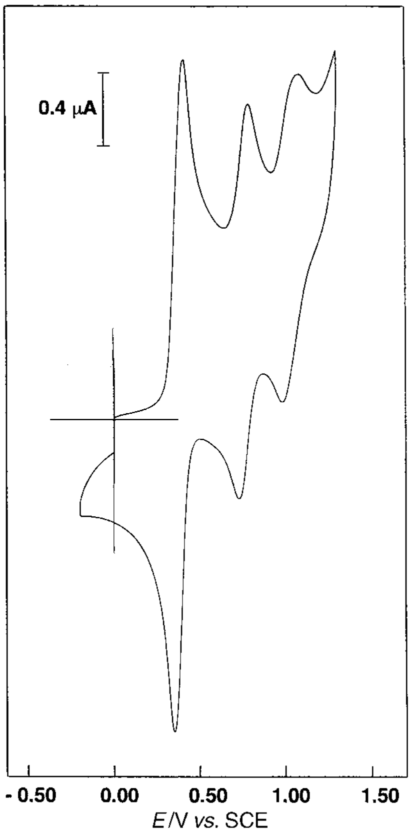
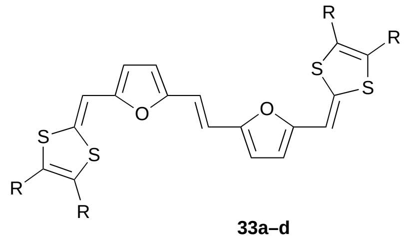
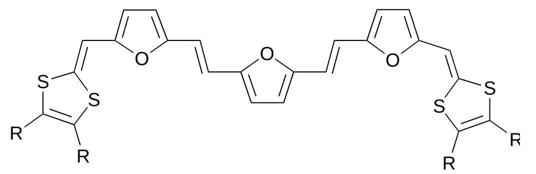


Fig. 7 Cyclic voltammogram of **32a** (1×10^{-4} M) in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, ref. SCE, scan rate 100 mV s^{-1} (Reprinted from ref. 69. Copyright 1996, Elsevier)



33a–d



34a–c

a R = CO_2Me
b R = SMe
c R = Pr
d R = H

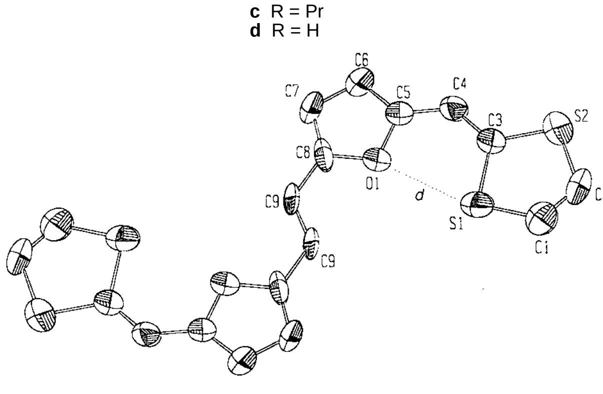


Fig. 8 ORTEP view of **33d** (Reprinted from ref. 72. Copyright 1996, Royal Society of Chemistry)

the dithiole cycle, with a non-bonded contact distance (d = 2.88 Å) smaller than the sum of the van der Waals radii of sulfur and oxygen (3.30 Å) but larger than a covalent S–O bond (1.75 Å).

The electronic absorption spectra of **33** and **34** reveal behaviour reminiscent of their nTV-based analogues. The increase in the electron-releasing effect of R produces a bathochromic shift of λ_{max} according to the sequence R = CO_2Me, H, SMe and propyl. Chain extension produces a red shift of λ_{max} (*e.g.* from 477 to 508 nm for **33c** and **34c** respectively). However, for a given spacer length, these compounds absorb at slightly shorter wavelengths than their nTV-based analogues (*ca.* 10 nm). The absence of saturation of effective conjugation and the persistence of the vibronic fine structure in the optical spectrum shows that as for nTVs, nFV spacers allow the related π-donors to keep a planar and rather rigid structure.

