FEATURE ARTICLE

Design and synthesis of TCNQ and DCNQI type electron acceptor molecules as precursors for 'organic metals'

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The main types of cyano-containing electron acceptor molecules, particularly those derived from TCNQ and DCNQI acceptors, have been reviewed. Ring substitution, the presence of heteroatoms and extended π-conjugation have been used as the principal structural modifications on the acceptor framework. Recent examples of C_{60} based electron acceptors bearing an acceptor organic addend and other single-component donor–acceptor systems exhibiting semiconducting behaviour are also discussed.

The synthesis of the highly conducting charge transfer (CT) complex formed by tetracyano-*p*-quinodimethane (TCNQ) and tetrathiafulvalene (TTF), as electron acceptor and electron donor components respectively, has opened up the field of molecular organic conductors.[1] A large number of different CT complexes have been prepared in the search for electrical properties. The synthesis of the so called 'organic metals' or 'synthetic metals' has mainly focused on the modification of the donor fragment and, as has been often stated, much less synthetic effort has been devoted to the preparation of novel acceptors.[2] In this review we discuss some highlights in the design and synthesis of electron acceptors as precursors of electrically conducting materials.

Taking into account the fact that the requirements needed to obtain a conducting molecular arrangement have been reviewed in detail by different authors[3–11] and given that the possibility of designing organic conducting materials has been recently reviewed by Khodorkovsky and Becker,[12] we will focus our attention on the main types of acceptors according to their different molecular nature. In particular, we will focus on derivatives of the parent molecules TCNQ, dicyano-*p*-quinone diimine (DCNQI), other polycyano derivatives, and some interesting cases in the emerging chemistry of modified fullerenes, as shown in Fig. 1.

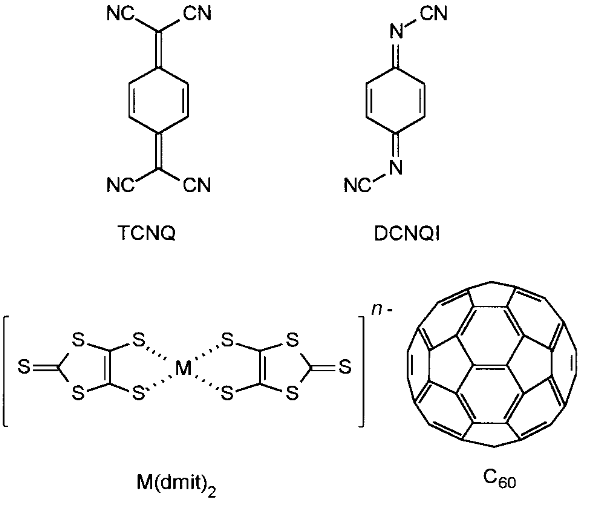


Fig. 1 Selected representative electron acceptor molecules

Other remarkable and structurally different acceptor molecules containing sulfur or selenium atoms on the periphery are represented by the [M(dmit)$_2$] complexes (dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolate, Fig. 1) with ten peripheral sulfur atoms, thus increasing the intra- and inter-stack interactions. Such compounds derived from transition metal complexes are, together with the more recent fullerides, the only materials in which an organic acceptor molecule (dmit and C_{60}) is responsible for superconductivity.

Formation of sulfur-containing donor molecules from the dmit ligand has been recently reviewed by Svenstrup and Becher[13] and the state of the art on the M(dmit)$_2$ systems such as crystal growth, stacking, oxidation state and conducting and superconducting properties have been excellently reviewed by Cassoux and Valade.[14]

Despite the lack of superconducting properties in salts and complexes formed from TCNQ and DCNQI derivatives, these two molecules and other structurally related analogues have been the subject of striking synthetic efforts and a wide variety of electrically conducting salts and charge transfer complexes have been obtained from these unique molecules.

A few years ago, a review article dealing with DCNQIs as a new type of electron acceptor was published by Hünig and Erk.[15] We are herein concerned with recent advances on the chemistry and properties of the most significant electron acceptor molecules (TCNQ and DCNQI) and other cyano containing related molecules. We will highlight some of the novel acceptors prepared as precursors of materials with relevant conducting, magnetic and optical properties.

Electron Acceptors: Design and Structural Modifications

After the discovery of TTF–TCNQ,[1] chemical research focused on synthesizing a remarkable number of new derivatives of TTF and TCNQ. Three general synthetic approaches have been used for the modification of the acceptor structure, which have been used for both TCNQ and DCNQI derivatives: (i) ring substitution with the aim of tuning the redox behaviour through careful choice of substituents, (ii) introduction of heteroatoms or heterocyclic rings into the TCNQ skeleton in order to increase inter- and intra-stack interactions which enhance the dimensionality of the corresponding charge transfer complexes, and (iii) extension of the π-system which leads to a lowering of the intramolecular Coulomb repulsion in the charged species.

Ring substitution on TCNQ and DCNQI rings

TCNQ derivatives. In an important early paper, Wheland and Martin from the Dupont company characterized 21 TCNQ derivatives,[16] and their complexes with TTF and some other donors were obtained.[17,18] These syntheses most frequently started with the corresponding *p*-xylylene dihalide **2** prepared by direct bis(chloromethyl)ation from the appropriate substituted benzene **1** as shown in Scheme 1. Although this procedure is not general and involves the use of the highly toxic cyanogen chloride to form intermediate **4**, it allowed the preparation of a wide variety of substituted TCNQs.

In general, it has been found that substitution on the basic TCNQ skeleton results in CT complexes that are less conducting than those of TCNQ itself.[2] This behaviour could be explained in some cases by lower acceptor properties or may be due to the complete charge transfer of stronger electron acceptors in other cases. However, interest in TCNQ derivatives for the preparation of novel organic conductors and, more recently, their potential application as organic rectifiers,[19] non-linear optical materials[20] or organic ferromagnets[21] led to the search for other, simpler, synthetic routes.

One of the alternative routes for preparing TCNQ derivatives is the reaction of 1,4-diiodobenzenes with malononitrile anion in the presence of a palladium catalyst to yield phenylenedimalononitrile derivatives, which after oxidation form the TCNQ system.[22] Nevertheless, the most widely used synthetic procedure for the preparation of TCNQ derivatives, first reported by Hünig,[23] takes place by direct condensation of the appropriate quinone **6** with Lehnert's reagent (malononitrile, $TiCl_4$ and pyridine)[24] (Scheme 1). Although this method has been said to be capricious,[25] the reaction seems to be of general applicability at least for the preparation of tri- or tetra-substituted TCNQ derivatives **5**.[26]

Theoretical calculations have been carried out to understand the reduction process of TCNQ.[27] The evolution of the geometry and electron structure of the molecule upon reduction have been calculated for TCNQ and also for its anion and dianion. As is shown in Scheme 2, the introduction of one electron into the TCNQ molecule to form the radical anion induces an aromatization of the planar TCNQ ring with a reduction of the quinoid character, as can be seen in the lengthening of the double bonds and the shortening of the single bonds. The introduction of the second electron completes the aromatization process of the TCNQ, leading to the dianion.

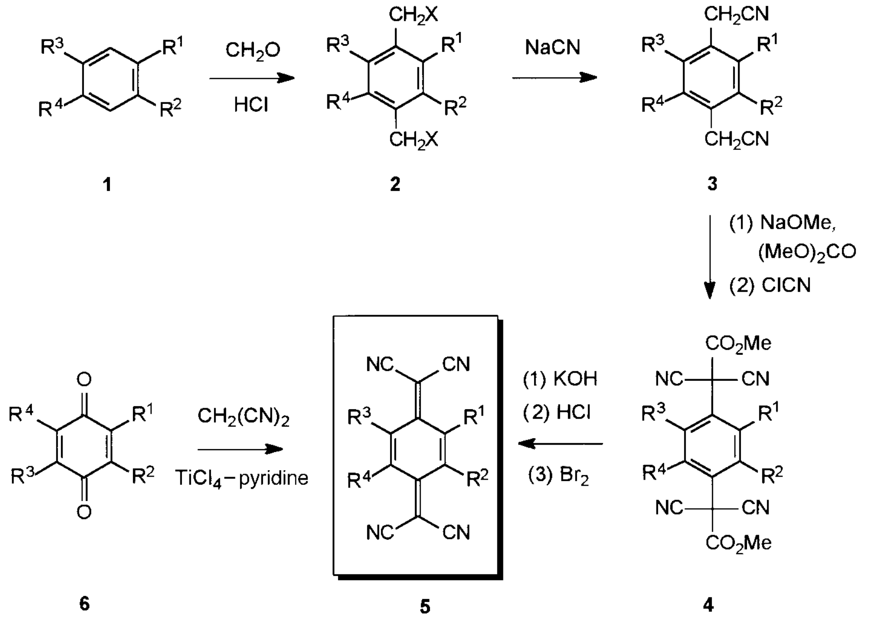
In agreement with the excellent EPR and ENDOR study previously reported for the radical anions of π-extended TCNQs,[28] the attached electrons are accommodated in the dicyanomethylene units, the extra negative charges taken by each $C(CN)_2$ unit being $0.38e^-$ for the radical anion and $0.83e^-$ for the dianion. The stability of the radical anion of TCNQ explains the two one-electron reduction waves observed for the parent TCNQ in the cyclic voltammetric studies.

DCNQI derivatives. Taking into account the chemical analogy between C=O and $C{=}C(CN)_2$ and between $C{=}C(CN)_2$ and C=N—CN, Hünig reported the *N,N′*-dicyanoquinone diimines **8** (DCNQIs) as a new class of efficient electron acceptor molecules[29] in the preparation of CT complexes and especially in highly conducting CT salts. These acceptors are readily available from the corresponding quinones in a one-step procedure by reaction with bis(trimethylsilyl)carbodiimide **7** (BTC) in the presence of titanium tetrachloride. Considering the synthetic availability of the starting quinones, a great variety of DCNQI derivatives have been prepared by following the general synthetic route shown in Scheme 3(*a*).[30]

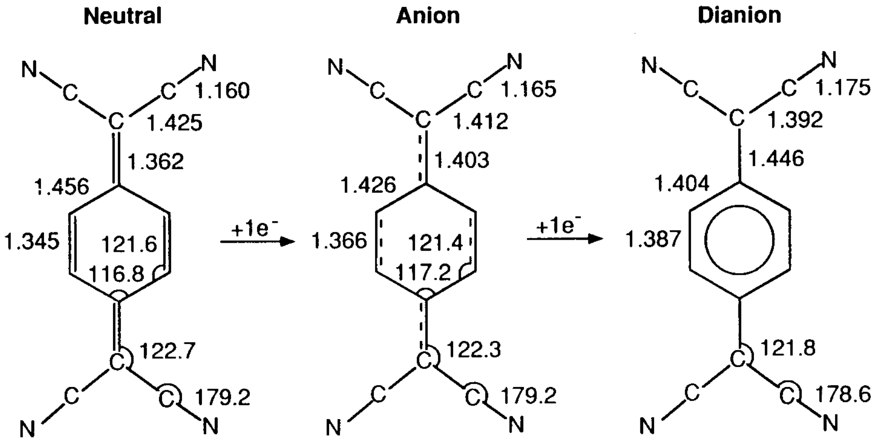
Theoretical calculations (AM1)[31] carried out on the DCNQI molecule reveal that the LUMO energy of TCNQ is 0.4 eV lower than the LUMO of DCNQI. Although the symmetries and atom coefficients of the LUMO orbital of TCNQ and DCNQI are almost identical (Fig. 2), the electron density on the nitrogen atom of the cyano group is larger in DCNQI, thus increasing the solvation energy. This has been used to explain the similar values found for the reduction potentials of both TCNQ and DCNQI molecules.[15]

In contrast to the above TCNQ derivatives and in addition to the easy synthetic route from the readily available quinones, DCNQI derivatives have the flexible and less sterically demanding C=N—CN group, resulting in planar molecules even for the tetrasubstituted derivatives.[32]

The acceptor ability of the DCNQI molecule is similar to that of TCNQ and the reduction potential can easily be tuned within a wide potential range by means of the substituents.



