Crystal Structures and Electrical Conductivities of TXC$_n$-TTF (X=Sulfur, Selenium, Tellurium; n=2,3)·TCNQ Charge-Transfer Complexes

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The crystal structures and the electrical conductivities have been studied for tetrakis(alkylchalcogeno)tetrathiafulvalene (TXC$_n$-TTF (X=sulfur, selenium, tellurium; n=2,3)) complexes with tetracyanoquinodimethane (TCNQ). All the complexes with a composition of 1 : 1 had the same crystal system (triclinic) and the same space group ($P\bar{1}$). The donor and acceptor molecules were alternately stacked in their crystals. (TSeC$_2$-TTF)TCNQ was obtained as plate and needle crystals. The molecular structure of TSeC$_2$-TTF and the overlapping mode between TSeC$_2$-TTF and TCNQ molecules of the two complexes were subtly different. All the complexes were semiconductors because of their mixed-stack structures. (TTeC$_2$-TTF)TCNQ showed the lowest resistivity (5 Ω cm at room temperature). Its good conductivity was brought about by the effective degree of charge-transfer and the favorable overlap between TTeC$_2$-TTF and TCNQ molecules. An overall discussion on the structural and physical properties of a series of TCNQ complexes with TXC$_n$-TTF (X=sulfur, selenium, tellurium; n=1,2,3) is presented.
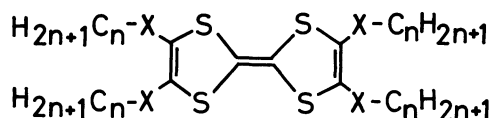
Tetrakis(alkylchalcogeno)tetrathiafulvalene (TXC$_n$-TTF) has exhibited novel electronic properties as a consequence of the intermolecular interactions between the tetrachalcogeno-TTF conjugated π systems and the alkyl side chains. TTC$_n$-TTF compounds with long alkyl chains had relatively low resistivities because of a reduction of the interplanar distances between the TTF skeletons through the van der Waals interactions of the alkyl side chains between molecules. This was termed "a molecular fastener effect".[1-4] This finding was significant since high conductivities in single-component organic solids are produced not by an external pressure but by an internal pressure derived from attractive forces between attached organic functional groups. TTeC$_1$-TTF is a new organic semiconductor with high electrical conductivity and high carrier mobility, which does not belong to the category of molecular fasteners. The unusual properties of TTeC$_1$-TTF are caused by a formation of regular Te chains through quasi-covalent Te–Te interatomic contacts between neighboring TTeC$_1$-TTF stacks.[5]

X = S : TTC$_n$-TTF
Se : TSeC$_n$-TTF
Te : TTeC$_n$-TTF

Scheme 1.

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TXC$_n$-TTF compounds are also attractive donors used in the formation of charge-transfer (CT) complexes.[6-9] TXC$_1$-TTF complexes with various acceptors have been actively investigated and a metallic conductivity has been found in (TTC$_1$-TTF)(I$_3$)$_{0.823}$.[10-13] TXC$_n$-TTF compounds with long alkyl side chains may form highly conductive CT complexes since they are expected to generate charge carriers in addition to their fastener effect. The present system allows us to systematically study how the chain length of alkyl groups and the variation of chalcogen atoms affect the physical properties of the complexes.

Various (TXC$_1$-TTF)–TCNQ complexes have been previously studied: the crystal structures and the physical properties of (TTC$_1$-TTF)TCNQ and (TTC$_1$-TTF)$_2$TCNQ were reported by Mori et al.[14] and those of (TSeC$_1$-TTF)TCNQ and (TTeC$_1$-TTF)TCNQ were reported by Iwasawa et al.[9,15,16] In this work, we prepared single crystals of TXC$_n$-TTF (X=S, Se, Te; n=2,3) complexes with TCNQ. We present the experimental results of their crystal structure determinations and electrical conductivity measurements. The correlation between the structure and the conductivity is discussed on the basis of the degree of charge-transfer (ionicity) and the molecular overlap between the donor and the acceptor.

Experimental

Black single crystals of TXC$_n$-TTF (X=S, Se, Te; n=2,3)·TCNQ were prepared by mixing hot CH$_3$CN solutions of each component and then keeping the solutions cool in a refrigerator (5 °C) or a freezer (−20 °C) for several days. (TTC$_2$-TTF)-TCNQ, (TSeC$_3$-TTF)TCNQ, (TTeC$_2$-TTF)TCNQ, and (TTeC$_3$-TTF)TCNQ crystallized in needles, while (TTC$_3$-TTF)TCNQ crystallized in plates. In the case of (TSeC$_2$-TTF)TCNQ, two kinds of crystals were obtained depending on

