Chem. Soc. Rev., 1991, **20**, 355–390

Recent Progress on Conducting Organic Charge-Transfer Salts

By Martin R. Bryce
DEPARTMENT OF CHEMISTRY. UNIVERSITY OF DURHAM,
DURHAM. DH1 3LE

1 Introduction

The past two decades have witnessed unabated interest in the synthesis and characterization of organic charge-transfer (CT) salts that display unusual solid-state properties. Metallic conductivity and superconductivity are the most glamorous phenomena to have been discovered in these materials, and recently attention has also been directed to the novel magnetic and optical properties which CT salts can display. This is a multi-disciplinary field that challenges the skills of synthetic chemists, crystallographers, applied physicists, theoreticians, and materials scientists. The motivation behind research on these exotic materials is twofold: (i) there is a wealth of fundamental solid-state chemistry and physics to be uncovered and (ii) there are potentially many far-reaching technological applications within the arena of molecular electronic devices. The same is true of conducting polymers (*e.g.* polyacetylene and polythiophene) and progress in the two areas (CT salts and conducting polymers) has largely gone hand-in-hand. Herein, we are concerned with CT salts that are electronic conductors and we will highlight some of the materials that are currently at the forefront of attention. The vast majority of work has involved studies on single crystals. However, innovative results are emerging with Langmuir–Blodgett film materials. It is, therefore, timely to devote a significant part of this review to this new area. This article is written by a chemist, and the approach to the subject will, therefore, be different from that of a scientist from another discipline studying the same materials. Several review articles,[1] books,[2] and detailed conference proceedings[3]

---

[1] (*a*) J. B. Torrance, *Acc. Chem. Res.*. 1979, **12**. 79; (*b*) D. Jérome and H. J. Schultz, *Adv. Phys.*. 1982, **31**, 299; (*c*) K. Bechgaard and D. Jérome, *Sci. Am.*, 1982, **247**, 52; (*d*) F. Wudl, *Acc. Chem. Res.*, 1984, **17**. 227; (*e*) M. R. Bryce and L. C. Murphy, *Nature*, 1984. **309**, 119; (*f*) T. J. Marks. *Science*. 1985. **227**. 881; (*g*) J. M. Williams, M. A. Beno, H. H. Wang, P. C. W. Leung. T. J. Emge. U. Geiser, and K. D. Carlson, *Acc. Chem. Res.*. 1985, **18**, 261; (*h*) D. O. Cowan and F. M. Wiygul. *Chem. Eng. News*. 1986. **64(29)**, 28; (*i*) P. M. Chaikin and R. L. Greene, *Physics Today*, 1986, **39(5)**. 24; (*j*) J. M. Williams. H. H. Wang. T. J. Emge, U. Geiser, M. A. Beno, K. D. Carlson, R. J. Thorn, A. J. Schultz, M.-H. Whangbo. *Prog. Inorg. Chem.*, 1987. **35**, 51; (*k*) D. O. Cowan, in 'New Aspects of Organic Chemistry I', ed. Z. Yoshida. T. Shiba. and Y. Oshiro, V.C.H. Publishers, New York, 1989, 177.

[2] (*a*) J. R. Ferraro and J. M. Williams, 'Introduction to Synthetic Electrical Conductors'. Academic Press, London, 1987; (*b*) T. Ishiguro and K. Yamaji, 'Organic Superconductors'. Springer-Verlag. Berlin, 1990.

[3] (*a*) Proceedings of ICSM 1988, Santa Fe, published in *Synth. Met.*, 1988 and 1989. **27–29**; (*b*) Proceedings of ICSM 1990, Tübingen, published in *Synth. Met.*, 1991, **41–43**; (*c*) 'The Physics and Chemistry of Organic Superconductors', ed. G. Saito and S. Kagoshima, Springer-Verlag. Berlin. 1990; (*d*) 'Organic Superconductivity', ed. V. Z. Kresin and W. A. Little. Plenum Press, New York. 1990.

are recommended for comprehensive coverage of the field.

2 Historical Perspective

In 1954 Japanese workers reported that an unstable perylene–bromine salt was conducting,[4] and during the 1960s many salts of TCNQ were found to be organic semiconductors.[5] Thus the foundations were laid for the discovery, in 1973, that the crystalline 1 : 1 CT complex formed by the donor tetrathiafulvalene (TTF) (1)[6] and the acceptor tetracyano *p*-quinodimethane TCNQ (14) exhibited metallic behaviour (σ_{rt} = 500 Scm^{-1}, σ_{max} = 10^{4} Scm^{-1} at 59 K).[7] This was a fulfilment of the prediction made in 1911 that organic solids might exhibit electrical conductivity comparable with that of metals,[8] and the science of organic conductors was now truly inaugurated. Also, in the 1970s it was found that the conductivity of polyacetylene could be increased by *ca.* 13 orders of magnitude by doping it with various donor or acceptors species;[9] this initiated a major research effort into the study of conjugated organic polymers. At about the same time, two other important classes of synthetic metals emerged: *viz.*, polymers of certain main group elements, notably $(SN)_x$,[10] and linear-chain chelated transition metal compounds where intra-chain overlap involves the ligand π-system as well as metal–metal interactions.[11] Major landmarks in the development of organic conductors based on CT complexes and ion radical salts are presented below (Table 1) in chronological order. Some of these compounds will be discussed in more detail in this review. Variable temperature conductivity values at ambient pressure for a range of highly conducting materials are shown in Figure 1.

Table 1

Year	*Discovery*
1954	Perylene–bromine salt. the first conducting molecular compound,[4] σ_{rt} = *ca* 1 Scm^{-1}.
1962	Semi-conducting salts of TCNQ reported.[5]
1973	TTF–TCNQ prepared the first organic metal; σ_{rt} = 500 Scm^{-1}; $T_{M\text{–}I}$ at 53 K [7]
1974	Tetraselenafulvalene (TSF)–TCNQ prepared· σ_{rt} = 700–800 Scm^{-1} and $T_{M\text{–}I}$ at *ca* 40 K. The metallic state is stabilized and transport properties are dominated by the donor stack.[12]

---

[4] H Akamatsu, H Inokuchi, and Y Matsunaga, *Nature*, 1954, **173**, 168

[5] L R Melby, R J Harder, W R Hertler, W Mahler, R E Benson, and W E Mochel, *J Am Chem Soc*, 1962, **84**, 3374

[6] TTF was first synthesized independently by two groups (*a*) F Wudl, G M Smith, and E J Hufnagel, *J Chem Soc*, *Chem Commun*, 1970, 1453, (*b*) S Hunig, G Kiesslich, D Scheutzow, R Zahradnik. and P Carsky, *Int J Sulphur Chem*, *Part C*, 1971, 109

[7] J Ferraris, D O Cowan, V V Walatka, and J H Perlstein, *J Am Chem Soc*, 1973, **95**, 948

[8] H N McCoy and W C Moore, *J Am Chem Soc*, 1911, **33**, 1273

[9] H Shirakawa, E J Louis, A G MacDiarmid, C K Chiang, and A J Heeger, *J Chem Soc*, *Chem Commun*, 1977, 578

[10] M M Labes, P Lowe, and L F Nichols, *Chem Rev*, 1979, **79**, 1

[11] (*a*) A E Underhill and D M Watkins, *Chem Soc Rev*, 1980, **9**, 429, (*b*) P I Clemenson, *Coord Chem Rev*, 1990, **106**, 171

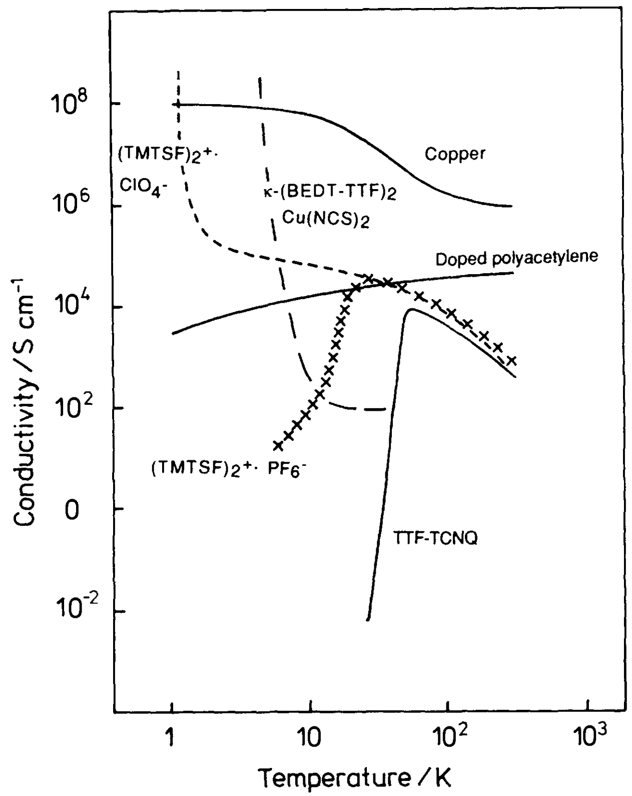


Figure 1 *Variable temperature conductivity values at ambient pressure for a range of highly conducting materials*

1975	HMTSF–TCNQ: metallic character retained down to <1 K; increased dimensionality due to close interstack Se•••N contacts.[13]
1978	HMTSF-2,5-DMTCNQ: T_{M-I} suppressed under pressure; $\sigma = 10^5\,\mathrm{S\,cm^{-1}}$ at 1 K and 10 kbar.[14]
1979	TMTTF–tetrahalo-*p*-benzoquinones: metallic behaviour without TCNQ, or derivative, as the acceptor.[15]
1980	$(\mathrm{TMTSF})_2$ X salts: organic superconductivity first reported at 0.9 K and 12 kbar for X = $\mathrm{PF_6^-}$, and at 1.4 K and ambient pressure for X = $\mathrm{ClO_4^-}$.[16]
1982	$(\mathrm{BEDT\text{-}TTF})_2\,\mathrm{ClO_4}$ (1,1,2-trichloroethane)$_{0.5}$: metallic conductivity over the temperature range 298—1.4 K in a sulphur-based system.[17]
1983	$(\mathrm{BEDT\text{-}TTF})_2\,\mathrm{ReO_4}$: the first sulphur-based organic superconductor; $T_c = 1.4$ K at 4 kbar.[18]
1984	β-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{I_3}$: T_c at 1.4 K and ambient pressure.[19]
1986	β-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{I_3}$: T_c raised to 8 K under anisotropic pressure.[20]
1986	$\mathrm{TTF[Ni(dmit)_2]_2}$: the first superconducting system based on a CT salt of a π-anion molecule; $T_c = 1.6$ K at 7 kbar.[21]

1987	Cu(2,5-DMDCNQI)$_2$ extremely high conductivity for a radical ion salt, metallic behaviour between 295—1 3K with σ = 5 × 10^5 Scm^{1} at 3 5K[22]
1987	(DMET)$_2$ Au(CN)$_2$ superconductivity first observed in a salt of an unsymmetrical donor, T_c = 1 1K at 2 5kbar[23]
1987	Me$_4$N[Ni(dmit)$_2$]$_2$ superconductivity in a π-anion molecule having a closed shell cation, T_c = 5 0K at 7kbar[24]
1988	TTeF–TCNQ synthesized,[25] σ_{rt} = *ca* 2000Scm^{1}
1988	(MDT–TTF)$_2$ AuI$_2$ sulphur-based superconductivity observed with an unsymmetrical donor, T_c = 3 5K at ambient pressure[26]
1988	κ-(BEDT–TTF)$_2$ Cu(SCN)$_2$ ambient pressure superconductivity at 10 4K[27]
1990	(BEDO–TTF)$_{2\ 4}$ I$_3$ the first organic metal of an oxygen-containing donor,[28] σ_{rt} = 100—280Scm^{1}
1990	(BEDO–TTF)$_3$ Cu$_2$(NCS)$_3$ superconductivity observed in an oxygen-containing donor, T_c = 1 0K at ambient pressure[29]
1990	κ-(BEDT–TTF)$_2$ Cu[N(CN)$_2$] X, X = Br, Cl currently the highest T_c organic superconductors, T_c = 11 6K at ambient pressure for X = Br,[30a] T_c = 12 5K at 0 3kbar for X = Cl[30b]

---

[12] E M Engler and V V Patel, *J Am Chem Soc*, 1974, **96**, 7376

[13] A N Bloch, D O Cowan, K Bechgaard, R E Pyke, and R H Banks, *Phys Rev Lett*, 1975, **34**, 1561

[14] C S Jacobson, K Mortensen, J R Anderson, and K Bechgaard, *Phys Rev*, 1978, **B18**, 905

[15] J B Torrance, J J Mayerle, V Y Lee, and K Bechgaard, *J Am Chem Soc*, 1979, **101**, 4747

[16] (*a*) D Jerome A Mazand, M Ribault, and K Bechgaard, *J Phys Lett*, 1980, **41**, L95 (*b*) K Bechgaard, C S Jacobsen, K Mortensen, H J Pedersen, and N Thorup, *Solid State Commun*, 1980, **33**, 1119

[17] G Saito, T Enoki, K Toriumi, and H Inokuchi, *Solid State Commun*, 1982, **42**, 557

[18] S S P Parkin, E M Engler, R R Schumaker, R Lagier, V Y Lee, J C Scott, and R L Greene, *Phys Rev Lett*, 1983, **50**, 270

[19] E B Yagubskii, I F Schegolev, V N Laukhin, P A Karatsovnik, M V Karatsovnik, A V Zvarykina, and L I Buravov, *J E T P Lett (Engl Trans)*, 1984, **39**, 12

[20] J E Schirber, L J Azevedo, J K Kwak, E L Venturini, P C W Leung, M A Beno, H H Wang, and J M Williams, *Phys Rev B*, 1986, **33**, 1987

[21] L Brossard, M Ribault, L Valade, and P Cassoux, *Physica B*, 1986, **143**, 378

[22] A Aumuller, P Erk G Klebe, S Hunig, J U von Schutz, and H -P Werner, *Angew Chem, Int Edn Engl*, 1986 **25**, 740

[23] K Kikuchi, K Murata, Y Honda, T Namiki, K Saito T Ishiguro, K Kobayashi, and I Ikemoto, *J Phys Soc Jpn*, 1987, **55**, 3435

[24] A Kobayashi, H Kim, Y Sasaki, H Kobayashi, S Moriyama, Y Nishio, K Kajita, and W Sasaki, *Chem Lett*, 1987, 1819