Scheme 1



Scheme 2

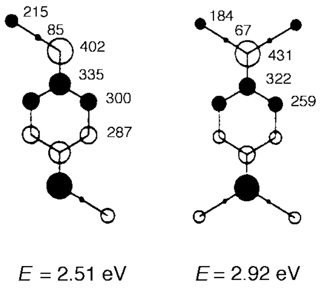


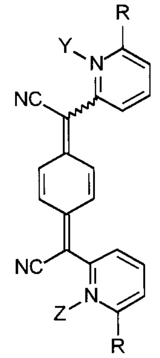
Fig. 2 LUMO energies of DCNQI and TCNQ (coefficients are given as 10^{-3})

Thus, Hünig reported an interesting electrochemical study by cyclic voltammetry of a series of substituted DCNQIs in different solvents and electrodes, finding a Hammett correlation for the substituent effect on the redox potentials.[33]

The unique properties exhibited by the DCNQI molecule are responsible for its excellent behaviour as electron acceptor component in the preparation of CT complexes and CT salts. Considering that the preparation of these electrically conducting materials has been the focus of several review articles,[15,34] we will mention only that in the last years and following the discovery of a metal–insulator–metal transition (re-entrant behaviour) in $(Me_2DCNQI)_2Cu$ at low pressure, the search for re-entrant phenomena at ambient pressure has attracted much interest. Selective deuteration of Me_2DCNQI [**9**, $R^1=R^3=Me$; $R^2=R^4=H$, Scheme 3(*a*)] has been performed.[35,36] By controlling the position and number of deuterium atoms, the low pressure region ($\leqslant 500$ bar) in the pressure–temperature phase diagram of $(Me_2DCNQI)_2Cu$ was reproduced at ambient temperature. The equivalency of the deuteration and pressure effects is explained by steric effects: 'contraction' caused by the slightly shorter C—D bond (steric isotope effect) and 'constriction' by pressure.[37–39]

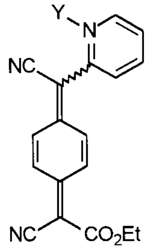
Other polycyano derivatives. During the last years a variety of novel acceptors, based on the TCNQ and DCNQI molecules have been reported. We will present some of the most significant modifications carried out on the quinoid skeleton. *N*,7,7-Tricyanoquinomethane imines **11** [Scheme 3(*b*)], which can be considered as hybrids of the TCNQ and DCNQI systems, were reported by Bryce and co-workers in 1989.[40] These new electron acceptors were prepared from the corresponding quinones **6** by treatment with Lehnert's reagent to form the dicyanoquinomethanes **9** which, on reaction with BTC, afforded the hybrid tricyano derivatives **11**. The acceptor strength of the parent compound ($R^1=R^2=R^3=R^4=H$) proved to be very close to those of TCNQ and DCNQI and the single crystal X-ray analysis of the trimethyl substituted derivative showed a geometry which was essentially planar, although it was highly distorted for the tetramethyl derivative.[40]

Another synthetic strategy for functionalizing quinodimethanes leading to new dicyanoquinodimethane electron acceptors **12** and **13** has been reported.[41] The multi-step synthesis takes place by substitution of α,α′-dicyano-*p*-xylene anions with electrophiles, followed by oxidative dehydrogenation. Unlike most of the other examples, the quinodimethanes are α substituted rather than ring substituted. These compounds, which are obtained as mixtures of *syn* and *anti* isomers, exhibit lower reduction potentials than the parent TCNQ and no CT complexes have been reported so far.



12

R = H, Y = Z = lp
R = H, Y = Z = Me (+)
R = H, Y = Me (+), Z = lp
R = $PO(OEt)_2$, Y = Z = lp
R = $PO(OH)_2$, Y = Z = lp

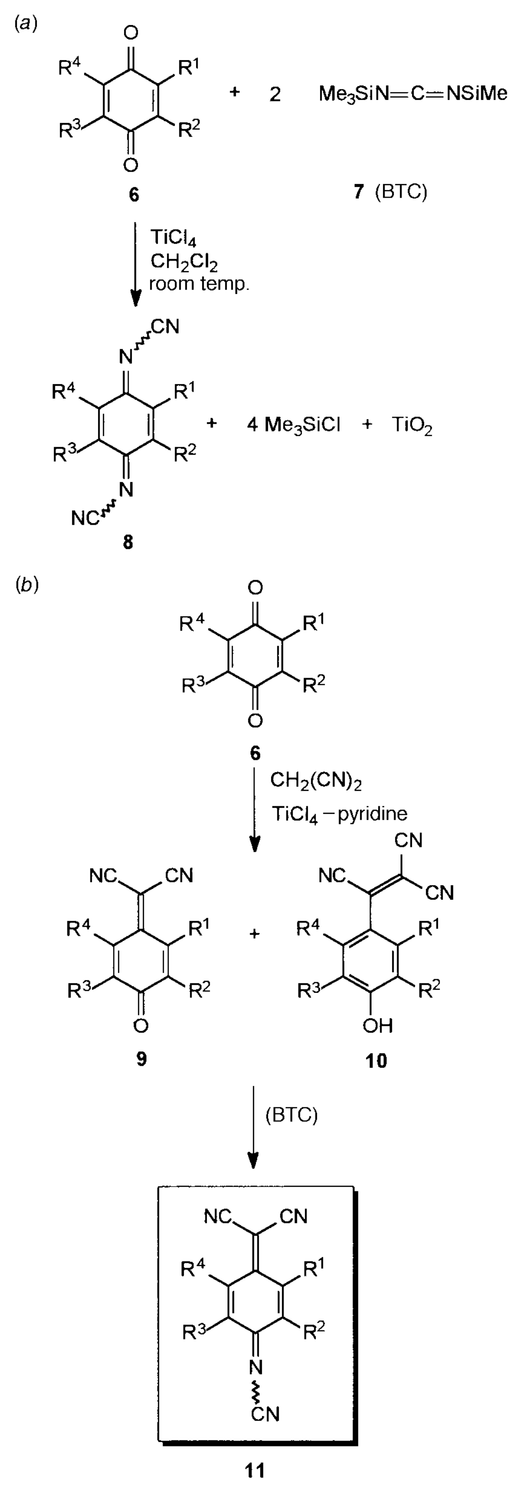


13

Y = lp
Y = Me (+)

lp = lone pair

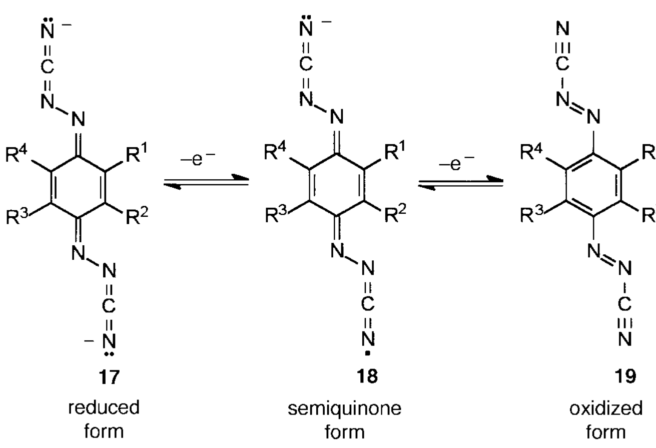
A very promising and totally different approach to the synthesis of novel acceptors was reported by Hünig in 1991.[42] The most important acceptor molecules, TCNQ and DCNQI, display two-stage reversible redox systems belonging to the Wurster type acceptors, in which the oxidized stage has quinone character.[43] Hünig's approach is based on the preparation of



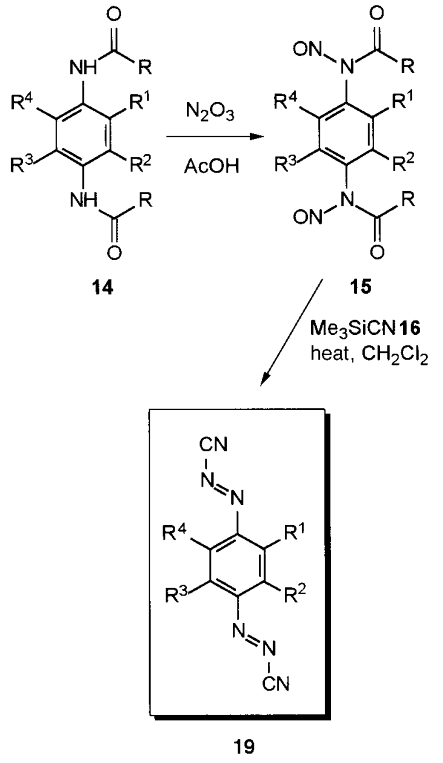
Scheme 3

two-stage redox systems of inverse Wurster type, that is, the aromatic oxidized stage.[42] Scheme 4 displays benzene-1,4-bis(diazocyanide)s (DCNAB), showing the different oxidation states (**17**–**19**), which were prepared as the first acceptors of the Wurster type.[42]

These aromatic diazocyanides **19** can be obtained by nitrosation of *N*-arylamides **14** and thermal rearrangement of intermediate **15** in the presence of trimethylsilyl cyanide **16** in an organic solvent to yield the diazocyanides **19** in good yields (Scheme 5).



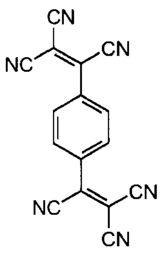
Scheme 4



Scheme 5

The redox potentials of these novel acceptors are similar to those of the TCNQ or DCNQI, and thus they form black CT complexes with donors such as TTF exhibiting a room temperature conductivity $\sigma = 120\ \mathrm{S\ cm^{-1}}$ and semiconducting behaviour.[42]

In addition to the benzenebis(diazocyanides), 1,4-bis(tricyanovinyl)benzene **20** has been previously reported by Wudl as a redox system of the inverse Wurster type.[44] This new type of acceptor can be considered a derivative from tetracyanoethylene **21** (TCNE) which is an excellent acceptor and the simplest of the symmetrical percyanoalkenes (cyanocarbons).[45] Following the discovery of TCNE, a series of neutral cyanocarbons, such as hexacyanobutadiene **22** (HCBD)[46] and a series of cyanocarbon acids such as pentacyanopropenide **23** ($\mathrm{PCP^-}$),[47] heptacyanopentadienide **24** ($\mathrm{HCP^-}$),[48] hexacyanotrimethylenemethanediide **25** ($\mathrm{HCTMM^{2-}}$)[49] and tris(dicyanomethylene)cyclopropandiide **26** ($\mathrm{HCP^{2-}}$)[50] were prepared.



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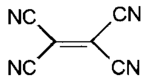
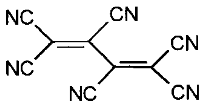
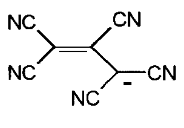


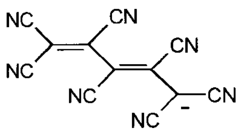
21 (TCNE)



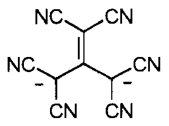
22 (HCBD)



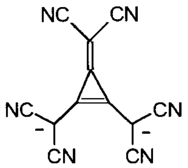
23 (PCP$^-$)



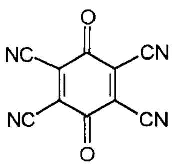
24 (HCP$^-$)



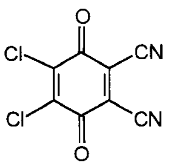
25 (HCTMM^{2-})



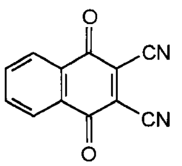
26 (HCP^{2-})



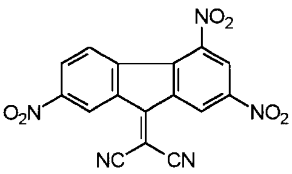
27 (Cyanil)



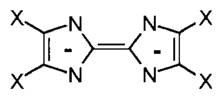
28 (DDQ)



29 (DCNQ)

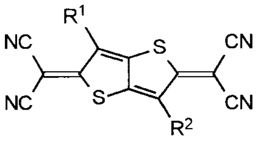


30 (DTF)



31 X = CN (TCTAF^{2-})

The work by Miller describing the new procedure for the synthesis and characterization of cyanil (tetracyano-*p*-benzoquinone, **27**) as the strongest isolated electron acceptor ($E_{red} = 0.90$ V *vs.* SCE in MeCN) and its reduced forms deserves attention.[51] The synthesis was carried out in a three-step procedure from commercially available 2,3-dichloro-5,6-dicyano-*p*-benzoquinone **28** (DDQ) and NaCN in methanol to form the tetracyanohydroquinone, which was transformed into the insoluble silver salt by treatment with silver nitrate followed by bromine oxidation to yield cyanil as a yellow crystalline material. Cyanil forms CT salts with a variety of donors. However, isolation of the radical anion in the solid state has not been achieved.[51] Other cyanoquinones like the already mentioned DDQ **28**[52] and 2,3-dicyano-1,4-naphthoquinone **29** (DCNQ)[53] have also been used in order to synthesize conducting CT complexes.