Table 1. Crystallographic Data of (TXC$_n$-TTF)TCNQ

	(TTC2-TTF)TCNQ	(TTC3-TTF)TCNQ	(TSeC2-TTF)TCNQ	(TSeC3-TTF)TCNQ	(TTeC2-TTF)TCNQ	(TTeC3-TTF)TCNQ
Chemical formula	$C_{26}H_{24}N_4S_8$	$C_{30}H_{32}N_4S_8$	$C_{26}H_{24}N_4S_4Se_4$	$C_{30}H_{32}N_4S_4Se_4$	$C_{26}H_{24}N_4S_4Te_4$	$C_{30}H_{32}N_4S_4Te_4$
FW	649.02	705.13	836.60	892.71	1031.16	1087.27
Crystal shape	Needle	Plate	Plate	Needle	Needle	Needle
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a/Å$	9.143(1)	9.107(1)	9.168(1)	9.203(2)	9.243(2)	10.285(2)
$b/Å$	11.374(2)	13.197(2)	11.418(1)	12.918(2)	11.287(2)	13.245(2)
$c/Å$	8.052(1)	8.168(1)	8.382(1)	8.494(3)	8.458(1)	8.467(2)
$\alpha/°$	95.37(1)	98.29(2)	92.14(1)	96.91(2)	90.80(1)	81.96(2)
$\beta/°$	105.83(1)	109.19(1)	110.66(1)	111.52(2)	107.90(1)	121.48(1)
$\gamma/°$	100.93(1)	101.58(1)	100.68(1)	101.88(2)	101.25(1)	108.09(2)
$V/Å^3$	781.5(2)	884.4(3)	801.8(2)	897.7(4)	821.0(2)	934.6(4)
Z	1	1	1	1	1	1
$D_x/g\,cm^{-3}$	1.379	1.324	1.733	1.651	2.086	1.932
R	0.048	0.078	0.057	0.060	0.038	0.039
$\mu(Mo\,K\alpha)/cm^{-1}$	5.71	5.10	48.03	42.95	37.96	33.39
$(\sin\theta/\lambda)_{max}$	0.7014	0.7009	0.7035	0.7026	0.7056	0.6965
No. of reflections	1205	1730	2516	2180	4074	1445

the temperature; plates formed at 5 °C and needles formed at −20 °C.

X-Ray diffraction data were collected at room temperature with a Rigaku AFC-5 automated four circle diffractometer with monochromatized Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation in the range of $2\theta < 60°$ using a θ–2θ scan technique. The unit cell parameters were determined by a least-squares fit of 50 reflections with $20° < 2\theta < 30°$. The crystallographic data are summarized in Table 1. The independent reflections ($|F_o| > 3\sigma(|F_o|)$) were used for structure analyses. The crystal structures were solved by the Patterson method for (TTeC3-TTF)TCNQ and the direct method using the MULTAN 78 program system[17] for the other complexes, and were refined by the block diagonal least-square method after an absorption correction. Anisotropic thermal parameters were adopted for non-hydrogen atoms and the hydrogen atoms were refined isotropically. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[18] All the calculations were carried out on a HITAC M-680H computer with the UNICS III program system.[19] The atomic parameters are listed in Table 2.[20]

The electrical conductivity along the long axis of the crystals, which corresponds to the a-axis, was measured between room temperature and 200 K with a four-probe method for (TTeC2-TTF)TCNQ and a two-probe method for the other complexes using a gold paste as electrical contacts.

Results and Discussion

Crystal Structure. The TXC$_n$-TTF (X=S, Se, Te; n=2,3) complexes with TCNQ crystallized in the triclinic system and the $P\bar{1}$ space group, as listed in Table 1. (TTC2-TTF)TCNQ and (TSeC3-TTF)TCNQ crystals were isomorphous to the (TSeC2-TTF)TCNQ needle-shaped crystal (abbreviated as n-(TSeC2-TTF)TCNQ). (TTC3-TTF)TCNQ and (TTeC2-TTF)TCNQ crystals were isomorphous to the (TSeC2-TTF)TCNQ plate-shaped crystal (abbreviated as p-(TSeC2-TTF)TCNQ). The crystal structure of (TTeC2-TTF)TCNQ was identical to that reported by Ahalon–Shalom et al.[21] Therefore, we have described the crystal structures of p-(TSeC2-TTF)TCNQ and n-(TSeC2-TTF)TCNQ only.

The molecular structures with atomic numbering schemes for p-(TSeC2-TTF)TCNQ and n-(TSeC2-TTF)TCNQ are illustrated in Figs. 1 and 2, respectively. The tetraseleno-TTF (C$_6$S$_4$Se$_4$) moieties in both complexes are nearly planar, in contrast to the nonplanar structure in the crystal of uncomplexed TSeC2-TTF.[22] The ethyl groups attached to Se(2) of p-(TSeC2-TTF)TCNQ lie almost coplanar to the C$_6$S$_4$Se$_4$ plane. The other ethyl groups attached to Se(1) are perpendicular to the C$_6$S$_4$Se$_4$ plane. This configuration of the molecule is denoted as the p-form. In constrast, the four ethyl groups of n-(TSeC2-TTF)TCNQ are perpendicular to the C$_6$S$_4$Se$_4$ plane. This configuration of the molecule is denoted as the n-form. The comparatively large temperature factors of the terminal carbon atoms of the ethyl groups in both complexes may be caused by large thermal vibrations. The molecular structure of TCNQ in these complexes is planar with a

Table 2. Positional Parameters (×10⁴) and Equivalent Isotropic Thermal Parameters (Å^2) of (TXC$_n$-TTF)TCNQ