As for the previous series, the electrochemical behaviour of these compounds depends on the nature of R and the length of the spacer. Thus, Epa1 decreases from 0.48 V for **33a** to 0.18 V for **33c**. Although compounds **33** show Epa1 values noticeably lower than their analogues with a single furan ring (**22**), further lengthening of the spacer to **34** has almost no effect on Epa1. The cyclic voltammograms of **33** and **34** exhibit a first single oxidation wave in the 0.18–0.32 V region and a second one around 1.00–1.35 V, depending on the R. Measurement of the peak width at half maximum and application of the Nicholson and Myers treatment[73] to the first wave gave Epa2 − Epa1 values of 40 mV for **33a** and 10 mV for **33b** and **33c**. For compounds **34** the zero value of this parameter indicates direct formation of the dication through a two-electron transfer, while a reversible one-electron wave corresponding to the tricationic state occurs around 1.00 V followed by a less reversible wave at 1.40 V, indicating possible formation of the tetracation (Fig. 9).

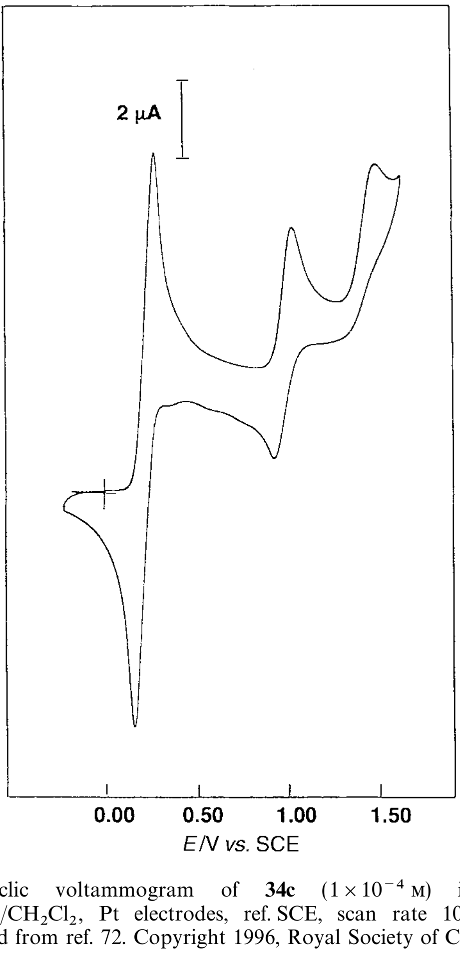
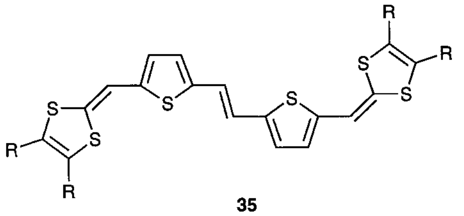


Fig. 9 Cyclic voltammogram of **34c** (1×10^{-4} M) in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, ref. SCE, scan rate 100 mV s^{-1} (Reprinted from ref. 72. Copyright 1996, Royal Society of Chemistry)

The X-ray structure of the electrogenerated cation radical salt **33b**·ClO_4 shows that the donor molecule adopts a *trans*, nearly planar geometry with 1,5-intramolecular S···O interactions between the dithiole and furan cycles. Donor molecules stack along the c axis with weak intermolecular interactions between the oxygen of the furan ring and a sulfur of the dithiole cycle. Despite a 1 : 1 stoichiometry, this material shows a weak but significant conductivity (10^{-4} S cm^{-1}).[70] This result might be related to the ease of formation of the dicationic state, which could contribute to some intra-stack delocalization.

In order to achieve a further decrease in the overall aromaticity of the spacer group, linearly extended TTF analogues in which the π-conjugating spacer involves two thiophene or furan rings separated by two or three double bonds have been synthesized (**35**–**38**).[74]



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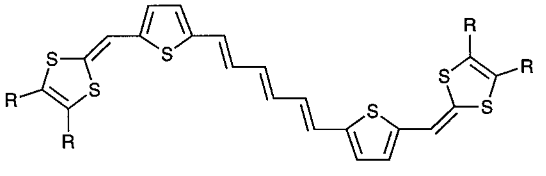