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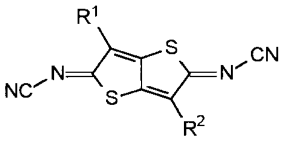

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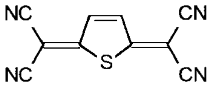

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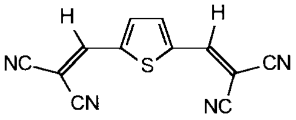

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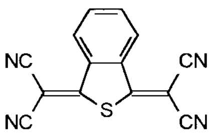

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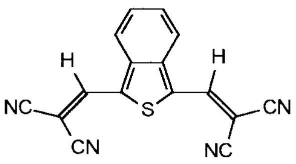

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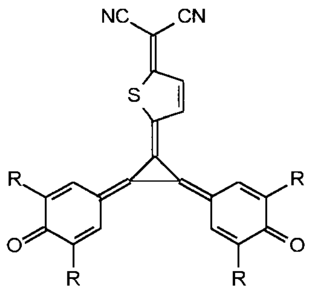
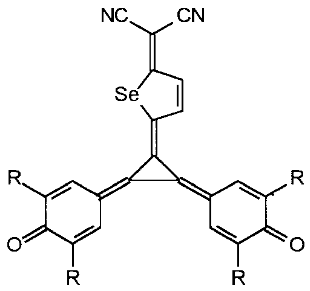


42a R = Bu^t
b R = Me



43

Finally, another type of cyano-containing electron acceptors with a completely different chemical structure is also worth mentioning. Thus, electron acceptors of the fluorene series[54] like 9-dicyanomethylene-2,4,7-trinitrofluorene **30** (DTF)[55] form solid charge transfer complexes with a number of aromatic hydrocarbons. Also, acceptor molecules with structural similarity to the strong donor system TTF have been recently reported to form charge transfer complexes. Thus, semiconducting charge transfer complexes of TTF with 4,4′,5,5′-tetracyano-1,1′,3,3′-tetraazafulvalene **31** (TCTAF)[56] have been synthesized.

Heteroquinoid electron acceptors

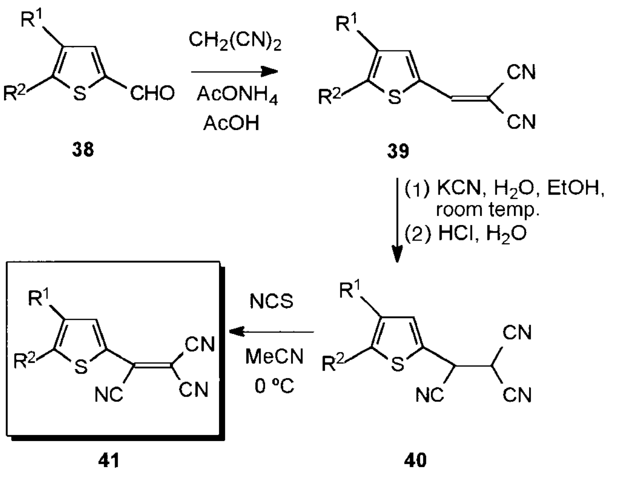
Most of the novel acceptors prepared have a modified quinoid backbone, with terminal dicyanomethylene or cyanoimine groups. A very successful variation leading to good conducting CT complexes was performed with the thieno[3,2-*b*]thiophene system. Thus, the novel sulfur-containing heteroquinoid electron acceptors 2,5-bis(dicyanomethylene)-2,5-dihydrothieno[3,2-*b*]thiophene **32**[57] and, more recently, 2,5-bis(cyanoimino)-2,5-dihydrothieno[3,2-*b*]thiophene **33** (DCNTT) were synthesised from the respective quinones and BTC.[58]

In this case, the standard conditions used for the preparation of DCNQIs were not satisfactory and the reaction had to be carried out in *o*-dichlorobenzene at 60 °C. These compounds showed good acceptor abilities which could be tuned within a wide range depending upon the substituents R^1 and R^2.

The search for increased dimensionality *via* interstack sulfur–sulfur contacts led to the synthesis of other acceptor molecules with the thiophene moiety. Thus, 2,5-bis(dicyanomethylene)2,5-dihydrothiophene **34**[57] and its vinilogue **35**[59] were prepared and, more recently, 1,3-bis(dicyanomethylene)-1,3-dihydrobenzo[*c*]thiophene **36** and its vinylogue **37**, as the first electron acceptor derived from isothianaphthene, were synthesized.[60] The half-wave redox potentials possess a weaker acceptor character in comparison with that of TCNQ. However, electron withdrawing substituents on the thienoquinoid ring increase the acceptor strength.

Tricyanovinylthiophenes **41** have been recently examined as electron acceptors for organic metals.[61] This molecule had been previously used as the acceptor moiety in D–π–A systems exhibiting non-linear optical properties.[62] The synthesis was carried out by condensation of thiophenecarbaldehyde **38** with malononitrile in the presence of acetic acid–ammonium acetate and azeotropic distillation of water to form the dicyanovinylthiophene **39**. Further treatment of **39** with potassium cyanide and then acidic conditions led to the tricyanoethane derivative **40** which was finally oxidized with *N*-chlorosuccinimide (Scheme 6). Although the X-ray data reveal an almost planar molecule, the reduction potentials lie far away from those of the parent TCNQ or TCNE molecules.

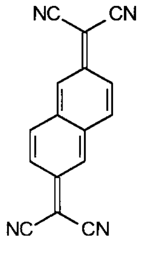
Radialene derivatives have also been used as promising acceptor components in the preparation of conducting materials. [3]Radialene derivatives **42** and **43** having a hybrid structure of 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene and tris (4-oxocyclohexa-2,5-dienylidene)cyclopropane have recently been reported as strong novel electron acceptors with interesting electrochemical properties. They form conducting 1 : 1 molecular complexes with TTF and other known electron donors.[63,64]



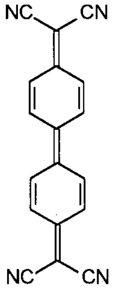
Scheme 6

π-Extended acceptor systems

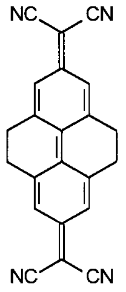
One of the most interesting aspects in the synthesis of tetracyano-*p*-quinodimethanes other than TCNQ was to increase the π-extension of the electron acceptors. From theoretical calculations, Garito and Heeger concluded, twenty years ago, that an extension of the π-system in such compounds would lead to a lowering of the intramolecular Coulomb repulsion in the anions of the acceptors, resulting in more stable radical anions and hence in highly conducting CT complexes.[3] Thus, in the last two decades novel acceptor structures such as 9,9,10,10-tetracyano-2,6-naphthoquinodimethane **44** (TNAP),[65,66] 7,7,7′,7′-tetracyano-4,4′-diphenoquinodimethane **45** (TCNDQ),[67,68] 11,11,12,12-tetracyano-4,5,9,10-tetrahydro-2,7-pyrenoquinodimethane **46** (TCNTHPQ)[68,69] and 11,11,12,12-tetracyano-2,7-pyrenoquinodimethane **47** (TCNPQ)[70] were prepared. However, some of these novel acceptors were not stable and, although some CT complexes have been described,[68,69,71,72] few solid state data have been reported due to their inability to form stable crystalline complexes. Thus, this approach was not as successful as was initially expected.



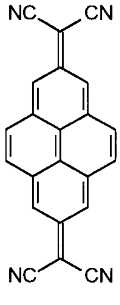
44 (TNAP)



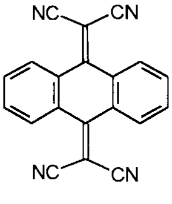
45 (TCNDQ)



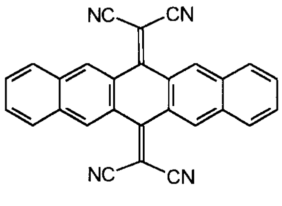
46 (TCNTHPQ)



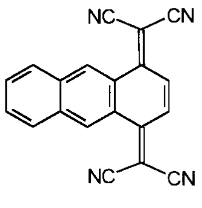
47 (TCNPQ)



48 (TCAQ)



49 (6,13-TCPQ)



50 (1,4-TCAQ)

Extended π-systems based on TCNQ and DCNQI analogues. Much less was known, however, on TCNQ analogues laterally fused with aromatic rings. 11,11,12,12-Tetracyano-9,10-anthraquinodimethane **48** (TCAQ) was prepared by four different groups during the period 1983–1985.[23,73–75] More π-extended linear systems have been described more recently by reaction of the corresponding quinones and malononitrile in the presence of Lehnert's reagent[76] (Table 1).

By following Hünig's methodology,[23] several synthetic routes have been used to prepare TCAQ, the most expeditious procedure being that reported for anthraquinone as starting material.[23,74] Cyclic voltammetry measurements of some of the π-extended acceptors are summarized in Table 1.

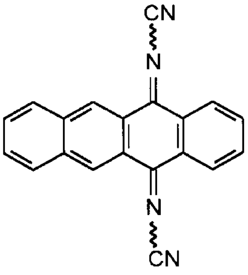
As is shown in Table 1, an increase in benzannulation results in a shift of the reduction potentials towards more negative values, due to the major influence of the molecular distortion of the fused benzene rings rather than to the electronic effect of increasing π-delocalization.[76]

In contrast to TCAQ and TBAQ, which show a two-electron reduction to the dianion,[77] the other π-extended molecules showed two single-wave reductions to the corresponding radical anion and dianion. The single-wave reduction involving two electrons was confirmed by coulometric analysis of TCAQ in DMF.[75] Therefore, the first reversible redox wave in the CV of TCAQ is an overall process leading to the dianion ($TCAQ^{2-}$). The formation of radical trianions in which the third electron is located in the aromatic skeleton is in agreement with the EPR observation of related systems.[28,78] The facile access to these radical trianions is related to that of the analogous dialkylsubstituted aromatic hydrocarbons.[75,79] The electrochemical data clearly show that benzannulated TCNQs are poorer acceptors than TCNQ and the charge transfer complexes formed proved to be poorer conductors.[80] To rationalize how the extension of the π-system affects the molecular geometry and the electronic properties, the molecular and electronic structures of 6,13-TCPQ **49** have recently been reported as a largely extended TCNQ derivative by using quantum-chemical methods.[81] The geometry found is highly distorted from planarity due to the strong steric interactions between the cyano groups and the hydrogens in the *peri* positions. To avoid this interactions, the TCNQ ring adopts a boat conformation with the dicyanomethylene units and the naphthalene rings folded in opposite directions. The 6,13-TCPQ molecule **49** adopts a butterfly-type structure, similar to that observed for TCAQ from X-ray data in which the lateral aromatic moieties preserve their planarity (Fig. 3).

The electronic structure of 6,13-TCPQ was calculated using its PM3-optimized geometry. Fig. 4 displays the Valence Effective Hamiltonian atomic orbital composition of the HOMO and the LUMO calculated for TCAQ and 6,13-TCPQ. The HOMO and the LUMO of TCAQ preserve the topology of the HOMO ($3b_{1u}$, -8.53 eV) and LUMO ($3b_{3g}$, -6.23 eV) of TCNQ showing, respectively, non-bonding and weak antibonding interactions with the outer carbon atoms. The LUMO of TCAQ is therefore destabilized by 1.01 eV with respect to the LUMO of TCNQ. An additional destabilization of 0.18 eV is calculated for the LUMO of 6,13-TCPQ which shows the same topology. Since the reduction process implies the introduction of an electron into the LUMO, the continuous destabilization of this orbital when passing from TCNQ to TCAQ and to 6,13-TCPQ explains the more negative reduction potential values observed in the CV measurements. Thus, the lowering of the acceptor ability with benzannulation is due to the loss of planarity, which reduces the bonding interactions in the LUMO of the TCNQ moiety, and also to the annulation itself, which gives rise to new destabilizing antibonding interactions.

