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Synthesis and Properties of Tetrakis(alkylseleno)tetrathiafulvalene

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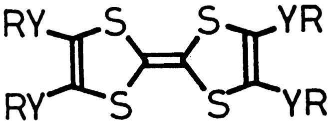
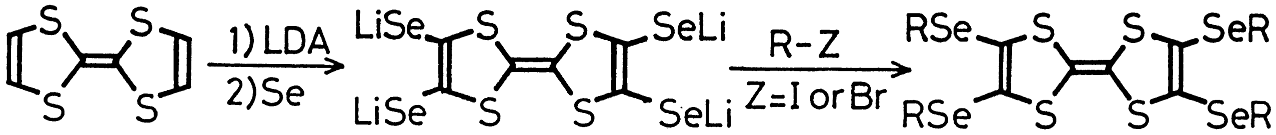
A series of tetrakis(alkylseleno)tetrathiafulvalene (TSeC$_n$-TTF; n = 1 - 18) has been synthesized. The melting points of this series showed the same dependency on the length of alkyl chains as the sulfur and the tellurium analogues. The g-values of the TYC$_1$-TTF cation radicals (Y = sulfur, selenium, and tellurium) are compared.

BEDT-TTF gives many cation radical salts which exhibit the metallic conductivity even at low temperature or ambient-pressure superconductivity. From the view point of the molecular design, BEDT-TTF is composed of central C_6S_4 group (TTF skeleton), outer four sulfur atoms, and ethylene groups. One can create new donor molecules by modifying each constituent. Previously, we prepared the series of TTC$_n$-TTF and TTeC$_n$-TTF which have four normal alkyl chains instead of the ethylene groups of BEDT-TTF.1,2) The electrical conductivities of the donor itself with long alkyl chains reach to a very high value of 10^{-6} S cm^{-1} as a single component organic compound. To realize this phenomenon, the concept of 'molecular fastener' has been derived from the manner of their crystal packing.3-5) It means that the central skeletons of C_6S_8 or $C_6S_4Te_4$ are fastened strongly by the van der Waals intermolecular interactions between the outer alkyl chains. On the other hand, TTeC$_1$-TTF showed a unique crystal structure in which two of the four tellurium atoms form the intermolecular zigzag quasi-covalent chains along the stacking axis. Consequently, this molecular crystal shows the extraordinarily high electrical conductivity of 10^{-5} S cm^{-1} and the high melting point of 175.2 - 176.2 °C.5) The situation is peculiar to this compound and has never occurred in both reported phases of the TTC$_1$-TTF.6) Moreover, the tellurium atoms of TTeC$_1$-TTF contribute to the intermolecular atomic contacts in the complex with TCNQ.7)



TYC$_n$-TTF
Y = Sulfur, Selenium, and Tellurium
R = $-C_nH_{2n+1}$

This paper describes the synthesis and the properties of TSeC$_n$-TTF which would supply the interesting complexes and the advanced comprehension to the series of TYC$_n$-TTF. The synthetic route of TSeC$_n$-TTF was the same as that of TTeC$_n$-TTF2,5,8,9) (Scheme 1). A typical procedure is as follows. A 100 ml, round-bottom, three-necked flask equipped with a thermometer and a magnetic stirrer was charged with 75 ml of dry THF and 1.55 ml of diisopropylamine (11.1 mmol). After



Scheme 1. Synthetic scheme of $TSeC_n$-TTF.