[25] (*a*) M D Mays, R D McCullough, D O Cowan, T O Poehler, W A Bryden, and T J Kistenmacher, *Solid State Commun*, 1988, **65**, 1089, (*b*) D O Cowan, M D Mays, T J Kistenmacher, T O Poehler, M A Beno, A M Kini, J M Williams, Y K Kwok, K D Carlson L Xiao, J J Nuova, and M -H Whangbo, *Mol Cryst Liq Cryst*, 1990, **181**, 43

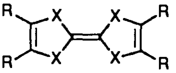
[26] G C Papavassiliou, G A Mousdis, J S Zambounis, A Terzis, A Hountas, B Hilti, C W Mayer and J Pfeiffer, *Synth Met*, 1988, **B27**, 379

[27] H Urayama, H Yamochi, G Saito, K Nozawa, T Sugano, M Kinoshita, S Sato, K Oshima A Kawamoto, and J Tanaka, *Chem Lett*, 1988, 55

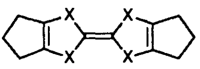
[28] (*a*) F Wudl, H Yamochi, T Suzuki, H Isotalo, C Fite, H Kasmai, K Liou, G Srdanov, P Coppens, K Maly and A Frost-Jensen, *J Am Chem Soc*, 1990, **112**, 2461, (*b*) F Wudl, H Yamochi T Suzuki H Isotalo C Fite K Liou H Kasmai, and G Srdanov, in ref 3*c*, p 358

[29] M A Beno, H H Wang, A M Kini, K D Carlson, U Geiser, W K Kwok, J E Thompson J M Williams J Ren and M -H Whangbo *Inorg Chem*, 1990, **29** 1599

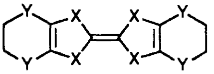
[30] (*a*) A M Kini, U Geiser, H H Wang, K D Carlson J M Williams, W K Kwok K G Vandervoot J E Thompson, D L Stupka, D Jung, and M -H Whangbo, *Inorg Chem* 1990, **29** 2555, (*b*) J M Williams, A M Kini, H H Wang, K D Carlson, U Geiser, L K Montgomery, G J Pyrka D M Watkins J K Kommers S J Boryschuk, A V Crouch, W K Kwok, J E Schirber D L Overmyer D Jung, and M -H Whangbo, *Inorg Chem*, 1990, **29**, 3274



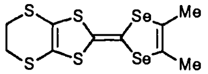
	X	R	
(1)	S	H	TTF
(2)	Se	H	TSF
(3)	S	Me	TMTTF
(4)	Se	Me	TMTSF
(5)	Te	H	TTeF



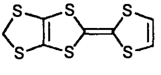
(6) X = S HMTTF
(7) X = Se HMTSF



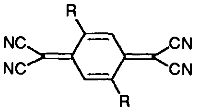
	X	Y	
(8)	S	S	BEDT-TTF
(9)	S	O	BEDO-TTF
(10)	Se	Se	BEDS-TSF
(11)	S	Se	BEDS-TTF



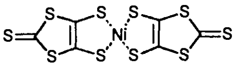
(12) DMET



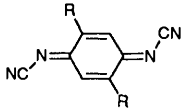
(13) MDT-TTF



(14) R = H TCNQ
(15) R = Me 2,5-DMTCNQ



(16) Ni(dmit)$_2$



(17) R = H DCNQI
(18) R = Me 2,5-DMDCNQI

3 Physical Concepts

Rigorous treatment of this topic is available elsewhere.[1b,i] A few basic points outlined here are of particular relevance to chemists engaged in the design and study of new materials. Conducting CT salts are composed of highly ordered arrays of donor [*e.g.* (1)—(13)] and acceptor [*e.g.* (14)—(18)] species, one or both of which must be a radical ion which is thermodynamically stable. The materials can be either single-chain conductors, *e.g.* (TMTSF)$_2^{+\bullet}$ X$^-$ salts where the anion is a closed shell species, or two-chain conductors, *e.g.* TTF$^{+\bullet}$–TCNQ$^{-\bullet}$ charge-transfer complexes in which both components are open shell molecules. The presence of a supermolecular orbital provides a mechanism for metallic delocalization of electrons, with the width of the conduction band dependent upon interactions between molecular orbitals on neighbouring molecules. However, the extensive interaction of molecular orbitals is not enough in itself to produce metallic (or even semiconducting) properties in a material. The occupancy of these energy bands is critically important: when the energy gap between the valence band (derived from the HOMO of the molecules) and the conduction band (derived from the LUMO of the molecules) is large, the material is an insulator. As the band gap decreases, thermal excitation of electrons from the valence band to the conduction band is possible and the material is an intrinsic semiconductor. Metallic behaviour requires partially filled bands in which it is possible for a large number of electrons to move easily into infinitesimally higher energy states within the band (Figure 2). The highest occupied state is called the Fermi level and it is the electrons in energy states very near to this level that influence the physical properties. In CT complexes these states are derived from the HOMOs of the donor species and the LUMOs of the acceptor species. The temperature dependence of conductivity in organic (and inorganic) metals is dominated by the interaction (scattering) of electrons with vibrations of the atomic lattice (phonons); as the temperature is lowered there are fewer lattice vibrations which, in effect, increases the intermolecular orbital overlap, so the conductivity increases. In contrast to this, the conductivity of a semiconductor

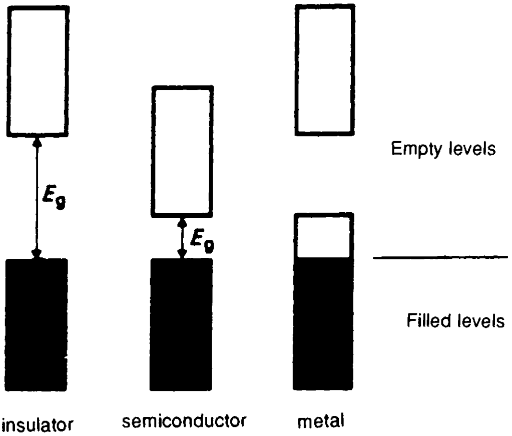


Figure 2 *Band structure of a solid; this determines the electrical properties.* E_g *is the energy gap between occupied and empty states*

decreases as the temperature is lowered, because there is less energy available to excite charge carriers across the band gap.

Superconductivity (the passage of an electric current without resistance) as described by the Bardeen, Cooper, and Shrieffer theory for inorganic materials, is caused by the highly coordinated motion of electron pairs (Cooper pairs.)[31] This mechanism is clearly distinct from metallic conduction for which individual electrons are the charge carriers. Electron pairing can be driven by phonons below a critical temperature, T_c, if a strict set of structural and electronic energy conditions is fulfilled; at higher temperatures the thermal agitation of the electrons dissociates the pairs and superconduction is lost. Currently it is not clear whether or not BCS theory can adequately explain organic superconduction.[2b]

In order to obtain efficient intermolecular interactions in a CT salt, the structural and redox properties of the constituent molecules are clearly of crucial importance. (There are, of course, other important design constraints, and these have been discussed recently.[1k]) The donor and/or acceptor moieties are typically planar (or nearly planar) molecules that form either segregated stacks or planar sheets. Thus the resultant electrical properties of the salt are highly anisotropic, *i.e.* associated with a unique direction within the crystal. Many organic metals are therefore termed quasi-one-dimensional metals. The behaviour of such a system was discussed over thirty years ago when Fröhlich[32] and Peierls[33] pointed out that at low temperature a quasi-one-dimensional metal could not sustain long-range order but would be unstable with respect to lattice distortions. (The chemical analogue is the well-known Jahn–Teller distortion.) The degree of

[31] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.*, 1957, **108**, 1175.

[32] H. Fröhlich, *Proc. R. Soc. London., Ser. A*, 1954, **223**, 296.

[33] R. E. Peierls, 'Quantum Theory of Solids', Oxford University Press, London, 1955.

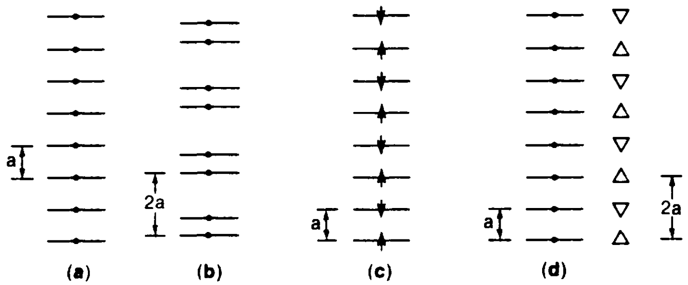


Figure 3 *Several possible configurations of a one-dimensional stack of molecules with one electron in the HOMO: (a) metal with uniform lattice constant a; (b) insulator with dimerization resulting from a Peierls transition; (c) SDW insulator with spin (↑) periodicity caused by Coulomb interactions; (d) insulator with periodicity caused by ordering of non-symmetric anions*
(Redrawn from R. L. Greene and G. B. Street, *Science*, 1984, **226**, 651)

instability depends upon the level of band filling (*i.e.*, in simple terms, the number of radical ionic and neutral molecules in the stack). A half-filled band has no neutral molecules in the stack, and as each molecule has an unpaired spin there is an electronic driving force for spin pairing. When molecules dimerize in this way there is concomitant creation of an energy gap between bonding and antibonding energy levels and so metallic conduction is lost. This is known as the Peierls distortion and the alternating regions within the lattice of higher and lower charge density result in the generation of a charge density wave (CDW). When neutral molecules are present in the stack, the resulting band will be less than half filled. For non-integral fractions of band filling the CDW periodicity will no longer be commensurate with the lattice and the CDW will be free to translate to new positions, so acting as a charge carrier.[34] For the complex TTF–TCNQ, the bandwidths of the TTF and TCNQ stacks are quite different, and although the CDW and the lattice periodicities are incommensurate (the charge on each stack is non-integral, *viz.* 0.59) ordering of the CDWs on different stacks, relative to each other, provides a mechanism for the Peierls instability which leads to an insulating state below *ca.* 40 K.[35]

In low-dimensional conductors, metal–insulator transitions can also be driven by either spin density waves (SDW) or anion ordering (Figure 3). The former instability was first identified in the salt $(TMTSF)_2\ PF_6$: the electron spins order antiferromagnetically (alternating spin up and spin down) which restricts electron mobility by introducing an energy gap in the electronic band.[36] Application of external pressure on crystals of TMTSF salts may suppress this transition, and for some systems, result in a superconducting ground state.[1c] Why a magnetic (SDW) transition and not a Peierls (CDW) transition should occur in

---

[34] D. Jérome and H. J. Schultz, *Springer Ser. Solid State Phys.*, 1981, **23**, 239.

[35] P. Coppens, V. Petricek, D. Levendis, F. K. Larsen, A. Paturle, G. Yan, and A. D. LeGrand, *Phys. Rev. Lett.*, 1987, **59**, 1695.

[36] W. M. Walsh, F. Wudl, E. Aharon-Shalom, L. W. Rupp, J. M. Vandenberg, K. Andres, and J. B. Torrance, *Phys. Rev. Lett.*, 1982, **49**, 885.

these salts is not clear at present The effect of anion ordering on metal–insulator transitions was also first appreciated from studies of a series of $(TMTSF)_2$ X salts (X = PF_6, AsF_6, ReO_4, ClO_4 *etc*)[1b,i] At room temperature the anions have random orientations, whereas at low temperature they orient to give three-dimensional superstructures If the periodicity of this superstructure matches that of the electrons at the Fermi level, an energy gap will open

4 New Conducting CT Materials; Design, Synthesis, and Properties

A. General Aspects—The global challenge for chemists working on conducting CT salts is the preparation of new molecular systems which meet the stringent requirements, both at the intra- and inter-molecular level, for high conductivity or superconductivity Since our ability to induce molecules to pack within a crystal lattice in a prescribed fashion (*e g* in dimer pairs or in sheets) is still very limited, the rational design of new conducting salts is essentially restricted to controlling the key properties of the individual molecules which can be deduced *a priori*, *e g* planarity, ionization potential/electron affinity, extent of conjugation [Some control over intermolecular arrangements in CT salts can be obtained in the form of Langmuir–Blodgett films (Section 6)] When a new donor or acceptor molecule is in hand it is invariably necessary to crystallize several salts and screen their properties (*e g* conductivity, magnetic susceptibility, and *X*-ray crystal structure)—only then will the effects of the new structural modification become apparent †

The desire to prepare CT systems with increased dimensionality of structural, and hence electrical, properties has been prevalent in the work of many groups This stems from the fact that the superconducting salts of TMTSF (4)[1c,37] and BEDT–TTF (8)[1i,j] were quickly recognized to be two-dimensional materials (not one-dimensional like TTF–TCNQ) with a strong network of inter-stack, as well as intra-stack, chalcogen–chalcogen interactions playing a key role in eliminating the Peierls transition While TMTSF salts do form donor stacks with close Se$\cdots$Se contacts, the structures of $(BEDT\text{-}TTF)_2$ X salts are dominated by short *inter*-stack S$\cdots$S interactions rather than intra-stack interactions, leading to little or no columnar stacking, and, for some BEDT–TTF salts, conductivity values are higher in the 'sheet' rather than in the 'stack' direction (*cf* Figures 4 and 5)

An increase in dimensionality can be encouraged in two ways (i) by placing polarizable heteroatoms (usually S, Se, or Te) at peripheral sites in the constituent donor or acceptor molecules, (ii) by judicious (or serendipitous!) choice of the inorganic counterions for subsequent CT salt formation Three major goals of recent years have been (i) to stabilize the metallic state down to the lowest observable temperatures by thwarting the Peierls distortion, (ii) to increase the critical temperature for the onset of superconductivity, (iii) to

---

† Two general methods are available for salt formation slow cooling of a saturated solution of the donor and acceptor (*e g* TTF—TCNQ) and electrolysis The latter method is particularly suitable when the anion is an inorganic species *e g* $(TMTSF)_2$ X or $(BEDT\ TTF)_2$ X Indeed this is the only method by which most of these salts are obtained

[37] F Wudl *J Am Chem Soc* 1981 **103** 7064

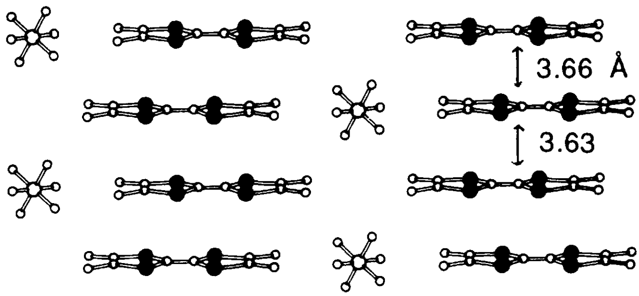


Figure 4 X-*Ray crystal structure of* $(\mathrm{TMTSF})_2^{+\cdot}$ PF_6^- *which is a superconductor under pressure. Selenium atoms are shaded. The overlap of selenium π-orbitals along the stacks forms a conduction band with a width of ca.* 1 eV
(Redrawn from N. Thorup, G. Rindorf, H. Soling, and K. Bechgaard, *Acta. Cryst.*, 1981, **B37**, 1236)

discover new families of metallic and superconducting salts based on new donor or acceptor molecules that are structurally quite different from those already known.

