Conducting Salts Composed of Selenium Analogues of TMET-TTP

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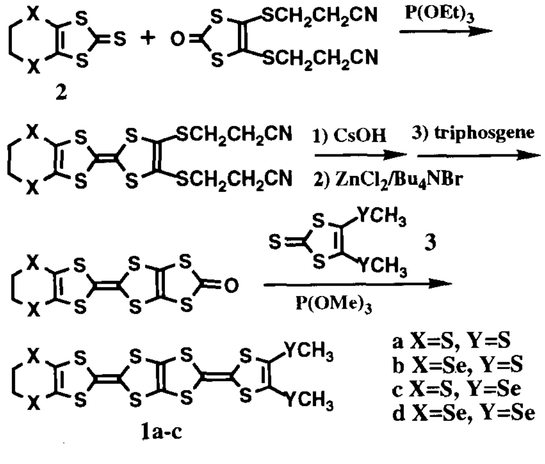
Selenium analogues of TMET-TTP (2-(4,5-bisthiomethyl-1,3-dithiol-2-ylidene)-5-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) **1b**-**d** have been synthesized. The iodine salt (**1b**)$_4$I$_3$ exhibits moderately high conductivity (σ_{rt} =13 S cm^{-1}) with semiconducting temperature dependence, and the donor arrangement is θ-type. The present θ-type salt as well as TMET-TTP salts is located at the insulating limit in the universal phase diagram of θ-phases.

Radical-cation salts of TTP(tetrathiapenetalene)-series donors have two-dimensional networks which are advantageous to stabilizing metal-like conductivity down to low temperatures.[1,2] Among them TMET-TTP (**1a**) forms θ-type salts regardless of the counter anions.[3] These salts show semiconducting conductivity below 200 K (σ_{rt} = 10 - 40 Scm^{-1}). Conducting properties of θ-type salts change systematically from an insulator to a metal as a function of the dihedral angle between the molecular planes.[4] The dihedral angles of θ-phase TMET-TTP salts are around 128 °, which falls into the insulating region. As an attempt to explore the influence of the molecular structure to the dihedral angle and to investigate the change of resulting properties, we have synthesized selenium analogues of TMET-TTP (**1b**-**d**) where the outer sulfur atoms of TMET-TTP are substituted by selenium atoms.



The target molecules were prepared by two steps of phosphite-mediated cross coupling.[5,6] Starting materials **2b** and **3c** were prepared according to Nigrey's method.[7] As a protecting group, cyanoethyl group was used instead of acetoxybenzyl group.[8] As shown in Table 1, these donors showed four-step oxidations characteristic of the TTP donors. Methylseleno substituted donors **1c** and **1d** showed by 0.03-0.04 V lower E_1 but by 0.05-0.12 V higher E_3, whereas E_2 was almost the same; these tendencies are the same as tetramethylseleno-TTP.[5]

Table 1. Redox potentials

Donor	E_1	E_2	E_3	E_4	E_2-E_1
1a (TMET-TTP)	0.48	0.70	0.98	1.11	0.22
1b	0.47	0.69	0.97	1.15	0.22
1c	0.45	0.71	1.03	1.19	0.26
1d	0.43	0.70	1.09	1.25	0.27

vs. Ag/AgCl in Bu$_4$NPF$_6$/PhCN at a Pt working electrode.

Table 2. Composition and Conductivity of (**1**)A$_x$

Donor	Anion	Solvent	x^a	σ_{rt}/S cm^{-1}	E_a/eV
1b	I$_3$	THF	0.27(I), 0.25(X)	13	0.07
	AuI$_2$	THF	0.29(Au), 0.27(I)	15	0.06
1c	PF$_6$	THF	0.61(P)	1.6	0.05
	ClO$_4$	TCE	0.62(Cl)	>10^{-4}	
	TCNQ	THF		3.3	0.04

^{a}Determined by the energy dispersion spectroscopy from the ratio of sulfur and the elements designated in the parentheses. X represents the value determined from the single crystal X-ray structure analysis.

Several radical-cation salts were grown by the electrochemical method (Table 2). Salts of **1b** exhibited moderately high conductivity; the values of room-temperature conductivity are about the same as those of the TMET-TTP salts.[3] Although many TMET-TTP salts showed almost flat temperature dependence down to 200 K, the present salts showed a gradual increase from room temperature, and an upturn around 200 K was less obvious.