In order to obtain more planar π-extended acceptors, the synthesis and characterization of 11,11,12,12-tetracyano-1,4-anthraquinodimethanes **50** (1,4-TCAQs) was reported.[26] From a synthetic point of view only the parent unsubstituted 11,11,12,12-tetracyano-1,4-anthraquinodimethane (1,4-TCAQ) had been previously reported from 1,4-bis(bromomethyl)-anthracene using a multistep procedure in a very low yield.[73] Although the use of Lehnert's reagent seemed to be only partially applicable to the synthesis of TCNQ derivatives, we have proved the validity of this reagent for preparation of tri- and tetrasubstituted derivatives.[26] These molecules show differing electrochemical behaviour depending upon the substitution pattern. Although the reduction potentials are shifted to negative values, related to TCNQ, substitution with chlorine atoms results in reduction potential values similar to that of the parent TCNQ. The geometries and electronic structures of TCAQs have also been studied, and follow a similar trend to that predicted for the above π-extended systems.[81]

Taking advantage of the more flexible and less sterically demanding C=N−CN bond in comparison with the $C{=}C(CN)_2$ moiety, a series of fused aromatic DCNQI derivatives **51**–**54** have been synthesised by reaction of the corresponding quinones with BTC, in which the π-system has been systematically extended in order to correlate the degree of conjugation with the acceptor ability of these molecules.[82]



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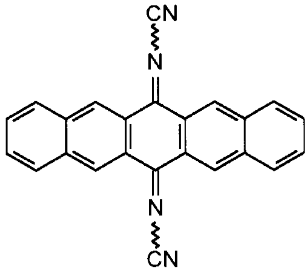

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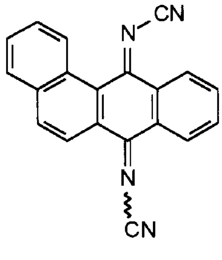

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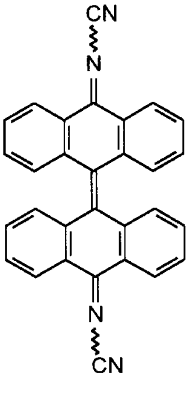


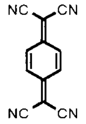
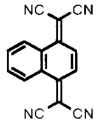
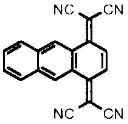
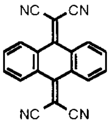
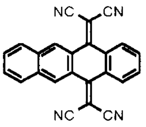
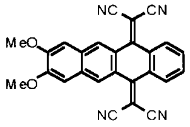
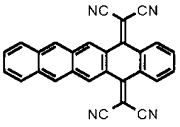
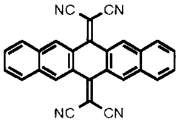
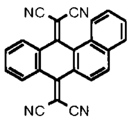
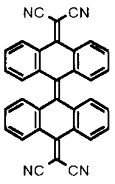
54

The CV measurements reveal that the increase in benzannulation results in a shift of the reduction potentials towards more negative values, following the same trend observed for the TCNQ analogues mentioned above. More planar π-extended DCNQI derivatives **56** have been prepared from substituted 1,4-anthracenediones **55** by reaction with BTC and $TiCl_4$ in dichloromethane[83] (Scheme 7).

Molecular mechanics calculations indicate that these DCNQI derivatives are nearly planar. Even the presence of two bromine atoms does not seem to disturb the planarity of the molecule, all of the dihedral angles being smaller than 2°.

Heterocyclic fused TCNQ and DCNQI analogues acceptors. A different approach, intended to increase the π-extension of the electron acceptor, involves the use of heterocyclic systems

Table 1 CV data for TCNQ and fused aromatic ring derivatives

			potential/*V vs.* SCE				
compound	formula	solvent	$E^1_{1/2}$	$E^2_{1/2}$	$\lvert E^2_{1/2}-E^1_{1/2}\rvert$	$E^3_{1/2}$	ref.
TCNQ		CH_3CN	0.08	−0.48	0.56	—	23
		BuCN	−0.09	−0.75	0.66		75
		DMF	−0.12	−0.72	0.59		75
benzo-TCNQ		CH_3CN	−0.04	−0.41	0.37	—	73
		BuCN	−0.26	−0.74	0.48		75
		DMF	−0.30	−0.73	0.43		75
naphtho-TCNQ		CH_3CN	−0.18	−0.48	0.30	—	73
TCAQ		CH_3CN	−0.285		—	−2.06	75
		BuCN	−0.71				75
		DMF	−0.705				75
TCTQ		CH_3CN	−0.44	−0.93	0.49	−1.85	76(*a*),(*b*)
$(MeO)_2$-TCTQ		CH_3CN	−0.44	−0.89	0.45	−1.59	76(*a*),(*b*)
5,14-TCPQ		CH_3CN	−0.50	−0.92	0.42	−1.54	76(*a*),(*b*)
6,13-TCPQ		CH_3CN	−0.57	−0.91	0.34	−1.61	76(*a*),(*b*)
BDCNBA		CH_3CN	−0.44	—	—	—	76(*c*)
TBAQ		DMF	−0.70		—	—	76(*d*)

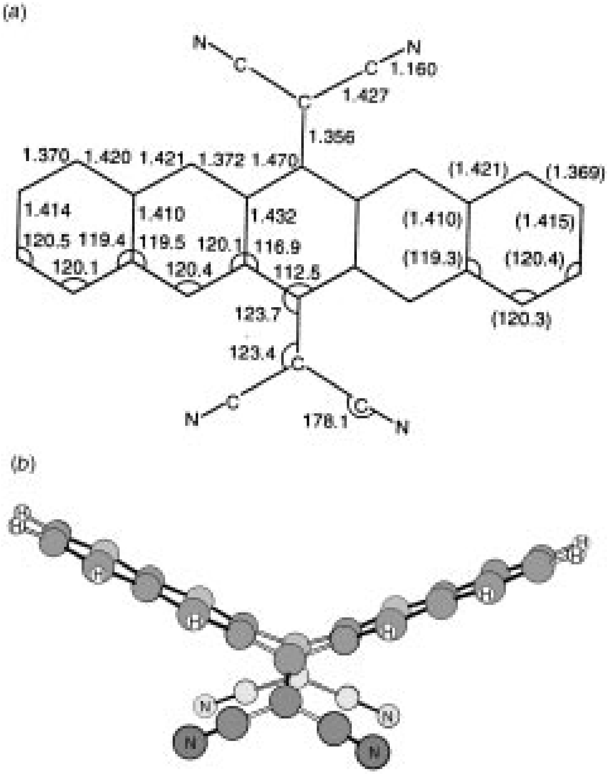
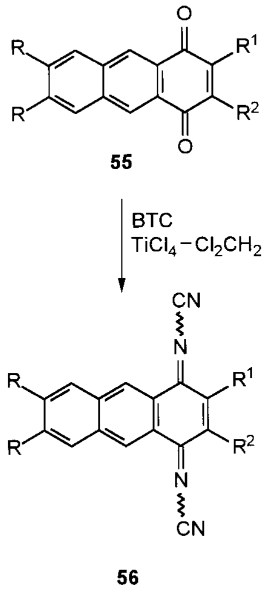


Fig. 3 (*a*) PM3-optimized bond lengths (in Å) and bond angles (in degrees) of TCPQ. The PM3 parameters calculated for the naphthalene molecule are included on the right within parentheses. (*b*) View showing the distortions from planarity of the molecule.



Scheme 7

which, despite the steric crowding introduced by ring fusing, has proven experimentally that planar molecules are formed when pentagonal heterocyclic systems, bearing no *peri* hydrogen atoms, are fused to the TCNQ ring.

Although the synthesis of thiophene-fused TCNQs was firstly reported in 1986 by Kobayashi and Gajurel,[84] a few years later, in 1992, the preparation and physicochemical

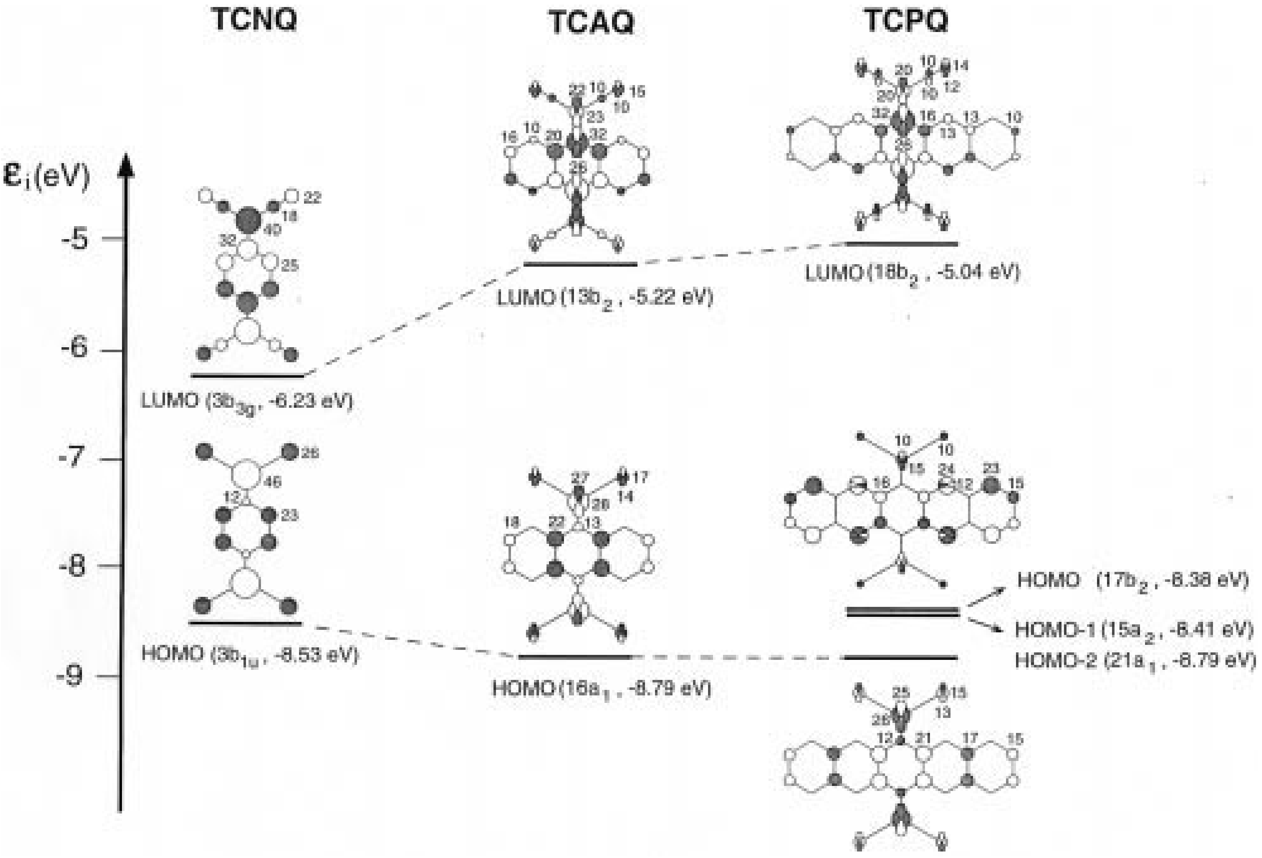
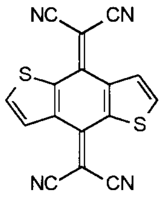


Fig. 4 VEH atomic orbital calculations of the HOMO and the LUMO for TCNQ, TCAQ and 6,13-TCPQ

properties of an isomeric series of thiophene-fused TCNQs were reported.[85] Their crystal and molecular structures,[86] the crystal structure of CT complexes with the strong donor TTF[87] and also the crystal structure of a 2:3 CT salt with the tetraethylammonium cation[88] were described. The conductivities of the complexes are strikingly high for **57**–TTF ($\sigma = 4.78\ \mathrm{S\ cm^{-1}}$) and **58**–TTF ($\sigma = 0.89\ \mathrm{S\ cm^{-1}}$) and very low for **59**–TTF ($\sigma < 10^{-6}\ \mathrm{S\ cm^{-1}}$). On the other hand, the radical anion salt of **57** with tetraethylammonium as counter cation exhibits a high conductivity at room temperature ($\sigma = 0.46\ \mathrm{S\ cm^{-1}}$).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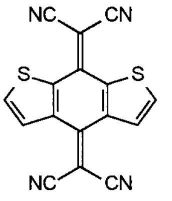
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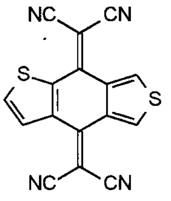
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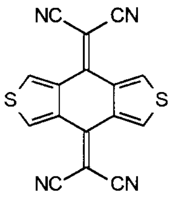
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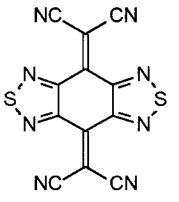
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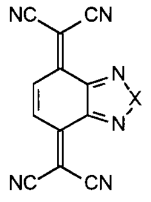
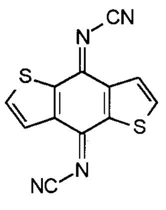