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
	(TTC$_2$-TTF)TCNQ					(TSeC$_2$-TTF)TCNQ Needle Crystal			
S1	7501(2)	−2321(2)	8709(3)	6.6	Se1	7527(1)	−2231(1)	8941(1)	5.7
S2	5586(2)	−3383(2)	4543(3)	6.4	Se2	5636(1)	−3482(1)	4718(1)	5.6
S3	9510(2)	−461(1)	7407(2)	5.2	S1	9506(2)	−397(2)	7403(3)	4.7
S4	7897(2)	−1421(1)	3700(2)	4.7	S2	7973(2)	−1442(1)	3802(3)	4.3
C1	9471(6)	−398(5)	5236(8)	4.3	C1	9487(8)	−381(6)	5269(9)	3.8
C2	7981(7)	−1762(5)	6929(8)	4.7	C2	8009(8)	−1685(6)	6.993(9)	4.2
C3	7246(6)	−2192(5)	5250(8)	4.4	C3	7321(8)	−2147(6)	5374(9)	3.9
C4	9202(9)	−2843(7)	9680(9)	7.7	C4	9373(12)	−2847(9)	9787(12)	8.2
C5	9504(9)	−3829(7)	8540(11)	12.2	C5	9587(13)	−3814(10)	8593(14)	9.3
C6	5656(8)	−4132(6)	2508(9)	7.8	C6	5642(11)	−4070(9)	2489(12)	8.7
C7	6856(9)	−4795(7)	2667(12)	9.7	C7	6864(13)	−4770(10)	2476(16)	10.6
CC1	6184(6)	847(5)	6263(8)	4.7	CC1	6157(8)	865(7)	6205(9)	4.6
CC2	6002(6)	869(5)	4427(8)	4.4	CC2	6002(8)	835(6)	4444(9)	4.1
CC3	4754(7)	−19(5)	3207(8)	4.8	CC3	4791(9)	−62(7)	3246(9)	4.7
CC4	6965(7)	1711(5)	3866(8)	4.8	CC4	6965(8)	1658(7)	3829(10)	4.9
CC5	8203(7)	2609(5)	5062(8)	5.5	CC5	8160(9)	2570(7)	4980(11)	5.5
CC6	6810(7)	1762(5)	2058(9)	6.2	CC6	6806(9)	1661(8)	2038(10)	6.1
N1	9181(7)	3327(5)	6038(8)	7.7	N1	9111(8)	3281(7)	5918(10)	7.5
N2	6679(8)	1799(6)	633(8)	9.4	N2	6698(10)	1674(8)	641(10)	9.1
	(TTC$_3$-TTF)TCNQ					(TSeC$_3$-TTF)TCNQ			
S1	8771(3)	1963(2)	9721(3)	7.1	Se1	7178(1)	−2041(1)	8234(1)	6.3
S2	7877(3)	3041(2)	6222(3)	7.5	Se2	5159(1)	−3166(1)	3657(1)	6.4
S3	9706(2)	366(2)	7563(3)	6.3	S1	9420(2)	−403(2)	7174(3)	4.9
S4	8889(2)	1287(2)	4416(3)	6.0	S2	7788(2)	−1313(2)	3436(3)	4.7
C1	9713(8)	338(5)	5412(9)	5.5	C1	9415(8)	−368(5)	5127(10)	4.4
C2	9010(8)	1504(5)	7723(9)	5.6	C2	7789(8)	−1558(5)	6472(10)	4.2
C3	8640(8)	1936(5)	6315(9)	5.5	C3	7056(8)	−1985(5)	4796(10)	4.2
C4	10835(11)	2534(7)	11164(10)	9.7	C4	9236(10)	−2310(6)	9631(10)	5.8
C5	11617(13)	3525(12)	10730(13)	19.1	C5	9646(10)	−3238(7)	8818(11)	5.6
C6	12835(22)	4187(12)	11747(18)	21.5	C6	8482(12)	−4317(7)	8531(13)	7.5
C7	7877(13)	3325(7)	4105(12)	10.8	C7	6003(12)	−4155(7)	2447(13)	8.5
C8	7424(16)	4221(8)	3761(14)	14.2	C8	6899(15)	−4733(9)	3573(17)	10.8
C9	7264(17)	4448(8)	2027(15)	14.8	C9	7430(15)	−5585(8)	2610(16)	10.1
CC1	5155(8)	−68(5)	6747(8)	5.1	CC1	6268(8)	828(5)	6325(9)	3.9
CC2	4549(7)	762(5)	5978(8)	4.8	CC2	6054(7)	747(5)	4569(9)	3.8
CC3	4427(7)	788(5)	4191(8)	5.0	CC3	4753(8)	−113(5)	3237(9)	4.0
CC4	4114(8)	1504(5)	6958(8)	5.5	CC4	7097(9)	1462(5)	4098(9)	4.3
CC5	4193(8)	1493(5)	8753(9)	6.2	CC5	8377(9)	2340(6)	5372(10)	4.9
CC6	3528(9)	2341(5)	6301(9)	6.4	CC6	6938(9)	1388(6)	2341(11)	5.3
N1	4528(8)	1467(5)	10168(8)	8.3	N1	9410(8)	3027(6)	6370(9)	7.2
N2	3053(8)	3019(5)	5761(9)	8.8	N2	6810(9)	1332(6)	951(9)	7.5
	(TSeC$_2$-TTF)TCNQ Plate Crystal					(TTeC$_2$-TTF)TCNQ			
Se1	8557(1)	2166(1)	9394(1)	5.7	Te1[a)	83735(3)	21556(2)	95134(3)	4.1
Se2	7802(1)	3657(1)	5759(1)	5.7	Te2[a)	77926(3)	38785(2)	57381(3)	3.7
S1	9605(2)	345(1)	7392(2)	4.8	S1	9505(1)	302(1)	7332(1)	3.8
S2	8897(2)	1537(1)	4252(2)	4.7	S2	8946(1)	1570(1)	4286(1)	3.7
C1	9703(6)	392(4)	5363(6)	4.2	C1	9679(4)	392(3)	5347(5)	3.4
C2	8881(6)	1657(4)	7384(6)	4.1	C2	8777(4)	1614(3)	7327(4)	3.1
C3	8567(6)	2210(4)	5971(6)	4.0	C3	8530(4)	2216(3)	5943(4)	3.0
C4	10790(9)	2762(7)	10824(8)	7.8	C4	10802(6)	2840(5)	10834(6)	6.1
C5	11649(9)	3744(7)	10241(10)	8.7	C5	11602(6)	3767(5)	10048(8)	6.7
C6	8001(12)	4117(8)	3428(14)	12.5	C6	7667(7)	4076(5)	3186(6)	6.2
C7	6666(15)	3704(12)	2494(17)	19.0	C7	6117(9)	3921(8)	2043(8)	10.8
CC1	5062(6)	−131(5)	6681(6)	4.2	CC1	4995(4)	−169(3)	6635(4)	3.4
CC2	4461(5)	839(4)	5822(6)	4.0	CC2	4395(4)	807(3)	5788(4)	3.3
CC3	4424(6)	932(5)	4102(6)	4.3	CC3	4435(4)	935(3)	4115(5)	3.4
CC4	3919(6)	1656(5)	6611(6)	4.5	CC4	3798(4)	1597(3)	6561(5)	3.7
CC5	3906(7)	1550(5)	8300(7)	5.5	CC5	3747(5)	1474(4)	8221(5)	4.4
CC6	3352(7)	2649(5)	5797(7)	5.9	CC6	3236(5)	2599(4)	5764(6)	4.5
N1	3879(7)	1455(5)	9641(6)	7.9	N1	3691(6)	1359(4)	9539(5)	6.5
N2	2892(8)	3430(5)	5140(7)	8.5	N2	2777(6)	3389(4)	5098(6)	6.3