B. Metals and Superconductors Based on π-Donors.—(i) *Sulphur-based Systems.* Since the discovery in 1983 of superconductivity in salts of BEDT–TTF (8),[18] sulphur-based systems have attracted the most attention. More than half the known ambient pressure superconductors are salts of BEDT–TTF (8).[2b] The first reported synthesis of the neutral donor (8) was by Cava *et al.*[38] from dithiolate salt (19).[39] This procedure has recently been improved,[40] and an alternative route from (24) is equally efficient[41] (Scheme 1). The non-planar structure of donor (8) together with the large thermal vibration of the peripheral ethylene bridges impedes good π-overlap along a face-to-face stacking axis. This fact, combined with prevalent intercolumn S···S networks, leads to increased dimensionality in the structural and transport properties of BEDT–TTF salts.

The study of cation radical salts of BEDT–TTF (8) is complicated by the existence of multiple stoicheiometries and structural phases for the same anion. For example, four stoicheiometrically unique phases, termed α, β, θ, and κ phases, are known for the $(\mathrm{BEDT{-}TTF})_2\,\mathrm{I}_3$ salt! While the α-phase is a metal ($T_{\mathrm{M-I}}$ at 135 K) the other three phases are ambient pressure superconductors with T_c 1.5 K (8 K at 0.5 kbar), 3.6 K, and 3.6 K, respectively. The intricate relationship between crystal packing and solid state properties of salts of (8) has been extensively studied, notably by American[1j,42] and Japanese teams.[43] Two

---

[38] M. Mizuno, A. F. Garito, and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1978, 18.

[39] G. Steimecke, H.-J. Sieler, R. Kirmse, and E. Hoyer, *Phosphorous and Sulfur*, 1979, 7, 49.

[40] K. S. Varma, A. Bury, N. J. Harris, and A. E. Underhill, *Synthesis*, 1987, 837.

[41] J. Larsen and C. Lenoir, *Synthesis*, 1989, 134.

[42] A. M. Kini, M. A. Beno, K. D. Carlson, J. R. Ferraro, U. Geiser, A. J. Schultz, H. H. Wang, J. M. Williams, and M.-H. Whangbo, in ref. 3c, p. 334.

[43] H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, A. Tamaka, T. Mori, Y. Maruyama, and H. Inokuchi, *Chem. Lett.*, 1985, 463 and references therein.

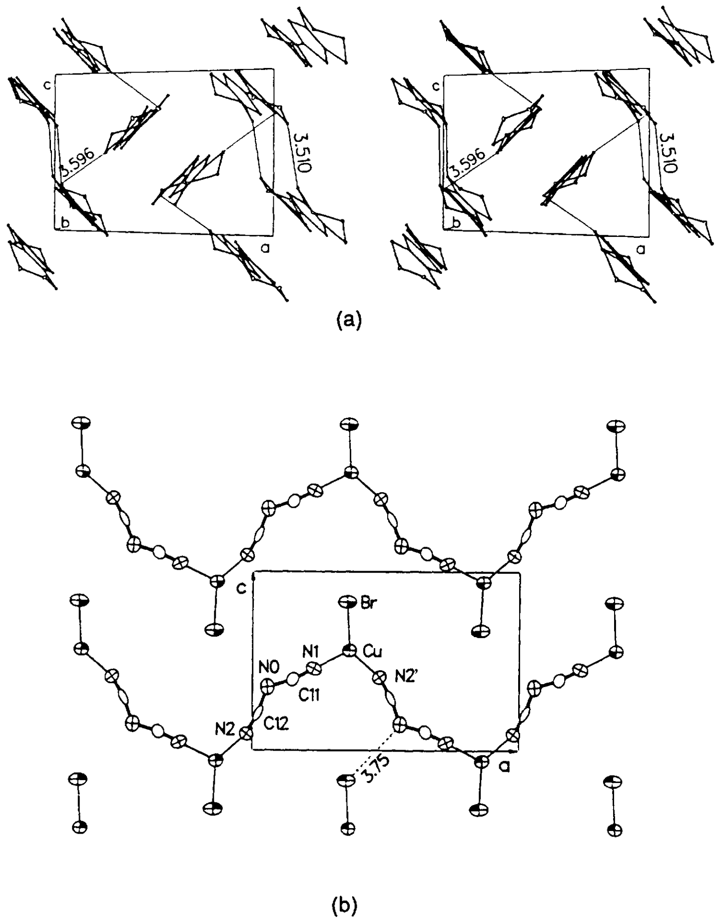
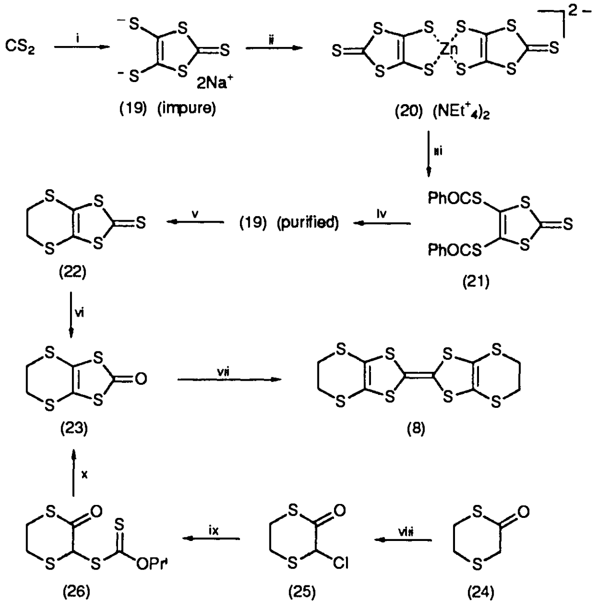


Figure 5 X-*Ray crystal structure of the superconductor* κ-(BEDT–TTF)$_2$ Cu[N(CN)$_2$]Br (*a*) *stereoview of the donor layer showing Kappa arrangement of orthogonal dimers, and intermolecular* S•••S *contacts shorter than* 3.60 Å; (*b*) *polymeric anion layer*
(From reference 30*a*; figures kindly supplied by Professor A. M. Kini)

common structural features of the (BEDT–TTF)$_2$ X salts that are known to have T_c values in excess of 10 K [*viz.* X = Cu(NCS)$_2$,[27] Cu[N(CN)$_2$]Br,[30a] and Cu[N(CN)$_2$] Cl[30b] have been identified.[30] First, there is κ-type packing of the BEDT–TTF molecules: this motif does not comprise stacks or sheets of the donors, but, instead, interacting dimers which are positioned approximately orthogonal to each other forming a conducting two-dimensional S•••S network (Figure 5a). Secondly, the anions in these three salts form insulating V-shaped polymeric chains (Figure 5b). The use of these anions followed from the observation that T_c for BEDT–TTF salts increases concomitantly with increased



Reagents: i, Na, DMF; ii, $ZnCl_2$, Et_4NBr; iii, PhC(O)Cl; iv, NaOEt; v, NH_4OAc, $BrCH_2CH_2Br$; vi, $Hg(OAc)_2$; vii, $P(OEt)_3$; viii, *N*-chlorosuccinimide; ix, $K^+ \, {}^-SC(S)OPr^i$; x, H_2SO_4

Scheme 1

linear anion length.[1j] Currently the highest T_c organic superconductor at ambient pressure, is κ-(BEDT–TTF)$_2$ Cu[N(CN)$_2$]Br with $T_c = 11.6$K;[30a] the isostructural chloride salt has $T_c = 12.5$K at 0.3kbar pressure[30b] (Figure 6). Both these salts were discovered by Kini, Williams, and co-workers at Argonne. The κ-type dimer structure is not unique to (BEDT–TTF)$_2$; it is present in cation radical salts derived from three other donor systems, *viz.* (BMDT–TTF)$_2$ Au(CN)$_2$ (metallic),[44] (MDT–TTF)$_2$AuI$_2$ (superconducting),[26,45] and the mixed S,Se system (DMET)$_2$AuBr$_2$ (superconducting).[46] It is notable that these last three donors are unsymmetrical molecules and it is tempting to suggest that this favours the formation of the κ-structure. However, as pointed out by Kini *et al.*,[42] there are, as yet, no clear guidelines to follow in this respect.

---

[44] P. J. Nigrey, B. Morosin, J. F. Kwak, E. L. Venturini, and R. J. Baughman, *Synth. Met.*, 1986, **16**, 1.

[45] A. M. Kini, M. A. Beno, D. Son, H. H. Wang, K. D. Carlson, L. C. Porter, U. Welp, B. A. Vogt, J. M. Williams, D. Jung, M. Evain, M.-H. Whangbo, D. L. Overmyer, and J. E. Schirber, *Solid State Commun.*, 1989, **69**, 503.

[46] K. Kikuchi, Y. Honda, Y. Ishikawa, K. Saito, I. Ikemoto, K. Murata, H. Anzai, T. Ishiguro, and K. Kobayashi, *Solid State Commun.*, 1988, **66**, 405.

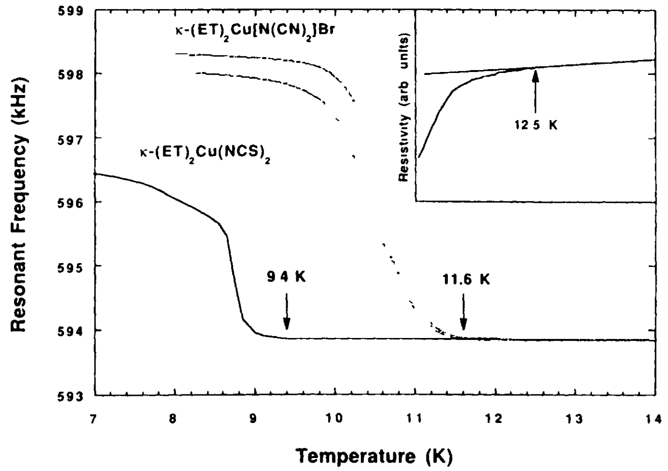


Figure 6 *Evidence of superconducting transition for crystals of* κ-(BEDT–TTF)$_2$ Cu[N(CN)$_2$]Br *and* κ-(BEDT–TTF)$_2$ Cu(NCS)$_2$
(From reference 30*a*)

Many other all-sulphur organic donors that are variants of TTF (1) or BEDT–TTF (8) have been reported recently.[3] Only one of these, MDT–TTF (13), has provided new superconductors. Papavassiliou *et al.* first reported that the gold iodide salt (MDT–TTF)$_2$ AuI$_2$ is a superconductor with $T_c = 3.5$K at ambient pressure.[26] (It should be noted that neither of the parent symmetrical donors, *i.e.* TTF and BMDT–TTF, yield superconductors.) The discovery of this second family of superconductors based on an unsymmetrical donor [the first was DMET (12) (Section 4Bii)] has highlighted the need for efficient synthetic routes to unsymmetrical systems.[47] While a few new approaches have been published, none is yet established as a general route.[48] Studies on most unsymmetrical TTF and BEDT–TTF analogues are, therefore, still hampered by synthetic problems.

A quite different skeletal variation to the donor system, *viz.* vinylogous derivatives of TTF (1) and BEDT–TTF (8) have attracted attention for the following reasons: increased separation of the 1,3-dithiole rings should lead to considerably reduced on-site Coulombic repulsion in the dication redox state,[49] and hence, a non-correlated type of conductivity may be possible. Yoshida *et al.* were the first to prepare extended TTFs of this type, *e.g.* compound (27).[50] We

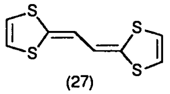
---

[47] For a review of the synthesis of TTF systems. see A Krief, *Tetrahedron*, 1986, **42**, 1209

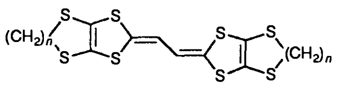
[48] For examples see (*a*) A M Kini, S F Tytko, J E Hunt, and J M Williams, *Tetrahedron Lett*, 1987, **28**, 4153, (*b*) K Lerstrup, I Johannsen, and M Jorgensen, *Synth Met*, 1988, **27**, B9. (*c*) K Lerstrup. M Jorgensen, I Johannsen, and K Bechgaard, in ref 3*c*, p 383, (*d*) M R Bryce, A J Moore, D Lorcy, A S Dhindsa, and A Robert, *J Chem Soc , Chem Commun* , 1990, 470

[49] *Cf* other highly conjugated redox systems discussed previously S Hunig and H Berneth, *Top Curr Chem* , 1980, **92**, 1

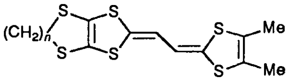
[50] (*a*) Z Yoshida, T Kawase, H Awaji, I Sugimoto, T Sugimoto. and S Yoneda, *Tetrahedron Lett*. 1983, **24**, 3469, (*b*) T Sugimoto, H Awaji, I Sugimoto, Y Misaki, T Kawase, S Yoneda. and Z Yoshida, *Chem Mater* . 1989, **1**, 535



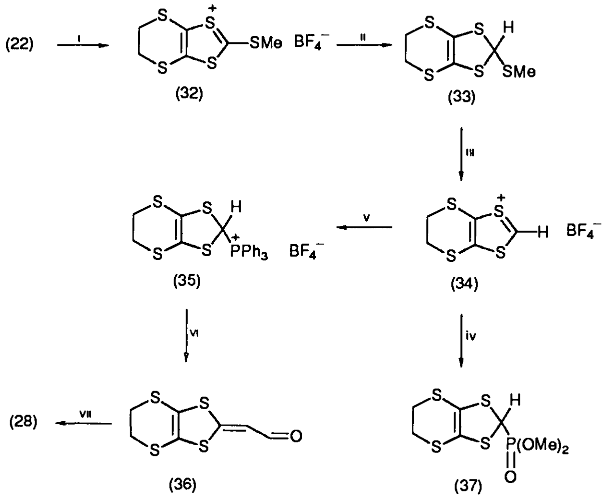
(27)



(28) $n = 2$
(29) $n = 3$



(30) $n = 2$
(31) $n = 3$



Reagents: i, $(MeO)_2SO_2$, AcOH, HBF_4; ii, $NaBH_4$; iii, Ac_2O, HBF_4; iv, $P(OMe)_3$, NaI; v, PPh_3; vi, Et_3N glyoxal; vii, (37), Bu^nLi

Scheme 2

have recently reported the synthesis of (28), the first vinylogous derivative of BEDT–TTF (8), along with several other new, extended donors, *e.g.* molecules (29)–(31).[51] Two other groups have independently prepared compound (28).[52,53] Our synthesis of (28) is shown in Scheme 2.[51a,54] It is notable that this methodology is readily adaptable to the preparation of unsymmetrical systems, *e.g.* (30) and (31). Compound (30) has furnished the first *X*-ray crystal structure of a vinylogous donor of the TTF or BEDT–TTF families: molecule (30) is significantly more planar than BEDT–TTF (8) (Figure 7).