62 X = S, Se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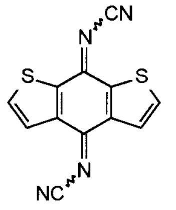
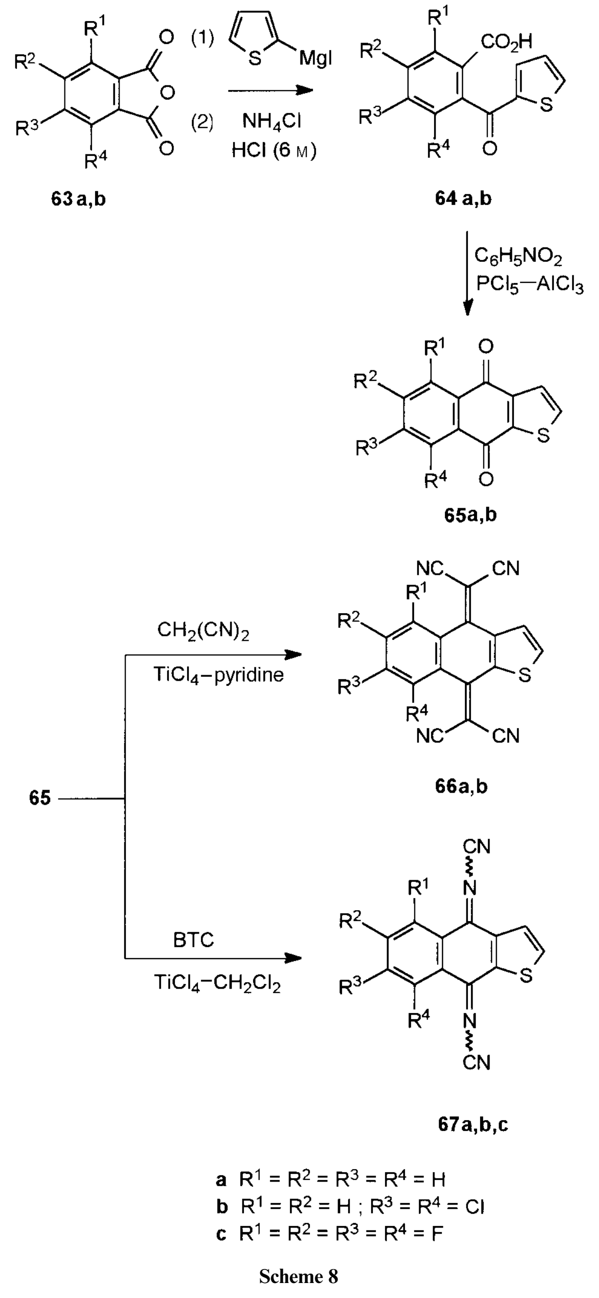

69

The synthesis was carried out from the corresponding heterocyclic quinones by treatment with Lehnert's reagent following the Hünig's procedure reported for the carbocyclic TCAQ.[23] The molecular structures of molecules **57**, **58** and **59** were determined by X-ray analysis,[88] and showed a butterfly shape, although much less distorted than the benzene-fused TCAQ molecule and closer to that of benzo-TCNQ.[89] Thus, acceptors **57**, **58** and **59** formed 1:1 CT complexes with TTF, whereas **60** did not form complexes due to its poor acceptor ability and highly deformed structure.[86,87]

Another interesting type of heterocyclic-fused TCNQ acceptors are the thiadiazole-fused TCNQ derivatives **61** and **62** reported by Yamashita, who described TCNQ acceptors bearing one[90] or two[91] thiadiazole units fused to the TCNQ ring. These compounds display good acceptor properties and their planar geometry, in addition to the presence of S···N contacts, allowed the preparation of charge transfer complexes exhibiting high electrical conductivities.[92] Owing to the large size of the chalcogen atoms, the interstack as well as the intrastack interactions are increased, and as a consequence, the conductivity and stabilization of the metallic state are enhanced.[93]

The synthesis, electrochemistry and crystallographic study of 9,9,10,10-tetracyanothieno[2,3-*b*][1,4]naphthoquinodimethanes **66**[94] has also been reported. In them, the TCNQ moiety is simultaneously fused to both benzene and thiophene rings as a hybrid acceptor between the TCAQ molecule and the dithiophene-fused TCNQ acceptors (Scheme 8). Compounds **66** are better acceptors than TCAQ, providing a more planar structure due to the presence of the thiophene ring.

DCNQI analogues have also been synthesized by reaction of quinones **65** (Scheme 8) with BTC following Hünig's procedure.[94,95] Their high resolution ^1H NMR spectra suggest a favoured configuration with the cyano groups pointing to the thiophene ring, in agreement with the X-ray data obtained for compound **67a**.



Scheme 8

The CV measurements showed two one-electron reduction waves to the corresponding radical anion and dianion. Replacing the benzene ring with a thiophene ring leads to a better acceptor due to the lowering of steric hindrance. The presence of four fluorine atoms on the benzene ring (**67c**) significantly decreases the reduction potential values. Unlike compounds **67a,b**, fluorine-substituted **67c** showed evidence of complexation in solution with the strong donor *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and forms a copper salt by reaction with copper(I) iodide.[95]

Isomeric thiophene-fused dicyanoquinone diimines **68** and **69** have been prepared and reacted with copper(I) iodide to afford a novel class of highly conducting complexes of CuI which exhibited metallic behaviour down to *ca.* 170 K with room temperature conductivities of 45 and 100 S cm^{-1}, respectively.[96] X-Ray powder diffraction studies suggested a highly layered structure and thermoelectric powder and X-ray photoelectron spectroscopy suggested that the electrical transport properties occur *via* hole conduction along the CuI chains.

In order to evaluate the effect of the presence of heteroatoms on the electronic properties of the acceptors without affecting the geometry of the molecule, we synthesized the aza-TCAQ analogue 11,11,12,12-tetracyano-2-azaanthraquinodimethane (TCAAQ) as a new nitrogen containing acceptor in a fused pyridine ring.[97] The presence of the electronegative heteroatom led to a slightly less negative reduction potential in comparison with TCAQ, resulting in a better acceptor molecule. These results can be generalized in the sense that they allow a correlation of the acceptor ability of fused TCNQ derivatives with the π-deficient or π-excessive character of the heterocyclic rings.

[60]Fullerene Based Acceptors

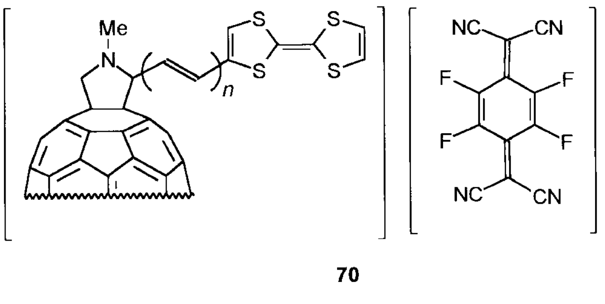
Since the preparation of fullerene C_{60} on a large scale in 1990[98] a great deal of effort has been devoted to the exploration of the chemical and physical properties of this new allotrope of carbon.[99]

The electron acceptor ability of the C_{60} molecule in solution has been measured by charge transfer absorption energy and also by redox potentials, and it has been concluded that C_{60} is a weak acceptor molecule, comparable to *p*-benzoquinone or 2,3-dichloro-1,4-naphthoquinone, the adiabatic electron affinity of the C_{60} molecule being estimated as 2.10 ± 0.1 eV.[100]

The finding of superconducting properties of salts prepared for C_{60} and alkali and alkaline-earth metals with relatively high transition temperatures ($T_c \leqslant 33$ K) led to the observation that the temperature T_c of the superconductivity of these fullerides was related to the size of the metallic atoms and the lattice constant.[101] Consequently, the preparation of complexes with bigger organic donor molecules was thought to increase the T_c values and a number of charge transfer complexes with a variety of donor molecules have been prepared.[100]

Complexation with strong electron donors such as cobaltocene[102] or tetrakis(dimethylamino)ethylene (TDAE)[103] formed fully ionic CT complexes which proved to be electrically insulating, although with interesting magnetic properties.[104]

Complexation with other donor organic molecules such as ferrocene,[105] hexamethylenetetratellurafulvalene,[106] bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)[107] or the dimer of BEDT-TTF[108] gave insulating neutral CT complexes in which C_{60} cocrystallizes with the donor unit.



70

Recently, CT complexes from [60]fullerene–tetrathiafulvalene (C_{60}–TTF) systems **70** have been reported to show semiconducting behaviour by reaction with the very strong electron acceptor tetrafluorotetracyano-*p*-quinodimethane ($TCNQF_4$).[109] In contrast, no intramolecular electronic interactions were observed in solution for C_{60}–TTF,[110] although a specific solid state interaction cannot be ruled out.[111]

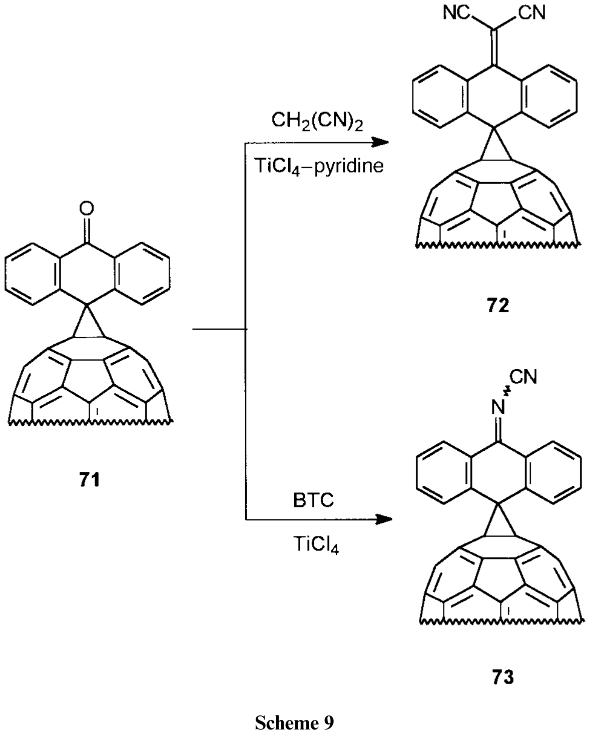
A dumbbell type [60]fullerene dimer in which both C_{60} units are covalently attached to a double donor spacer has also recently been prepared by a double cycloaddition of azomethine ylide to C_{60}.[112]

The C_{60} molecule can be derivatized with organic groups to yield organofullerenes exhibiting redox properties different than those of C_{60}.[113–116] Wudl and co-workers have reported the synthesis and redox behaviour of spiroannulated methanofullerenes exhibiting better reduction ability than the parent C_{60} molecule.[117–120] In these molecules the aromatic rings are held rigidly perpendicular to the surface of the ball, and a 'periconjugative effect' takes place between the p_z orbitals of the addends and the p_z orbitals of the fullerene carbon atoms adjacent to the bridge atom.

TCNQ and DCNQI type spiromethanofullerenes **72** and **73** were obtained from the quinone-type **71** by reaction with malononitrile and bis(trimethylsilyl)carbodiimide respectively in the presence of $TiCl_4$ and pyridine (Scheme 9). The cyclic voltammetry measurements of the novel acceptors show that the methanofullerene derivatives are slightly better acceptors than the parent C_{60}.

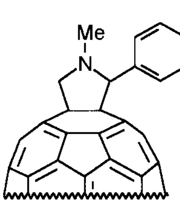
In comparison with the quinone-type precursor spiromethanofullerene **71**, the reduction potentials of compounds **72** and **73** are shifted toward less negative values (70–80 mV) due to the stronger electron-withdrawing effect of the dicyanomethylene and cyanoimino groups.

A different approach towards the search for novel organofullerenes showing better acceptor abilities than the parent C_{60} have been recently carried out in our group.[121] Thus, the C_{60} cage is covalently linked to strong electron-acceptor moieties

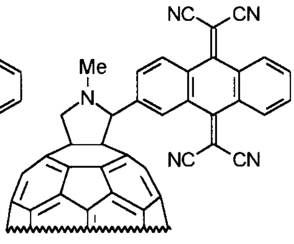


Scheme 9

derived from DCNQI **74** and TCNQ **75** as precursors for novel C_{60} based organic metals.



