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Highly polarized electron donors, acceptors and donor–acceptor compounds for organic conductors

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New types of π-electron donors and acceptors with high polarizability are reviewed. TTF derivatives with polarizable substituents, π-extended TTF analogues fused with nitrogen-containing heterocycles and non-TTF donors (*i.e.* electron donors) and chalcogen atom-containing quinones, TCNQ and DCNQI analogues (*i.e.* electron acceptors) are described. Donor–acceptor compounds showing electrochemically amphoteric properties are also discussed.

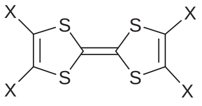
Introduction

Recently much attention has been focused on molecular-based organic conductors and superconductors.[1] Development of new electron donors and acceptors affording them is particularly important in order to make progress in this field. For this purpose many kinds of electron donors and acceptors have been designed and synthesized.[2–4] Among them highly polarized molecules containing heteroatoms have attracted considerable attention. Polarized molecules can be produced by introduction of polarizable substituents into donor or acceptor skeletons, or linkage of electron-donating units and accepting ones. In the latter compounds donor or acceptor properties appear depending on the strength of their electron-donating or -accepting abilities. The highly polarized molecules have several advantages as components for affording organic conductors. First, intermolecular interactions can be enhanced by electrostatic interactions, which increase dimensionality in the complexes and suppress metal–insulator transitions. Such interactions may lead to the formation of unique molecular networks which have special functions such as inclusion properties. Second, in the donor–acceptor systems intermolecular charge-transfer (CT) interactions can be expected, which may be useful for crystal engineering. Third, π-extended systems have reduced on-site Coulomb repulsion which is one of the important requirements for the molecular design of organic conductors. Fourth, unstable strong electron donors can be stabilized by introduction of electron-withdrawing groups to give polarized electron donors. Similarly unstable strong electron acceptors can be stabilized by electron-donating groups. Finally, highly polarized molecules have low excitation energies, and interesting optical properties such as non-linear optical ones are expected. When the electron-donating and -accepting abilities are balanced in the donor–acceptor compounds, they show amphoteric properties. Such compounds are of special interest as candidates for single-component conductors showing intrinsic conductivities. We will highlight here highly polarized donors, acceptors and donor–acceptor compounds.

Polarized electron donors

TTF derivatives

The derivatives of TTF such as BEDT-TTF have played a major role in the development of organic conductors and superconductors.[2] The synthetic methods of TTF derivatives have been improved and several derivatives containing polarizable substituents have been prepared. In the halogenated TTF derivatives **1**, halogen-halogen contacts are expected to lead to strong intermolecular interactions in the crystals. However, attachment of halogen atoms reduces electron-donating ability and the tetra-substituted derivatives **1** (X = Cl, Br) do not afford conducting materials.[5] On the other hand, the tetraiodo derivative **1** (X = I) affords cation radical salts. Although the I_3^- salt is an insulator due to its 1 : 1 stoichiometry, strong I···I interactions are observed, which connect the stacks of cation radicals in a three-dimensional structure.[6]



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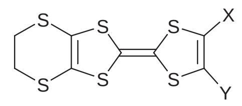

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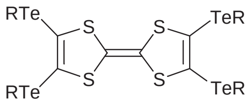

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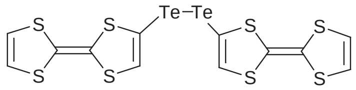

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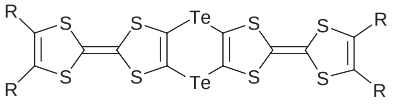

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Unsymmetrical TTF derivatives **2** have been prepared to increase donating abilities as well as to use intermolecular interactions involving sulfur atoms. The donor **2** (X = I, Y = H) affords a complex with Pd(dmit)$_2$ which shows metallic properties down to 4.2 K.[7] X-Ray analysis reveals strong and directional I···S donor–acceptor interactions. The donor **2** (X = Y = I) affords metallic cation radical salts $\mathbf{2}_4\mathrm{M(CN)}_4$(M = Ni, Pd, Pt).[8] In the crystals there are two kinds of short I···NC contacts resulting in unusual three-dimensional structures. In the CT complex of **2** (X = Y = Cl) with TCNQ, Cl···Cl short contacts are observed, which control the packing in the crystal.[9] In spite of the mixed stacking structure, its conductivity ($\sigma = 1$ S cm^{-1}) is high.

Compounds containing highly polarizable tellurium atoms tend to form molecular networks through the heteroatom contacts. This property can be used to increase the intermolecular interactions between TTF molecules. In the tetrakis(alkyltelluro)-TTFs **3**, a two dimensional network based on Te···Te contacts is observed, which leads to an unusually high conductivity (*ca.* 10^{-5} S cm^{-1}) as a single component.[10] The crystal of tetrakis(phenyltelluro)-TTF **3** (R = Ph) has Te···S interstack and Te···Te intrastack interactions, resulting in a single-component conductivity of 10^{-6} S cm^{-1}.[11] TTF-di-substituted ditellu-

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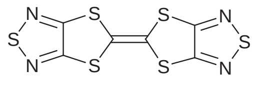
ride **4** prepared by Becker *et al.* also shows a high single-component conductivity (5×10^{-5} S cm^{-1}).[12] The crystal has a stacking structure where several short Te···S contacts are observed. TTF derivative **5** has been obtained by a one-pot reaction of 2,3-dimethyl-TTF with bis(phenylacetylenyl) telluride.[13] The TTF units are significantly bent and both Te···S and Te···Te contacts are observed.

Introduction of heterocycles containing C=N bonds on the TTF units is of interest since such heterocycles are electron-withdrawing and so polarized structures leading to strong intermolecular interactions are expected. In addition, the extended π-conjugation decreases on-site Coulomb repulsion. In this context, 1,2,5-thiadiazole- and pyrazine-fused TTF derivatives have been synthesized. Bis[1,2,5]thiadiazolo-TTF **6** has been prepared independently by Underhill *et al.* and us.[14] In the crystal structure of the neutral molecule a unique molecular network is formed by short S···N and S···S contacts. However, this molecule has not afforded CT complexes with electron acceptors due to its poor electron-donating ability. In order to enhance this ability, unsymmetrical molecules **7** have been synthesized.[15] The donor **7** (R = SC_2CH_2S) affords radical cation salts with 1:1 stoichiometries. The conductivities are fairly good in spite of their being 1:1 salts. X-Ray analysis reveals short S···N and S···S contacts (Fig. 1).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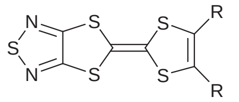
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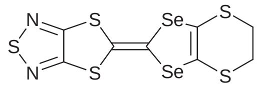
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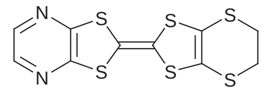
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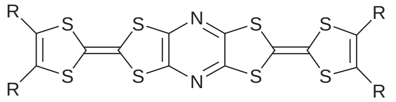
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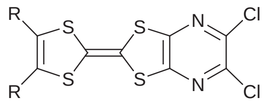
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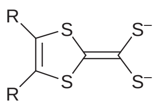
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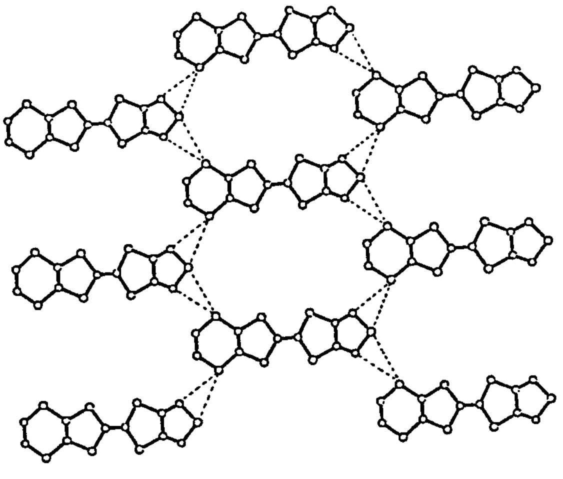


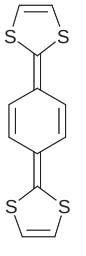
Fig. 1 Two-dimensional network in the crystal of (**7**)(ClO_4) (reprinted with permission from ref. 15)

On the other hand, the diselenium analogue **8** forms 2:1 salts showing metallic behaviour down to 20 K.[16] In the crystal a two dimensional network of S···N interactions in addition to S···S(Se) ones is formed. Since there are no distinctive donor columns, the thiadiazole network is considered to afford a conduction path.

Papavassiliou *et al.* have prepared the pyrazine derivative **9**. This molecule affords a cation radical salt $\mathbf{9}_3I_3$ which is considered to be a three-dimensional conductor due to the S···N intermolecular interactions.[17] Pyrazine-fused TTF derivatives **10** and **11** have been prepared by nucleophilic reaction of dianion **12** with tetrachloropyrazine.[18] The bis-TTF derivative **10** (R = hexyl) exhibits four reversible sequential one-electron oxidation steps with potentials of 0.49, 0.71, 1.24 and 1.50 V *vs.* SCE.