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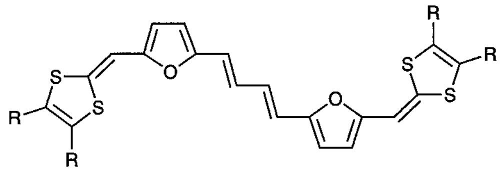
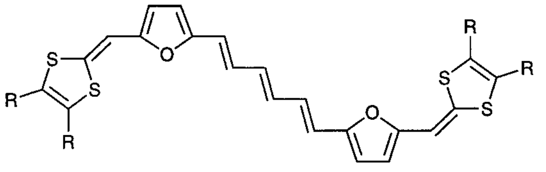


37



38

a R = CO_2Me
b R = SMe
c R = Pr

The X-ray structure determination of the dicarbaldehyde precursor of compound **36** reveals the all-*trans* configuration of the ethylenic spacer and shows the planar conformation adopted by the molecule (Fig. 10).

Optical data show that for a given R substituent, thiophene-based compounds absorb at longer wavelengths than their furan analogues. However, the increase in the number of double bonds tends to minimize this difference and, for example, **36c** and **38c** exhibit identical λ_{max} (512 nm) and HOMO–LUMO gap values (2.09 eV). Increasing the electron-releasing effect of R leads to the expected red shift of λ_{max} and decrease of ΔE. However, for furan-containing compounds **37** and **38**, introduction of electron-donating R substituents produces a loss of resolution of the vibronic fine structure. This suggests that the electronic effects of R indirectly affect the rigidity of the system *via* a modification of the 1,5-intramolecular interaction between the oxygen of the furan ring and a sulfur atom of the dithiole cycle.[75]

In addition to the expected dependence of the oxidation potential on the nature of the R substituent, cyclic voltammetric data show that all these compounds are directly oxidized into their dication state through a single-step two-electron transfer. For both thiophene and furan series, the lengthening of the spacer leads to a very small negative shift of *E*pa1 (20–50 mV). Furan-based compounds **37** and **38** show *E*pa values *ca.* 100 mV lower than their thiophene analogues, a difference which can be related to the lower aromatic resonance energy of furan. Compounds **38** exhibit very low oxidation potentials, the value of 0.16 V *vs.* SCE obtained for **38c** lying among the lowest observed so far in the TTF series (Fig. 11).

Comparison of the electrochemical and optical data for all of the above discussed series of linearly extended TTF analogues shows that, independent of the structure of the spacer, the decrease in the HOMO–LUMO gap resulting from the extension of the spacer is much larger than the negative shift of *E*pa1.

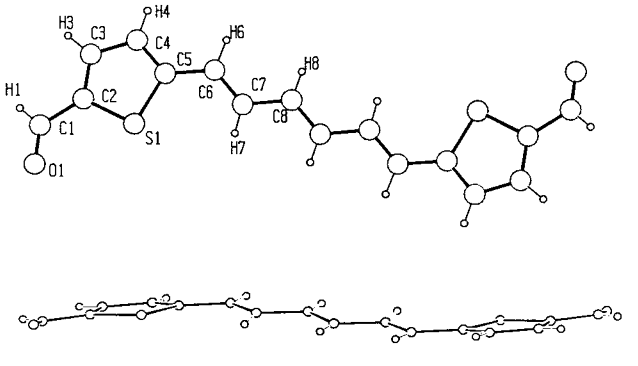


Fig. 10 ORTEP view of the dicarbaldehyde precursor of **36** (Reprinted from ref. 74. Copyright 1996, American Chemical Society)

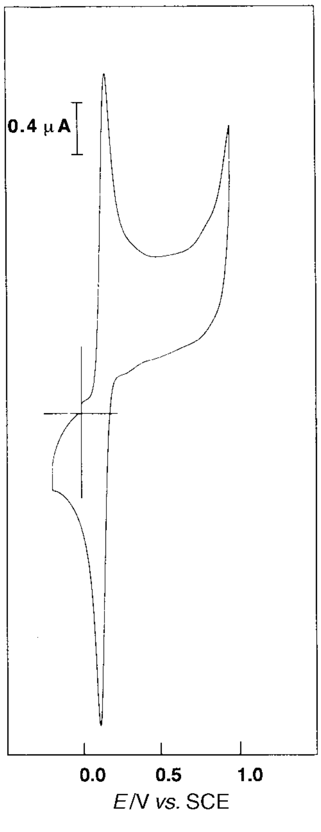


Fig. 11 Cyclic voltammogram of **38c** (5×10^{-5} M) in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, ref. SCE, scan rate 100 mV s^{-1} (Reprinted from ref. 74. Copyright 1996, American Chemical Society)