Table 2.   (Continued)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
					(TTeC$_3$-TTF)TCNQ				
Te1	13007(1)	2064(1)	11344(1)	5.9	C8	13140(24)	4690(16)	6840(28)	15.3
Te2	15039(1)	3224(1)	8396(1)	6.0	C9	12332(21)	5563(12)	5240(23)	11.3
S1	10667(3)	420(2)	7796(4)	4.5	CC1	4799(12)	−113(8)	11532(14)	3.9
S2	12170(3)	1285(2)	5582(4)	4.4	CC2	6088(11)	698(7)	11538(13)	3.4
C1	10584(11)	355(8)	5699(13)	4.0	CC3	6237(11)	796(7)	9933(13)	3.7
C2	12287(11)	1528(8)	8689(13)	3.9	CC4	7158(11)	1405(8)	13047(13)	3.9
C3	12984(11)	1933(8)	7700(14)	3.9	CC5	7049(13)	1321(9)	14641(15)	5.2
C4	10757(13)	2306(9)	10442(15)	5.4	CC6	8427(12)	2235(8)	13089(16)	5.0
C5	10373(14)	3231(9)	9215(16)	5.7	N1	6990(12)	1259(8)	15973(13)	6.9
C6	11408(16)	4302(11)	10058(20)	8.1	N2	9450(12)	2930(8)	13136(15)	7.2
C7	13756(22)	4335(13)	6176(24)	13.4					

a) Positional parameters (×10^5).

maximum deviation of only 0.033 Å for CC(1). The planar structure is commonly observed in many TCNQ complexes.

Figures 3(a) and 3(b) show the intermolecular overlap between the donor and the acceptor of p-(TSeC$_2$-TTF)TCNQ and n-(TSeC$_2$-TTF)TCNQ, respectively. In the case of p-(TSeC$_2$-TTF)TCNQ, a six-membered ring of TCNQ overlaps one of the two five-membered rings of TSeC$_2$-TTF. This overlapping manner is denoted as the p-mode. On the other hand, n-(TSeC$_2$-TTF)TCNQ has a disadvantageous donor–acceptor overlap with a smaller overlap between a six-membered ring of TCNQ and a five-membered ring of TSeC$_2$-TTF. This overlapping manner is denoted as the n-mode.
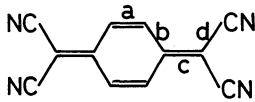
Figures 4(a) and 4(b) show the crystal structures of p-(TSeC$_2$-TTF)TCNQ and n-(TSeC$_2$-TTF)TCNQ, respectively. In both complexes, the donor and acceptor molecules alternately stack along the a-axis. The molecular short axis of the C$_6$S$_4$Se$_4$ molecular plane is nearly parallel to the c-axis.

The molecular structure of TTeC$_3$-TTF in the (TTeC$_3$-TTF)TCNQ complex is analogous to that of TSeC$_2$-TTF in n-(TSeC$_2$-TTF)TCNQ and the donor–acceptor

overlapping mode is analogous to that of p-(TSeC$_2$-TTF)TCNQ. The characteristic difference between (TTeC$_3$-TTF)TCNQ and the other complexes is that in the (TTeC$_3$-TTF)TCNQ complex the stacking axis is [101] which is different from the growing axis [100] of the crystal.

We have observed interchain atomic contacts in the (TXC$_2$-TTF)TCNQ complexes which are shorter than the sum of the van der Waals radii. n-(TSeC$_2$-TTF)-TCNQ possesses a contact between the outer chalcogen atoms, while (TTeC$_2$-TTF)TCNQ possesses a contact between the outer chalcogen atom and the nitrogen atom. The shortest distances are 3.58 Å (Se(2)–Se(2) in n-(TSeC$_2$-TTF)TCNQ) and 3.28 Å (Te(2)–N(2) in (TTeC$_2$-TTF)TCNQ). In contrast, (TXC$_3$-TTF)TCNQ complexes do not possess any interchain atomic contacts due to a disturbance of the longer propyl groups elongated in the interchain direction.