TTF analogues with quinoid structures

Such TTF analogues are of interest due to their high electron-donating abilities and reduced on-site Coulomb repulsion.[4]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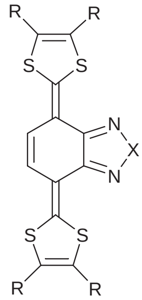
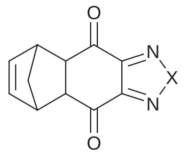

14 X = S
15 X = Se
16 X = CH=CH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Although a TTF analogue **13** has been prepared with this aim, it is unstable in solution due to its extremely low oxidation potential.[19] Introduction of electron-withdrawing heterocycles is expected to enhance stability as well as intermolecular interaction and π-delocalization.

TTF analogues fused with 1,2,5-thiadiazole **14**, selenadiazole **15** and pyrazines **16** have been prepared by a Wittig–Horner reaction of the corresponding carbanions derived from phosphonate esters with diones **17** followed by a retro-Diels–Alder reaction.[20] They are air-stable violet solids. Their absorption maxima are observed at 482–522 nm due to intramolecular charge transfer from the 1,3-dithiole units to the nitrogen-containing heterocycle. The oxidation potentials are lower than those of TTF, as shown in Table 1, indicating that they are stronger donors than TTF although they contain electron-

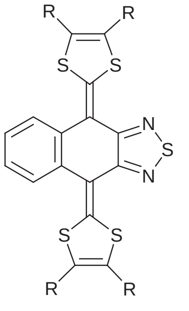
Table 1 Oxidation potentials of donors[a]

	E/V *vs.* SCE			
compound	E_1	E_2	ΔE	ref.
TTF[a]	0.46	0.87	0.41	20(*a*)
13[b]	−0.11	−0.04	0.07	19
14 (R = H)[a]	0.36	0.53	0.17	20(*a*)
15 (R = H)[a]	0.37	0.55	0.18	20(*b*)
16 (R = H)[a]	0.23	0.43	0.20	20(*c*)
18 (R = H)[a]	0.63		0.01	22
19[a]	0.76	0.85	0.09	23
20[a]	0.68		0.05	26
25 (X = S)[b]	0.54	1.30	0.76	31
26[b]	0.15	0.95	0.80	32
28 (R = H)[a]	0.22	0.66	0.44	33
29 (R = Me)[c]	0.59	0.75	0.16	34
30 (R = Me)[a]	0.27	0.57	0.30	35

[a] In PhCN. [b] In MeCN. [c] In CH_2Cl_2.

withdrawing heterocycles. The differences between the first and second oxidation potentials are smaller than that for TTF. This fact shows that on-site Coulomb repulsion is decreased in these molecules due to the extended π-conjugation. The donors **14** (R = Me) and **15** (R = Me) afford cation radical salts showing metallic behavior down to 100 K. The structures are similar to those of superconducting TMTSF salts.[21]

Organic conductors are usually obtained from planar molecules; the planar geometry is considered to be necessary for good π-overlapping *via* stacking. However, it seems possible to use non-planar molecules to increase dimensionality *via* multi-dimensional interactions in the crystal. In this context, bis(1,3-dithiole) compounds **18**, which are non-planar owing to steric interactions caused by the peri hydrogens, are interesting.[22] These molecules are butterfly-shaped and there are intramolecular S···N interactions between the heterocycles, which suppress a large conformational change upon oxidation. They undergo one-stage two-electron oxidation, indicating that the cation radicals are thermodynamically unstable. However, some compounds afford the cation radical salts as stable single crystals. The donor molecule **18** (R, R = benzo) affords 1 : 1 salts where butterfly-shaped molecules are uniformly stacked.[22] The overlap of molecules is an alternative mode due to the intermolecular CT interaction. Although the conductivities are fairly high (8.3 to 10^{-2} S cm^{-1}), they show semiconducting behavior due to completely charged salts.



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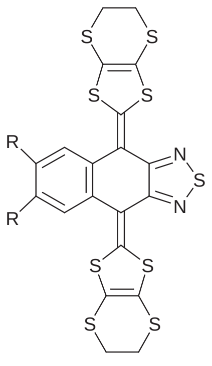
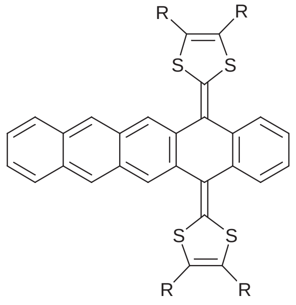


19 R, R = benzo
20 R = Me



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On the other hand, a naphthalene-fused derivative **19** affords cation radical salts incorporating solvent molecules whose composition is 2 : 1 : 1 (donor : cation : solvent).[23] The PF_6 salt involving THF shows metallic behavior down to 3 K.[24] The crystal structure is shown in Fig. 2 where good overlap between the butterfly-shaped molecules is observed. The physical properties are strikingly dependent on the incorporated solvent molecules. Thus, in contrast to the THF incorporated salt, 2,5-dihydrofuran (DHF) and 1,3-dioxolane (DO) incorporated ones undergo a metal–insulator transition at 150 and 100 K, respectively.[25] Since their crystal structures are almost the same, the difference is attributed to the ordering of the incorporated solvent molecules. The dimethyl derivative **20** also gives cation radical salts incorporating solvent molecules with a composition of $\mathbf{20}_2(PF_6)$(solvent) where THF, DHF and DO are used as solvent.[26] Although their conductivities at room temperature are all 10 S cm^{-1}, the properties at low temperature are dependent on the solvent molecules. Thus, the THF salt is metallic down to 180 K, while the DHF and DO ones show semiconducting behavior at room temperature. No distinctive difference in crystal structure between the metallic and semiconducting salts is observed. The difference of the ordering of the solvent is considered to appear in the salts of **20** at room temperature.

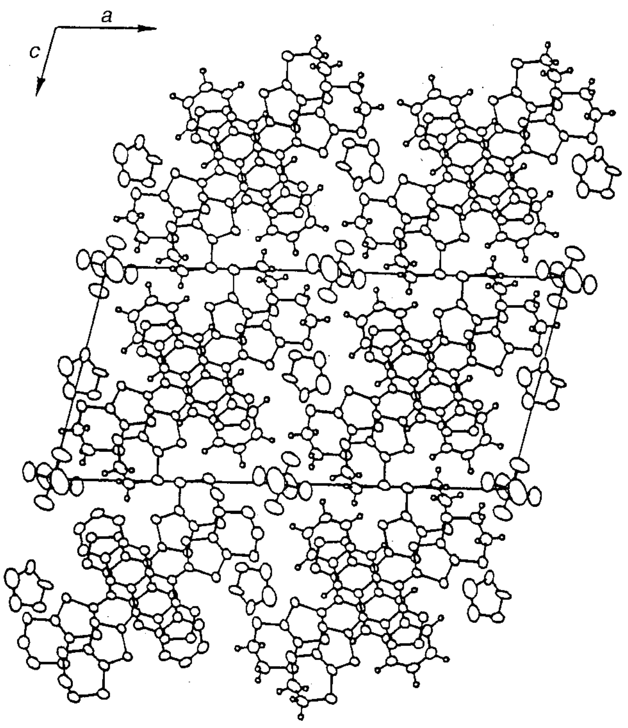


Fig. 2 Crystal structure of $(\mathbf{19})_2(PF_6)$(THF) (reprinted with permission from ref. 23)

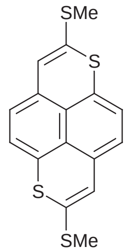
Martín *et al.* have recently reported larger π-extended compounds **21**, where a charge transfer from the 1,3-dithiol-2-ylidene moieties to the fused anthracene is observed.[27]

Non-TTF donors

Most molecular conductors are formed from donor molecules based on TTF and its derivatives. However, it is important to explore new classes of electron donors which do not contain such skeletons to extend the range of conductors. We describe here non-TTF donors with high polarizability.

Dithiapyrene derivative **22** forms metallic CT complexes with TCNQ, chloranil and bromanil.[28] On the other hand, the more polarized nitrogen-containing molecule **23** also affords metallic cation radical salts where several S···S contacts are observed.[29]

5,10-Dimethyl-5,10-dihydrophenazine (DMPH) is a strong electron donor due to its 16π-electron ring system and affords conducting CT complexes with acceptors.[30] On the other hand, 1,4-dimethyl-1,4-dihydroquinoxaline **24** with a 12π-electron ring system is unstable and has not been isolated. We have replaced the benzene rings with 1,2,5-thiadiazole or -selenadiazole rings to give **25** and **26** in order to enhance their stability as well as polarizability, leading to strong intermolecular interactions. The absorption maxima of **25** are red-shifted by *ca.* 50 nm compared with those of DMPH due to the polarization effect.[31] Their electron-donating abilities are comparable to that of dibenzo-TTF and they give cation radical salts and CT complexes. The 12π-electron ring system **26** is a stronger electron donor than TTF in spite of the presence of the



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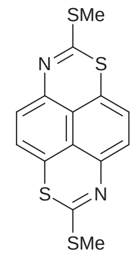

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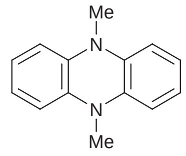
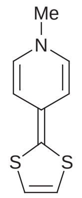


DMPH



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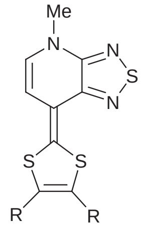

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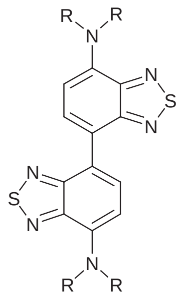

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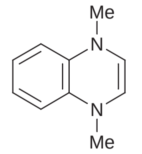

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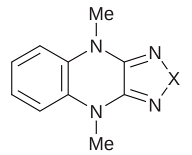
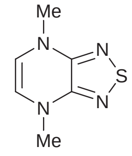


25 X = S, Se



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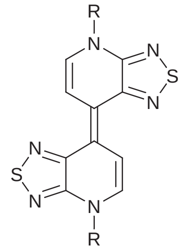
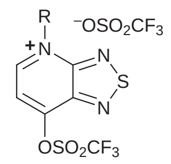


30 R = Me, Et



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electron-withdrawing heterocycle (Table 1).[32] In the crystal the molecules are connected by S···N contacts (3.05 Å) to form a coplanar dyad which is held together by hydrogen bonding between the olefinic hydrogens and nitrogens to form a sheet-like network (Fig. 3). The sheet is stacked to give a three-dimensional structure. The strong S···N interactions are attributed to electrostatic effects caused by the polarized structure. This molecule affords conducting complexes with acceptors containing a 1,2,5-thiadiazole or -selenadiazole ring although no complex with TCNQ is formed.