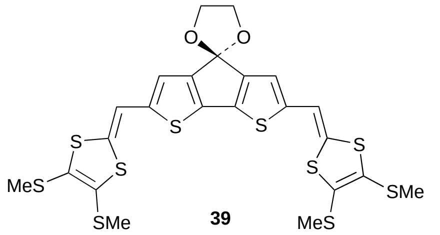
In fact, in several instances chain extension leads to a rapid convergence of *E*pa1 to a constant value, while optical data indicate that the HOMO–LUMO gap still decreases. These results confirm, in agreement with previous conclusions of Sugimoto *et al.*,[40] that in these systems, the end 1,3-dithiafulvenyl groups provide the main contribution to the HOMO energy level, while that of the LUMO is essentially determined by the nature and the length of the π-conjugating spacer.

Extended TTF analogues with rigid π-conjugated spacers

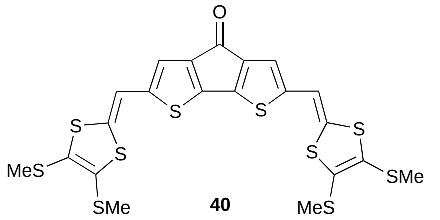
The synthesis of small bandgap linear π-conjugated materials has recently become one of the major challenges in the chemistry of conjugated polymers and oligomers.[21] In addition to the long term prospect of reaching intrinsically conductive materials, bandgap control is of crucial importance for future development of the technological applications of π-conjugated systems, as most of their relevant electronic properties are more or less directly determined by the width of the bandgap.

The increase of the quinoid character of the PT backbone to the detriment of its aromaticity has been known for several years as an efficient approach to the design of small bandgap polymers.[21] The most well-known illustration of this approach is poly(isothianaphthene), which exhibits a bandgap of 1.15 eV, *i.e.* about 1.00 eV smaller than that of PT.[76] More recently, rendering the π-conjugated system more rigid has been shown to represent an efficient alternative strategy for bandgap control. Thus, conjugated polymers obtained by electropolymerization of bridged thiophene oligomers[77] or dithienylethylenes[78] exhibit significantly smaller bandgaps than their analogues derived from non-rigid precursors. In this context, the use of such bridged systems as building blocks for the synthesis of extended TTF analogues appears particularly attractive in order to develop more stable systems with smaller HOMO–LUMO gaps.

A first step in this direction has involved the synthesis of compounds **39**–**41** in which bridged bithiophenes diversely substituted at the bridging carbon are used as spacer groups.[79]



39



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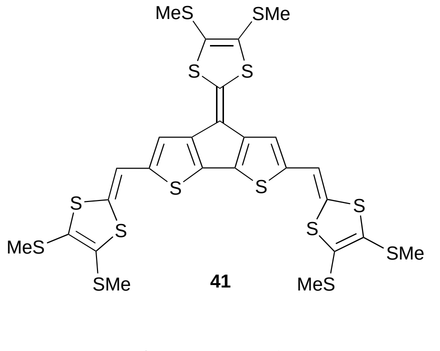
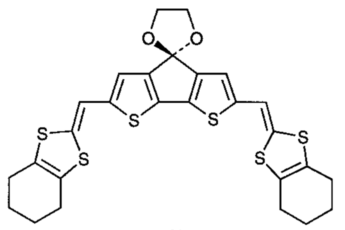