Cyclic voltammetry has established the solution redox behaviour of the new

---

[51] (*a*) A. J. Moore, M. R. Bryce, D. Ando, and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1991, 320; (*b*) A. J. Moore and M. R. Bryce, manuscript in preparation.

[52] V. Y. Khodorkovskii, L. N. Veselova, and O. Ya. Neiland, *Khim. Geterotsikl. Soedin.*, 1990, 130; (*Chem. Abs.*, 1990, **113**, 22868t).

[53] T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. M. Metzger, and J. Becher, *J. Org. Chem.*, 1991, **56**, 2720.

[54] A. J. Moore and M. R. Bryce, *Synthesis*, 1991, 26.

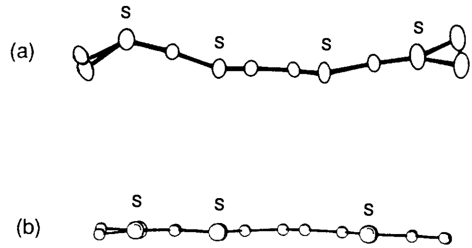


Figure 7 *Molecular structure of the neutral donors (a)* BEDT TTF (8) *and (b) molecule* (30) *as determined by single crystal* X *ray analysis a view along the best plane formed by the sulphur atoms Note the marked deviation from planarity of* BEDT TTF

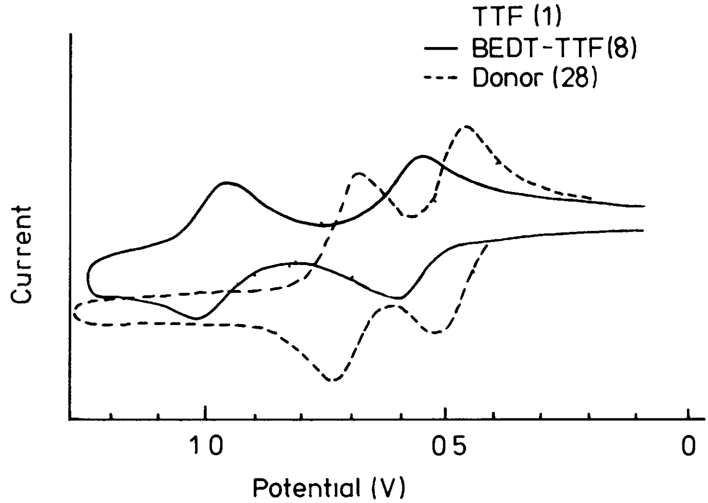
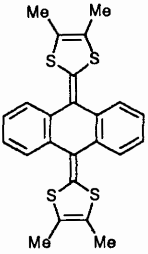


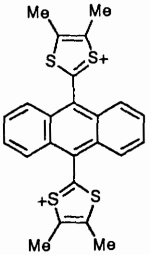
Figure 8 *Cyclic voltammetric data for* TTF (1) BEDT TTF (8) *and vinylogous* BEDT TTF *derivative* (28) (Pt *electrode* versus Ag/AgCl, *electrolyte* EtN_4^+ PF_6 *in* CH_2Cl_2)

vinylogues (28)—(31) They undergo two, reversible, single-electron oxidations (as do TTF and BEDT–TTF) and two important consequences of 'stretching' the conjugated π-system in this way are observed (i) both the first and second oxidation potentials of (28) are substantially lowered in comparison with BEDT–TTF, *i e* molecule (28) is a stronger donor than BEDT–TTF (8), and $E_2^{\frac{1}{2}}$ (the radical cation–dication redox wave) for (28) and TTF (1) are seen at very similar potentials, (ii) the difference between the two redox waves, $\Delta E^{\frac{1}{2}}$, is also reduced in the vinylogue (Figure 8) [51] These stretched donors appear, therefore, to be very promising candidates for the preparation of new families of organic metals and superconductors that could be structurally and electronically very different from their predecessors

Donor (38), which can also be viewed as a stretched TTF system, has been



(38) reduced form



(38') oxidized form

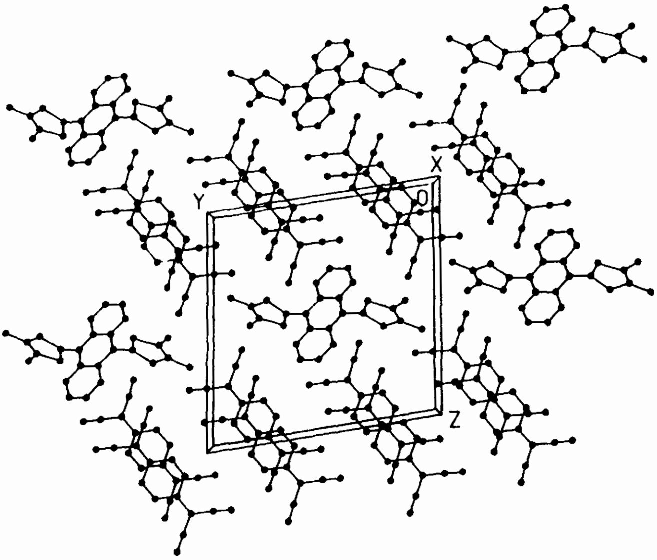


Figure 9 X-*Ray crystal structure of the conducting* 1:4 *complex formed by donor* (38) *and* TCNQ (14), i.e. $(38')^{2+}$-$(TCNQ)_4^{2-}$

studied recently.[55] An unusual 1:4 salt is formed with TCNQ, and magnetic susceptibility data establish that the donor is present in the dication redox state (38'). The *X*-ray structure reveals four TCNQ stacks surrounding each dication molecule (Figure 9). The two 1,3-dithiolium cations in structure (38') are almost orthogonal to the planar anthracene ring, which is a conformation very different from the butterfly shape adopted by the neutral donor (38). The conductivity of the salt derives from charge delocalization on the uniform TCNQ stacks; at room temperature $\sigma_{rt} = 60 \mathrm{S cm^{-1}}$ and this value is maintained down to *ca.* 100K when the salt becomes insulating. This work establishes that (i) extended conjugation between the two heterocyclic rings reduces on-site Coulombic repulsion such that

---

[55] M. R. Bryce, A. J. Moore, M. Hasan, G. J. Ashwell, A. T. Frazer, W. Clegg, M. B. Hursthouse, and A. I. Karaulov, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 1450.

in the solid state the dication redox form is stable and (ii) interesting materials can result from the study of TTF analogues which have very distorted (non-planar) structures

(ii) *Selenium- and Tellurium-containing Systems* In the late 1970s and early 1980s organoselenium donors provided a bonanza for the physicists the metallic state was stabilized to very low temperatures (*e g* HMTSF–TCNQ)[13] and the first generation of organic superconductors [*viz* the (TMTSF)$_2$X salts] were discovered by Bechgaard [16] Much work concerned the specific role played by the inorganic anions with respect to the ground state of these salts, which can be either insulating, metallic, or superconducting The origin of the insulating ground state appears to be related to the symmetry of the anion For centrosymmetric anions, *e g* PF$_6$ and AsF$_6$, the ground state is due to formation of a spin density wave phase ($T_c < 12$ K) while in the salts with non-centrosymmetric anions, *e g* ReO$_4$ and FSO$_3$, the metal-to-insulator phase transition is driven by ordering of the anions (see Section 3) In both cases, when single crystals are subjected to a finite external pressure the insulating phase is suppressed, leading to metallic behaviour and eventually a superconducting ground state Within the TMTSF series, the perchlorate salt remains the only one to superconduct at ambient pressure

More recently, selenium-containing systems have been overshadowed by their sulphur bretheren in comparison, the selenium donors are invariably much harder to synthesize,[56] are insoluble, and the oxidation potential is raised by sequential selenium incorporation [48d,57] In contrast to BEDT–TTF (8), superconductivity has not been found in salts of the selenium analogues BEDS–TSF (10)[58] or BEDS–TTF (11),[59] even though the β-phase of the triiodide salt (BEDS–TTF$_2$)I$_3$ is isostructural[59] with (BEDT–TTF$_2$)I$_3$, which has $T_c = 8$ K under pressure [20]

Of the many mixed S,Se donors that are now known,[60] only the DMET system (12) has so far yielded superconducting salts [61] The synthesis of DMET (12) is shown in Scheme 3 [62] The desired product (12) has to be separated from the symmetrical products TMTSF (4) and BEDT–TTF (8), which is the problem inherent in the synthesis of an unsymmetrical donor by a cross-coupling reaction An efficient synthesis of selenone (43) had been reported previously [63] The gold

---

[56] Review D Cowan and A Kini *in* The Chemistry of Organic Selenium and Tellurium Compounds Vol 2 ed S Patai J Wiley 1987 p 463

[5] E M Engler F B Kaufman D C Green C E Klots and R N Compton *J Am Chem Soc* 1975 **97** 2921

[58] (*a*) V Y Lee E M Engler R R Schumaker and S S P Parkin *J Chem Soc Chem Commun* 1983 235 (*b*) R Kato H Kobayashi and A Kobayashi *Chem Lett* 1986 785

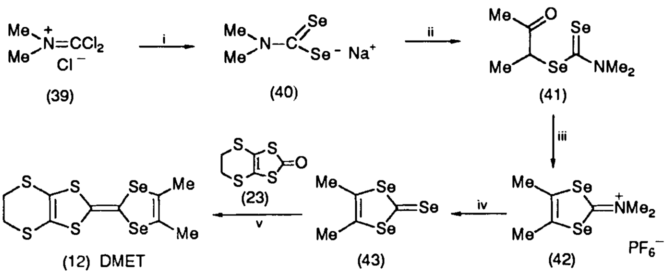
[59] H W Wang L K Montgomery H Geiser L C Porter K D Carlson J R Ferraro J M Williams C S Cariss R L Rubinstein and J R Whitworth *Chem Mater* 1989 1 140 and references therein

[60] (*a*) V Y Lee *Synth Met* 1987 **20** 161 (*b*) G C Papavassiliou G A Mousdis S Y Yiannopoulos V C Kakoussis and J S Zambounis *Synth Met* 1988 **27** B373

[61] K Kikuchi Y Honda Y Ishikawa K Saito I Ikemoto K Murata Y Anzai I Ishiguro and K Kobayashi *Solid State Commun* 1988 **66** 405

[62] K Kikuchi T Namiki I Ikemoto and K Kobayashi *J Chem Soc Chem Commun* 1986 1472

[63] A Moradpour V Peyrussen I Johannsen and K Bechgaard *J Org Chem* 1983 **48** 388



Reagents: i, NaHSe, Et_3N; ii, 2-chlorobutanone; iii, H_2SO_4, HPF_6; iv, NaHSe, AcOH; v, $P(OMe)_3$

Scheme 3

cyanide salt $(DMET)_2$ $Au(CN)_2$ was the first superconductor in this series, reported in 1987 by Japanese workers.[23] This material broke new ground as the donor (12) is an unsymmetrical molecule [it can be viewed as a hybrid of the TMTSF (4) and BEDT–TTF (8) molecules]. A range of electronic transport properties, from insulator to superconductor, are displayed by siblings of the $(DMET)_2$ X family, the highest T_c being 1.9 K at ambient pressure for the $AuBr_2$ salt.[61] Some DMET salts have the important κ-type structure discussed earlier (Section 4.2a). Overall the behaviour of DMET superconductors is intermediate between that of the TMTSF and BEDT–TTF systems.

Within the whole field of organic metals, the preparation of tetratellurafulvalene (TTeF) derivatives has proved to be one of the most daunting synthetic challenges. Work in the mid 1970s established that the substitution of the sulphur atoms of TTF with selenium generally had beneficial effects on the properties of the TCNQ salt: *viz.* increased room temperature conductivity and a lower M–I transition temperature; also, transport properties become dominated by the donor stack.[12] Further advantages that tellurium substitution could afford (over and above selenium) were identified by Cowan *et al.*:[64] *viz.* (i) the more diffuse *p* and *d* orbitals centred on Te should give larger conduction bandwidths (enhanced metallic conductivity) due to increased intrastack interactions, (ii) interchain interactions (*i.e.* two- and three-dimensional contacts) should be favoured which, in turn, should suppress Peierls distortions, (iii) the greater polarizability of Te should reduce on-site Coulombic repulsion in the dication state (*i.e.* $TTeF^{2+}$) [*cf.* compounds (28) and (38) discussed in Section 4.B(i)].

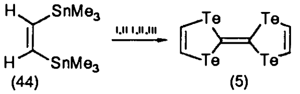
The first substituted TTeF derivatives were reported in 1982[65] and the long-awaited parent tellurium donor TTeF (5) arrived in 1987.[66] The five-step, one-

---

[64] D. O. Cowan, M. Mays, M. Lee, R. McCullough, A. Bailey, K. Lerstrup, F. Wiygul, T. Kistenmacher, T. Poehler, and L.-Y. Chiang, *Mol. Cryst. Liq. Cryst.*, 1985, **125**, 191.