Degree of Charge-Transfer. The degree of CT (γ) for the TCNQ complexes was estimated from the bond lengths of TCNQ by the procedure developed by Kistenmacher et al.[23]   Table 3 presents the calculated values of γ for the present TCNQ complexes.

Table 3.   Bond Lengths of TCNQ and Degree of Charge-Transfer for (TXC$_n$-TTF)TCNQ

	a/Å	$b^{a)}$/Å	c/Å	$d^{a)}$/Å	$c/(b+d)$	γ	
(TTC$_2$-TTF)TCNQ	1.331(9)	1.439(8)	1.369(9)	1.429(8)	0.477	0.04	
(TTC$_3$-TTF)TCNQ	1.327(10)	1.443(10)	1.377(10)	1.433(11)	0.479	0.13	
(TSeC$_2$-TTF)TCNQ							
Plate	1.350(8)	1.436(8)	1.383(8)	1.430(8)	0.483	0.29	
Needle	1.343(11)	1.426(10)	1.397(11)	1.435(11)	0.488	0.50	
(TSeC$_3$-TTF)TCNQ	1.363(11)	1.434(9)	1.393(11)	1.435(10)	0.486	0.42	
(TTeC$_2$-TTF)TCNQ	1.340(6)	1.434(6)	1.386(6)	1.428(6)	0.484	0.33	
(TTeC$_3$-TTF)TCNQ	1.352(13)	1.426(17)	1.395(12)	1.404(18)	0.493	0.71	
TCNQ	1.346(3)	1.448(4)	1.374(3)	1.441(3)	0.476	0	Ref. 23
TCNQ$^-$	1.373(4)	1.423(4)	1.420(4)	1.416(4)	0.500	1	Ref. 23

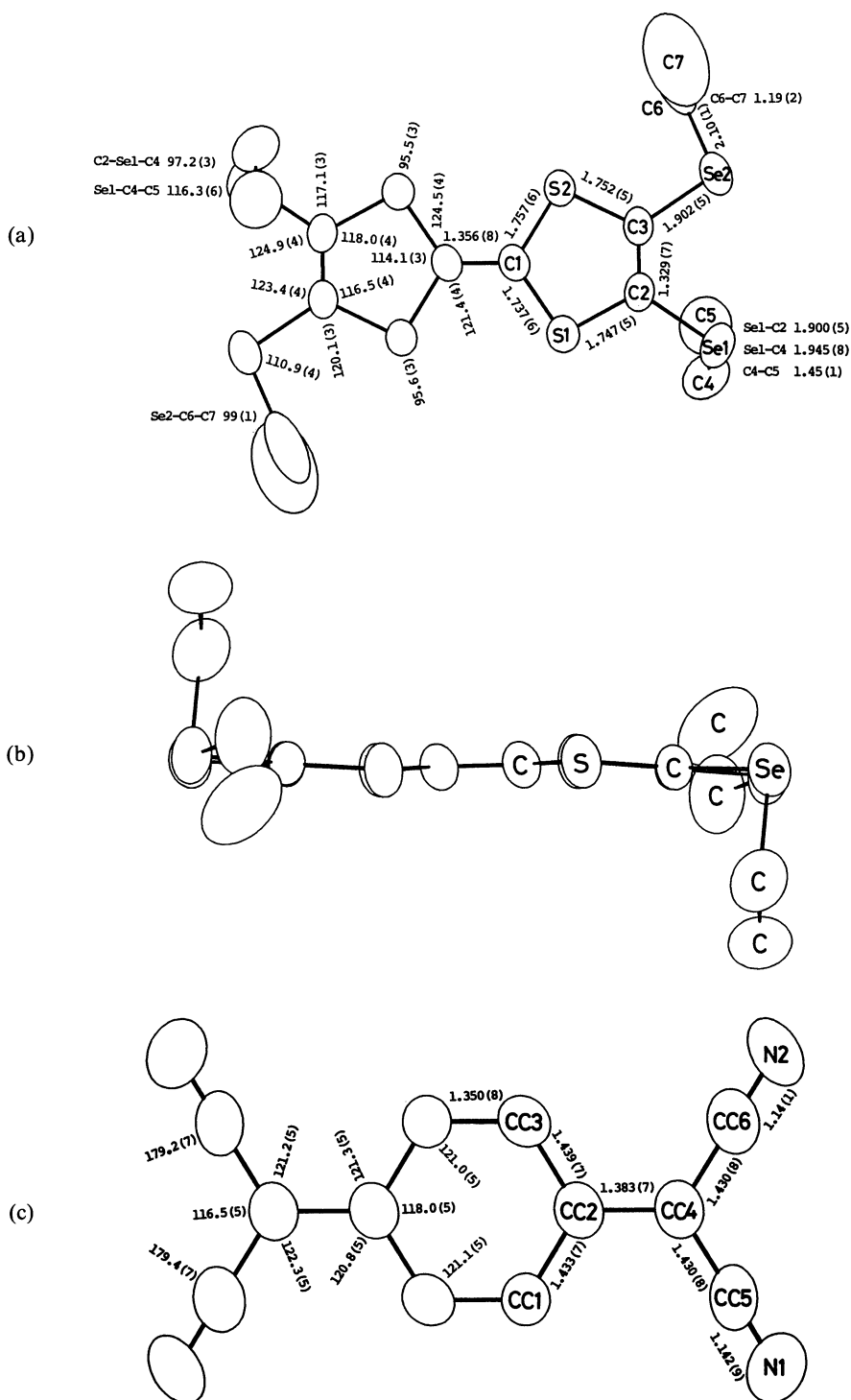a) The average value of the two equivalent bond lengths.