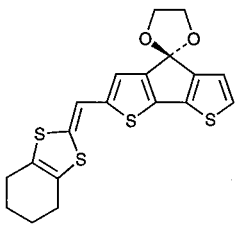
41

The electronic absorption spectra of compounds **39**–**41** differ from that of their non-bridged analogue **27c** by the emergence of an additional weak absorption band extending towards long wavelength. The absorption onset leads to estimated ΔE values of 1.50–1.60 eV for **41** and 1.20–1.30 and 1.30–1.40 eV for **39** and **40**, respectively, considerably smaller than that of **27c** (2.30 eV).[61] Cyclic voltammetric data show that the bridging of the bithiophene spacer produces a large negative shift of Epa1. Thus Epa1 decreases from 0.54 V for **27c** to 0.18 V for **41**, as could be expected with the grafting of a third 1,3-dithiole cycle on to the bridging carbon. However, the fact that introduction of a carbonyl group at the bridging carbon (**40**) also produces a decrease in Epa1 to 0.38 V shows that the electron-withdrawing effect of the C=O group is largely offset by the suppression of rotational disorder. As shown in Fig. 12, the bridging of the bithiophene spacer induces a considerable positive shift of the reduction potential, while multiple oxidation and reduction states become accessible. The difference between the first oxidation and reduction potentials indicates a ΔE value as low as 0.90 eV for **39**. The electronic absorption spectrum of a vacuum-evaporated thin film of **39** shows a bandgap of 1.20–1.30 eV, consistent with the small ΔE value observed on the molecule.[80]

More detailed information on the structure–property relationships in this class of π-donors has been gained by comparing the optical and electrochemical properties of **42** with those of the model compounds **43** and **44**.



42



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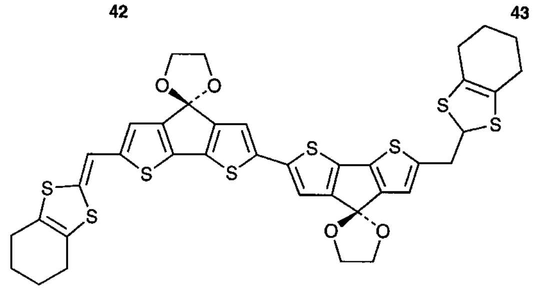


44

Whereas **42** shows an Epa1 value of 0.33 V, that of **43** occurs as expected at a higher potential (0.45 V) due to the absence of the second 1,3-dithiafulvenyl group. Surprisingly, the CV of the extended analogue **44** obtained by duplication of **43** shows an almost identical Epa1 value of 0.48 V. Furthermore, comparison of the optical spectra of the three compounds shows that **43** and **44** have similar $\lambda_{\max}$ (431 and 436 nm, respectively) at considerably shorter wavelengths than **42** (496 nm).[81] These two sets of data demonstrate that there is practically no increase in effective conjugation between **43** and **44**. This implies that in **44** the two halves of the molecule form a dihedral angle close to 90°. This angle value, which largely exceeds that reported for oligothiophenes in solution (*ca.* 30°) confirms, in agreement with previous conclusions,[61] that the grafting of 1,3-dithiafulvenyl moieties on to both ends of *n*Ts considerably enhances rotational disorder within the spacer. An important consequence of these results is that in order to be fully effective the rigidification must imperatively include the whole π-conjugated system.

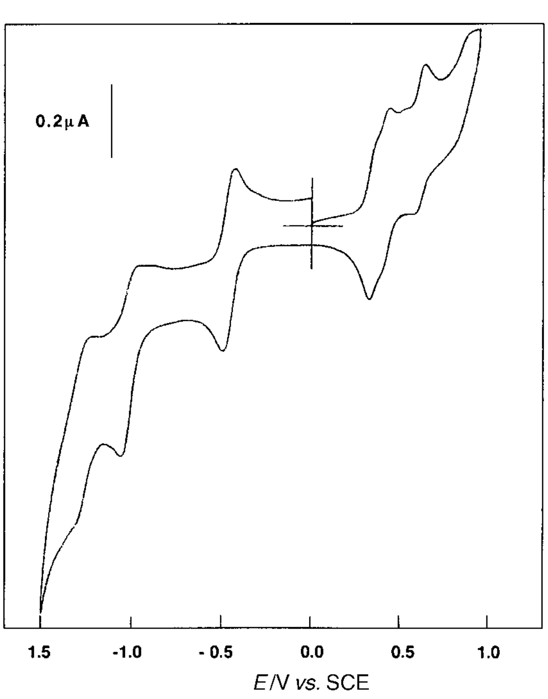
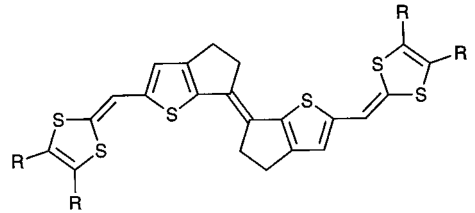