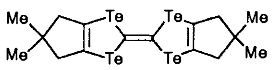
[65] (*a*) K. Lerstrup, D. Talham, A. Bloch, T. Poehler, and D. Cowan, *J. Chem. Soc., Chem. Commun.*, 1982, 336; (*b*) F. Wudl and E. Aharon-Shalom, *J. Am. Chem. Soc.*, 1982, **104**, 1154.

[66] (*a*) R. D. McCullough, G. B. Kok, K. A. Lerstrup, and D. O. Cowan, *J. Am. Chem. Soc.*, 1987, **109**, 4115; (*b*) for an improved synthesis of TTeF see: R. D. McCullough, M. D. Mays, A. R. Bailey, and D. O. Cowan, *Synth. Met.*, 1988, **27**, B487.

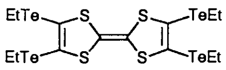


Reagents i, Bu^{n}Li, −78 °C, ii, Te, −78 °C, iii, $Br_2C{=}CBr_2$

Scheme 4



(45)



(46)

pot synthesis of (5) developed in Cowan's laboratory is shown in Scheme 4.[66b] Electrochemical data, obtained by cyclic voltammetry, indicate an ionization potential for TTeF intermediate between that of TTF and TSF, with the difference between the first and second oxidation waves, $\Delta E^{\frac{1}{2}}$, following the expected trend TTeF < TSF < TTF.[66a] The conductivity of the complex TTeF–TCNQ is very high, $\sigma_{rt} = 2200 \pm 300\,\mathrm{S\,cm^{-1}}$, and this value increases down to 2K (*i.e.* there is no Peierls distortion).[25] It has, therefore, been established that within the TXF–TCNQ series, electrical conductivity increases as X varies from S to Se to Te, and this increase is primarily caused by conductivity enhancement in the donor stacks. The *X*-ray crystal structure of TTeF–TCNQ reveals layers of donor molecules with close inter- and intra-stack Te···Te contacts. This mode of packing is quite different from that of TXF–TCNQ (X = S, Se) which possess no interstack chalcogen interactions, and is more like the structure found for most $(TMTSF)_2$ X and $(BEDT\text{–}TTF)_2$ X salts. TTeF–TCNQ is, therefore, considered to be a two-dimensional metal.[25b]

Some new TTeF derivatives, *e.g.* tetramethylhexamethylene–TTeF (45), have been reported,[67] although tetramethyl–TTeF and molecules with mixed S, Te or Se, Te atoms in the fulvalene core are still unknown. However, attachment of tellurium atoms to the periphery of the TTF frame is relatively straightforward to accomplish by reaction of elemental tellurium with lithiated TTF species.[68] Several alkyltelluro sidechains have been attached in this way, *e.g.* to yield molecule (46), which forms a semi-conducting complex with TCNQ.[69]

(iii) *Oxygen-containing Systems.* Analogues of TTF (1) where any of the sulphurs in the fulvalene core have been replaced by oxygen are unknown. The first derivative with oxygen bonded directly to the periphery of TTF was the symmetrical BEDO–TTF molecule (9) reported by Wudl's group in 1989.[70] The synthesis is presented in Scheme 5.[70] Contrary to the popular view that the more

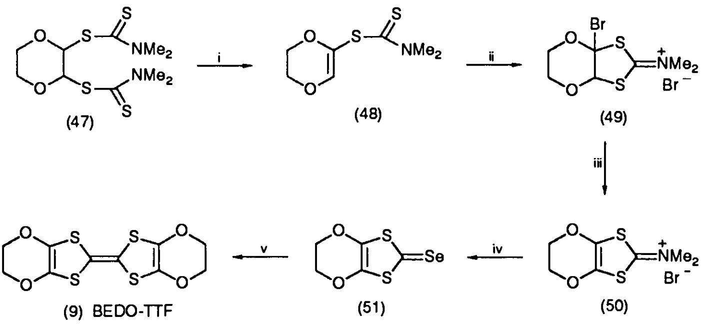
---

[67] A R Bailey, R D McCullough, M D Mays, D O Cowan, and K A Lerstrup, *Synth Met*, 1988, **27**, B425

[68] (*a*) E Aharon-Shalom, J Y Becker, J Bernstein, S Bittner, and S S Shaik, *Tetrahedron Lett*. 1985, **26**. 2783, (*b*) J Y Becker, J Bernstein, S Bittner, J A R P Sharma. and L Shahal, *Tetrahedron Lett*. 1988, **29**. 6177, (*c*) N Iwasawa, F Shinozaki, G Saito, K Oshima, T Mori, and H Inokuchi. *Chem Lett*, 1988, 215

[69] E Aharon-Shalom, J Y Becker, J Bernstein, S Bittner. and S Shaik, *Synth Met*, 1985, **11**, 213

[70] T Susuki, H Yamochi. G Srdanov. K Hinkelmann, and F Wudl, *J Am Chem Soc*, 1989, **111**, 3108



Reagents: i, 110 °C, DMSO; ii, Br_2; iii, 110 °C, 25 Torr; iv, H_2Se; v, $(MeO)_3P$

Scheme 5

polarizable chalcogens Se and Te offered the best hopes for metallic and superconducting behaviour, [Section 4.B(ii)], Wudl reasoned that oxygen substitution was a promising way forward.[70] First, according to BCS theory of superconductivity, the lighter the component atoms within a series of donors, the higher should be the T_c value in an isostructural salt.† Secondly, there may be a remote link between O-containing organic superconductors and the 'high T_c' copper oxide superconductors, where oxygen radical cations may be involved in the conduction process.‡

Studies on the first organic metal formed by this new donor, $(BEDO\text{–}TTF)_{2.4}$ I_3, suggest that oxygen substitution can increase the metallic bandwidth: the metallic state is stabilized down to low temperatures and the physical behaviour is reminiscent of a classical 3-dimensional metal. The *X*-ray structure reveals short interstack S•••S and S•••O contacts.[28] One superconducting salt of BEDO–TTF has been discovered: this is $(BEDO\text{–}TTF)_3$ $Cu_2(NCS)_3$ with $T_c =$ 1.06 K.[29] Some unsymmetrically substituted ethylenedioxytetrathiafulvalene donors have been synthesized but their salts have not yet been characterized.[71]

5 Metals and Superconductors Based on Organic π-Acceptors

In recent years two families of π-acceptor molecules have provided exciting results: these are the $metal(dmit)_2$ and DCNQI systems. We will consider these in turn and then briefly mention a few other promising acceptor systems.

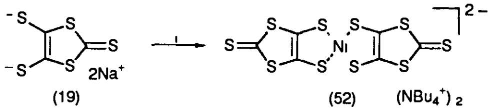
A. Metal(dmit)$_2$ Acceptors.—These acceptors (52) which are metal complexes of the 1,2-dithiolene ligand (19) have three notable features: (i) the $M(dmit)_2$ system is nearly planar; (ii) there are ten peripheral sulphur atoms which can engage in

---

† For a BCS superconductor, T_c should vary inversely with the square root of the mass of the ions in the lattice.

‡ Other workers have commented on some general similarities between organic CT salts and CuO superconductors: *e.g.* both types of compound are layered, narrow band structures with close proximity of superconducting and antiferromagnetic ground states.[3c,d]

[71] (*a*) A. M. Kini, T. Mori, U. Geiser, S. M. Budz, and J. M. Williams, *J. Chem. Soc., Chem. Commun.*, 1990, 647; (*b*) T. Mori, H. Inokuchi, A. M. Kini, and J. M. Williams, *Chem. Lett.*, 1990, 1279.



Reagents i $NiCl_4$ NBu_4Br

Scheme 6

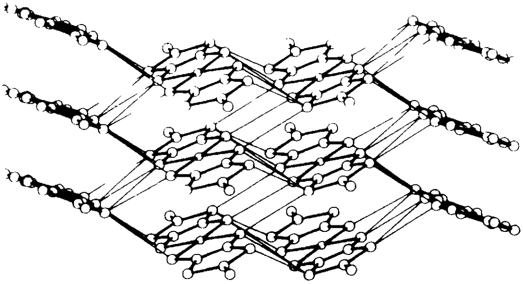


Figure 10 X-*Ray crystal structure of* TTF[Ni(dmit)$_2$]$_2$ *viewed in the plane of the* TTF *ring Thin lines indicate* S··· S *distances shorter than* 3 70 Å
(From reference 72a)

intra- and inter-stack interactions, and (iii) the redox properties can be tuned by varying the central metal atom (Ni, Pt, Pd, *etc*) The metal complexes (52) are synthesized from ligand (19) as shown in Scheme 6[39] (*cf* Scheme 1) Metal(dmit)$_2$ anions have been studied in combination with alkali metal cations, open shell organic cations (*eg* TTF)[21 72 73] and closed shell organic cations (*eg* tetraalkylammonium salts)[24 74] Superconductivity has been found in the last two classes of material

It was first reported by Cassoux *et al* in 1984 that TTF[Ni(dmit)$_2$]$_2$ remained metallic at very low temperatures and that the crystal structure was essentially three-dimensional, comprising segregated stacks of donors and acceptors with close lateral interstack S···S contacts (Figure 10)[75] The electronic structure of the system is, however, still under discussion and, based on extended Huckel band calculations, Kobayashi *et al* concluded that the lateral interactions are very weak and the salt should be considered as a one-dimensional metal The origin of the stable metallic state in TTF[Ni(dmit)$_2$]$_2$ lies not in the multi-dimensionality of the band structure, but rather in the nature of the multi-Fermi

---

[72] (*a*) M Bousseau L Valade J P Legros P Cassoux M Garbauskas and L V Interrante *J Am Chem Soc* 1986 **108** 1908 (*b*) P Cassoux L Valade J P Legros C Tejel J P Ulmet and L Brossard in ref 3c p 22

[73] (*a*) L Brossard H Hurdequint M Ribault L Valade J P Legros and P Cassoux *Synth Met* 1988 **27** B157 (*b*) L Brossard M Ribault L Valade and P Cassoux *J Phys France* 1989 **50** 1521

[74] K Kajita Y Nishio S Moriyama R Kato H Kobayashi W Sasaki A Kobayashi H Kim and Y Sasaki *Solid State Commun* 1988 **65** 361

[75] M Bousseau L Valade M F Bruniquel P Cassoux M Garbauskas L V Interrante and K Kasper *Nouv J Chim* 1984 **8** 653

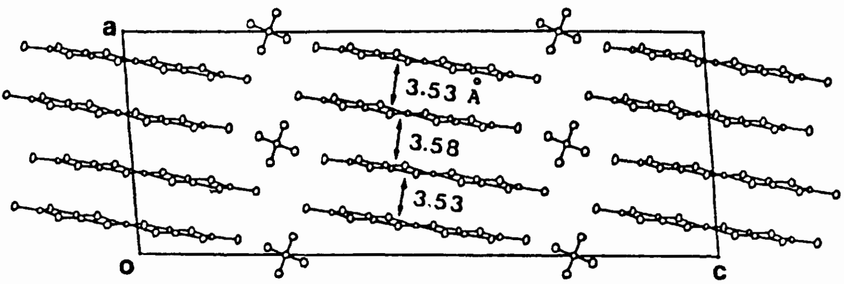
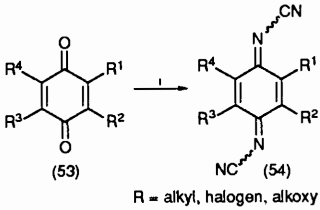


Figure 11 X-*Ray crystal structure of the anion stack superconductor* $Me_4N^+[Ni(dmit)_2]_2^-$ (From reference 24)



Reagents i, $TiCl_4$, $Me_3SiN{=}C{=}NSiMe_3$

Scheme 7

surface.[76] The salt shows superconductivity under pressure ($T_c = 1.6$ K at 7 kbar).[21]

Replacement of Ni by Pd affords the salt TTF$[Pd(dmit)_2]_2$, one phase of which (the α' phase) has the highest T_c value (6.5 K at 20 kbar) within the metal $(dmit)_2$ series of compounds.[73] This material provides the first example of competition at very low temperatures between a charge density wave and superconductivity [*cf.* it is a spin density wave that operates in salts of TMTSF and BEDT–TTF]. The partially oxidized TTF stacks, as well as the anion stacks, play an important role in the conduction process in these $M(dmit)_2$ salts, which are, therefore, two-chain conductors.

Salts of $Ni(dmit)_2$ anions with closed shell cations have also provided very interesting materials: the mixed valence salt $NMe_4[Ni(dmit)_2]_2$ is an anion-stack superconductor[24] ($T_c = 5$ K at 7 kbar) and the sodium salt $Na[Ni(dmit)_2]$ remains metallic down to at least 25 mK.[77] The *X*-ray crystal structure of the tetramethylammonium salt (Figure 11) reveals stacks of planar $Ni(dmit)_2$ anions separated by channels which contain the inorganic cations. This is the reverse situation to that of the TMTSF salts (*cf.* Figure 4).

B. *N,N'*-Dicyanoquinonediimine (DCNQI) Acceptors

This family of acceptors, which has been developed by Hünig and co-workers,

---

[76] A Kobayashi, H Kim, Y Sasaki, R Kato, and H Kobayashi, *Solid State Commun*, 1987, **62**, 57

[77] A Clark, A E Underhill, R H Friend, M Allen, I Marsden, A Kobayashi, and H Kobayashi, in ref 3c, p 28

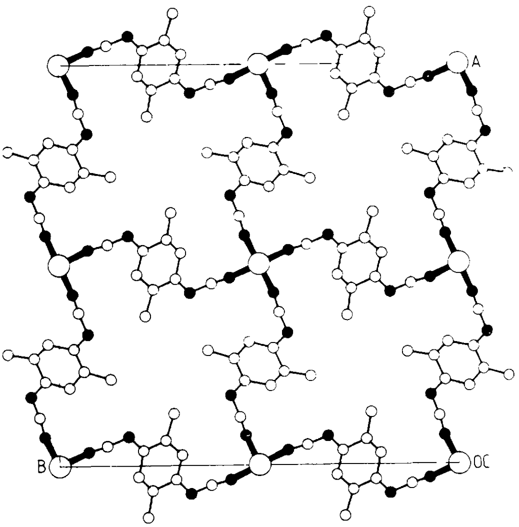


Figure 12 X-*Ray crystal structure of* Cu(2,5-DMTCNQI)$_2$, *nitrogen atoms are shaded* (From reference 22)

has three attractive features: (i) synthesis—DCNQIs (54) are produced in good yield in a one-pot synthesis from benzoquinones (53) (Scheme 7);[78] (ii) structure—since the =NCN group is flexible, and sterically less demanding than the =C(CN)$_2$ group, planarity of the DCNQI system is retained even upon tetrasubstitution[79] so close face-to-face stacking can occur in a wide range of derivatives [*cf.* tetrasubstituted TCNQ derivatives (14) have a buckled ring],[79] (iii) redox properties—the acceptor strength of DCNQI is similar to that of TCNQ and by appropriate substitution, the electron affinity can be finely tuned.