74



75

Each of the cyclic voltammograms of compounds **74** and **75** shows a reduction wave for each of the organic addends, in addition to the first three one-electron quasi-reversible reduction waves corresponding to the reduction steps of the fullerene moiety. The first reduction potential for these fulleropyrrolidines is shifted to more positive values related to the parent C_{60}, TCAQ and DCAQI, these novel [60]fullerene based electron acceptors being suitable precursors for the preparation of intermolecular CT complexes by reaction with strong electron donor molecules.

TCNQ and DCNQI Based Intramolecular Acceptor–Donor Systems

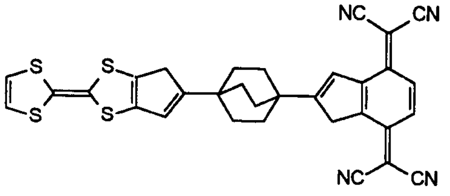
The design of novel organic molecules containing electron donor (D) and electron acceptor (A) moieties constitutes a promising field of study due to the interesting optical and electronic properties they can display. D–σ–A structures are the basis for the development of molecular electronic devices,[122–124] and for the design of artificial photosynthetic systems constituted by electron donor–spacer–electron acceptor compounds[125] using long spacers such as proteins and peptides.[126] Other biomimetic novel compounds resembling the pigments of nature have also been constructed from porphyrins and quinones[127] (Fig. 5).

Donor–acceptor (D–A) conjugated systems have been used for the preparation of molecular chromophores exhibiting nonlinear optical response.[128] On the other hand, organic compounds exhibiting semiconducting properties based on a single component have only recently been described.[129–131]

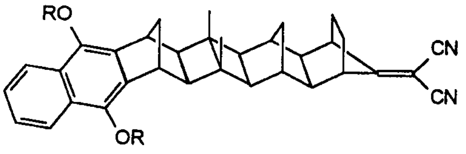
TCNQ derivative 2,5-dibenzyl-7,7,8,8-tetracyano-*p*-quinodimethane **76** (DBTCNQ) reported by Becker in 1983 was designed as a novel and interesting prototypical donor–acceptor–donor (D–A–D) system.[132]

Other DBTCNQ derivatives with electron-withdrawing substituents on the phenyl ring or naphthalene units as donor fragments were latter published, and a significant difference in the colour of these compounds depending upon the donating strength was observed in the solid state.[133]

The characteristic architectural finding in the structure of compound **76** was a packing motif of isolated triplets D···A···D formed by the central TCNQ ring of a molecule and two phenyl rings of two other neighbouring molecules. The donor phenyl ring moieties are orthogonal to the acceptor TCNQ moiety as a consequence of the steric hindrance of the phenyl rings and the olefinic hydrogens on the TCNQ, thus preventing donors from properly stacking.[132,133] In order to mitigate this steric hindrance, we carried out the synthesis and electrochemical and crystallographical studies of the novel molecules 7,7,8,8-tetracyano-2,5-bis(3-phenylpropyl)-*p*-quinodimethane **77** and *N,N′*-dicyano-2,5-bis(3-phenylpropyl)-*p*-quinone diimine **78** in which an extension of the linking chains units between the donor and acceptor moieties has been performed.[134] However, this modification of the chain length has no influence on the stacking motif in comparison with compound **76**, the two phenyl rings being nearly orthogonal to the TCNQ moiety, thus preventing the formation of segregated stacks of donor and acceptor moieties, which is one of the structural requirements to obtain an electrically conducting arrangement.



From ref. 123(*b*)



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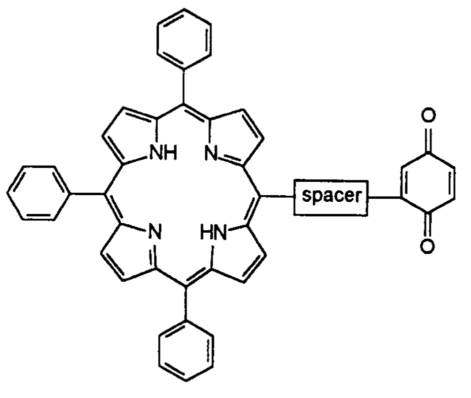


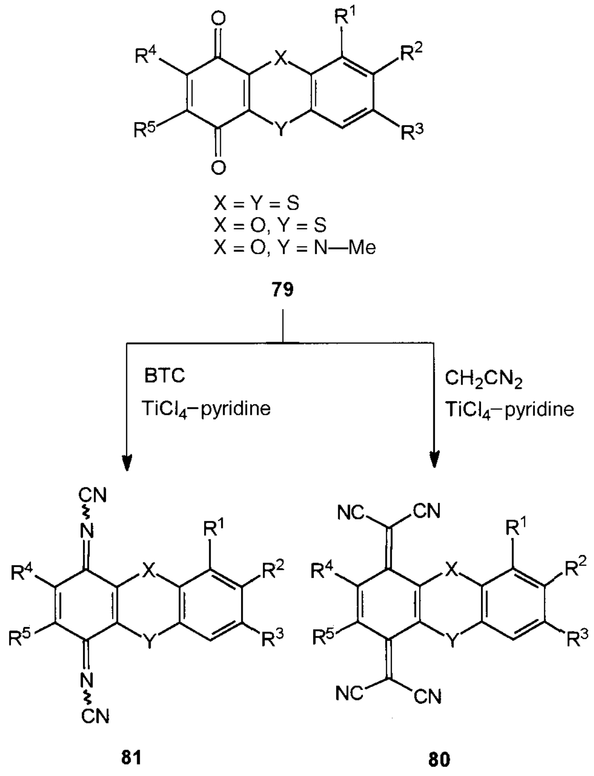
From ref. 127

Fig. 5 Representative donor–spacer–acceptor compounds

In order to avoid the orthogonality of the phenyl rings, we have prepared a new type of single-component donor–acceptor compounds in which the donor and acceptor moieties are linked by two heteroatoms (sulfur, oxygen or nitrogen)[27,135–137] This type of molecules presents, in principle, the following advantages: (i) as the above D–A–D system, the molecule contains a prefixed D:A stoichiometric ratio, and consequently, it would be possible to tune the electron transfer by using different substituents; (ii) the presence of two heteroatom bridges overcomes the orthogonal relative geometry between donor and acceptor moieties found when only one bridge is present;[132,134] (iii) the crystal packing in the solid state can be modified by changing the intermolecular connectivity; and (iv) the presence of heteroatoms, and particularly the presence of sulfur atoms, may reinforce the intermolecular interactions, thus increasing the dimensionality in the solid state.

The target molecules **80** and **81** were prepared by reaction of the corresponding quinones **79** with malononitrile and Lehnert's reagent and with BTC in the presence of $TiCl_4$, respectively (Scheme 10).

Interestingly, previous attempts to prepare TCNQ derivatives **84** from the corresponding quinone **82** were unsuccessful,

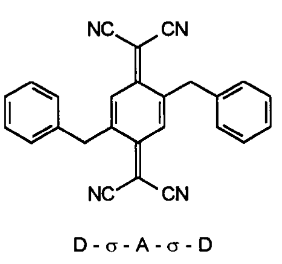


Scheme 10

leading to the tricyano derivative **83** instead of the expected TCNQ derivative.[138]

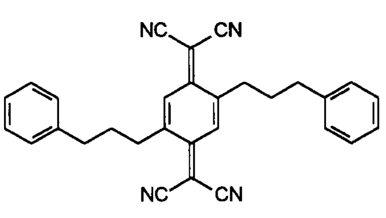
Substitution of sulfur or nitrogen atoms by one or two oxygen atoms in the dioxine 6,11-quinone results in a favoured 1,2-addition of malononitrile to both carbonyl groups. The reaction of quinones with nucleophilic agents has recently been reviewed considering modern mechanistic aspects.[139]

The electronic spectra of the starting quinones and TCNQ and DCNQI derivatives show, in addition to the expected bands in the UV region, the presence of a charge-transfer band as a low energy absorption in the visible region which is shifted bathochromically when the donor fragment bears electron-releasing methyl groups. This feature suggests an intramolecular electron transfer from the donor to the acceptor part of the molecule. The intramolecular character of this electronic transition was confirmed by UV–VIS dilution experiments.



D - σ - A - σ - D

76 (DBTCNQ)



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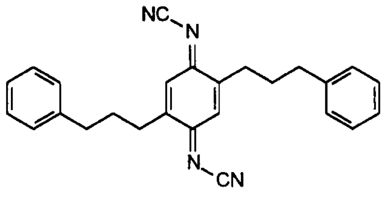

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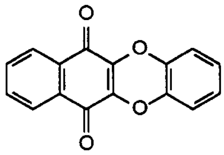
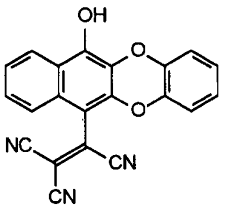
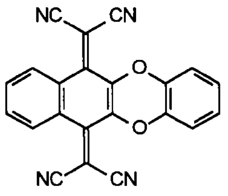




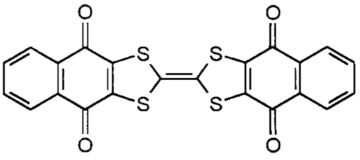
82 **83**



84

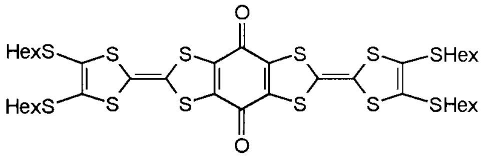
The cyclic voltammetry measurements performed on compounds **79**, **80** and **81** show, together with the reduction waves corresponding to the quinoid moiety, an oxidation wave at positive potential value due to the oxidation of oxathiine, dithiine and oxazine fragments which give rise to stable cation radicals. This behaviour has also been observed in sulfur-containing twin-DCNQI-type acceptors.[140]

Semiempirical PM3 molecular orbital calculations predict that TCNQ and DCNQI derivatives **80** and **81** show a non-planar conformation in which the acceptor and the donor moieties are bent. Distortions from planarity are found to be larger for the TCNQ derivative owing to the presence of the more voluminous and rigid dicyanomethylene units.



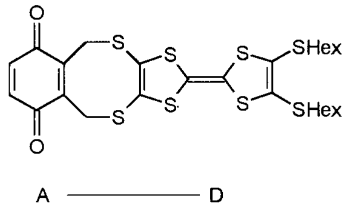
A —— D —— A

85



D —— A —— D

86



87

The electronic properties of these compounds have been studied using the non-empirical VEH method.[27,135,137] The HOMO–LUMO transition corresponds to an electronic transfer from the donor to the acceptor moieties, thus supporting the charge-transfer nature of the lowest energy absorption observed experimentally.

The X-ray structural analysis performed for the DCNQI derivative **81** [$X=Y=S$; $R^1=R^2=R^3=H$; R^4, $R^5=-(CH=CH)_2-$, Scheme 10] shows that these molecules adopt a non-planar conformation and are packed in vertical stacks where donor and acceptor moieties alternate their position. In agreement with this aggregation in mixed stacks [···(A–D)(D–A)(A–D)···], the electrical conductivity of this compound is less than 10^{-6} S cm^{-1}.[137]

A different approach for the preparation of intramolecular CT complexes consists of the synthesis of donor–σ–acceptor systems bearing the strong donor TTF. Until now, only the TTF quinones **85** and **86** have been reported as fused donor and acceptor units. However, the poor solubility of **85** prevented its further functionalisation and also the structural study of this A–D–A system. In addition, the cyclic voltammetry studies did not show the oxidation waves corresponding to the TTF donor fragment.[141]

In contrast to **85**, the cyclic voltammetry of compound **86** reveals only two two-electron oxidation waves corresponding to the two TTF moieties.[142] No data were reported on the electrochemical behaviour of the *p*-benzoquinone acceptor fragment.

We have recently presented our preliminary results on the preparation of a novel and soluble donor–σ–acceptor molecule **87** in which the TTF fragment is linked to a *p*-benzoquinone ring by two methylenethio (CH_2-S) spacers.[143] These spacers allow minimal conjugation between the D and A fragments, so that each component retains its original identity. Thus, the electroactive character of both donor and acceptor partners can be clearly observed in the CV measurements.