Fig. 12 Cyclic voltammogram of **39** (1×10^{-3} M) in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, ref. SCE, scan rate 100 mV s^{-1} (Reprinted from ref. 79. Copyright 1994, Royal Society of Chemistry)

More recently, this approach has been extended to the synthesis of π-donors **45** built around a bridged dithienylethylene (DTE) spacer.[82]



45

a R = CO_2Me
b R = SMe
c R = Pr

Except for the alkyl substituents, the molecule adopts a fully planar geometry ensured by the combined effects of the bridged DTE spacer and 1,5-intramolecular interactions already observed for their analogues (Fig. 13). Rigidification of the spacer induces as expected a decrease in oxidation potential, however the negative shift of Epa1 (*ca.* 100 mV) is noticeably smaller than for compounds **39**–**41**. This smaller effect is related to the fact that the structure of the unbridged reference compounds (**29**) is already planar. Comparison of the X-ray data for both types of structure has shown that the bridging of the dithienylethylene spacer induces important changes in bond distances along the conjugated path, with a lengthening of double bonds and a compression of single bonds that results in a significant decrease in bond length alternation.[78,82]

Contrary to compounds **29**, for which the dication is formed *via* a single-step two-electron transfer, the CV of compounds **45** exhibits two successive one-electron oxidation waves (Fig. 14). The splitting of the two-electron wave results from a decrease in the potential needed to form the cation radical while the potential corresponding to the formation of the dication remains unchanged. This unusual behaviour is related to the specificity of the spacer structure. Oxidation of TTF analogues containing a DTE spacer **29** and **45** to the cation radical state induces geometrical changes in the conjugated path; the thiophene rings adopts a quinoid structure while the