Fig. 1. Molecular structures and atomic numbering schemes of the donor (top view (a) and side view (b)) and the acceptor (c) of p-(TSeC$_2$–TTF)TCNQ.

Furthermore, γ was also estimated by the IR procedure established by Chappell et al.[24] The calculated γ from the CN stretching vibration frequencies in the nujol samples are listed in Table 4.

The electronic spectra in the KBr pellets showed the charge-transfer bands. These CT absorption energies are also listed in Table 4. The charge-transfer transition energy (E_{CT}) in a neutral complex with a mixed-stack can be expressed by the following equation:[25]

$$E_{CT} = I_p - E_A - E_M,$$

Fig. 2. Molecular structures and atomic numbering schemes of the donor (top view (a) and side view (b)) and the acceptor (c) of n-(TSeC$_2$-TTF)TCNQ.

where I_p is the ionization potential of a donor, E_A is the electron affinity of an acceptor, and E_M is a crystal Madelung energy value. A large E_{CT} gives a small γ, while a small E_{CT} gives a large γ.

The X-ray and IR methods gave somewhat different estimated values of γ. However, TTC$_n$-TTF(n=2,3)·TCNQ, TSeC$_n$-TTF(n=2,3)·TCNQ, and TTeC$_n$-TTF(n=2,3)·TCNQ had about the same CT absorption energies (6100—5200 cm^{-1}, 4700—4600 cm^{-1}, and 4200—3900 cm^{-1}, respectively). This fact suggested that γ of
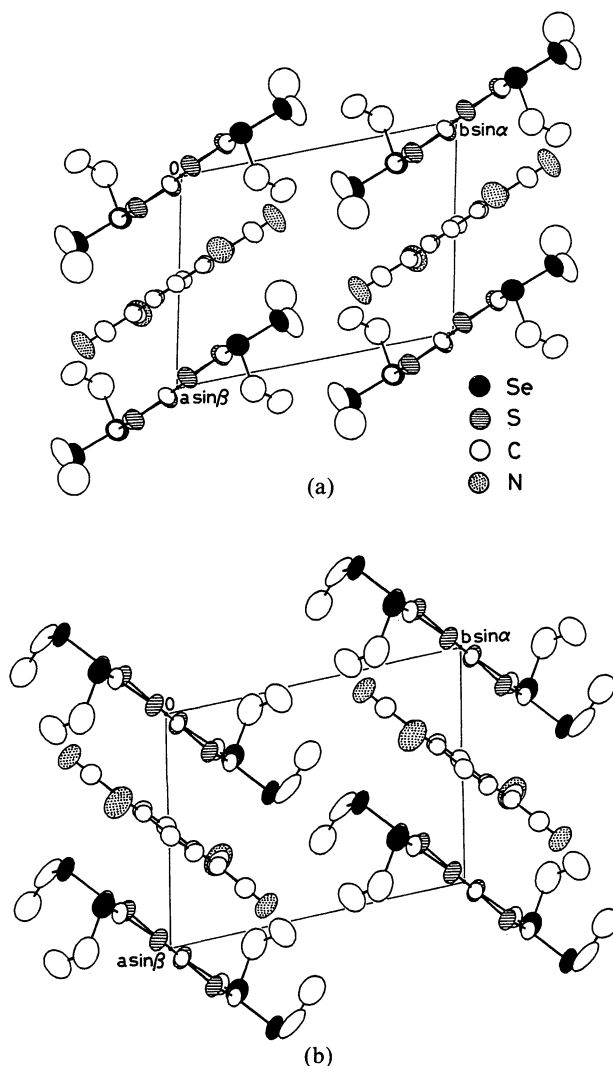
Table 4. Degree of Charge-Transfer (γ) Calculated by the IR Method, Charge-Transfer
Absorption Energy (E_{CT}), and Electrical Properties of (TXC$_n$-TTF)TCNQ

	ν_{CN}/cm^{-1}	γ	E_{CT}/cm^{-1}	ρ_{RT}/Ω cm	E_a/eV
(TTC$_2$-TTF)TCNQ	2214	0.30	6100	3.6×10^7	0.35
(TTC$_3$-TTF)TCNQ	2214	0.30	5200	1.2×10^6	0.33
(TSeC$_2$-TTF)TCNQ					
Plate	2212	0.34	4700	3.5×10^3	0.09
Needle	2216	0.25	4700	2.3×10^5	0.29
(TSeC$_3$-TTF)TCNQ	2214	0.30	4600	2.2×10^6	0.39
(TTeC$_2$-TTF)TCNQ	2206	0.48	4200	5.0	0.06
(TTeC$_3$-TTF)TCNQ	2204	0.52	3900	7.5×10^3	0.18

(a)