On the other hand, 4-(1,3-dithiol-2-ylidene)-1-methyl-1,4-dihydropyridine **27** has not been prepared because of the instability of the ring system. We have replaced one amino group of **26** by a 1,3-dithiol-2-ylidene unit to give **28**.[33] These molecules are stronger electron donors than TTF. Their absorption maxima are observed around 515 nm, and are regarded as intramolecular CT bands. The crystal structure of **28** (R = H) is constructed of four columns which interact with each other *via* S···S contacts (Fig. 4). These donors form highly conducting CT complexes with TCNQ.

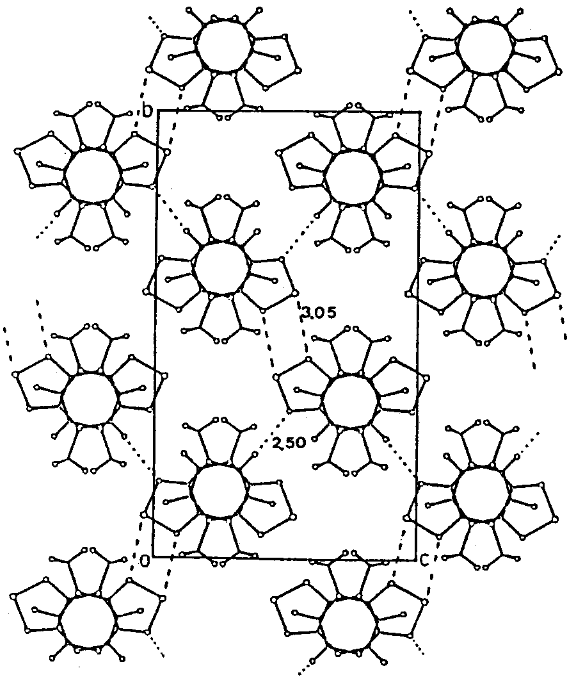


Fig. 3 Sheet-like network of **26**; broken line: S···N interactions and hydrogen bonding (reprinted with permission from ref. 32)

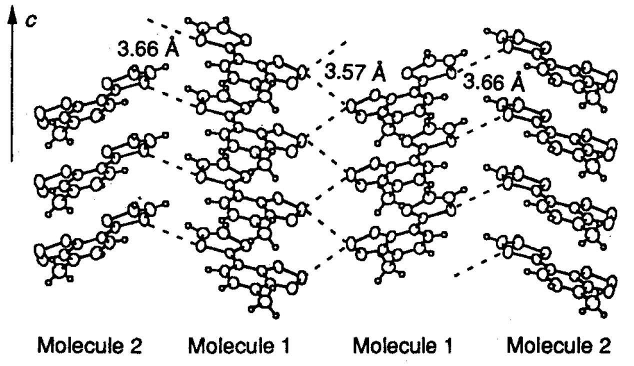


Fig. 4 Crystal structure of **28**; broken lines: S···S contacts (reprinted with permission from ref. 33)

Introduction of fused 1,2,5-chalcogenadiazole units to benzidines which are known as strong Wurster type electron donors leads to new polarized donors **29**.[34] They have absorption maxima in the 500–550 nm region assignable to intramolecular CT bands. X-Ray analyses reveal that the twisted geometry of the neutral molecule **29** becomes planar upon one-electron oxidation, and a coplanar tape-like network is formed by S···N contacts in the crystal of the PF_6 salt.

1,1-Dihydro-4,4′-bi(pyridylidene) has also been used as a strong electron-donating skeleton. Highly polarized electron donors **30** containing this unit have been synthesized by reductive coupling of pyridinium compounds **31**.[35] The absorption maxima are observed at 623 (R = Me) and 627 nm (R = Et) in CH_2Cl_2. They are stronger donors than TTF (Table 1) and afford conductive CT complexes with TCNQ and cation radical salts. In the crystal structure of the PF_6 salt the donor molecules form two-dimensional columnar stacks and a tape-like network is also formed by short S···N contacts (3.05 Å) (Fig. 5).

Polarized electron acceptors

Quinones

Quinones bearing sulfur-containing substituents are considered to be polarized electron acceptors. 2,3 : 5,6-Bis(ethylenedithio)-1,4-benzoquinone **32** is obtained, by reaction of chloranil and ethane-1,2-dithiol, as green crystals.[36] Quinones **33** bearing a 1,4-dithiine unit have been prepared by an unusual reaction of the corresponding dichloro-substituted quinones with phos-

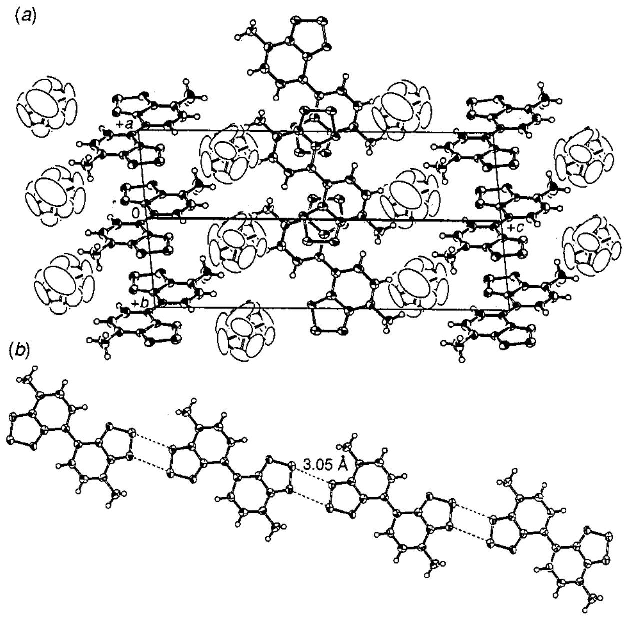
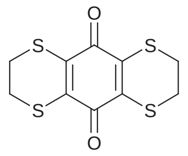


Fig. 5 Crystal structure of (**30**)PF_6 (reprinted with permission from ref. 35)



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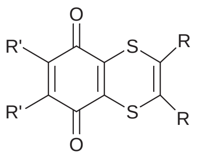

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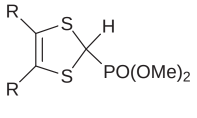

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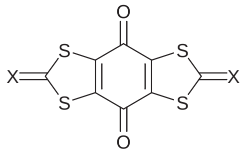
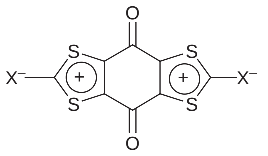


35 X = C(CN)$_2$, S, O



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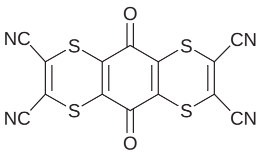

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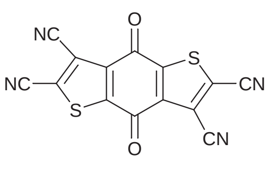
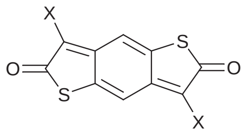


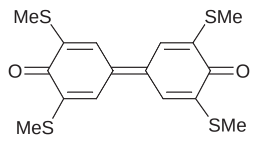
37

phonate esters **34**.[37] The absorption maximum of **33** (R = H, R′, R′ = benzo) is observed at 546 nm due to intramolecular charge transfer. These quinones are weaker electron acceptors and have not been used as components for conducting materials.

On the other hand, quinones **35–37** fused with electron-accepting sulfur-containing heterocycles are stronger electron acceptors than chloranil.[38] The first reduction potential of **35** [X = C(CN)$_2$, 0.30 V *vs.* SCE] is comparable to that of TCNQ. The quinones **35** have a large contribution of resonance structure **35′** which leads to high electron affinities.[39] These quinones afford highly conducting CT complexes with some electron donors.