X-ray single crystal structure analysis of (**1b**)$_4$I$_3$ has been carried out.[9] The structure is essentially isostructural to the TMET-TTP salts except for the doubling along the *c* (stacking) axis (Figures 1 and 2). Since I$_3$ is about 9.4 Å in length, *c* = 5 Å is too short to incorporate an I$_3$ anion, resulting in the doubling. However, the donors have θ-type arrangement. Two donors are crystallographically independent and I$_3$ is located on an inversion center. So the composition is 4:1; this is the same as many TMET-TTP salts.[3] The methyl groups extend out of the molecular plane; this is in accordance with the low degree of charge transfer.

The donors make pseudo stacks along the c axis, but the molecular planes are inclined by 64° from the c axis. Then the dihedral angle between the molecular planes of adjacent stacks is 128 °; this value is the same as TMET-TTP salts. In the stack the donors slide not only along the molecular short axis (1.8 Å) but also along the molecular long axis (3.0 Å) (Figure 3). By contrast usual BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) θ-phase does not have any slide along the molecular long axis.

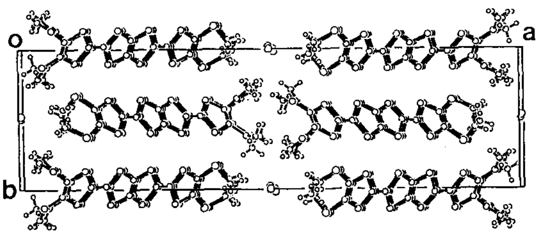


Figure 1. Crystal structure of (**1b**)$_4$I$_3$, projection along the c axis.

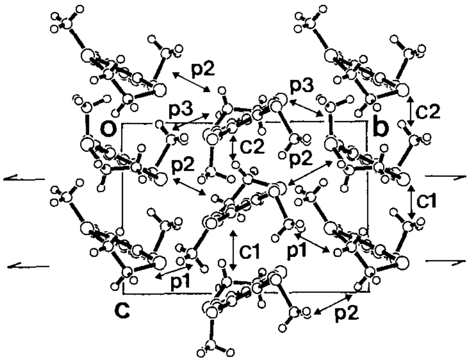


Figure 2. Donor arrangement of (**1b**)$_4$I$_3$.

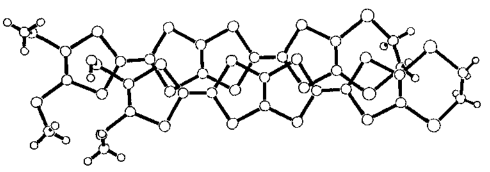


Figure 3. Overlap mode in (**1b**)$_4$I$_3$.

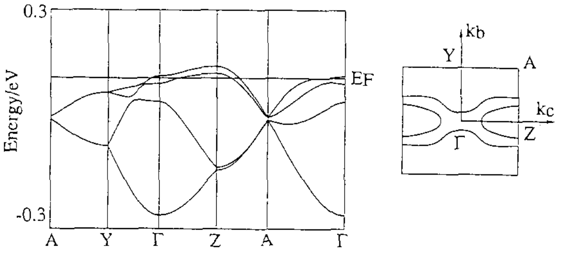


Figure 4. Energy band structure and Fermi surface of (**1b**)$_4$I$_3$.

Overlap integrals of HOMO are calculated to be c1 = 3.8, c2 = 3.5, p1 = 3.8, p2 = 5.4, and p3 = 4.5 x 10^{-3}. The tight-binding energy band structure and Fermi surface are depicted in Figure 4. Owing to the lattice doubling along the c axis, the Fermi surface is not a θ-like ellipse but folded at the ZA zone boundary to be separated to closed and open parts like that of α-phase.[10] Total bandwidth is comparatively small (0.45 eV) similarly to the TMET-TTP salts.

In conclusion the substitution of outer sulfur atoms to selenium atoms in TMET-TTP affords similar salts to TMET-TTP, which are located at the insulating limit in the universal phase diagram of θ-phases.

References and Notes

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6 **1b**: 28% yield; Mp 256 °C (dec.); ^{1}H NMR (δ in CDCl$_3$-CS$_2$) 2.40 (s, 6H), 3.33 (s, 4H). **1c**: 19% yield; Mp 214-217 °C (dec.); ^{1}H NMR 2.34 (s, 6H), 3.30 (s, 4H). **1d**: 17% yield; Mp 229 °C (dec.); ^{1}H NMR 2.34 (s, 6H), 3.36 (s, 4H).

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9 Crystal data of (**1b**)$_4$I$_3$: F_w=3007.97, monoclinic, space group P2$_1$/n, a= 40.15(1), b=11.286(8), c=10.019(4) Å, β= 94.02(2) °, Z=2, ρ_{calc}=2.2057 g cm^{-3}, and V=4529(9) Å^3. The final R=0.076 (R_w=0.083) for independent 4172 reflections (I>3σ(I)).

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