(b)
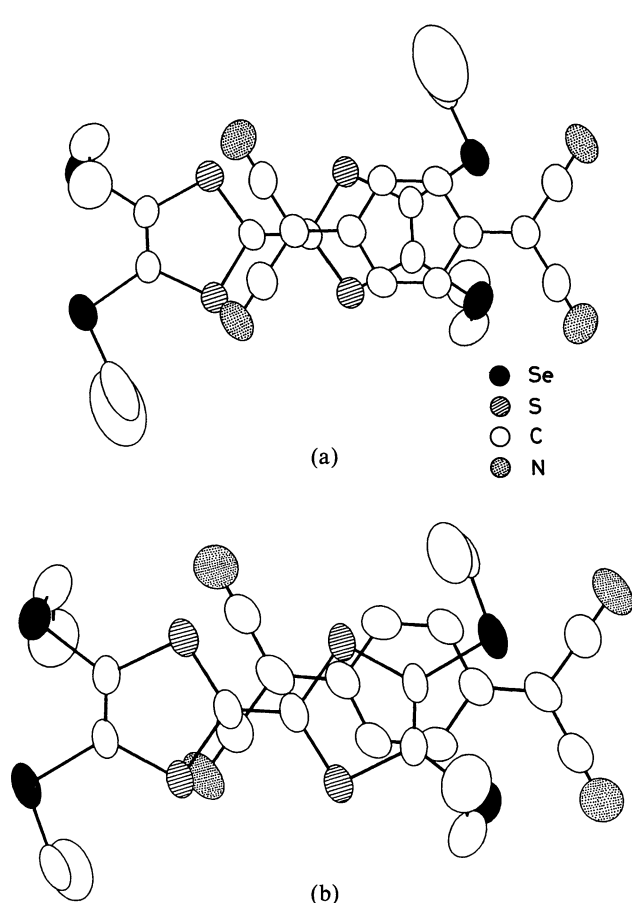
Fig. 3. Overlapping modes between the donor and
acceptor molecules; (a) p-(TSeC$_2$-TTF)TCNQ, (b) n-
(TSeC$_2$-TTF)TCNQ.

(a)

(b)

Fig. 4. Crystal structures projected along the c-axis; (a)
p-(TSeC$_2$-TTF)TCNQ, (b) n-(TSeC$_2$-TTF)TCNQ.

TTC$_n$-TTF(n=2,3)·TCNQ, TSeC$_n$-TTF(n=2,3)·TCNQ,
and TTeC$_n$-TTF(n=2,3)·TCNQ were in the ranges of
0.04—0.30, 0.25—0.50, and 0.33—0.71, respectively.

In the present system, γ increased in the order TTC$_n$-
TTF(n=2,3)·TCNQ<TSeC$_n$-TTF(n=2,3)·TCNQ<
TTeC$_n$-TTF(n=2,3)·TCNQ. According to the cyclic
voltammetry studies of TXC$_n$-TTF (X=S, Se, Te; n=1—
18),[9] the first redox potentials of TXC$_n$-TTF com-
pounds were independent of n and decreased in the order
TTC$_n$-TTF>TSeC$_n$-TTF>TTeC$_n$-TTF. Thus, the
tendency of the ionicity observed in the present system
could be explained by the decrease of (I_p-E_A).

Electrical Conductivity. The electrical resistivity at
room temperature (ρ_{RT}) and the activation energy (E_a) are
given in Table 4. (TTeC$_2$-TTF)TCNQ showed a
markedly low resistivity of 5 Ω cm, which was smaller
than the value (ca. $10^2 \Omega$ cm) reported by Aharon–
Shalom et al.[21] The measurement by Aharon–Shalom
et al. may have included a contact resistance. p-(TSeC$_2$-
TTF)TCNQ and (TTeC$_3$-TTF)TCNQ also showed

relatively low resistivities of 3.5×10^3 and 7.5×10^3 Ω cm, respectively. The other complexes showed comparatively high resistivities of 10^5—10^7 Ω cm. The temperature dependence of the resistivities for all the complexes was simply semiconductive, which resulted from the alternate stacks of the donor and acceptor molecules in their crystal structures. (TTeC$_2$-TTF)-TCNQ, which had the lowest resistivity, had the lowest E_a (0.06 eV).

The electrical conductivity is universally expressed by a simple relation: $\sigma=ne\mu$. The carrier number n and the carrier mobility μ are believed to depend on γ and the magnitude of the molecular orbital overlap of the donor and the acceptor in the crystal, respectively. According to the band calculation by the extended Hückel method,[26] the intermolecular overlap integrals between the highest occupied molecular orbital (HOMO) of TSeC$_2$-TTF and the lowest unoccupied molecular orbital (LUMO) of TCNQ along the stacking direction were -8.78×10^{-3} and 7.36×10^{-3} for p-(TSeC$_2$-TTF)TCNQ and n-(TSeC$_2$-TTF)TCNQ, respectively. The p-mode had an overlap integral larger than of the n-mode.

The high resistivities of (TTC$_2$-TTF)TCNQ and (TTC$_3$-TTF)TCNQ are easily understood in terms of the smaller γ values. n-(TSeC$_2$-TTF)TCNQ and (TSeC$_3$-TTF)TCNQ also showed high resistivities due to the n-mode overlap with a smaller overlap integral (as shown in Fig. 3(b)) in spite of having a larger γ than the S analogues.

The best planes for the C$_6$S$_4$X$_4$(X=S, Se, Te) moieties of the donor and TCNQ were parallel to each other. The interplanar distances were 3.45, 3.44, 3.51, 3.49, 3.43, 3.57, and 3.47 Å for (TTC$_2$-TTF)TCNQ, (TTC$_3$-TTF)-TCNQ, p-(TSeC$_2$-TTF)TCNQ, n-(TSeC$_2$-TTF)TCNQ, (TSeC$_3$-TTF)TCNQ, (TTeC$_2$-TTF)TCNQ, and (TTeC$_3$-TTF)TCNQ, respectively. These complexes had nearly the same interplanar spacings, which meant that the complexes including Se and Te atoms with larger van der Waals radii had stronger intermolecular interactions than the S analogues. The lower resistivities of p-(TSeC$_2$-TTF)TCNQ, (TTeC$_2$-TTF)TCNQ, and (TTeC$_3$-TTF)TCNQ compared with the S analogues are qualitatively explained in terms of the difference of the van der Waals radii of the chalcogen atoms. (TTeC$_2$-TTF)TCNQ had the lowest resistivity among the present complexes, owing to the p-mode overlap with a larger overlap integral (as shown in Fig. 3(a)) and the effective γ.