Conducting DCNQI radical anion salts have been characterized with π-donors (*e.g.* TTF), organic cations (*e.g.* tetramethylammonium) and metal cations.[80] The last class of compounds is the most interesting, especially those containing 2,5-disubstituted DCNQI acceptors, *e.g.* (18). Very high conductivities are achieved with a variety of metal monocations in salts of general formula M$^+$ (2,5-DMDCNQI)$_2^{-\bullet}$ (M = Cu, Ag, Tl, Ni, Na, K, Rb).[80] The *X*-ray crystal structure of Cu(2,5-DMDCNQI)$_2$ reveals that each metal atom is tetrahedrally coordinated to four DCNQI ligands by strong Cu···N interactions (d = 1.99 Å) and the acceptor forms one-dimensional columns (just like TCNQ) with an intrastack distance of 3.2 Å (Figure 12).[22] Many of the M(2,5-X$_2$DCNQI)$_2$ salts possess this structure[81] and the distance between the cations (3.78—3.97 Å) is too large

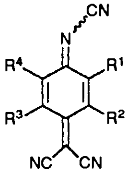
---

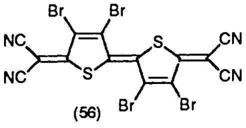
[78] A Aumuller and S Hunig, *Angew Chem, Int Ed Engl*, 1984, **23**, 447

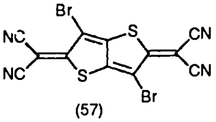
[79] U Schubert, S Hunig, and A Aumuller, *Liebigs Ann Chem*, 1985, 1216

[80] S Hunig and P Erk, *Adv Mater*, 1991, **3**, 225 and references therein

[81] S Hunig, H Meixner, T Metzenthin, U Langohr, J U von Schutz, H-C Wolf, and E Tillmans, *Adv Mater*, 1990, **2**, 361


(55) R^1—R^4 = H or Me


(56)


(57)

for electron transport to occur along a metal ion chain; conductivity is, therefore, ascribed to a partially filled band formed by the LUMOs of the DCNQI molecules.

The conductivity of the salt Cu(2,5-DMDCNQI)$_2$ is $\sigma_{rt} = 10^3\,\mathrm{Scm^{-1}}$ and this value steadily increases as the temperature is lowered to 1.3K without any interruption from a Peierls distortion.[22] Indeed at 3.5K, $\sigma = 5 \times 10^5\,\mathrm{Scm^{-1}}$. This conductivity is pseudo-three-dimensional with a value as high as $100\,\mathrm{Scm^{-1}}$ perpendicular to the stacking axis, with the N···Cu···N bridges providing a channel for conduction in this direction.[82] Based on low temperature *X*-ray diffraction and *X*-ray photoelectron spectra, Kobayashi *et al.* conclude that the copper atoms are present in a mixed valence state, *viz.* $\mathrm{Cu}^{1\ 3+}$, which could arise from admixture of the 3*d* orbitals on copper with the *p*π conduction band of the DMDCNQI ligands.[83] The spin susceptibility is Pauli paramagnetic and larger than that of most organic metals. Electron spin resonance studies indicate that the unpaired electrons residing on the Cu ions order antiferromagnetically below 10K through the organic π-system.[84]

Some other Cu(2,5-XY-DCNQI)$_2$ salts (X,Y = Me, I; MeO, MeO) retain metallic behaviour at very low temperatures, while many in this series (X,Y = Me, Cl; Me, Br; Cl, Cl; Cl, Br; Br, Br) undergo a metal-to-insulator transition at low temperatures, due to extensive deformation of the tetrahedral coordination around copper and a CDW instability on the DCNQI stacks.[83b]

C. Other Acceptors.—A few other quinonoid acceptor systems have been characterized recently. Several derivatives of compound (55), which is a hybrid of the TCNQ (14) and DCNQI (17) systems, yield semiconducting copper salts.[85] Incorporation of sulphur into the acceptor ring system with a view to increasing dimensionality has led to heterocyclic TCNQ and DCNQI analogues, *e.g.* compounds (56)[86] and (57),[87] respectively, which have provided some complexes with TTF of high conductivity.

---

[82] T Mori, K Imaeda, R Kato, A Kobayashi, H Kobayashi, and H Inokuchi, *J Phys Soc Jpn*, 1987, **56**, 3429

[83] (*a*) A Kobayashi, R Kato, H Kobayashi, T Mori, and H Inokuchi, *Solid State Commun*, 1987, **64**, 64, (*b*) R Kato, H Kobayashi, and A Kobayashi, *J Am Chem Soc*, 1989, **111**, 5224

[84] H-P Werner, J U von Schutz, H C Wolf, R Kremer, M Gehrke, A Aumuller, P Erk, and S Hunig, *Solid State Commun*, 1988, **65**, 809

[85] M R Bryce and S R Davies, *J Chem Soc, Chem Commun*, 1989, 328

[86] (*a*) K Yui, Y Aso, T Otsubo, and F Ogura, *Bull Chem Soc Jpn*, 1989, **62**, 1539, (*b*) F Ogura, K Yui, H Ishida, Y Aso, and T Otsubo, in ref 3*c*, p 403

[87] E Gunther, S Hunig, K Peters, H Rider, H G von Schering, J-U von Schutz, S Soderholm, H-P Werner, and H C Wolf, *Angew Chem, Int Ed Engl*, 1990, **29**, 204

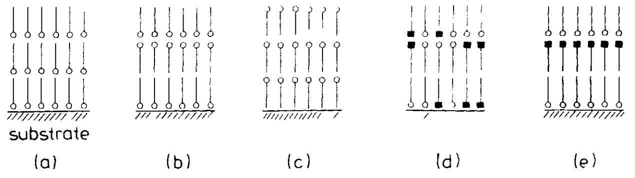


Figure 13 *Schematic representation of molecular arrangements of amphiphilic molecules in LB films (a) X-structure, (b) Y-structure, (c) Z-structure, (d) mixed structure, (e) alternate layer structure*

6 Langmuir–Blodgett (LB) Films of CT Salts

General Aspects.—Currently there is burgeoning interest, from both the scientific and practical viewpoint, in using the LB technique to produce highly-conducting, ultra-thin films of CT salts. LB films offer the possibility for preparing organic structures with a greater level of control over the molecular architecture than in the corresponding single crystal materials. Practical interest stems from the electrical and optical properties of CT salts being available in the form of thin films which should be far easier to fabricate into electronic devices than would frail single crystals. It is, therefore, the combination of tailor-made, intermolecular chemistry within the LB film, together with interactions that can occur at the LB film–solid surface interface, that may provide novel advanced technological applications.[88] Before reviewing the CT materials that form conducting films, a brief description of the fundamentals of LB films is appropriate as many chemists are not familiar with the technique.

An amphiphilic compound (which may be a neutral molecule or a salt) is dissolved in a volatile organic solvent and spread at the air–water interface of an LB trough. Compression of the resulting monomolecular layer orients the molecules at the interface, and in this condensed, oriented state, transfer of the monolayer is achieved onto a solid substrate (*e.g.* a glass slide) as it is dipped perpendicularly through the air–water interface. A single monolayer on the substrate will exhibit quasi two-dimensional character and subsequent deposition of film layers (which may consist of different chemical compounds) will assemble a three-dimensional superstructure, with the film thickness being controlled precisely by the number of dipping cycles. The structure of the amphiphile and the nature of the substrate (*i.e.* hydrophobic or hydrophilic surface) will determine whether deposition occurs during both the up- and down-strokes, or only during either the up- or the down-strokes. Alternate-layer films comprising two different amphiphiles (*e.g.* a donor and an acceptor molecule) can be assembled in successive layers using a specially designed LB trough. The different molecular orientations that can result are shown in Figure 13.

This degree of control over the orientation of individual molecules is clearly one of the most attractive features of the LB technique when applied to the formation of layers (which, in effect, are segregated stacks) of π-donor or π-

---

[88] (*a*) B Tieke, *Adv Mater*, 1990, **2**, 222, (*b*) H Fuchs, H Ohst, and W Prass, *Adv Mater*, 1991, **3**, 10

acceptor species. Structural studies show that most LB films possess a crystalline, lamellar structure consisting of domains with diameters of 0.1—10 μm. Water molecules or adventitious ions may be present in the hydrophilic interlayers. Oxidation (doping) of the molecules within the LB film is frequently needed to yield a mixed-valence conducting system. This is most readily achieved chemically, by exposure of the film to a gaseous oxidant, *e.g.* iodine or bromine, for 1—2 min. Electrochemical oxidation of a film, during, or after, deposition on a conducting support is an alternative method, by which a wider range of dopant anions (ClO_4, PF_6, BF_4, *etc.*) can be introduced into the structure.[88a]

Film preparation takes place under ambient conditions where most amphiphilic organic molecules are stable; however, the monolayer is in a metastable state far removed from thermodynamic equilibrium. Consequently, spontaneous reorientation of the molecules can occur on transfer to the substrate, resulting in structural defects in the assembled multilayer structure. A major short-coming of the LB technique is, therefore, the lack of long-term chemical, thermal, and mechanical stability of the films.

B. Anion Radical Salts.—The materials used to fabricate conducting LB films have been collated elsewhere.[88a,89] Initial work on CT salts concerned long-chain pyridinium cation–TCNQ anion radicals salts first reported by Barraud and co-workers in 1985.[90] LB films of the 1:1 charge-transfer complex *N*-docosylpyridinium-TCNQ (58), as deposited, exhibited low lateral conductivity. However, on doping with iodine vapour, higher conductivity films (σ_{rt} = *ca.* $10^{-1}\,Scm^{-1}$) were produced. Detailed investigations by Richard *et al.*[91] revealed that the precursor film consisted of sheets of $(TCNQ^{-\bullet})_2$ dimers with their molecular planes almost parallel to the plane of the substrate: the effect of the iodination process was to re-orient the TCNQ molecules so that they stood edge-on with their molecular planes and long axes roughly aligned to the substrate normal.

Work on the same system by the group of Nakamura *et al.*[92] has also shown that, as deposited, the films were not highly conducting ($\sigma_{rt} = 10^{-5}$—$10^{-7}\,Scm^{-1}$); these studies also indicated, however, that the orientation of the TCNQ molecules could be changed by varying the LB deposition conditions. Subsequently, this group reported on the properties of the 1:2 complex (59) of the same charge-transfer system; LB films of this material exhibited a high conductivity (*ca.* $10^{-2}\,Scm^{-1}$) even without doping or any further treatment.[93] It should be noted that two distinct means of evaluating the lateral conductivity of multilayer films from the measured resistance values exist in the literature. In the first method, used by Barraud and co-workers,[90] the calculation neglects the

---

[89] T. Nakamura and Y. Kawabata, *Techno Japan.*, 1989, **22**, 8.

[90] (*a*) A. Ruaudel-Teixier, M. Vandevyver, and A. Barraud, *Mol. Cryst. Liq. Cryst.*, 1985, **120**, 319; (*b*) A. Barraud, A. Ruaudel-Teixier, M. Vandevyver, and P. Leisieur, *Nouv. J. Chim.*, 1985, **2**, 365.

[91] J. Richard, M. Vandevyver, P. Lesieur, A. Ruaudel-Teixier, A. Barraud, R. Bozio, and C. Pecile, *J. Chem. Phys.*, 1987, **86**, 2428.

[92] T. Nakamura, M. Tanaka, T. Sekiguchi, and Y. Kawabata, *J. Am. Chem. Soc.*, 1986, **108**, 1302.

[93] M. Matsumoto, T. Nakamura, F. Takei, M. Tanaka, T. Sekiguchi, M. Mizuno, E. Manda, and Kawabata, *Synth. Met.*, 1987, **19**, 675.

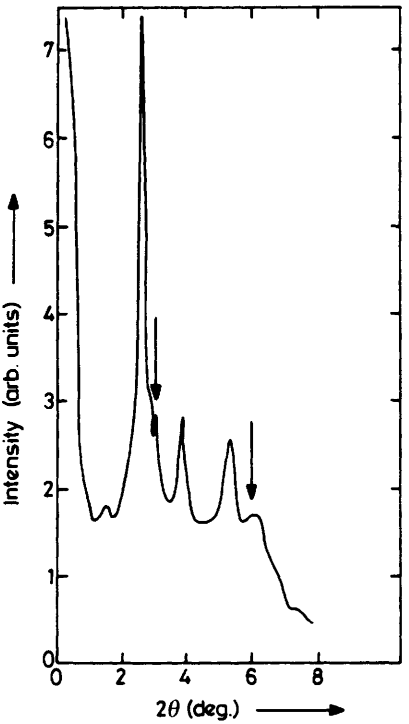


Figure 14 *Low angle X-ray diffraction data for 42 LB layers of salt* (60). [*The arrows identify maxima due to a second phase* (< 10% *of the sample volume*) *within the film*]
(From reference 94*b*)

insulating (hydrocarbon) portion of the molecules; in contrast, in the work of Nakamura and co-workers[92] the full length of the substituted charge-transfer system is used. The former technique can produce a conductivity figure up to an order of magnitude larger than the latter method.