The quinone moiety of **87** can be used as a precursor for other, stronger acceptor moieties, *e.g.* DCNQI or TCNQ, which will allow access for the first time to molecules which contain simultaneously strong acceptors such as TCNQ or DCNQI together with the strong donor TTF, thus resembling the Aviram–Ratner rectifier.[123b]

Conclusions

The main classes of cyano-containing acceptor molecules have been highlighted in this article, stressing those acceptors of the TCNQ and DCNQI types. The synthetic approaches used for the structural modifications of the acceptor framework, such as ring substitution, presence of heteroatoms and π-system extension, have been discussed. In this regard, although extensive studies have been carried out in the search for better acceptors forming stable radical anions, an increase in dimensionality remains a major goal in the chemistry of electron acceptor molecules. It is clear from this article that novel electron acceptors capable of hydrogen bonding or chalcogen–chalcogen interactions deserve more study and represent a challenge for synthetic chemistry.

Despite the lack of superconducting properties in TCNQ and DCNQI derivatives or other cyano containing acceptors, highly conducting salts have been well-characterized, particularly the copper salts of 2,5-disubstituted DCNQIs reported by Hünig, which exhibit metallic conductivity and are among the better studied acceptors.

We have also pointed out the first examples from the emerging chemistry of C_{60} based electron acceptors, which pave the way for the preparation of novel CT complexes in which the conducting properties of CT complexes are combined with the unique properties of fullerenes, thus resulting in novel multiproperty materials.

TCNQ and DCNQI based intramolecular acceptor–donor (A–D) systems constitute a promising field of application for the known acceptor molecules due to the interesting optoelectronic properties they can exhibit. In particular, conjugated D–A molecules bearing TCNQ or DCNQI derivatives as the acceptor moiety constitutes an unexplored area within the field of non-linear optical (NLO) materials.

The authors are indebted to all those who collaborated in this research and whose names appear in the references given. We also acknowledge financial support from CICYT (Grants PB-89-0495, PB-92-0237 and PB-95-0428-C02) and Complutense University for research grants and fellowships.

References

1 (*a*) J. Ferraris, D. O. Cowan, V. V. Walatka and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948; (*b*) L. B. Coleman, M. J. Cohen, A. J. Sandman, F. G. Yamagishi, A. F. Garito and A. J. Heeger, *Solid State Commun.*, 1973, **12**, 1125.
2 M. R. Bryce and L. C. Murphy, *Nature*, 1984, **309**, 119.
3 A. F. Garito and A. Heeger, *Acc. Chem. Res.*, 1974, **7**, 232.
4 J. H. Perlstein, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 519.
5 G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2141.
6 S. S. Shaik, *J. Am. Chem. Soc.*, 1982, **104**, 5328.
7 F. Wudl, *Acc. Chem. Res.*, 1984, **17**, 227.
8 T. K. Marks, *Angew. Chem., Int. Ed. Engl.*, 1990, **62**, 467.
9 J. Y. Becker, J. Bernstein, S. Bittner and S. S. Shaik, *Pure Appl. Chem.*, 1990, **62**, 467.
10 M. R. Bryce, *Chem. Soc. Rew.*, 1991, **20**, 355.
11 N. Martín and C. Seoane, *Mundo Científico (Spanish edition of La Recherche)*, 1991, **116**, 820.
12 V. Khodorkovsky and J. Y. Becker, *Organic Conductors, Fundamental and Applications* ed. J.P. Farges Marcel Dekker, New York, 1994, ch. 3, pp. 75–114.
13 N. Svenstrup and J. Becher, *Synthesis*, 1995, 215.
14 P. Cassoux and L. Valade, *Molecular Inorganic Superconductors*, in *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, Wiley, New York, 1992.
15 S. Hünig and P. Erk, *Adv. Mater.*, 1991, 225.
16 R. C. Wheland and E. L. Martin, *J. Org. Chem.*, 1975, **40**, 3101.
17 R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, 1976, **98**, 3926.
18 R. C. Wheland, *J. Am. Chem. Soc.*, 1976, **98**, 3926.
19 R. M. Metzger, R. R. Shumaker, M. P. Cava, R. K. Laidlaw, L. A. Panetta and E. Torres, *Langmuir*, 1988, **4**, 298.
20 G. J. Ashwell, E. J. C. Dawney, A. P. Kuczynski, M. Szablewski, I. M. Sandy, M. R. Bryce, A. M. Grainger and M. Hasan, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1117.
21 J. S. Miller, J. C. Calabrese, R. L. Harlow, D. A. Dixon, J. H. Zhang, W. M. Reiff, S. Chittipeddi, M. A. Selover and A. J. Epstein, *J. Am. Chem. Soc.*, 1990, **112**, 5496.
22 (*a*) M. Uno, K. Seto, M. Masuda, W. Ueda and S. Takahashi, *Tetrahedron Lett.*, 1985, **26**, 1553; (*b*) S. Yamaguchi, K. Nagareda and T. Hanafusa, *Synth. Met.*, 1989, **30**, 401.
23 A. Aumüller and S. Hünig, *Liebigs Ann, Chem.*, 1984, 618.
24 (*a*) W. Lehnert, *Tetrahedron Lett.*, 1970, 4723; (*b*) W. Lehnert, *Synthesis*, 1974, 667.
25 M. R. Bryce, A. M. Grainger, M. Hasan, G. J. A. Ashwell, P. A. Bates and M. B. Hursthouse, *J. Chem. Soc., Perkin. Trans 1*, 1992, 611.
26 N. Martín, J. L. Segura, C. Seoane, P. de la Cruz, F. Langa, E. Orti, P. M. Viruela and R. Viruela, *J. Org. Chem.*, 1995, **60**, 4077.
27 P. Bando, N. Martín, J. L. Segura, C. Seoane, E. Orti, P. M. Viruela, R. Viruela, A. Albert and F. H. Cano, *J. Org. Chem.*, 1994, **59**, 4618.
28 F. Gerson, R. Heckendorn, D. O. Cowan, A. M. Kini and M. Maxfield, *J. Am. Chem. Soc.*, 1983, **105**, 7017.

29 A. Aumüller and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 447.
30 A. Aumüller and S. Hünig, *Liebigs Ann. Chem.*, 1986, 142.
31 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
32 U. Schubert, S. Hünig and A. Aumüller, *Liebigs Ann. Chem.*, 1985, 1216.
33 A. Aumüller and S. Hünig, *Liebigs Ann. Chem.*, 1986, 165.
34 (*a*) S. Hünig, *Pure Appl. Chem.*, 1990, **62**, 395; (*b*) P. Erk, S. Hünig, J. U. von Schütz, H. P. Werner, H. C. Wolf, D. Jérome, S. Tomic, R. T. Henriques and D. Schmeisser, *Organic Superconductivity*, ed. V.Z. Kresin and W.A. Little, Plenum Press, New York, 1990, pp. 325–334.
35 S. Hünig, K. Sinzger, M. Jopp, D. Bauer, W. Bietsch, J. U. von Schütz and H. C. Wolf, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 859.
36 K. Sinzger, S. Hünig, M. Jopp, D. Bauer, W. Bietsch, J. U. von Schütz, H. C. Wolf, R. K. Kremer, T. Metzenthin, R. Bau, S. I. Khan, A. Lindbaum, C. L. Lengauer and E. Tillmanns, *J. Am. Chem. Soc.*, 1993, **115**, 7696.
37 S. Aonuma, H. Sawa, R. Kato and H. Kobayashi, *Chem. Lett.*, 1993, 517.
38 T. Yanagimoto, K. Takimiya, T. Otsubo and F. Ogura, *J. Chem. Soc., Chem. Commun.*, 1993, 519.
39 S. Aonuma, H. Sawa and R. Kato, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1541.
40 (*a*) M. R. Bryce and S. R. Davies, *J. Chem. Soc., Chem. Commun.*, 1989, 328; (*b*) M. R. Bryce, S. R. Davies, A. M. Grainger, J. Hellberg, M. B. Hursthouse, M. Mazid, R. Bachman and F. Gerson, *J. Org. Chem.*, 1992, **57**, 1690.
41 H. E. Katz and M. L. Schilling, *J. Org. Chem.*, 1991, **56**, 5318.
42 H. Almen, T. Bauer, S. Hünig, V. Kupcik, U. Langohr, T. Metzenthin, K. Meyer, H. Rieder, J. V. von Schütz, E. Tillmans and H. C. Wolf, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 561.
43 K. Deucher and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 875.
44 F. Wudl, P. M. Allemand, P. Delhaes, Z. Soos and H. Hinkelman, *Mol. Cryst. Liq. Cryst.*, 1989, **171**, 179.
45 T. L. Cairus, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick and W. J. Middleton, *J. Am. Chem. Soc.*, 1957, **79**, 2340.
46 O. W. Webster, *J. Am. Chem. Soc.*, 1962, **84**, 3370.
47 J. K. Williams, D. W. Wiley and B. C. McKusick, *J. Am. Chem. Soc.*, 1962, **84**, 2216.
48 H. Yamochi, T. Tsuji, G. Saito, T. Miyashi, C. Kabuto and T. Suzuki, *Synth. Met.*, 1988, **27**, A479.
49 W. L. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.*, 1958, **80**, 2795.
50 T. Fukunaga, *J. Am. Chem. Soc.*, 1976, **98**, 610.
51 C. Vázquez, J. C. Calabrese, D. A. Dicon and J. S. Miller, *J. Org. Chem.*, 1993, **58**, 65.
52 D. Walker and J. D. Hiebert, *Chem. Rev.*, 1967, **67**, 153.
53 G. A. Reynolds and J. A. Vanallen, *J. Org. Chem.*, 1964, **29**, 3591.
54 I. F. Perepichka, A. F. Popov, T. V. Orekhove, M. R. Bryce, A. N. Vdovichenko, A. S. Batsanov, L. M. Goldenberg, J. A. K. Howard, N. I. Sokolov and J. L. Megson, *J. Chem. Soc., Perkin. Trans. 2*, 1996, 2453.
55 T. K. Mukherjee and L. A. Levassen, *J. Org. Chem.*, 1965, **30**, 644.
56 S. Prassana and T. P. Radhakrishnan, *Synth. Met.*, 1996, **78**, 127.
57 (*a*) K. Yui, H. Ishida, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 1987, **22**, 39; (*b*) K. Yui, H. Ishida, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 1987, **22**, 1069; (*c*) K. Yui, H. Ishida, Y. Aso, T. Otsubo, F. Ogura, A. Kawamoto and J. Tanaka, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1547; (*d*) F. Ogura, T. Otsubo and Y. Aso, *Pure Appl. Chem.*, 1993, **65**, 683.
58 E. Günther, S. Hünig, K. Peters, H. Rieder, H. G. von Schnering, J. U. von Schütz, S. Söderholm, H. P. Werner and H. C. Wolf, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 204.
59 M. V. Joshi, M. P. Cava, M. V. Lashnikantham, R. M. Metzger, H. Abdeldayem, M. Henry and P. Venkateswarlu, *Synth. Met.*, 1993, **55–57**, 3974.
60 D. Lorcy, K. D. Robinson, Y. Okuda, J. L. Atwood and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1993, 345.
61 A. I. de Lucas, N. Martín, P. de Miguel, C. Seoane, A. Albert and F. H. Cano, *J. Mater. Chem.*, 1995, **5**, 1141.
62 Special issue on NLO, in *Chem. Rev.*, 1994, **94**.
63 K. Takahashi and S. Tarutani, *J. Chem. Soc., Chem. Commun.*, 1994, 519.
64 K. Takahashi and S. Tarutani, *Adv. Mater.*, 1995, **7**, 639.
65 J. Dieckman, W. R. Hertler and R. Benson, *J. Org. Chem.*, 1963, **28**, 2719.
66 D. J. Sandman and A. F. Garito, *J. Org. Chem.*, 1974, **39**, 1165.
67 A. W. Addison, N. S. Dalal, Y. Hoyano, S. Huizinga and L. Weiler, *Can. J. Chem.*, 1977, **55**, 4191.
68 E. Aharon-Shalom, J. Y. Becker and I. Agranat, *Nouv. J. Chim.*, 1979, **3**, 643.
69 M. R. Maxfield, D. O. Cowan, A. N. Bloch and T. O. Poehler, *Nouv. J. Chim.*, 1979, **3**, 647.
70 N. Acton, D. Hov, J. Schwarz and T. J. Katz, *J. Org. Chem.*, 1982, **47**, 1011.
71 P. A. Berger, D. J. Dahm, G. P. Johnson, M. G. Miles and J. D. Wilson, *Phys. Rev.*, 1975, **B12**, 4085.
72 K. Bechgaard, G. S. Jacobsen and N. H. Anderson, *Solid State Commun.*, 1978, **25**, 875.
73 S. Yamaguchi, H. Tatemitsu, Y. Sakata and S. Misumi, *Chem. Lett.*, 1983, 1229.
74 B. S. Ong and B. Keoshkerian, *J. Org. Chem.*, 1984, **49**, 5002.
75 A. M. Kini, D. O. Cowan, F. Gerson and R. Möckel, *J. Am. Chem. Soc.*, 1985, **107**, 556.
76 (*a*) N. Martín and M. Hanack, *J. Chem. Soc., Chem. Commun.*, 1988, 1522; (*b*) N. Martín, R. Behnisch and M. Hanack, *J. Org. Chem.*, 1989, **54**, 2563; (*c*) T. Suzuki, C. Kabuto, Y. Yamashita, T. Mukai, T. Miyashi and G. Saito, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 483; (*d*) S. Yamaguchi, T. Hanafusa, T. Tanaka, M. Sawada, K. Kondo, M. Irie, H. Tatemitsu, Y. Sakata and S. Misumi, *Tetrahedron Lett.*, 1986, **27**, 2411.
77 Two one-electron reduction waves at −0.46 and −0.65 V in acetonitrile have also been reported (see ref. 73).
78 M. Scholz, G. Gescheidt, U. Schöberl and J. Daub, *J. Chem. Soc., Perkin Trans. 2*, 1995, 209.
79 K. Maruyama, H. Imahori, K. Nakagawa and N. Tanaka, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1626.
80 T. Mukai, T. Suzuki and Y. Yamashita, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2433.
81 (*a*) R. Viruela, P. M. Viruela, E. Orti and N. Martín, *Synth. Met.*, 1995, **70**, 1031; (*b*) E. Orti, R. Viruela and P. M. Viruela, *J. Mater. Chem.*, 1995, **5**, 1697.
82 N. Martín, J. A. Navarro, C. Seoane, A. Albert, F. H. Cano, J. Y. Becker, V. Khodorkowsky, E. Harlev and M. Hanack, *J. Org. Chem.*, 1992, **57**, 5726.
83 (*a*) E. Barranco, N. Martín, J. L. Segura, C. Seoane, P. de la Cruz, F. Langa, A. González and J. M. Pingarrón, *Tetrahedron*, 1993, **49**, 4881; (*b*) E. Barranco, A. González, N. Martín, J. M. Pingarrón, J. L. Segura and C. Seoane, *Synth. Met.*, 1993, **55–57**, 1717.
84 K. Kobayashi and C. L. Gajurel, *J. Chem. Soc., Chem. Commun.*, 1986, 1779.
85 K. Kobayashi, C. L. Gajurel, K. Umemoto and Y. Mazaki, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2168.
86 F. Iwasaki, S. Hironaka, N. Yamazaki, M. Yasui and K. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2173.
87 F. Iwasaki, S. Hironaka, N. Yamazaki and K. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2180.
88 M. Yasui, M. Hirota, Y. Endo, F. Iwasaki and K. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2187.
89 F. Iwasaki, *Acta Crystallogr.*, 1971, **B27**, 1360.
90 (*a*) C. Kabuto, T. Suzuki, Y. Yamashita and T. Mukai, *Chem. Lett.*, 1986, 1433; (*b*) T. Suzuki, C. Kabuto, Y. Yamashita, T. Mukai, T. Miyashi and G. Saito, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 483.
91 T. Suzuki, Y. Yamashita, C. Kabuto and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, 1989, 1102.
92 Y. Yamashita, J. Eguchi, T. Suzuki, C. Kabuto, T. Miyashi and S. Tanaka, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 643.
93 K. Kobayashi, *Phosphorus, Sulphur Silicon*, 1989, **43**, 187.
94 P. de la Cruz, N. Martín, F. Miguel, C. Seoane, A. Albert, F. H. Cano, A. González and J. M. Pingarrón, *J. Org. Chem.*, 1992, **57**, 6192.
95 N. Martín, P. de Miguel, C. Seoane, A. Albert and F. H. Cano, *J. Mater. Chem.*, 1997, **7**, 25.
96 K. Kobayashi, Y. Mazaki, H. Namba, K. Kikuchi, K. Saito, I. Ikemoto, S. Hino and N. Kosugi, *J. Mater. Chem.*, 1995, **5**, 1625.
97 N. Martín, C. Seoane, J. L. Segura, J. L. Marco and M. Hanack, *Synth. Met.*, 1991, **41–43**, 1873.
98 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Hoffman, *Nature*, 1990, **347**, 354.
99 (*a*) A. Hirsch, *The Chemistry of Fullerenes*, Thieme, Stuttgart, 1994; (*b*) Special issue on Buckminsterfullerenes, *Acc. Chem. Res.*, 1992, **35**; (*c*) F. Diederich and C. Thilgen, *Science*, 1996, **271**, 317; (*d*) Special issue on Fullerene Chemistry, *Tetrahedron*, 1996, **52**.
100 G. Saito, T. Teramoto, A. Otsuka, Y. Sugita, T. Ban, M. Kusunoki and K. Sakaguchi, *Synth. Met.*, 1994, **64**, 359.
101 A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy,

