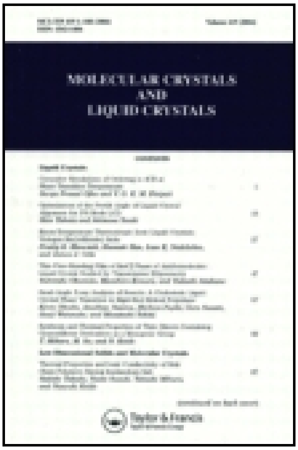

Molecular Crystals and Liquid Crystals

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The Organic Metallic State[1]

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The Organic Metallic State[1]

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The development of the organic metallic state is traced from our original synthesis and study of TTF–TCNQ to the new conductor HMTSF–TCNQ, the first organic substance which remains metallic as T → 0.

The organic charge-transfer salt tetrathiafulvalenium tetracyanoquinodimethanide (TTF–TCNQ),[2] one of the best organic conductors known, exhibits a transition from metallic to non-metallic conductivity as the temperature is decreased below 60 K.[2–4] (See Table I.) The structure of TTF–TCNQ consists of parallel columns of separately stacked TTF (donor) and TCNQ (acceptor) molecules.[5,6] Electrical conductivity occurs mainly along these chains,[7] and it now seems likely that the metal-insulator transition is associated with a Peierls instability of a quasi-one-dimensional metal.[8]

The following postulates have been used in part by our group to help design new highly conducting organic materials.[9]

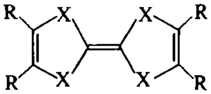
Constituent molecular cations and anions should both be:

a) Nominally divalent, so that both can form conducting chains of radical cations or radical anions.
b) Planar, with inhomogeneous charge distribution to facilitate stacking.
c) Small and polarizable, to diminish the correlation energy.
d) Symmetric, to reduce static potential fluctuations.

In this lecture we will indicate how the heteroatoms and substitutents associated with the donor portion (TTF) of the salt can be changed in order to optimize bandwidths, change the band overlap, charge transfer and interchain coupling. A number of these conducting complex salts prepared in our laboratories and in others are listed in Table I.

TABLE I

Organic semimetals; 1 : 1 TCNQ salts of:



	R	X	σ_{RT} ($cm^{-1}\ \Omega^{-1}$)	σ_{max}/σ_{RT}	T_m	Ref.
TTF	—H	S	500	20	59	2–4
DMTTF	2—H, 2—CH_3	S	50	25	~50	3
TMTTF	—CH_3	S	1,000	1	—	11
	—CH_3	S	350	15	60	12
HMTTF	—$CH_2CH_2CH_2$—	S	500	4	80	13
TSF	—H	Se	800	12	40	14
DTDSF	—H	2S, 2Se	500	7	64	15
TMTSF	—CH_3	Se	1,000	6	71	16
HMTSF	—$CH_2CH_2CH_2$—	Se	2,000	No Transition		10

Of particular interest is the electrical conductivity of HMTSF–TCNQ. The room-temperature d.c. conductivity of this material is the largest of any known organic substance (2,000 Ω^{-1} cm^{-1}). In addition, the magnitude of the conductivity remains metallic to temperatures at least as low as 0.045 K.[10] The higher crystal symmetry, reduced interchain coupling, and lack of three-dimensional long-range order all suggest possible modes for suppression of the insulating state.

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