We have studied multilayers of the 1:1 salt (60), as deposited, and found conductivity values of $\sigma_{rt} = 10^{-2}\,\mathrm{Scm}^{-1}$ (calculated using the full molecular length). UV–visible dichroism and polarized IR spectra indicate that in these films of salt (60) the TCNQ molecules and the alkyl chains have their long axes inclined at an angle of *ca.* 30° to the substrate normal. From low angle *X*-ray diffraction data (Figure 14) the Bragg spacing was found to be 3.2 nm; taken together these data are consistent with the interdigitated multilayer structure represented schematically in Figure 15. This structure is in contrast to the orientation of salt (58) discussed above.[91] The nature of the conduction process in films (60) is uncertain (a 1:1 salt should be a Mott insulator[1a]). It seems likely that the films are unintentionally doped, with an anion such as OH^-, during deposition.[94c]

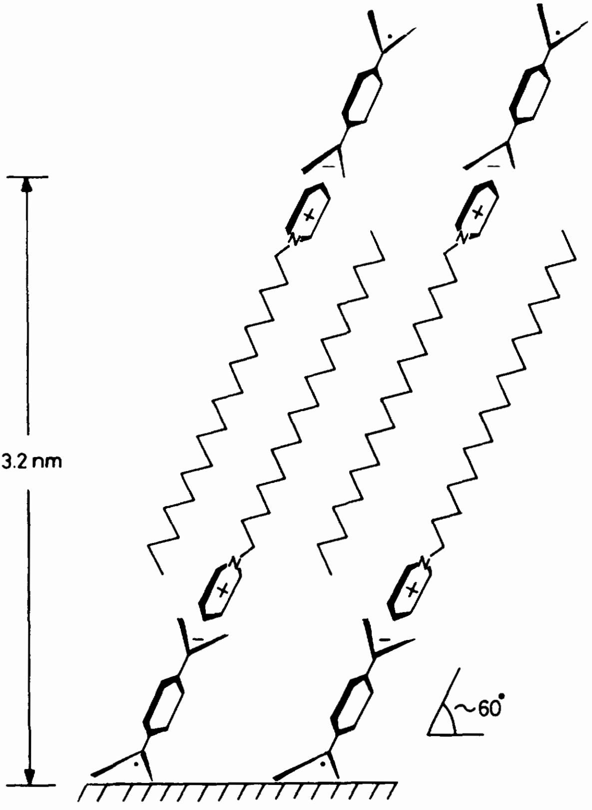


Figure 15 *Schematic diagram showing the proposed average orientation of salt* (60) *in LB film form*
(From reference 94*b*)

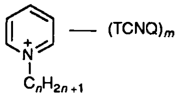
LB films of a 1 : 1 salt formed by TCNQ and the dimethyloctadecylsulphonium cation are conducting after iodine doping; from spectroscopic analysis of the films it was concluded that the TCNQ molecules exist as dimers with their long axes parallel to the substrate,[95] in a similar fashion to salt (58).[91]

C. TTF–TCNQ CT Complexes.—LB films that incorporate both TTF and TCNQ derivatives have been fabricated: a long hydrophobic chain is attached

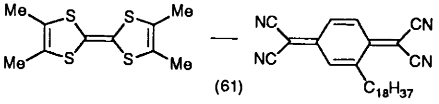
---

[94] (*a*) A. S. Dhindsa, M. R. Bryce, J. P. Lloyd, and M. C. Petty, *Synth. Met.*, 1987, **22**, 185; (*b*) A. S. Dhindsa, G. H. Davies, M. R. Bryce, J. Yarwood, J. P. Lloyd, M. C. Petty, and Y. M. Lvov, *J. Mol. Elect.*, 1989, **5**, 135; (*c*) R. J. Ward, A. S. Dhindsa, M. R. Bryce, M. C. Petty, and H. S. Munro. *Thin Solid Films*, 1991, **198**, 363.

[95] A. Barraud, M. Lequan, R. M. Lequan, P. Lesieur, J. Richard, A. Ruaudel-Teixier, and M. Vandevyver, *J. Chem. Soc., Chem. Commun.*, 1987, 797.



	n	m
(58)	22	1
(59)	22	2
(60)	18	1



(61)

either to (i) the TCNQ moiety, or (ii) the TTF moiety, or (iii) both components. The first TTF–TCNQ films were reported by Japanese workers who prepared the 1:1 complex (61).[96] The conductivity of the films is $\sigma_{rt} = 10^{-2}\,\mathrm{Scm^{-1}}$, without doping, which is an order of magnitude higher than a compressed pellet of the complex. No anistropy of the conductivity was observed in the film plane, and the temperature dependence of the conductivity showed typical semiconductivity behaviour with $E_a = 0.08\,\mathrm{eV}$.[97] We have studied LB films of a TTF–TCNQ complex in which a long, hydrophobic chain is attached to the TTF moiety, *viz.* complex (62) which has a relatively low conductivity value ($\sigma_{rt} = 10^{-3}\,\mathrm{Scm^{-1}}$) that is further reduced to $\sigma_{rt} = 10^{-6}\,\mathrm{Scm^{-1}}$ upon iodine doping.[98]

French workers have studied in detail the complex (63) formed by a double-chain tetrathio-TTF donor and $\mathrm{TCNQF_4}$. In the deposited form, LB films are insulating, due to complete charge-transfer, but the films become conducting ($\sigma_{rt} = 5 \times 10^{-2}\,\mathrm{Scm^{-1}}$) after iodine doping, *i.e.* on formation of a mixed-valance, ternary complex.[99] Spectroscopic data suggest that the $\mathrm{TCNQF_4}$ molecules are fully ionized both before and after doping and are, therefore, not involved in the conduction process. Doping converts the donor into a mixed valence species and it is these molecules, not I_3^-, that are directly responsible for the conductivity.

By using a specially designed LB trough, we have alternated layers of octadecyl–TCNQ and octadecanoyl–TTF (64) to afford the semiconducting multilayer structure represented schematically in Figure 13e,[100] for which $\sigma_{rt} = 5 \times 10^{-3}\,\mathrm{Scm^{-1}}$. This procedure provides a novel way of enforcing segregated stacking on a donor–acceptor complex. Further studies on amphiphilic TTF and TCNQ derivatives that have different structures and redox potentials are needed

---

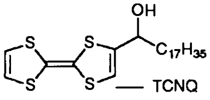
[96] T Nakamura, F Takei, M Tanaka, M Matsumoto, T Sekiguchi, E Manda, Y Kawabata, and G Saito, *Chem Lett*, 1986, 323

[97] Y Kawabata, T Nakamura, M Matsumoto, M Tanaka, T Sekiguchi, H Komizu, E Manda, and G Saito, *Synth Met*, 1987, **19**, 663

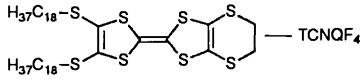
[98] A S Dhindsa, C Pearson, M R Bryce, and M C Petty, *J Phys D Appl Phys*, 1989, **22**, 1586

[99] (*a*) J Richard, M Vandevyver, A Barraud, J P Morand, R Lapouyade, P Delhaes, J F Jacquinot, and M Roulliay, *J Chem Soc*, *Chem Commun*, 1989, 754, (*b*) J P Morand, R Lapouyade, P Delhaes, M Vandevyver, J Richard, and A Barraud, *Synth Met*, 1988, **27**, B569

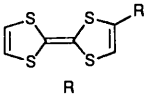
[100] C Pearson, A S Dhindsa, M R Bryce, and M C Petty, *Synth Met*, 1989, **31**, 275



(62)



(63)



R

(64) $-C(O)-C_{17}H_{35}$
(65) $-C(O)-C_{15}H_{31}$
(66) $-C(S)-O-C_{16}H_{33}$
(67) $-C(O)-O-C_{16}H_{33}$
(68) $-S-C_{18}H_{37}$
(69) $-Se-C_{18}H_{37}$
(70) $-Te-C_{18}H_{37}$
(71) $-C(O)-(CH_2)_4CH_2Br$

to determine if the conductivity values of alternate layer structures of this type can be increased to the level of single crystals of TTF–TCNQ.

D. Cation Radical Salts.—Cation radical salts of amphiphilic π-donors have provided the best quality data for conducting LB films: to date, the temperature dependence of the conductivity is that of a semiconductor not a metal ($\sigma_{max} = 1\,Scm^{-1}$). A multilayer film of the neutral donor is assembled which is then oxidized to form a conducting salt of general formula (Donor$^{+\bullet}$), $(X^-)_n$, where $n < 1$, which has a partially filled band structure. The presence of only one bulky component, *i.e.* the donor, favours a more regular film structure than that of the binary or ternary compounds discussed above, where two bulky species must be ordered. Our strategy has been to decorate the TTF ring with one hydrophobic tail, *e.g.* molecules (64)—(70),[101] for which a chain length of at least sixteen atoms is needed to give a stable monolayer. The acyl, thioester, and ester groups in compounds (64)—(67) appear to play a key role in ordering the structure of the LB films which form by Y-type deposition (Figure 13*b*). These electron-withdrawing groups reduce the donor ability of the TTF system [by *ca.* 0.18 V for $E_1\frac{1}{2}$ relative to TTF], and their presence has the beneficial effect of significantly increasing the polar, hydrophilic nature of the TTF ring. Indeed, the single crystal *X*-ray structure of acyl-TTF derivative (71) shows that the carbonyl group lies in the same plane as the TTF ring, thereby maximizing its π-conjugative effect.[101]

Hexadecanoyl-TTF (65) was the first derivative to be studied.[102] Upon doping with iodine vapour the LB films initially remain insulating, then after several hours in air, semiconducting behaviour is established, $\sigma_{rt} = 10^{-2}\,Scm^{-1}$, $E_a = 0.19\,eV$. This doping process has been monitored by UV–visible, IR, and *X*-ray photoelectron spectroscopy: immediately upon doping, the TTF system is oxidized to a full charge transfer (insulating) state, then with time a partial release of iodine occurs to afford the stable mixed-valence (conducting) state. In contrast to this, films doped with bromine remain insulating. Absorption spectra

---

[101] M. R. Bryce, G. Cooke, A. S. Dhindsa, D. Lorcy, A. J. Moore, M. C. Petty, M. B. Hursthouse, and A. I. Karaulov, *J. Chem. Soc., Chem. Commun.*, 1990, 816.

[102] (*a*) A. S. Dhindsa, M. R. Bryce, J. P. Lloyd, and M. C. Petty, *Thin Solid Films*, 1988, **165**, L97; (*b*) A. S. Dhindsa, R. J. Ward, M. R. Bryce, Y. M. Lvov, H. S. Munro, and M. C. Petty, *Synth. Met.*, 1990, **35**, 307; (*c*) A. S. Dhindsa, M. R. Bryce, H. Ancelin, M. C. Petty, and J. Yarwood, *Langmuir*, 1990, **6**, 1680.

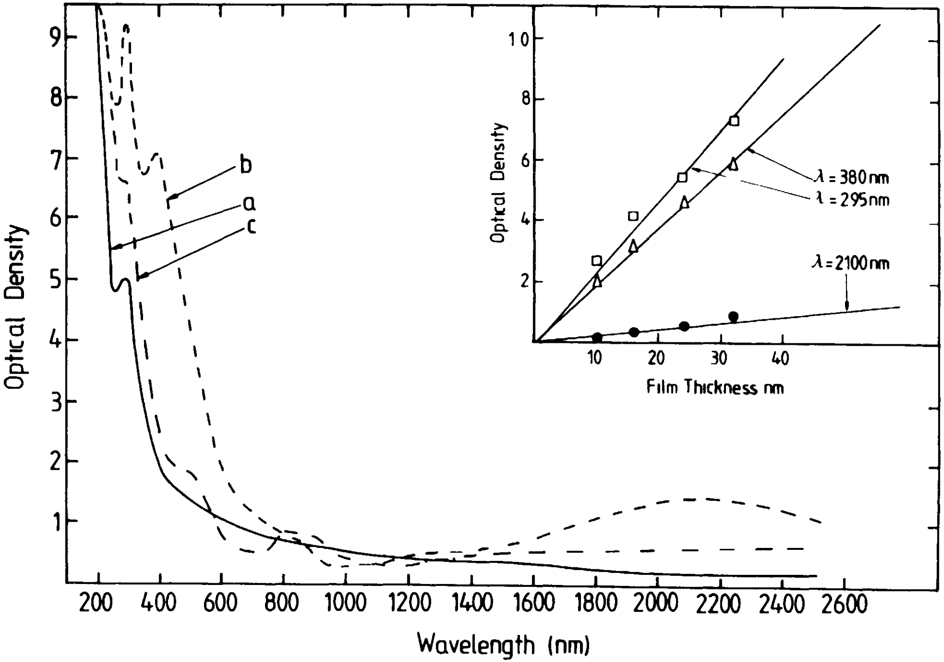


Figure 16 *Absorption spectra of LB films of compound* (65) *Curve a* 40 *layers as deposited Curve b* 40 *layers* 20h *after iodine doping* (i e *in the conducting state*) *Curve c* 50 *layers* 48h *after bromine doping The inset shows the variation of optical density with thickness for the iodine-doped film* (*measured* 20h *after iodination*)
(From reference 102*b*)

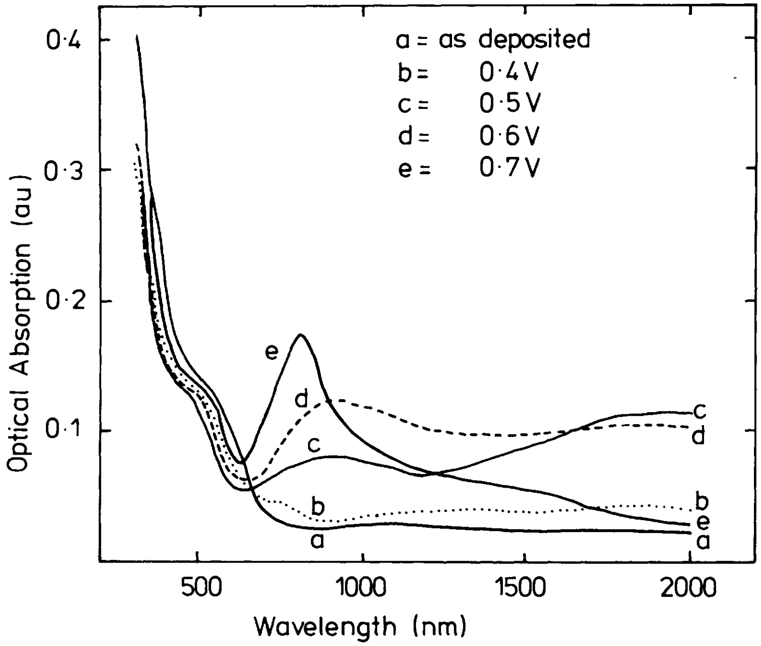
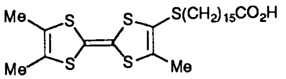


Figure 17 *Absorption spectra for a* 40 *layer LB film of octadecanoyl-TTF* (64). *The different curves correspond to different applied voltages in the electrochemical cell*
(From reference 103)

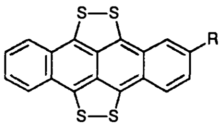
of LB films of compound (65) are shown in Figure 16. The intermolecular CT band at *ca.* 2100nm for the iodine doped films is characteristic of an organic conductor. The optical density of the iodine-doped film scales approximately linearly with the number of layers in the LB assembly. Thus the ordered nature of the multilayers is not disrupted upon doping, and we conclude that doping is uniform throughout the forty layers (Figure 16, inset). Low angle *X*-ray diffraction and polarized IR spectra of films of (65) point to near-vertical alignment of the donor molecules on the substrate surface, with lateral electron mobility *via* well-ordered, partially oxidized TTF rings.[102c] More controlled oxidation of films of an analogous acyl-TTF derivative, *viz.* octadecanoyl-TTF, (64), has been achieved electrochemically in aqueous tetrabutylammonium perchlorate solution.[103] The doping process was monitored by measuring the optical spectra at different applied voltages (Figure 17). The charge-transfer band at *ca.* 2000nm starts to develop at 0.4V, is at a maximum at 0.5—0.6V and then decreases at higher applied voltages, when the full charge-transfer state of the TTF system has been reached. This is supported by the steady increase in

---

[103] M. C. Petty, A. S. Dhindsa, C. Pearson, A. P. Monkman, and M. R. Bryce, Proceedings IEEE/EMBS, ed. P. C. Pederson and B. Onoral, 1990, 1693.