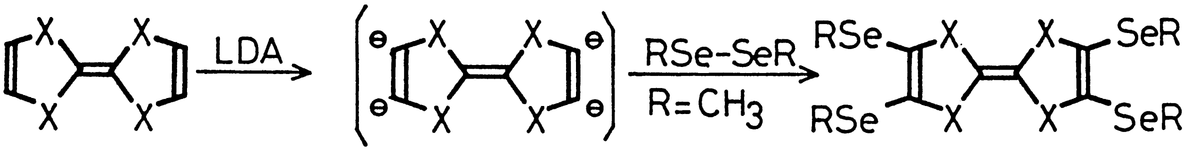
cooling in a dry-ice/acetone bath, the hexane solution containing 9.8 mmol of butyllithium was added and stirred for 50 min. TTF (0.5 g, 2.46 mmol) was added at once and stirring continued for 65 min under chilled conditions. Selenium powder (<100 mesh)(0.77 g, 9.75 mmol) was added to the yellow suspension. After an additional stirring for 40 min at that temperature, the cold bath was removed and stirring was continued for 7 hours at ambient temperature. When selenium had completely dissolved, a brownish suspension formed. The reaction mixture was cooled to ca. -40 °C and an excess amount of alkylhalide (ca. 20 mmol) was added. The cold bath was removed, and the stirring was continued overnight. All of the above procedures were carried out under Ar. The post-treatment was as follows. The reaction mixture was again cooled to 0 °C and water was added. The crude product was extracted with ether, washed with water and with brine, and dried with $MgSO_4$. After evaporation of the solvent, the residue was chromatographed over silica gel using a hexane-benzene mixture as an eluate. Repetitional recrystallizations from the solvents denoted in Table 1 gave the pure products which satisfy the elemental analyses. For n = 11 to 18, the quenching by water gave orange yellow precipitates which were isolated by filtration, washed with water, dried, and recrystallized several times. The yields and the melting points were summarized in Table 1.

From the point of the organic synthesis, dialkyldiselenide may react with TTF anions to give the target molecules directly (Scheme 2). In fact, the employment of dimethyldiselenide instead of the two-step introduction of selenium and methyliodide gave $TSeC_1$-TTF in 1.1% yield (not optimized). Our preliminary experiment showed that this reagent works more effectively in the preparation of the TSeF derivative. Pure $TSeC_1$-TSeF was obtained in 43% yield

Table 1. Yields, melting points, and the solvents for recrystallization of $TSeC_n$-TTF

n	Yield[a)] %	Mp θm/°C	Recryst.[b)] from
1	51.6	93.5 - 93.7	HB
		109.5 -109.7	H
2	69.8	62.7 - 63.5	HB
3	62.9	37.4 - 38.3	HB
4	55.2	38.8 - 39.3	H
5	55.9	29.9 - 30.7	H
6	56.3	32.5 - 32.9	H
7	61.6	39.0 - 39.7	H
8	68.7	48.7 - 49.2	HB
9	65.1	56.0 - 56.8	HB
10	83.8	62.2 - 62.8	HB
11	65.1	66.2 - 67.5	H
12	70.1	74.3 - 75.2	H
13	77.6	79.7 - 80.3	H
14	72.5	83.3 - 84.1	H
15	78.0	86.0 - 86.6	H
16	74.9	87.7 - 89.2	H
17	70.5	90.4 - 91.3	H
18	76.7	94.2 - 94.6	H

a) Based on TTF after the first recrystallization. b) H : hexane HB : hexane + benzene



Scheme 2. Synthetic scheme of $TSeC_1$-TTF using dimethyldiselenide (X = Sulfur, Selenium).

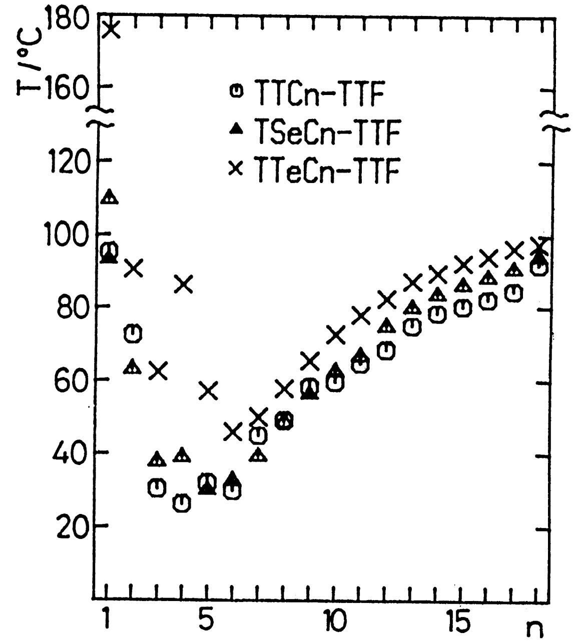


Fig. 1. Melting points of TYC$_n$-TTF.

