# Synthesis of Unsymmetrical Tetrathiafulvalenes and Electrical Conductivities of Their Tetracyanoquinodimethane Complexes

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The preparation of some unsymmetrical tetrathiafulvalenes and the electrical conductivities of their charge transfer complexes with tetracyanoquinodimethane (TCNQ) are described; the ethylenedithio(trimethylene)tetrathiafulvalene–TCNQ complex exhibited higher conductivity than complexes of tetrathiafulvalene, tetramethyltetrathiafulvalene, and hexamethylenetetrathiafulvalene with TCNQ.

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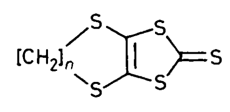
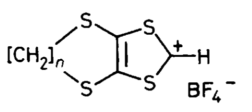
Since the discovery of highly conductive cation radical salts of tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) derivatives, much effort has been put into the synthesis of donor molecules that endow their salts with metallic properties. Recently it has been reported that radical cation salts of unsymmetrically-alkylated TTF and TSF showed higher conductivities than symmetrical salts, maintaining the metallic state to lower temperature.[1] Considering that bis(ethylenedithio)tetrathiafulvalene (**23**) forms highly conductive radical salts indicating two-dimensional metallic properties owing to their intermolecular $S \cdots S$ contacts along the transverse direction in the crystal,[2] the formation of unsymmetrical TTF derivatives by incorporating heterorings with different ring sizes or related substituents might also be expected to form highly conducting complexes.[1]

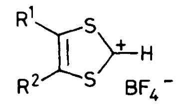
We now report the synthesis of several unsymmetrical donors and investigation of the steric and electronic effects of substituents on their electrical conductivities. Dithiolium salts (**3**) and (**4**) were obtained from the corresponding trithiocarbonates (**1**)[3] and (**2**)[4] by a four-step sequence: methylation with dimethyl sulphate, treatment with tetrafluoroboric acid, reduction with sodium borohydride in methanol, and reaction



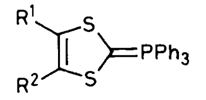
(1) $n = 2$
(2) $n = 3$



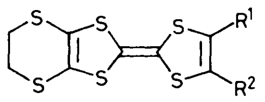
(3) $n = 2$
(4) $n = 3$



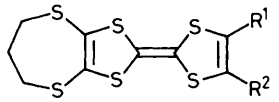
(5) $R^1 = R^2 = H$
(6) $R^1 = R^2 = Me$
(7) $R^1 = R^2 = MeS$
(8) $R^1, R^2 = -[CH_2]_3-$



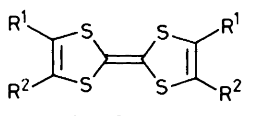
(9) $R^1, R^2 = -S[CH_2]_3S-$
(10) $R^1 = R^2 = Me$



(11) $R^1 = R^2 = H$
(12) $R^1 = R^2 = Me$
(13) $R^1 = R^2 = MeS$
(14) $R^1, R^2 = -[CH_2]_3-$



(15) $R^1 = R^2 = H$
(16) $R^1 = R^2 = Me$
(17) $R^1 = R^2 = MeS$
(18) $R^1, R^2 = -S[CH_2]_2S-$



(19) $R^1 = R^2 = H$
(20) $R^1 = R^2 = Me$
(21) $R^1 = R^2 = MeS$
(22) $R^1, R^2 = -[CH_2]_3-$
(23) $R^1, R^2 = -S[CH_2]_2S-$
(24) $R^1, R^2 = -S[CH_2]_3S-$

with $HBF_4$ in acetic anhydride afforded (**3**) and (**4**) in overall yields of 77 and 62%, respectively.[5] Unsymmetrical donors were easily prepared in a moderate yield (21—50%) by cross coupling of two ditholium salts with triethylamine in acetonitrile according to known methods,[6] followed by separation of the resulting mixture into three component tetrathiafulvalenes using fractional crystallization and/or gel permeation chromatography.

Two compounds, (**18**) and (**16**), were prepared by an improved route using phosphorane because of the difficult separation of the desired component from the reaction mixture. Thus, (**18**) was prepared in 22% yield by coupling of (**3**) and phosphorane (**9**) which was derived from (**4**) by successive treatments with triphenylphosphine and $Bu^nLi$.[7] Similarly, (**16**) was obtained in 62% yield from (**4**) and phosphorane (**10**), derived from (**6**). The known symmetrical compounds, (**23**) and (**24**),[7,8] were prepared by self-coupling of (**3**) and (**4**), respectively, with triethylamine in acetonitrile as an alternative synthesis.

Cyclic voltammetry of the donors (Table 1) showed two reversible one-electron oxidations in all cases. The potentials of the donors attached *via* the ethylenedithio group are very close to those of donors with propylenedithio groups, indicating the same effect of both groups on the electronic state of TTF. Complexation of the donors with tetracyanoquinodimethane (TCNQ) in acetonitrile, chloroform, chlorobenzene, or 1,1,2-trichloroethane gave black 1:1 complexes as fine needles or powders. D.c. conductivity measurements were made by a two probe technique on their compressed pellets at room temperature (Table 1).

**Table 1.** Redox potentials and electrical conductivities of TCNQ complexes.

| Compound | $E^1_{1/2}$/V[a] | $E^2_{1/2}$/V[a] | Conductivity[b]/S cm$^{-1}$ |
|---|---|---|---|
| (**24**) | 0.500 | 0.775 | $1.7 \times 10^{-2}$ ($1.8 \times 10^{-2}$)[c] |
| (**18**) | 0.490 | 0.765 | [d] |
| (**23**) | 0.486 | 0.739 | $4.9 \times 10^{-7}$ ($5.0 \times 10^{-8}$)[c] |
| (**17**) | 0.480 | 0.729 | $3.9 \times 10^{-7}$ |
| (**13**) | 0.479 | 0.718 | $9.4 \times 10^{-2}$ |
| (**21**) | 0.474 | 0.700 | $1.0 \times 10^{-5}$[e] |
| (**15**) | 0.412 | 0.730 | $1.9 \times 10^{-1}$ |
| (**11**) | 0.390 | 0.690 | $8.4 \times 10^{-2}$ |
| (**12**) | 0.369 | 0.670 | $2.4 \times 10^{-3}$ |
| (**14**) | 0.368 | 0.661 | 1.4 |
| (**16**) | 0.364 | 0.685 | $1.1 \times 10^{-1}$ |
| (**19**) | 0.319 | 0.701 | $3.9 \times 10^{-1}$ |
| (**22**) | 0.270 | 0.604 | $4.6 \times 10^{-1}$ |
| (**20**) | 0.240 | 0.598 | $2.4 \times 10^{-1}$ |

[a] V *vs.* standard calomel electrode at a glassy carbon electrode, 0.1 M $Et_4NClO_4$–MeCN, scan rate 100mV/s. [b] Measured at room temperature on compressed pellets. [c] Ref. 9. [d] No complex was formed. [e] Ref. 7.

It is noteworthy that the TCNQ complex of (**14**) exhibits higher conductivity than that of TTF (**19**), tetramethyltetrathiafulvalene (**20**), and hexamethylenetetrathiafulvalene (**22**). Table 1 shows that a trimethylenedithio group attached to a TTF framework seems to increase the conductivity compared with the corresponding ethylenedithio group, although little difference in redox potentials of each type of donors is observed.

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