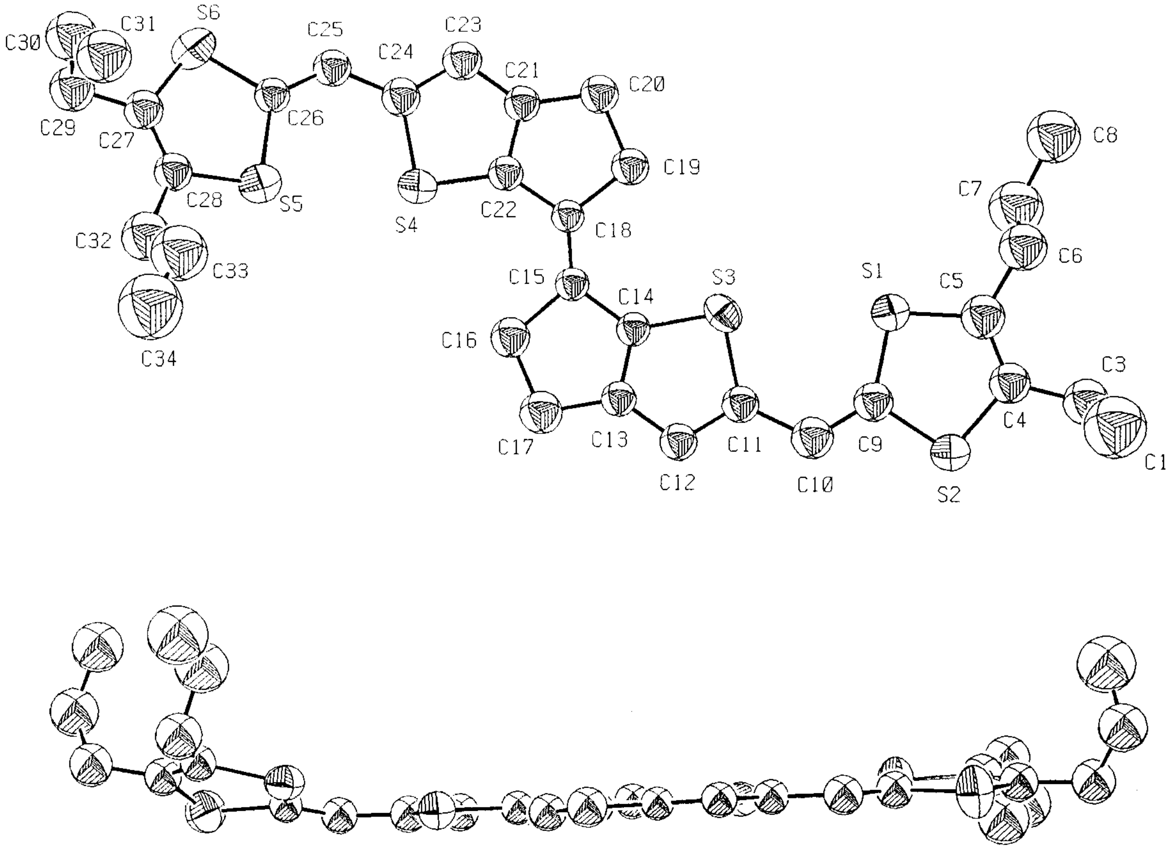


Fig. 13 ORTEP view of **45c** (Reprinted from ref. 82. Copyright 1997, Royal Society of Chemistry)

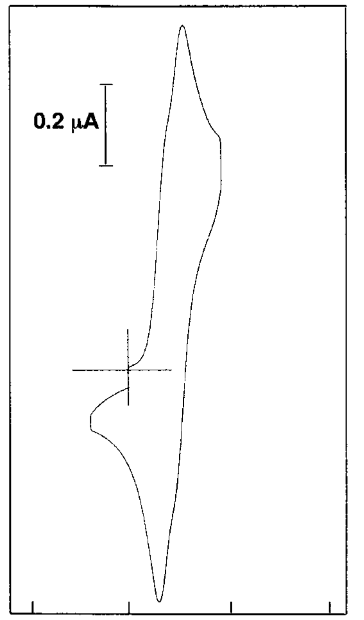
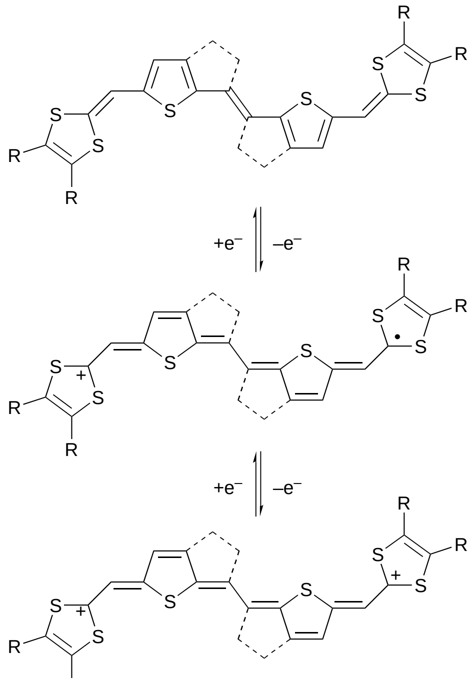


Fig. 14 Cyclic voltammogram of **45c** (1×10^{-4} M) in 0.1 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, scan rate 100 mV s^{-1} (Reprinted from ref. 82. Copyright 1997, Royal Society of Chemistry)



Scheme 2

central ethylene linkage acquires the character of an essentially single bond (Scheme 2).

However, in the case of **45** the bridging of the spacer leads to an anticipation of these modifications in bond distance; consequently, oxidation into the cation radical requires less energy than for the unbridged system. On the other hand, as there is much less difference between the geometry of the cation radical of the bridged and unbridged systems than between their respective neutral forms, the potential of the second oxidation step remains almost unchanged. The difference between the bridged and unbridged systems in the neutral state has been confirmed by theoretical calculations which indicate that, whereas for the unbridged system the highest coefficients of the HOMO are located on the 1,3-dithiafulvenyl