38 X = Br, Cl



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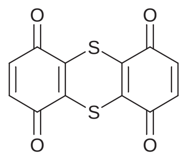

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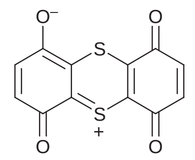

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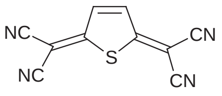
Quinones **38** with extended π-conjugation also have strong electron-accepting abilities and afford conducting complexes with tetrathiatetracene.[40] 4,4′-Biphenoquinone **39** has recently been prepared using oxidative coupling of the corresponding phenol.[41] This molecule shows the longest absorption maximum at 562 nm. Bis(*p*-benzoquinone) **40** has a resonance form **40′** and is deep violet with an absorption maximum of 508 nm.[42] This quinone can be reduced to a stable tetraanion species.

Heterocyclic analogues of TCNQ

Chalcogen atom-containing TCNQ analogues are highly polarized and are expected to have strong intermolecular interactions *via* heteroatom contacts. In this context, thiophene-TCNQ **41**,[43] its π-extended analogue **42**,[44] and fused heteroquinonoid compound **43**[45] have been prepared. These and related molecules, which are called hetero-TCNQs, have recently been reviewed by Ogura and Otsubo.[46] Therefore, we will focus our attention on the TCNQ analogues containing fused heterocycles.



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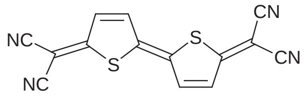

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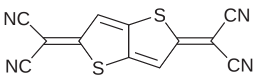

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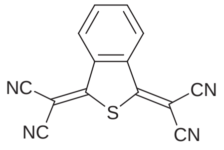

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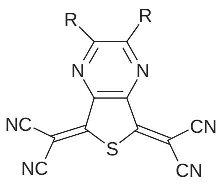

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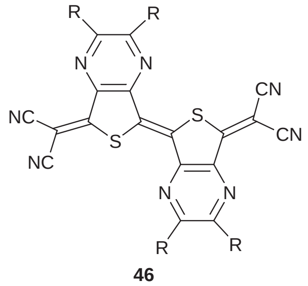

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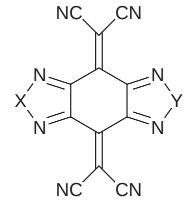
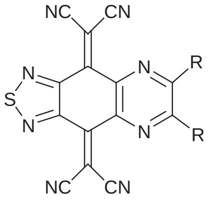
Benzothiophene-TCNQ **44** has been prepared to extend the π-conjugation of thiophene-TCNQ.[47] However, this molecule is a weak electron acceptor due to the fused benzene ring. In order to enhance its acceptor ability, we have replaced the benzene ring with an electron-withdrawing pyrazine ring to give **45**.[48] These molecules have been prepared together with **46** by reaction of 5,7-dibromothieno[3,4-*b*]pyrazine with tetracyanoethylene oxide (TCNEO), although the yields are low. In the crystal of **45** (R = H) there exist three kinds of short S···N contacts between the S atom of the thiophene ring and the N atoms of the pyrazine ring, leading to an interesting molecular network with a helical structure (Fig. 6). This acceptor affords two kinds of CT complexes with TTF, in which unique structures are constructed by S···N interactions between the S atoms of TTF and the N atoms of the CN group.

TCNQ analogues fused with sulfur-containing heterocycles are also polarized electron acceptors. Bis(thiadiazolo)-TCNQ **47** (BTDA) has been prepared from the corresponding dione by reaction with malononitrile in the presence of $TiCl_4$.[49] The reduction potentials of BTDA are lower than those of TCNQ, as shown in Table 2. The difference between the first and second reduction potentials is smaller than that of TCNQ, indicating that on-site Coulomb repulsion is reduced. The CT complex of BTDA **47** with tetraselenotetracene shows metallic behavior down to 1.5 K without undergoing a Peierls transition.[50] The acceptor forms a sheet-like network by S···N interactions in the crystal (Fig. 7).[51] The selenium analogues **48** and **49** form similar crystal structures. These molecular networks are used to selectively incorporate aromatic hydrocarbons such as xylene.[52]



47 X = Y = S (BTDA)
48 X = S, Y = Se (TSDA)
49 X = Y = Se (BSDA)



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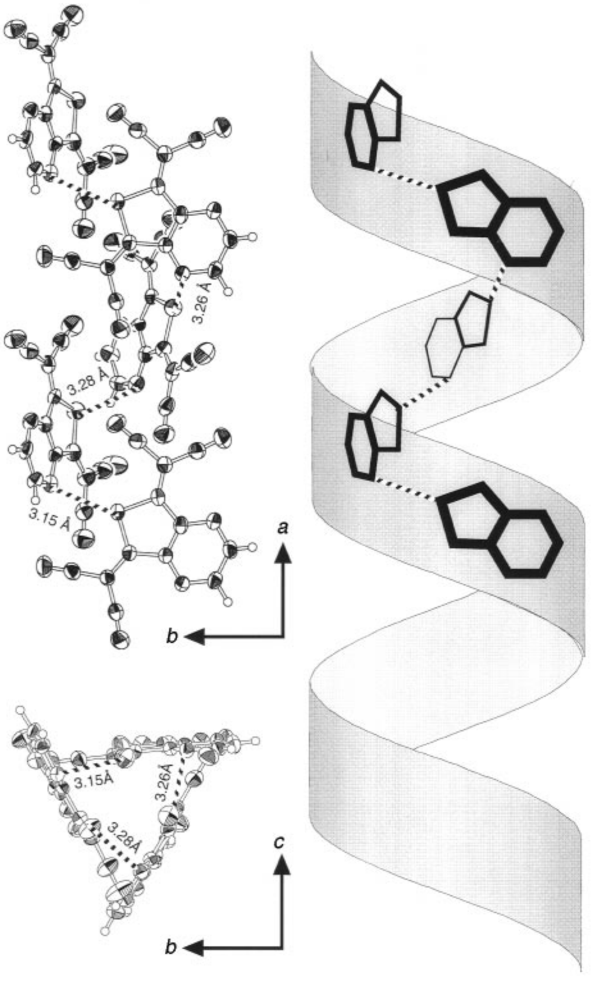


Fig. 6 Crystal structure of **45** (reprinted with permission from ref. 48)

Table 2 Reduction potentials of acceptors

compound	E_1	E_2	ΔE	ref.
	E/V *vs.* SCE			
TCNQ	0.18	−0.36	0.54	49
35 [X = C(CN)$_2$]	0.30	−0.44	0.74	38
35 (X = S)	0.14	−0.60	0.74	38
35 (X = O)	0.05	−0.70	0.75	38
36	0.27	−0.39	0.66	38
37	0.04	−0.66	0.70	38
47	−0.02	−0.49	0.47	49
48	−0.12	−0.55	0.43	52
49	−0.23	−0.55	0.32	52
50 (R = H)	−0.01	−0.46	0.45	53
51	0.12	−0.38	0.50	54
52	0.04	−0.43	0.47	56
53	0.22	−0.29	0.51	56

Thiadiazolopyrazino-TCNQs **50** have also been prepared from the corresponding dione.[53] Their reduction potentials are a little higher than those of BTDA **47** (Table 2). They undergo reversible four-stage one-electron reduction and give conductive CT complexes with electron donors. The X-ray analysis of **50** (R = H) reveals that the coplanar sheet-like network is formed by S···N heteroatom contacts and hydrogen bonding.

Thiadiazolo-TCNQ **51** has been prepared by reaction of dibromo compound **54** with malononitrile anion in the presence of a Pd catalyst followed by oxidation with PbO_2.[54] Compound **51** is a stronger acceptor than BTDA judging from the reduction potentials (Table 2). This acceptor affords highly conducting complexes with TTF in contrast to BTDA, which forms a mixed stacking with TTF due to its inclusion properties.[55] The selenium and oxygen analogues **52** and **53** have been similarly prepared.[56] They also afford highly conducting complexes with electron donors such as TMTTF.

Tetracyanodiphenoquinodimethane **55** fused with four thiadiazole rings has recently been prepared by Suzuki *et al.*[57]

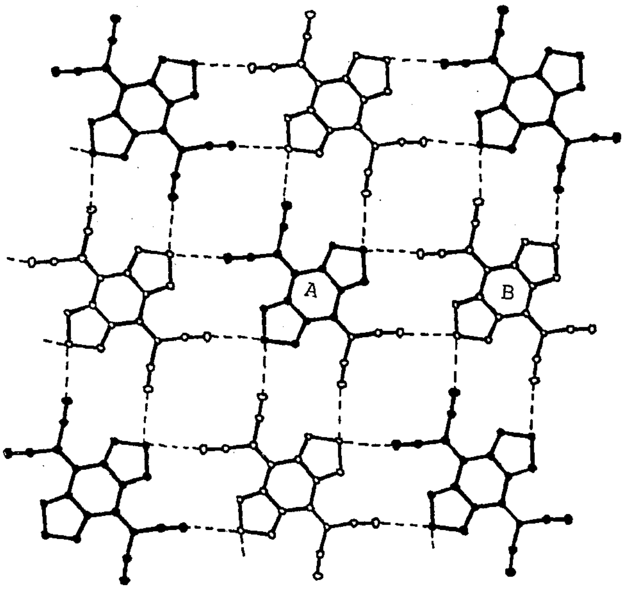
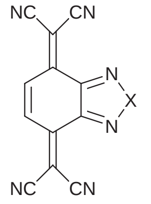
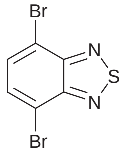


Fig. 7 Sheet-like network of BTDA **47** (reprinted with permission from ref. 51)



51 X = S
52 X = Se
53 X = O



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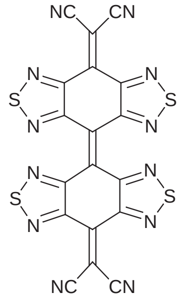
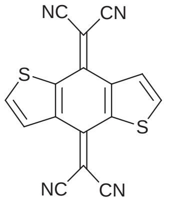


55

This molecule exhibits reversible mechano- and thermo-chromism involving the folded (yellow) and twisted (violet) conformers. The folded conformer forms a sheet-like network *via* electrostatic S···N interactions.

