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'Organic Metals': Acceptor Stack Doping in the Charge-transfer Salt Tetraselenafulvalene–Tetracyano-*p*-quinodimethane (TSeF–TCNQ)

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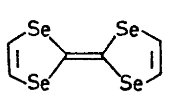
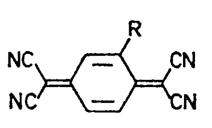
Summary Doping of methyltetracyano-*p*-quinodimethane into the 'organic metal' tetraselenafulvalene–tetracyano-*p*-quinodimethane obscures the phase transition at 28 K and increases the conductivity at 4 K by four orders of magnitude.

A LARGE part of research on metal-like charge-transfer salts, such as tetrathiafulvalene–tetracyano-*p*-quinodimethane (TTF–TCNQ),[1] is focused towards understanding the metal–insulator phase transition in these materials. The quasi-one-dimensional structure[2] of these segregated donor and acceptor stacked metals makes them susceptible to a lattice distortion which opens a gap in the conduction band, and is referred to as a Peierls transition.[3] Previously, the effect on the phase transition of varying the properties of the donor stack could be probed with the solid solutions TSeF$_x$TTF$_{1-x}$ TCNQ, where x can be continuously varied from 0 to 1.[4] We now report, for the first time, results on the controlled doping of the acceptor stack in the 'organic metal' tetraselenafulvalene–tetracyano-*p*-quinodimethane [TSeF–TCNQ; (**1**)–(**2**)].[5]


(1)


(2) R = H
(3) R = Me

The stringent structural requirements of the solid severely limit both the type and amount of dopant that can be introduced into the charge-transfer salt. Of the variety of ways in which the acceptor TCNQ could be modified[6] to act as a dopant, methyl substitution seemed to be the least demanding in terms of steric and electronic considerations.

Methyl-TCNQ (MTCNQ; **3**)[7] and TSeF[5] were prepared by earlier described procedures. To hot acetonitrile (60 ml) under nitrogen were added MTCNQ (2·2 mg, 0·1 mmol), TCNQ (18·4 mg, 0·9 mmol) and TSeF (39·6 mg, 1 mmol). Slow cooling to room temperature in an insulated Dewar flask gave black needle-like crystals. Elemental analysis showed the crystals to be predominantly TSeF–TCNQ (%C and H for TSeF–TCNQ: calculated 36·27, 1·35; found 36·41, 1·38) but suggestive of some MCTNQ incorporation. *X*-Ray diffraction, however, provided stronger evidence of MTCNQ doping in TSeF–TCNQ. The structure of the MTCNQ-doped crystals was found to be isomorphic with TSeF–TCNQ,[5,8] but with a slightly expanded unit cell ($a_0 = 12{\cdot}60$, $b_0 = 3{\cdot}89$, $c_0 = 18{\cdot}49$, $\beta = 104{\cdot}3°$). The a_0 constant, which is across the width of the molecules, increases the most because of the methyl substitution, as expected. In view of the relatively similar electronic and steric properties of TCNQ and MTCNQ, it seems reasonable to assume a random distribution of dopant in the acceptor stack. Based on this assumption, a rough estimate of the amount of MTCNQ incorporated was made using the increase in the a_0 constant and the known van der Waals radii of the constituent molecules and found to be *ca.* 10 mol %.

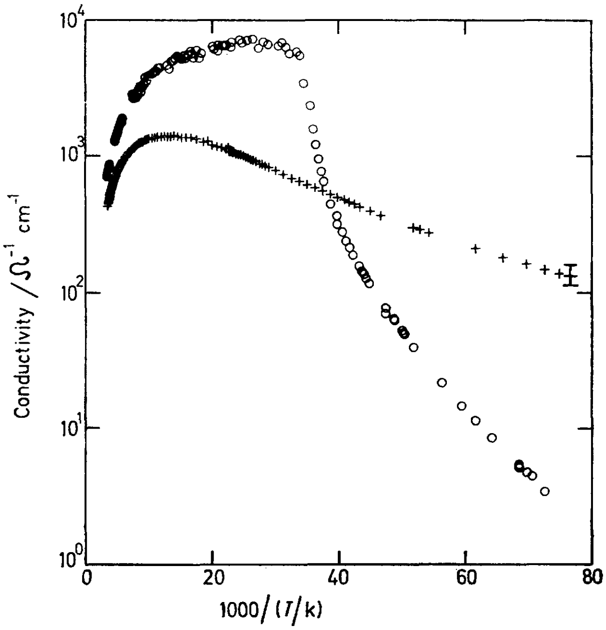


FIGURE. Conductivity of TSeF–TCNQ (circles) and TSeF–TCNQ doped with methyl–TCNQ (crosses) as a function of 1000/T. Error bar at 12 K indicates variation in conductivity among four samples at that temperature; smaller variations were found at higher temperatures.

As seen in the Figure, the conductivity behaviour of TSeF–TCNQ is dramatically altered by MTCNQ doping. The overall temperature dependence of the conductivity gives a much flatter curve when compared to that of the undoped material. The peak in the conductivity is moved from 40 to 75 K, and the sharp drop in conductivity at the 28 K phase transition is no longer seen. Although the conductivity is decreasing with decreasing temperature in the doped material below 28 K, the conductivity at 4 K (14·9 Ω^{-1} cm^{-1}; not shown in the Figure) is 10^4 times greater than that of undoped TSeF–TCNQ.[9] This result suggests that acceptor doping in TSeF–TCNQ leads to a decrease in the effective energy gap which opens at the phase transition. Decreasing the amount of MTCNQ doping produced intermediate changes in the conductivity–temperature profile.

The effect on the conductivity due to acceptor doping in TSeF–TCNQ contrasts sharply with the results of doping the donor stack in this system with TTF, where the phase transition remains relatively sharp and the effective activation energy at low temperature is essentially unchanged.[4,8] Both dopants introduce disorder into TSeF–TCNQ. However, TTF doping directly affects the band structure[4b] as a result of perturbing the band-forming orbital (HOMO) of the donor;[10] MTCNQ doping, on the other hand, is expected to have a much smaller effect on the corresponding band-forming orbital (LUMO) of TCNQ. The sensitivity of the effective energy gap to acceptor doping emphasizes the role of disorder in modifying the low-temperature behaviour.

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