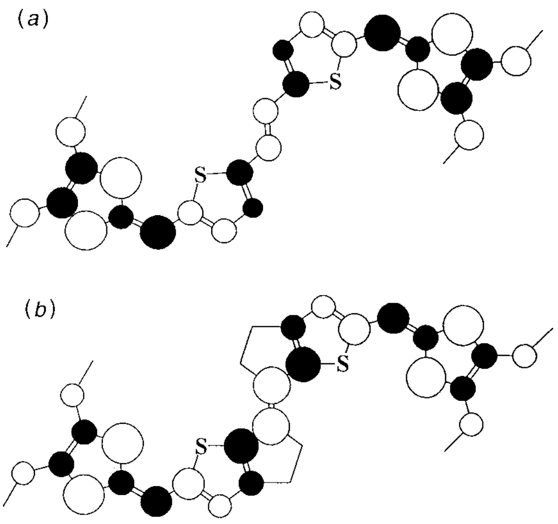


Fig. 15 Atomic orbital coefficients in HOMO; (*a*) **29b** and (*b*) **45b** (Reprinted from ref. 82. Copyright 1997, Royal Society of Chemistry)

units, the more homogeneous distribution found for **45** reveals an enhanced π-electron delocalization (Fig. 15).

Conclusion and Outlook

Whereas the chemistry of TTF derivatives already has a relatively long history, the combination of TTF and linear π-conjugated systems is a relatively recent research area. Conjugated polymers with TTF pendent groups can open interesting perspectives for the development of processible TTF-based conducting materials with higher dimensionality. A particularly exciting long-term prospect concerns the synthesis of polymers in which the two types of conduction mechanisms, namely mixed-valence migration in the TTF stacks and polaron/bipolaron translation in the linear conjugated backbone, coexist or eventually hybridize in a synergic way. Due to the multiple stringent prerequisites which must simultaneously be fulfilled, namely precise control of the position of the TTF moieties in order to ensure proper stacking, fine tuning of the oxidation potential of both the TTF moiety and the conjugated backbone and, above all, preservation of the aptitude for electropolymerization of the TTF-derivatized precursor, the design of the precursor structure poses complex problems and will require considerable further effort in synthetic chemistry. However, the recent synthesis of precursors with improved polymerizability will probably open interesting new perspectives in this area.

Extended TTF analogues involving linear π-conjugated systems have been initially investigated as a possible route towards conductive materials with increased dimensionality. The confirmation of the validity of this approach by the recent synthesis of the first superconductor based on a linearly extended TTF π-donor will certainly stimulate further synthetic work in this direction, while the theoretical and experimental investigation of the charge-transport properties of these new systems will acquire a growing importance in the near future. As a matter of fact, by precise control of the spacer length it should be possible to tune the conduction mechanism between the 'vertical' mixed-valence conduction of TTF charge transfer salts to the 'horizontal' polaron/bipolaron conduction of linear systems. Furthermore, access to multicationic states associated with the linear extension of these systems opens exciting perspectives, with the possibility of developing materials involving mixed valences between higher oxidation states (dication/trication radicals *etc.*)

The reverse of the medal is that the lengthening of the donor molecule seems to exert detrimental effects on its ability to electrocrystallize. In fact, among the large number of these new systems synthesized in the past five years, very few electrocrystallized cation radicals salts have been obtained. Thus, parallel to further investigations of the structure–property relationships, future progress in the study of this promising new class of π-donors will depend strongly on the development of a parallel research effort directed towards the preparation of good quality crystals.

With the recent development of systems of higher extension, these compounds appear more and more as a new class of conjugated oligomers in which dithiafulvenyl end groups bring original electronic properties. In addition to a strong decrease in the HOMO–LUMO gap, the grafting of 1,4-dithiafulvenyl groups on to both ends of a π-conjugated oligomer seems to highlight the relevant structural factors that control the effective conjugation such as planarity, charge delocalization *vs.* confinement, and bond length alternation. This better understanding of the relationship between molecular structure and electronic properties will certainly be helpful for the conception of new linear π-conjugating spacers for both new TTF π-donors or chromophores for quadratic and cubic nonlinear optics. Finally the association of a small bandgap with multiple oxidation and reduction states in a narrow potential range exhibited by some of these new systems makes them interesting candidates as organic semi-conductors for the realization of microelectronic devices. Thus, parallel to the exciting perspectives they open for basic research, organic materials resulting from the association of TTF and linear π-conjugated systems already possess a large technological potential in the field of electronic and optoelectronic devices, and these multiple aspects will probably strongly influence future work on these materials.

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