Kobayashi *et al.* have prepared a series of thiophene-fused TCNQs **56–59**.[58] They are non-planar due to the steric interactions caused by the peri hydrogens. The molecules **56** and **57** keeping the TCNQ skeleton are stronger acceptors than the others, and afford conductive CT complexes with TTF. Benzo derivative **60** is butterfly-shaped and a weaker acceptor.[59] There has been no report on their complexes with donors.



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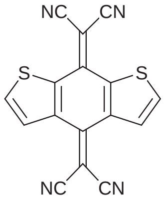

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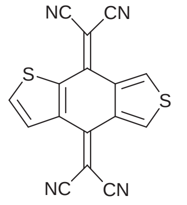

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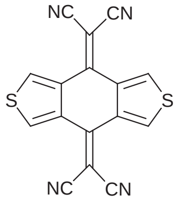

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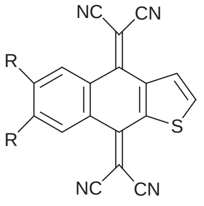


60 R = H, Cl

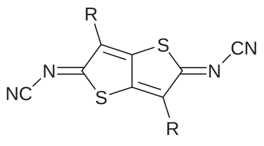
DCNQI derivatives

Hünig has reported *N,N′*-dicyanoquinone diimine (DCNQI) analogues **61** with a thieno[3,2-*b*]thiophene skeleton.[60] These compounds are obtained by reaction of the corresponding quinone with bis(trimethylsilyl)carobodiimide and $TiCl_4$. The acceptor **61** (R = Br) affords highly conductive complexes with electron donors.

Thiophene-fused DCNQI analogues **62** and **63** have been prepared by a similar method. They afford metallic complexes with CuI. An interesting structure composed of polynuclear CuI chains bridged by bidentate ligands **62** or **63** has been suggested.[61] Martín *et al.* have prepared benzo-fused derivatives **64** which are planar molecules in contrast to the corresponding butterfly-shaped TCNQ analogues **60**.[62] The presence of four fluorine atoms in **64** increases its accepting ability.

Others

[3]Radialenes containing a sulfur, selenium or tellurium atom **65** are highly polarized acceptors with strong electron accepting abilities. They afford metallic CT complexes with some donors in spite of the presence of the bulky *tert*-butyl groups.[63]



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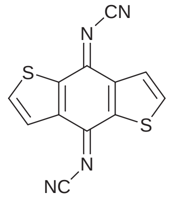

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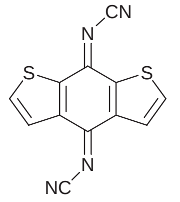

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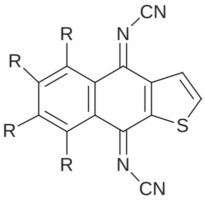

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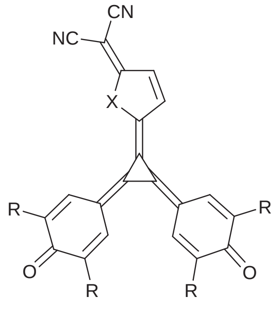
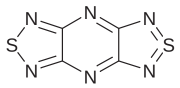


65 X = S, Se, Te
R = $\mathrm{Bu^t}$



66

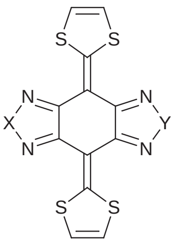
Heterocyclic compound **66** containing a hypervalent sulfur atom has been prepared by reaction of 5,6-diaminothiadiazolopyrazine with thionyl chloride.[64] Its first reduction potential (0.10 V) is higher than that of the corresponding TCNQ analogue **47** (0.02 V), indicating that **66** is a stronger electron acceptor than **47** although it has no electron-withdrawing substituents. This molecule has a unique three-dimensional network in the crystal, which is formed by S···N interactions.

Donor–acceptor compounds

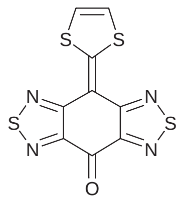
Compounds containing both electron donor and acceptor units are highly polarized due to intramolecular charge transfer. These compounds are expected to have small HOMO–LUMO gaps which lead to interesting properties such as absorption in the near-infrared region, nonlinear optical properties, and single component conductivity. We discuss here unusual donor–acceptor systems with electrochemically amphoteric properties.

Donor–π–acceptor systems

We have prepared bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT) **67** where the 1,3-dithiole units are the electron-donating parts and the thiadiazole ones are the electron accepting parts.[65] The conductivity of BTQBT is good (10^{-3} to 10^{-5} S cm^{-1}) as a single component. A high hall mobility for the single crystal has been observed.[66] In the crystal the planar molecule forms a sheet-like network *via* interactions between the S atoms of the 1,3-dithiole rings (Fig. 8). The S···S contact distance of 3.26 Å is much shorter than the sum of the van der Waals radii (3.70 Å). The molecules are uniformly stacked with a distance of 3.46 Å between the molecular planes. The ratio of the conductivity along the stacking direction to that along the intercolumnar direction is only 2. The selenadiazole analogues **68** and **69** have also been prepared.[65b] Their



67 X = Y = S (BTQBT)
68 X = S, Y = Se
69 X = Y = Se



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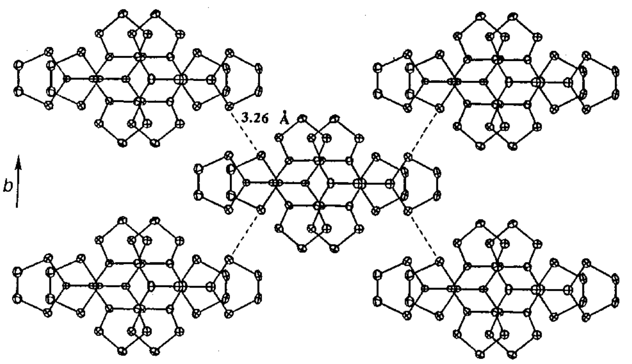
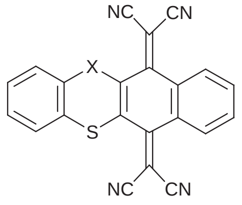


Fig. 8 Sheet-like network of BTQBT **67** [reprinted with permission from ref. 65(*a*)]

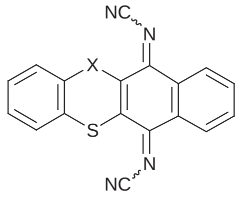
conductivities are a little higher than that of BTQBT due to the stronger intermolecular interactions caused by the selenium atom.

We have replaced one of the 1,3-dithiol-2-ylidene units of **67** by a carbonyl group to give **70** which is more highly polarized than **67**.[67] This molecule shows both oxidation and reduction potentials. In the crystal the planar molecules form a uniform stack, where short S···S and S···N contacts are observed between the columns. Compound **70** shows unusual non-ohmic behavior on measurement of the resistivity.

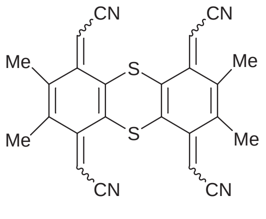
Martín and co-workers have prepared TCNQ analogues **71**[68] and DCNQI ones **72**[69] and **73**[70] containing a fused dithiine skeleton. These molecules show amphoteric properties and have intramolecular CT absorptions. For example, **72** (X = S) shows an absorption maximum at 628 nm, an oxidation potential at 1.51 V, and reduction potentials at 0.05 and −0.36 V.[68]



71 X = S, O



72 X = S, O



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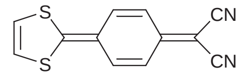

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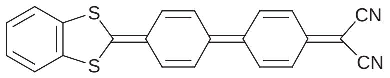

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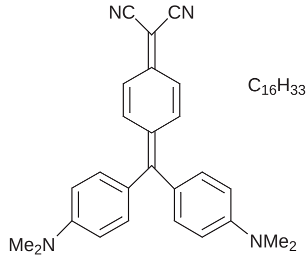

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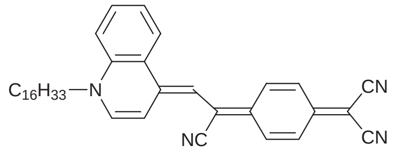
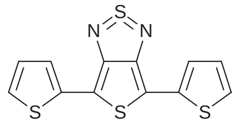


77

Push-pull types of conjugated π-electronic systems become highly-coloured chromphores.[71] Quinoid compound **74** containing a dicyanomethylene group shows a strong intramolecular CT band with a longest absorption maximum of 644 nm.[72] The CT absorption of diphenoquinoid compound **75** recently prepared is red-shifted to the near-infrared region (957, 1045 nm).[73] Dicyanodiaryl-*p*-quinodimethane **76** shows its longest absorption maximum at 698 nm.[74]

Metzger *et al.* have used highly polarized molecule **77** for electrical rectification.[75] Compound **77** shows an absorption maximum at 884 nm in dichloromethane. It shows both oxidation ($E_p = 0.49$ V) and reduction potentials ($E_{1/2} = -0.513$ V). Electrical rectification has been observed in Langmuir–Blodget multilayers and even a monolayer of **77**. This property is related to a transition of the zwitterionic ground-state to the neutral excited state.