Table 2. Redox potentials of TYC$_n$-TTF$^{a)}$

	$E^1_{1/2}$	$E^2_{1/2}$	ΔE
TTC$_n$-TTF	0.64	0.94	0.30
TSeC$_n$-TTF	0.58	0.93	0.35
TTeC$_n$-TTF	0.51	0.91	0.40

a) V vs. SCE in 0.1 M (TBA)BF$_4$/ClCH$_2$-CH$_2$Cl
ΔE = $E^2_{1/2} - E^1_{1/2}$.

by the usage of this reagent, whereas the two-step procedure afforded so many by-products not to be able to isolate the desired compound. The details will be reported soon.

It is worth noting that TSeC$_1$-TTF crystallizes in two phases. Recrystallization from the mixture of hexane and benzene gave only red needles having lower melting point. On the other hand, using pure hexane as the solvent gave red to reddish violet needles of the higher melting point phase, sometimes contaminated with the lower melting point one. The melting points were summarized with those of TTC$_n$-TTF and TTeC$_n$-TTF in Fig. 1. All the TYC$_n$-TTF show the similar dependencies on the length of the alkyl chains. Melting points decrease rapidly in the short chain regime, and then increase with the increment of the length of the alkyl chains with some exceptions. When n is greater than 9, the melting point increases in the order of Y = sulfur, selenium, and tellurium for the same n. Preliminary results of the conductivity measurements and this data indicate that the 'molecular fastener' should work in the TSeC$_n$-TTF with long alkyl chains.[10)] In the meanwhile, both phases of TSeC$_1$-TTF arouses our interest in their crystal structures because they melt at relatively low temperature and the low melting point phase has relatively high conductivity of 10^{-6} S cm^{-1}.[10)]

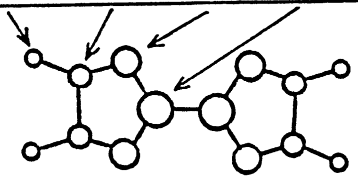
The redox potentials of TSeC$_n$-TTF were measured by cyclic voltammetry (vs. SCE, 0.1 M (Bu$_4$N)BF$_4$/CH$_2$Cl-CH$_2$Cl, Pt electrodes). The first and second redox potentials, $E^i_{1/2} = (E^i_{pa} + E^i_{pc})/2$ (i = 1,2) were independent on the length of the alkyl chains within the experimental error (maximum deviation is 0.02 V). This behavior is similar to those of TTC$_n$-TTF and TTeC$_n$-TTF. Table 2 summarizes the averaged values of each TYC$_n$-TTF. The $E^1_{1/2}$ values decrease in nuclear sequence of outer chalcogen atoms S, Se, and Te. This tendency reflects the electron affinity of each chalcogen atom. On the other hand, ΔE value also increases in that order, which is attributed mainly to the decrement of the resonance energy between the outer chalcogen atoms and carbon atoms. This realization is consistent with the Hückel MO parameters of each hetero atom.[11)]

In order to learn the distributions of the spin densities in the cation radicals, each TYC$_1$-TTF was oxidized electrochemically in the ESR cavity.[12)] Each of (TYC$_1$-TTF)$^+$ showed a symmetric absorption signal (the line widths were ca.

1.55, 1.74, and 1.88 Gauss for sulfur, selenium, and tellurium derivatives, respectively) The g values of these cation radicals were almost the same despite the large differences of the spin-orbit coupling constant of chalcogen atoms(Table 3). This fact suggests that the spin densities on the outer chalcogen atoms are so small as not to affect the g values. Under the rough approximation, this explanation is supported by the Hückel-McLachlan-type calculations using the hetero atom parameters taken from Ref. 11. The calculated spin densities were summarized in Table 3.

Table 3. g-Values and spin densities of TYC$_1$-TTF cation radicals

Y	g-Value	Calculated spin density			
S	2.0076	0.0056	0.053	0.10	0.17
Se	2.0075	0.0019	0.042	0.11	0.19
Te	2.0062	0.00016	0.037	0.11	0.20



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12) ESR spectra were measured by using a JEOL JES-FE1XG X-band (8.9 GHz) spectrometer equipped with the ESR-electrochemical cell (JEOL JES-EL-10). The g values were determined by comparing the resonance position with that of Li$^+$(TCNQ)$^-$ (g = 2.00263). 1,2-Dichloroethane containing 0.1 M (Bu$_4$N)BF$_4$ was used as the solvent. Before the electrolytic oxidation, the solution was degassed by passing argon gas for 30 min and then the appropriate voltage was applied.

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