(72)



(73) R = $-CF_3$
(74) R = $-O-C_{18}H_{37}$

intensity of the band at *ca.* 800 nm which has been assigned to the full CT state in crystalline TTF salts.

Similar structural ordering and doping characteristics are observed for LB films of TTF-thioester (66)[104] with one important difference: the lateral (in-plane) room temperature conductivity of films of (66) is two orders of magnitude higher ($\sigma_{rt} = 1.0$ S cm^{-1}, $E_a = 0.09$ eV) than for acyl- or ester-derivatives (65)[102] and (67).[105] Iodine doping has been monitored by IR spectroscopy (Figure 18). Before doping, the C=S band is present at 1250 cm^{-1} (Figure 18a); this band shifts immediately upon doping, consistent with oxidation having occurred, *i.e.* neutral (66) ⟶ radical cation (66). The new sharp band which appears at 1350 cm^{-1} is a vibronic coupling band and a broad CT band is present at *ca.* 5000 cm^{-1} (Figure 18b). Two hours after doping, when the conductivity value has reached its maximum, the CT band has shifted to lower wavenumber and the vibronic coupling band is much weaker (Figure 18c). A schematic representation of structural ordering within the conducting films of (66), based on low angle *X*-ray diffraction and polarized spectroscopic data, is shown in Figure 19. The role of the C=S group of compound (66) in improving the conduction properties of the LB films is not yet understood; it is tempting to speculate that intermolecular S···S interactions may be involved, but we have no evidence for this. The conductivity of (66) is presently the highest for a TTF LB film; it is, however, still considerably lower than that of single crystal TTF halide salts,[106] *e.g.* TTF-$Br_{0.77}$, σ_{rt} = *ca.* 800 S cm^{-1}, and a current goal is to achieve comparable values for LB films.

It is clear that LB film quality within the series of monochain-TTFs (65)—(70) is reduced when the C=O or C=S group is absent. Compounds (68)—(70) form less-ordered films of lower conductivity, $\sigma_{rt} = 10^{-3}$ after doping.[107] The related compound (72), which carries a terminal carboxylic acid group, prepared by Bechgaard and Lerstrup, is also a relatively poor LB film material.[107] LB films of tetraselenafulvalene derivatives have not yet been reported, but they are clearly prime targets.

Workers at Ciba-Geigy, Basel, have studied tetrathiotetracene (TTT) derivatives (73)[108] and (74).[109] These donors are not classical amphiphiles and LB film

---

[104] A. S. Dhindsa, J. P. Badyal, M. R. Bryce, M. C. Petty, A. J. Moore, and Y. M. Lvov, *J. Chem. Soc., Chem. Commun.*, 1990, 970.

[105] A. S. Dhindsa, Y. Song, M. R. Bryce, M. C. Petty, and J. Yarwood, to be published.

[106] B. A. Scott, S. J. Placa, J. B. Torrance, B. D. Silverman, and B. Welber, *J. Am. Chem. Soc.*, 1977, **99**, 6631.

[107] A. S. Dhindsa, G. Cooke, K. Lerstrup, K. Bechgaard, M. R. Bryce, and M. C. Petty, to be published.

[108] A. Wegmann, B. Tieke, C. W. Mayer, and B. Hilti, *J. Chem. Soc., Chem. Commun.*, 1989, 716.

[109] (*a*) B. Tieke and A. Wegmann, *Thin Solid Films*, 1989, **179**, 109; (*b*) B. Tieke, A. Wegmann, W. Fischer, B. Hilti, C. W. Mayer, and J. Pfeiffer, *Thin Solid Films*, 1989, **179**, 233.

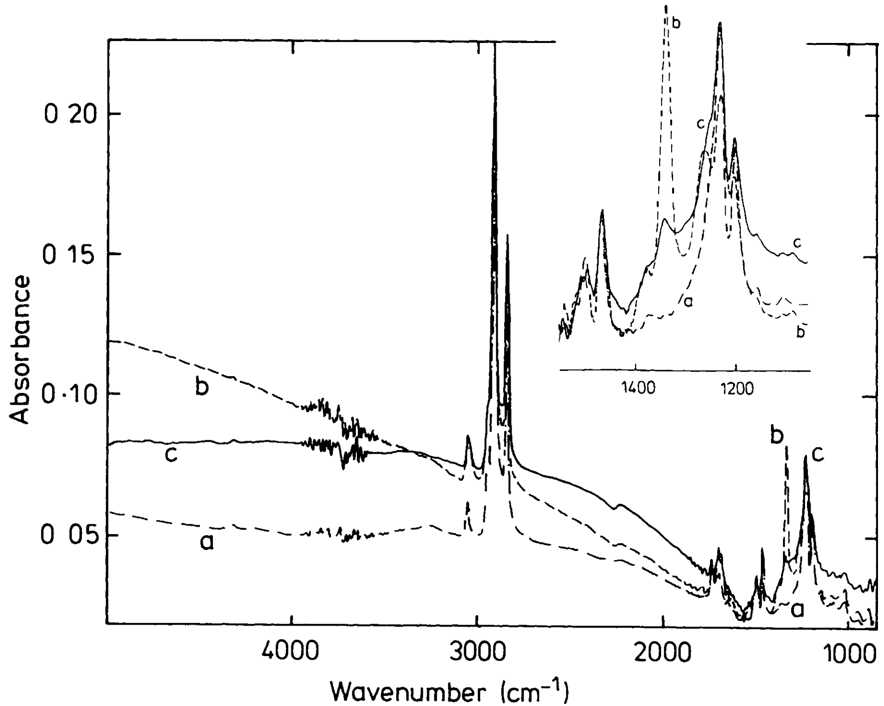


Figure 18 *Transmission IR spectra for LB films of compound* (66) (96 *layers*) *including an expansion of the* 1500—1100 cm^{-1} *region,* (*a*) *as deposited,* (*b*) 5 min *after iodine doping* (*c*) 2 h *after doping*
(From reference 104)

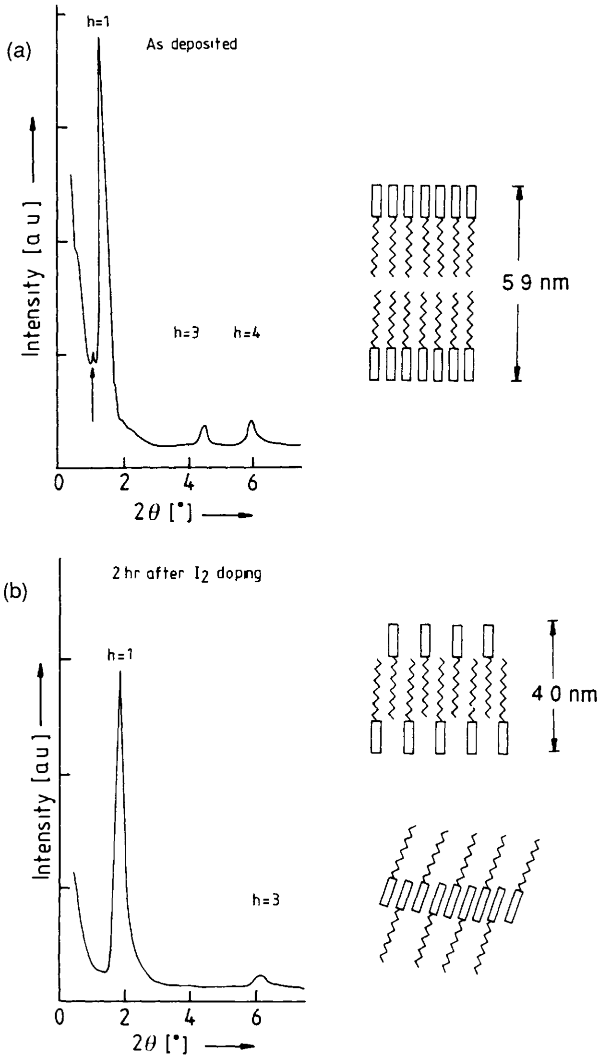
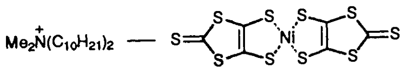


Figure 19 *Low angle X-ray diffraction data for LB layers of compound* (66) *and schematic diagrams showing the proposed average orientation of the molecules* (*a*) *Data for the film as deposited* (i e Y-*type deposition*) (*b*) *data for the conducting film* 2h *after iodine doping* [*The arrow in Figure* 19a *identifies maxima due to a second phase within the film which disappear upon doping*]

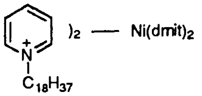
formation, as Y-type structures, required mixing the donor with methylarachidate (*ca* 3 1 ratio) The oxidized films of (74) were prepared in a variety of ways (i) by the usual iodine vapour method, (ii) by treatment with aqueous KI_3 solution



(75) Ni(dmit)$_2$

$Me\overset{+}{N}(C_{10}H_{21})_3$ — Au(dmit)$_2$

(76)



(77)

before or after film formation; (iii) by anodic oxidation with aqueous $LiClO_4$ solution either during, or after, film formation. The conductivity and ordering within the LB film varied with the doping method applied.[109] *X*-Ray studies revealed that doping resulted in considerable disordering of the layer structure. The deposited films are insulators (σ_{rt} = *ca.* 10^{-7} Scm^{-1}) and maximum conductivities obtained after doping are σ_{rt} = 1.3 × 10^{-4} Scm^{-1} and 10^{-2} Scm^{-1} for (73) and (74), respectively. In contrast to the doped, mixed-valence TTF films (65)—(67), which retain high conductivity values on storage in air for several weeks, the doped TTT films (73)[108] and (74),[109a] are quite unstable to loss of iodine, which is accompanied by a marked decrease in conductivity.

E. Organometallic Systems.—Conducting LB films of metal(dmit)$_2$ complexes with long-chain ammonium or pyridinium cations (75)—(77) have also been studied recently, with the aim of increasing dimensionality within the film structure (*cf.* Section 5A). The first reports came from Japanese workers[110] who found conductivity, σ_{rt} = 10^{-2} Scm^{-1}, in bromine-doped films of complex (75). However, the complex had to be mixed with as much as 50% icosonoic acid to prevent collapse of the monolayer on the water surface and transfer to the substrate required a horizontal lifting technique. Subsequently, the same group studied Au(dmit)$_2$ complex (76)—fatty acid mixtures which had significantly higher room temperature conductivity (σ_{rt} = 25 Scm^{-1}) and this value was retained on cooling down to *ca.* 200 K.[111] Both complexes (75) and (76) are reported to have 1 : 1 stoicheiometries.

Work in our laboratory has shown that complex (77) of 2:1 stoicheiometry produces stable films at the air-water interface without the need of added fatty acid, and efficient Y-type LB deposition of (77) proceeds in the normal way.[112] After iodine doping the films are conducting, σ_{rt} = 8 × 10^{-2} Scm^{-1}, and variable temperature data (300—100 K) provide evidence of space charge injection in both the undoped and doped films. The doping process has been probed by a

---

[110] (*a*) T. Nakamura, H. Tanaka, M. Matsumoto, H. Tachibana, E. Manda, and Y. Kawabata, *Chem. Lett.*, 1988, 1667; (*b*) *idem*, *Synth. Met.*, 1988, **27**, B601.

[111] T. Nakamura, K. Kojima, M. Matsumoto, H. Tachibana, M. Tanaka, E. Manda, and Y. Kawabata, *Chem. Lett.*, 1989, 367.

[112] A. S. Dhindsa, J. P. Badyal, C. Pearson, M. R. Bryce, and M. C. Petty, *J. Chem. Soc., Chem. Commun.*, 1991, 322.

combination of IR and XPS data it is clear that oxidation occurs in the vicinity of the nickel centre to yield a mixed-valence CT system

7 Future Directions

There are now six families of organic superconductor, *i e* those based on molecules (4), (8), (9), (12), (13), and (16) The study of these compounds has been most fruitful in recent years and is expected to remain so in the immediate future Exciting physics is provided by the close proximity of superconducting and antiferromagnetic (insulating) ground states, and the control of dimensionality in the solid state is a fascinating challenge for synthetic chemists Only where two-dimensional interstack interactions become predominant is superconductivity observed, it is essential that new donor and acceptor systems are synthesized so that the subtle factors which govern the structural, electrical, and magnetic properties of CT salts can be better understood *X*-Ray crystallographic studies at liquid helium temperatures, as well as at high pressures, are needed to shed light on the low temperature transitions that are characteristic of many charge-transfer organic conductors

The preparation and study of conducting thin films of CT salts is a growing topic where major developments can be expected Good quality Langmuir–Blodgett films are now available, but their conductivity values are still relatively low Nevertheless, novel properties and technological applications may result, especially from the controlled fabrication of superlattice structures The recent reports of superconductivity in polycrystalline compressed pellets of a BEDT–TTF salt[113] and a thin film of BEDT–TTF iodide, formed by vapour deposition,[114] may prove to be important milestones on the long road to device fabrication

---

[113] D Schweitzer E Gogu H Grimm S Kahlich and H J Keller *Angew Chem Int Ed Engl Adv Mater* 1989 **28** 953

[114] K Kawabata K Tanaka and M Mizutani *Adv Mater* 1991 **3** 157