Non-classical 1,2,5-thiadiazole containing a hypervalent sulfur atom has a high electron affinity. Introduction of electron-donating groups to a skeleton containing this unit affords new donor–acceptor systems. Terthiophene derivative **78** has an absorption maximum at 618 nm in dichloromethane.[76] This absorption is red-shifted to 990 nm in **79** where a pyrazine ring is inserted. Replacement of the thiophene rings in **79** by more electron-donating pyrrole rings results in a further red-shift.[77] The heterocycle **80** has an absorption maximum at 1345 nm and the end-absorption reaches to 2100 nm (0.6 eV).[78]



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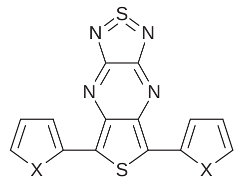
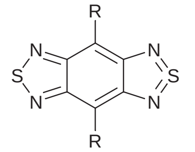


79 X = S
80 X = NH



81

The electronic spectra of **79** and **80** are shown in Fig. 9. This low energy gap is attributed to the low LUMO of the nonclassical heterocyclic part and the high HOMO of the pyrrole ring. These heterocycles **78–80** afford narrow bandgap polymers by electrochemical oxidation.[76–78] The bandgaps are dependent on the HOMO–LUMO gaps of the monomers. The electrochemical bandgaps of poly-**78**, -**79** and -**80** determined from their cyclic voltammograms (Fig. 10) are *ca.* 0.9, 0.3 and 0 eV, respectively.

Benzobis(thiadiazole)s **81** with electron-donating substituents also have small HOMO–LUMO gaps.[79] For example, the morpholine-substituted derivative shows an absorption maximum at 764 nm. X-Ray structure analysis of the diphenyl derivative reveals the formation of a tape-like network *via* short S···N contacts (Fig. 11). The derivative containing 2-thienyl groups has an absorption maximum at 702 nm and affords a narrow bandgap polymer with a bandgap below 0.5 eV by electrochemical oxidation.[80]

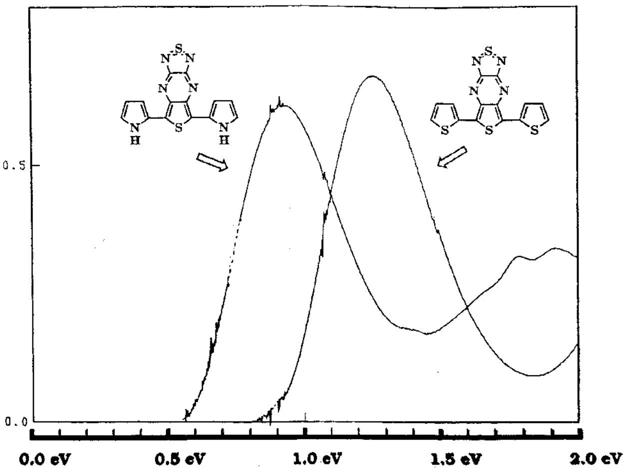


Fig. 9 Electronic spectra of **79** and **80**

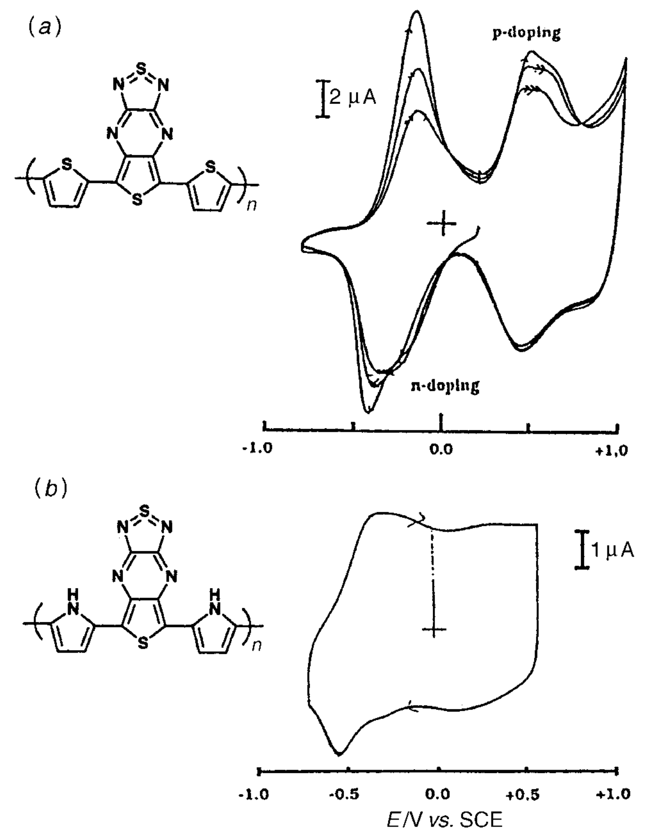


Fig. 10 Cyclic voltammograms of (*a*) poly-**79** and (*b*) poly-**80** (reprinted with permission from ref. 78)

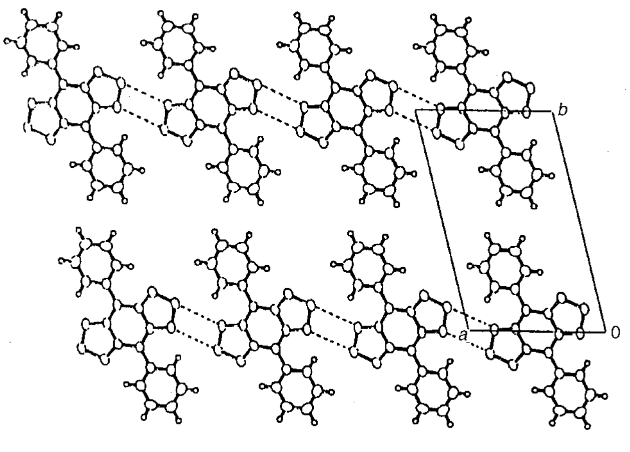
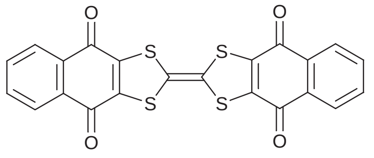


Fig. 11 Tape-like network of **81** (R = Ph) [reprinted with permission from ref. 79(*b*)]

TTF derivatives containing electron-accepting parts are promising donor–acceptor systems. The derivative **82** containing fused naphthoquinone units, which is slightly soluble in solvent, shows a reduction potential at −0.32 V, but no oxidation potential is reported.[81] On the other hand, bis-TTF molecules **83** show amphoteric properties.[82] Thus, **83** (R = n-butyl) shows oxidation potentials at 0.67 (2e) and 1.02 eV, and a reduction potential at −0.27 V. They show intramolecular CT absorptions in solution and in the solid state. The absorption maximum of **83** (R = n-hexyl) is observed at 819 nm in toluene and 1042 nm in the solid state.



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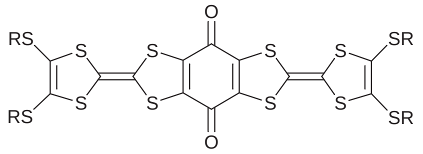

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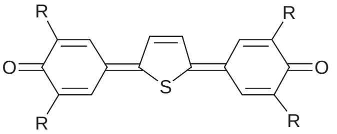
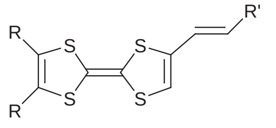


84 R = H, Me, Bu^t



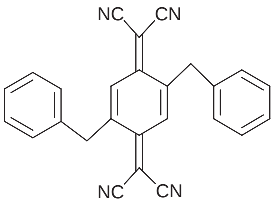
85 R' = CHO, CH=C(CN)$_2$

Quinonoid compounds **84** also show both oxidation and reduction potentials [**84** (R = H); $E_{red} = -0.12, -0.22$ V, $E_{ox} = +1.46$ V].[83] Their absorption maxima are observed at 531–558 nm.

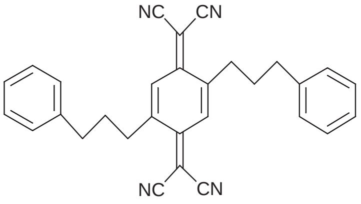
Very recently push-pull TTF derivatives **85** have been reported to exhibit high second-order NLO activities.[84] This report shows that highly polarized TTF molecules are promising candidates for materials showing NLO properties.