S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Cortan, *Nature*, 1991, **350**, 600.
102 J. Stinchcombe, A. Penicaud, P. Bhyrappa, P. D. W. Boyd and C. A. Reed, *J. Am. Chem. Soc.*, 1993, **115**, 5212.
103 P. M. Allemand, K. C. Khemani, A. Koch, F. Wudl, P.-M. Holczer, S. Donovan, G. Grüner and J. D. Thompson, *Science*, 1991, **253**, 301.
104 P. W. Stephens, D. Cox, J. W. Lanher, L. Mihaly, J. B. Wiley, P. M. Allemand, A. Hirsch, K. Holezer, Q. Li, J. D. Thompson and F. Wudl, *Nature*, 1992, **355**, 331.
105 J. D. Crane, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1764.
106 T. Pradeep, K. K. Singh, A. P. B. Sinha and D. E. Morris, *J. Chem. Soc., Chem. Commun.*, 1992, 1747.
107 A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, 1992, 1472.
108 A. Izuoka, T. Tachikawa, T. Sugawara, Y. Saito and H. Shinohara, *Chem. Lett.*, 1992, 1049.
109 N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín and J. Orduna, *Tetrahedron Lett.*, 1996, **37**, 5979.
110 M. Prato, M. Maggini, C. Giacometti, G. Scorrano, G. Sardonà and G. Farnia, *Tetrahedron*, 1996, **52**, 5221.
111 N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín, J. Orduna, E. Ortí, P. M. Viruela and R. Viruela, *J. Phys. Chem. Solids.*, in the press.
112 A. I. de Lucas, N. Martín, L. Sánchez and C. Seoane, *Tetrahedron Lett.*, 1996, **37**, 9391.
113 T. Suzuki, Y. Maruyama, T. Akasaka, W. Ando, K. Kobayashi and S. Nagase, *J. Am. Chem. Soc.*, 1994, **116**, 1359.
114 R. C. Haddon, *Science*, 1993, **261**, 1545.
115 F. Zhon, G. J. van Berkel and B. T. Donovan, *J. Am. Chem. Soc.*, 1994, **116**, 5485.
116 K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith, III, J. P. McCauley, Jr, D. R. Jones and R. T. Gallagner, *J. Am. Chem. Soc.*, 1992, **114**, 1103.
117 F. Wudl, T. Suzuki and M. Prato, *Synth. Met.*, 1993, **59**, 297.
118 M. Eiermann, R. C. Haddon, B. Knight, Q. C. Li, M. Maggini, N. Martín, T. Ohno, M. Prato, T. Suzuki and F. Wudl, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1591.
119 T. Ohno, N. Martín, B. Knight, F. Wudl and T. Suzuki, *J. Org. Chem.*, 1996, **61**, 1306.
120 N. Martín, B. Knight and F. Wudl, *Synth. Met.*, 1997, **86**, 2271.
121 B. Illescas, N. Martín and C. Seoane, *Tetrahedron Lett.*, 1997, **38**, 2015.
122 R. Metzger and C. Panetta, *New J. Chem.*, 1991, **15**, 209.
123 (*a*) *Molecular Electronic-Science and Technology*, ed. A. Aviram, Emgennering Foundation, New York, 1989; (*b*) A. Aviram and M. Ratner, *Chem. Phys. Lett.*, 1974, **29**, 277.
124 J. P. Lunnay, *Molecular Electronics*, in *Granular Nanoelectronics*, ed. D. K. Ferry, Plenum Press, New York, 1991.
125 *Photoinduced Electron Transfer*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988.
126 See for example: (*a*) S. S. Isied, *Prog. Inorg. Chem.*, 1984, **32**, 4436; (*b*) A. Vassilian, J. F. Wishart, B. Hemelryck, H. Schwarz and S. S. Isied, *J. Am. Chem. Soc.*, 1990, **112**, 7278; (*c*) M. S. Meier, M. A. Fox and J. R. Miller, *J. Org. Chem.*, 1991, **56**, 5380; (*d*) M. N. Paddon Row, *Acc. Chem. Res.*, 1994, **27**, 18.
127 (*a*) H. Kurrek and M. Huber, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 849; (*b*) M. A. Staab, A. Feurer and R. Hanck, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2428.
128 (*a*) P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991; (*b*) M. S. Nalwa, *Adv. Mater.*, 1993, **5**, 341; N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.
129 Y. Yamashita, S. Tanaka, K. Imaeda, H. Inakuchi and M. Sano, *J. Org. Chem.*, 1992, **57**, 5517.
130 A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. W. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 582.
131 Y. Tsubata, T. Suzuki, T. Miyashi and Y. Yamashita, *J. Org. Chem.*, 1992, **57**, 6749.
132 J. Y. Becker, J. Bernstein, S. Bittner, N. Levi and S. S. Shaik, *J. Am. Chem. Soc.*, 1983, **105**, 4468.
133 J. Y. Becker, J. Bernstein, S. Bittner, N. Levi and S. S. Shaik, *J. Org. Chem.*, 1988, **53**, 1689.
134 (*a*) N. Martín, J. L. Segura, C. Seoane, A. Albert and F. H. Cano, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2363; (*b*) N. Martín, J. L. Segura, C. Seoane, A. Albert and F. H. Cano, *Synth. Met.*, 1993, **55–57**, 1730; N. Martín and C. Seoane, in *New Organic Materials*, ed. C. Seoane and N. Martín, Universidad Complutense de Madrid, 1994, ch. 2, p. 20.
135 P. Bando, K. Davidkov, N. Martín, J. L. Segura, C. Seoane, A. González and J. M. Pingarrón, *Synth. Met.*, 1993, **55–57**, 1721.
136 (*a*) B. Illescas, N. Martín, J. L. Segura, C. Seoane, E. Ortí, P. M. Viruela and R. Viruela, *J. Org. Chem.*, 1995, **60**, 5643; (*b*) B. Illescas, N. Martín, J. L. Segura, C. Seoane, E. Ortí, P. M. Viruela and R. Viruela, *J. Mater. Chem.*, 1995, **5**, 1563.
137 N. Martín, J. L. Segura, C. Seoane, E. Ortí, P. M. Viruela, R. Viruela, A. Albert, F. H. Cano, J. Vidal-Gancedo, C. Rovira and J. Veciana, *J. Org. Chem.*, 1996, **61**, 3041.
138 T. Czekanski, M. Hanack, J. Y. Becker, J. Bernstein, S. Bittner, L. Kaufman-Orenstein and D. Peleg, *J. Org. Chem.*, 1991, **56**, 1569.
139 (*a*) A. A. Kutyrev, *Tetrahedron*, 1991, **47**, 8043; (*b*) *The chemistry of the quinoid compounds*, ed. S. Patai and Z. Rappoport, Wiley, 1988.
140 M. González, P. de Miguel, N. Martín, J. L. Segura, C. Seoane, E. Ortí, R. Viruela and P. M. Viruela, *Adv. Mater.*, 1994, **6**, 765 and references cited therein.
141 W. H. Watson, E. E. Ednok, R. P. Kashyap and M. Krawieck, *Tetrahedron*, 1993, **49**, 3035.
142 M. Adam and K. Müllen, *Adv. Mater.*, 1994, **6**, 439.
143 J. L. Segura, N. Martín, C. Seoane and M. Hanack, *Tetrahedron Lett.*, 1996, **37**, 2503.

Paper 7/02314F; *Received* 4*th April*, 1997