Donor–σ–acceptor systems

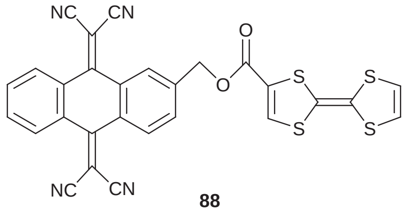
TCNQ derivative **86** has been designed to control the degree of charge-transfer.[85] However, the donor phenyl groups are



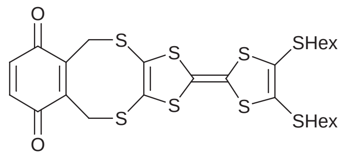
86



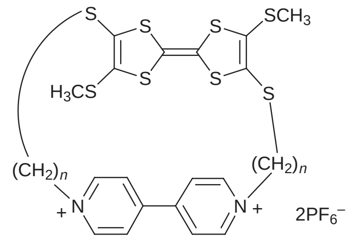
87



88



89



90 *n* = 4, 5

orthogonal to the TCNQ moiety due to steric interactions. TCNQ derivative **87** and the *N*-cyanoimine analogue bearing a longer methylene chain have similar stacking motifs and the formation of segregated stacks of donor and acceptor moieties has not been accomplished.[86]

Bryce has developed the novel donor–σ–acceptor compound **88** containing tetracyanoanthraquinodimethane (TCNAQ) and TTF moieties.[87] Compound **88** shows a very weak, low-energy intramolecular CT band at 420–680 nm. In this molecule clean oxidation of the TTF and reduction of the TCNAQ take place. TTF derivative **89** bearing a benzoquinone unit has also been prepared.[88] The interaction between the units is small and each component preserves its identity.

In compound **90** a TTF-derived donor is covalently tethered to a bipyrdinium acceptor.[89] The CT absorption maxima are observed at 673 ($n=4$) and 650 nm ($n=5$). The redox potentials of **90** ($n=4$) are observed at 0.72, 0.58, −0.36 and −0.85 V.

Donor–σ–acceptor systems composed of TTF and C_{60} moieties have recently been prepared.[90] They show oxidation potentials derived from the TTF unit and reduction potentials derived from the C_{60} unit. However, the interaction between the donor and acceptor units is so small that no CT interaction was observed.

Conclusion

Highly polarized molecules showing electron-donating, electron-accepting and amphoteric properties have been highlighted in this article. TTF derivatives containing polarizable substituents such as iodine or tellurium atoms afford conductors with unique three-dimensional crystal structures. Such substituents can be used to increase dimensionality so as to suppress metal–insulator transitions as well as to strengthen intermolecular interactions leading to wide bandwidths.

Nitrogen-containing heterocycles such as 1,2,5-thiadiazole or pyrazines are used as electron-accepting units in highly polarized donors. Negatively charged atoms electrostatically interact with positively charged chalcogen atoms to form interesting molecular assemblies. Interactions between the nitrogen and sulfur atoms of thiadiazole rings result in the formation of a molecular tape. Intermolecular CT interactions sometimes lead to alternative stacking of molecules. These facts suggest that such interactions can be used for crystal engineering.

Chalcogen atom-containing quinones, and TCNQ and DCNQI analogues are highly polarized acceptors. Short atom contacts between the chalcogen atoms and negatively charged heteroatoms are often observed in the crystals. They are promising electron acceptors to afford multi-dimensional conductors.

Donor–acceptor compounds showing amphoteric properties have small HOMO–LUMO gaps. This leads to interesting optical properties such as absorptions in the near-infrared region and non-linear optical properties. They are also candidates for single-component conductors. Some compounds show semiconducting behavior without doping. However, the synthesis of single-component organic metals has not been accomplished yet and the preparation of such molecules remains as a challenging theme.

References

1 *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, Wiley, vol. 1, 1997.
2 M. R. Bryce, *J. Mater. Chem.*, 1995, **5**, 1481.
3 N. Martín, J. L. Segura and C. Seoane, *J. Mater. Chem.*, 1997, **7**, 1661.
4 J. Roncali, *J. Mater. Chem.*, 1997, **7**, 2307.
5 M. Jorgensen and K. Bechgaard, *Synthesis*, 1989, 207; M. R. Bryce and G. Cooke, *Synthesis*, 1991, 263.
6 R. Gompper, J. Hock, K. Polborn, E. Dormann and H. Winter, *Adv. Mater.*, 1995, **7**, 41.
7 T. Imakubo, H. Sawa and R. Kato, *J. Chem. Soc., Chem. Commun.*, 1995, 1097.
8 T. Imakubo, H. Sawa and R. Kato, *J. Chem. Soc., Chem. Commun.*, 1995, 1667.
9 M. Iyoda, H. Suzuki, S. Sasaki, H. Yoshino, K. Kikuchi, K. Saito, I. Ikemoto, H. Matsuyama and T. Mori, *J. Mater. Chem.*, 1996, **6**, 501.
10 N. Okada, H. Yamochi, F. Shinozaki, K. Oshima and G. Saito, *Chem. Lett.*, 1986, 1861.
11 V. Y. Khodorkovsky, C. Wang, J. Y. Becker, A. Ellern, L. Shapiro and J. Bernstein, *Adv. Mater.*, 1994, **6**, 656.
12 J. Y. Becker, J. Bernstein, M. Dayan and L. Shahal, *J. Chem. Soc., Chem. Commun.*, 1992, 1048.
13 C. Wang, A. Ellern, V. Khodorkovsky, J. Y. Becker and J. Bernstein, *J. Chem. Soc., Chem. Commun.*, 1994, 2115.
14 A. E. Underhill, I. Hawkins, S. Edge, S. B. Wilkes, K. S. Varma, A. Kobayashi and H. Kobayashi, *Synth. Met.*, 1991, **42**, 2093; M. Tomura, S. Tanaka and Y. Yamashita, *Heterocycles*, 1993, **35**, 69.
15 M. Tomura and Y. Yamashita, *Synth. Met.*, 1997, **86**, 1871.
16 T. Naito, A. Kobayashi, H. Kobayashi and A. E. Underhill, *Chem. Commun.*, 1996, 521.
17 G. C. Papavassiliou, S. Y. Yiannopoulos and J. S. Zambounis,

J. Chem. Soc., *Chem. Commun.*, 1986, 820; V. Psycharis, A. Hountas, A. Terzis and G. Papavassiliou, *Acta Crystallogr.*, 1988, **C44**, 125.

18 K. Lahlil, A. Moradpour, C. Merienne and C. Bowlas, *J. Org. Chem.*, 1994, **59**, 8030.

19 Y. Yamashita, Y. Kobayashi and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1052.

20 (*a*) Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi and M. Sano, *Chem. Lett.*, 1992, 419; (*b*) Y. Yamashita, S. Tanaka and M. Tomura, *Phosphorus Sulfur Silicon*, 1992, **67**, 327; (*c*) Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi and M. Sano, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1132.

21 Y. Yamashita and S. Tanaka, *Chem. Lett.*, 1993, 73.

22 Y. Yamashita, K. Ono, S. Tanaka, K. Imaeda and H. Inokuchi, *Adv. Mater.*, 1994, **6**, 295.

23 Y. Yamashita, S. Tanaka and K. Imaeda, *Synth. Met.*, 1995, **71**, 1965.

24 K. Imaeda, Y. Yamashita, S. Tanaka and H. Inokuchi, *Synth. Met.*, 1995, **73**, 107.

25 Y. Yamashita, M. Tomura, S. Tanaka and K. Imaeda, *Synth. Met.*, 1997, **86**, 1795; K. Imaeda, Jröber, C. Nakano, M. Tomura, S. Tanaka, Y. Yamashita, H. Kobayashi, H. Inokuchi and A. Kobayashi, *Mol. Cryst. Liq. Cryst.*, 1997, **296**, 205.

26 Y. Yamashita, M. Tomura and K. Imaeda, *Chem. Commun.*, 1996, 2021.

27 N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela and R. Viruela, *J. Org. Chem.*, 1998, **63**, 1268.

28 K. Nakasuji, M. Sasaki, T. Kotani, I. Murata, T. Enoki, K. Imaeda, H. Inokuchi, A. Kawamoto and J. Tanaka, *J. Am. Chem. Soc.*, 1987, **109**, 6970.

29 J. S. Zambounis, E. Christen, J. Pfeiffer and G. Rihs, *J. Am. Chem. Soc.*, 1994, **116**, 925.

30 K. Dietz, H. J. Keller, D. Nöthe and D. Wehe, *J. Am. Chem. Soc.*, 1982, **104**, 7581.

31 Y. Yamashita, K. Saito, T. Mukai and T. Miyashi, *Tetrahedron Lett.*, 1989, **30**, 7071.

32 Y. Yamashita, J. Eguchi, T. Suzuki, C. Kabuto, T. Miyashi and S. Tanaka, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 643.

33 K. Ono, S. Tanaka, K. Imaeda and Y. Yamashita, *J. Chem. Soc., Chem. Commun.*, 1994, 899.

34 T. Suzuki, T. Okubo, A. Okada, Y. Yamashita and T. Miyashi, *Heterocycles*, 1993, **35**, 395.

35 Y. Yamashita, K. Ono, M. Tomura and K. Imaeda, *Chem. Commun.*, 1997, 1851.

36 T. Otsubo, Y. Nobuhara, K. Kanefuji, Y. Aso and F. Ogura, *J. Phys. Org. Chem.*, 1988, **1**, 275.

37 N. Martín, L. Sánchez, C. Seoane, J. Garín and J. Orduna, *Tetrahedron Lett.*, 1995, **36**, 7153.

38 Y. Yamashita, T. Suzuki, G. Saito and T. Mukai, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 1489.

39 T. Suzuki, C. Kabuto, Y. Yamashita and T. Mukai, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3459.

40 M. Nakatsuka, K. Nakasuji, I. Murata, I. Watanabe, G. Saito, T. Enoki and H. Inokuchi, *Chem. Lett.*, 1983, 905.

41 Y. Morita, A. Kashiwagi and K. Nakasuji, *J. Org. Chem*, 1997, **62**, 7464.

42 S. Hünig, K. Sinzger, R. Bau, T. Metzenthin and J. Salbeck, *Chem. Ber.*, 1993, **126**, 465.

43 S. Gronowitz and B. Uppström, *Acta Chem. Scand.*, 1974, **B28**, 981.

44 K. Yui, Y. Aso, T. Otsubo and F. Ogura, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 1816.

45 K. Yui, H. Ishida, Y. Aso, T. Otsubo, F. Ogura, A. Kawamoto and J. Tanaka, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1547.

46 F. Ogura and T. Otsubo, *Conductive Hetero-TCNQs*, in *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, Wiley, 1997, vol. 1.

47 D. Lorcy, K. D. Robinson, Y. Okuda, J. L. Atwood and M. P. Cava, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 345.

48 K. Suzuki, M. Tomura and Y. Yamashita, *J. Mater. Chem.*, 1998, **8**, 1117.

49 Y. Yamashita, T. Suzuki, T. Mukai and G. Saito, *J. Chem. Soc.*, *Chem. Commun.*, 1985, 1044.

50 A. Ugawa, K. Iwasaki, A. Kawamoto, K. Yakushi, Y. Yamashita and T. Suzuki, *Phys. Rev. B*, 1991, **43**, 14718.

51 C. Kabuto, T. Suzuki, Y. Yamashita and T. Mukai, *Chem. Lett.*, 1986, 1433.

52 T. Suzuki, H. Fujii, Y. Yamashita, C. Kabuto, S. Tanaka, M. Harasawa, T. Mukai and T. Miyashi, *J. Am. Chem. Soc.*, 1992, **114**, 3034.

53 Y. Tsubata, T. Suzuki, Y. Yamashita, T. Mukai and T. Miyashi, *Heterocycles*, 1992, **33**, 337.

54 T. Suzuki, Y. Yamashita, C. Kabuto and T. Miyashi, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1102.

55 T. Suzuki, C. Kabuto, Y. Yamashita and T. Mukai, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2111.

56 T. Suzuki, Y. Yamashita, T. Fukushima and T. Miyashi, *Mol. Crst. Liq. Cryst.*, 1997, **296**, 165.

57 T. Suzuki, T. Fukushima, T. Miyashi and T. Tsuji, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 2495.

58 K. Kobayashi and C. L. Gajurel, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 1779; K. Kobayashi, C. L. Gajurel, K. Umemoto and Y. Mazaki, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2168; F. Iwasaki, N. Toyoda, M. Hirota, N. Yamazaki, M. Yasui and K. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2173; F. Iwasaki, S. Hironaka, N. Yamazaki and K. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2187.

59 P. Cruz, N. Martín, F. Miguel, C. Seoane, A. Albert, F. H. Cano, A. González and J. M. Pingarrón, *J. Org. Chem.*, 1992, **57**, 6192.

60 E. Günther, S. Hünig, K. Peters, H. Rieder, H. G. von Schnering, J.-V. von Schütz, S. Söderholm, H.-P. Werner and H. C. Wolf, *Angew. Chem.*, *Int. Ed. Engl.*, 1990, **29**, 204.

61 K. Kobayashi, Y. Mazaki, H. Namba, K. Kikuchi, K. Saito, I. Ikemoto, S. Hino and N. Kosugi, *J. Mater. Chem.*, 1995, **5**, 1625.

62 N. Martín, P. de Miguel, C. Seoane, A. Albert and F. H. Cano, *J. Mater. Chem.*, 1997, **7**, 25.

63 K. Takahashi and S. Tarutani, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 519; K. Takahashi and S. Tarutani, *Adv. Mater.*, 1995, **7**, 639; S. Tarutani, T. Mori, H. Mori, S. Tanaka and K. Takahashi, *Chem. Lett.*, 1997, 627.

64 Y. Yamashita, K. Saito, T. Suzuki, C. Kabuto, T. Mukai and T. Miyashi, *Angew. Chem.*, *Int. Ed. Engl.*, 1988, **27**, 434.

65 (*a*) Y. Yamashita, S. Tanaka, K. Imaeda and H. Inokuchi, *Chem. Lett.*, 1991, 1213; (*b*) Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi and M. Sano, *J. Org. Chem.*, 1992, **57**, 5517.

66 K. Imaeda, Y. Yamashita, Y. Li, T. Mori, H. Inokuchi and M. Sano, *J. Mater. Chem.*, 1992, **2**, 115; K. Imaeda, Y. Li, Y. Yamashita, H. Inokuchi and M. Sano, *J. Mater. Chem.*, 1995, **5**, 861.

67 Y. Yamashita, K. Ono, S. Tanaka, K. Imaeda, H. Inokuchi and H. Sano, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1803.

68 P. Bando, N. Martín, J. L. Segura, C. Seoane, E. Ortí, P. M. Viruela, R. Viruela, A. Albert and F. H. Cano, *J. Org. Chem.*, 1994, **59**, 4618.

69 N. Martín, J. L. Segura, C. Seoane, E. Ortí, P. M. Viruela, R. Viruela, A. Albert, F. H. Cano, J. V.-Gancedo, C. Rovira and J. Veciana, *J. Org. Chem.*, 1996, **61**, 3041.

70 H. González, P. Miguel, N. Martín, J. L. Segura, C. Seoane, E. Ortí, R. Viruela and P. M. Viruela, *Adv. Mater.*, 1994, **6**, 765.

71 R. Gompper and H.-U. Wagner, *Angew. Chem.*, *Int. Ed., Engl.*, 1988, **27**, 1437.

72 R. Gompper, H.-U. Wagner and E. Kutter, *Chem. Ber.*, 1968, **101**, 4123.

73 S. Inoue, Y. Aso and T. Otsubo, *Chem. Commun.*, 1997, 1105.

74 T. Kawase, M. Wakabayashi, C. Takahashi and M. Oda, *Chem. Lett.*, 1997, 1055.

75 R. M. Metzger, B. Chen, U. Höpfner, M. V. Lakshmikantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer and G. J. Ashwell, *J. Am. Chem. Soc.*, 1997, **119**, 10455.

76 S. Tanaka and Y. Yamashita, *Synth. Met.*, 1993, **55–57**, 1251.

77 S. Tanaka and Y. Yamashita, *Synth. Met.*, 1995, **69**, 599.

78 S. Tanaka and Y. Yamashita, *Synth. Met.*, 1997, **84**, 229.

79 (*a*) K. Ono, S. Tanaka and Y. Yamashita, *Angew. Chem., Int. Ed., Engl.*, 1994, **33**, 1977; (*b*) Y. Yamashita, K. Ono, M. Tomura and S. Tanaka, *Tetrahedron*, 1997, **53**, 10169.

80 M. Karikomi, C. Kitamura, S. Tanaka and Y. Yamashita, *J. Am. Chem. Soc.*,1995, **117**, 6791.

81 W. H. Watson, E. E. Eduok, R. P. Kashyap and M. Krawiec, *Tetrahedron*, 1993, **49**, 3035.

82 S. Frenzel and K. Müllen, *Synth. Met.*, 1996, **80**, 175.

83 K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami and Y. Fukazawa, *J. Am. Chem. Soc.*, 1991, **113**, 4576.

84 A. I. de Lucas, N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín, J. Orduna, R. Alcalá and B. Villacampa, *Tetrahedron*, 1998, **54**, 4655.

85 J. Y. Becker, J. Bernstein, S. Bittner, N. Levi and S. S. Shaik, *J. Am. Chem. Soc.*, 1983, **105**, 4468; J. Y. Becker, J. Bernstein, S. Bittner, N. Levi and S. S. Shaik, *J. Org. Chem.*, 1988, **53**, 1689.

86 N. Martín, J. L. Segura, C. Seoane, A. Albert and F. H. Cano, *J. Chem. Soc.*, *Perkin Trans. 1*, 1993, 2363.

87 P. de Miguel, M. R. Bryce, L. M. Goldenberg, A. Beeby, V. Khodorkovsky, L. Shapiro, A. Niemz, A. O. Cuello and V. Rotello, *J. Mater. Chem.*, 1998, **8**, 71.

88 J. L. Segura, N. Martín, C. Seoane and M. Hanack, *Tetrahedron Lett.*, 1996, **37**, 2503.

89 K. B. Simonsen, K. Zong, R. D. Rogers, M. P. Cava and J. Becher, *J. Org. Chem.*, 1997, **62**, 679.

90 N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín and J. Orduna, *Tetraheron Lett.*, 1996, **37**, 5979; A. I. de Lucas, N. Martín, L. Sánchez and C. Seoane, *Tetrahedron Lett.*, 1996, **37**, 9391; C. Boulle, J. M. Rabreau, P. Hudhomme, M. Cariou, M. Jubault, A. Gorgues, J. Orduna and J. Garín, *Tetrahedron Lett.*, 1997, **38**, 3909; J. Llacay, M. Mas, E. Molins, J. Veciana, D. Powell and C. Rovira, *Chem. Commun.*, 1997, 659.

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