(TTeC$_3$-TTF)TCNQ possessed the p-mode overlap shown in Fig. 3(a) and the highest γ. However, (TTeC$_3$-TTF)TCNQ showed a higher resistivity than (TTeC$_2$-TTF)TCNQ, because of a mismatch between the measuring direction of the conductivity and the stacking direction of the donor and acceptor molecules. If we can measure along the stacking axis, a lower resistivity of (TTeC$_3$-TTF)TCNQ is expected to be observed.

Finally, we compared the crystal structures and the electrical properties of the TXC$_1$-TTF(X=S, Se, Te)-TCNQ complexes,[9,14-16] The structural and physical properties of TXC$_n$-TTF(X=S, Se, Te; n=1,2,3)-TCNQ complexes are presented in Table 5. The molecular structure of the donor and the donor(D)-acceptor(A) overlapping mode in TXC$_1$-TTF(X=S, Se, Te)·TCNQ were analogous to those of p-(TSeC$_2$-TTF)TCNQ. (TTeC$_1$-TTF)TCNQ made simple DA type stacks, similar to TXC$_n$-TTF (X=S, Se, Te; n=2,3)·TCNQ. In contrast, (TTC$_1$-TTF)TCNQ and (TSeC$_1$-TTF)TCNQ formed DDAA mixed-stacks, and (TTC$_1$-TTF)$_2$TCNQ formed a DDA mixed-stack.

(TTC$_1$-TTF)TCNQ and (TSeC$_1$-TTF)TCNQ had interchain atomic contacts between the outer chalcogen atom and the nitrogen atom, similar to (TTeC$_2$-TTF)TCNQ. In particular, (TTeC$_1$-TTF)TCNQ had a unique crystal structure with three-dimensional intermolecular interactions through two kinds of DA stacks along the [110] and [1$\bar{1}$0] direction and strong interchain Te–N contacts. These chalcogen–N interactions modulated the CN stretching vibration frequency and caused an overestimation of γ by the IR method for (TXC$_1$-TTF)TCNQ.

Judging from the value of γ calculated by the X-ray method and E_{CT}, (TTC$_1$-TTF)TCNQ, (TTC$_1$-TTF)$_2$-TCNQ, and (TSeC$_1$-TTF)TCNQ were in the neutral CT state, similar to TTC$_n$-TTF(n=2,3)·TCNQ. It was difficult to determine the ionicity of (TTeC$_1$-TTF)TCNQ by the IR and X-ray methods.

Summary

TXC$_n$-TTF (X=S, Se, Te; n=2,3) formed semiconductive 1 : 1 CT complexes with TCNQ, in which donor and acceptor molecules alternately stacked with a uniform spacing. This situation was in contrast to (TXC$_1$-TTF)-TCNQ complexes with a variety of stoichiometries and donor–acceptor stacks. It was of interst that (TSeC$_2$-TTF)TCNQ crystallized in plates and needles. These two phases had different crystal structures and showed different electrical properties. The crystal structures of the other complexes were isomorphous to either p-(TSeC$_2$-TTF)TCNQ or n-(TSeC$_2$-TTF)TCNQ.

The ionicity of TXC$_n$-TTF (X=Se, Te; n=2,3)·TCNQ was at the boundary between the neutral (N) and ionic (I) states. These complexes may exhibit an N–I phase transition induced by temperature and/or pressure.

(TXC$_1$-TTF)TCNQ and (TXC$_2$-TTF)TCNQ had two- or three-dimensional networks in the crystals through intrachain and interchain atomic contacts less than the van der Waals distance. On the other hand, (TXC$_3$-TTF)TCNQ was one-dimensional. TXC$_n$-TTF($n\geqslant$4) did not form CT complexes with TCNQ. The reason was speculated to be a decrease of lattice energy by further weakened interchain interactions, in addition to a size mismatch between the donor and TCNQ molecules.

Table 5. Summary of Structural and Physical Properties of (TXCₙ-TTF)–TCNQ Complexes

n = 1

	X=T (Sulfur)[a]		X=Se[a]	X=Te[a]
D:A	1:1	2:1	1:1	1:1
Stacking	DDAA	DDA	DDAA	DA
Spacing	Non-uniform	Non-uniform	Non-uniform	Uniform
	D··D A··A D··A	D··D D··A	D··D A··A D··A	
/Å	3.48 3.41 3.58	3.51 3.60	3.51 3.38 3.28	3.38
Molecular structure	p-Form[b]	p-Form	p-Form	p-Form
Mode of DA overlap	p-Mode[b]	p-Mode	p-Mode	p-Mode
γ (X-ray)	0.04	0.25	0.29	>1
γ (IR)	0.57	0.43	0.61	>1
E_{CT}/cm^{-1}	6000	5100	6000	4800
$\rho_{RT}/\Omega\,\mathrm{cm}$	3.8×10^5	5.5×10^4	1.5×10^5	1.0×10^2
E_a/eV	0.30	0.17	0.35	0.11
Melting point/°C	111—112	105	131—132	312—315

n = 2

	X=T (Sulfur)[a]	X=Se[a] Plate	X=Se[a] Needle	X=Te[a]
D:A	1:1	1:1	1:1	1:1
Stacking	DA	DA	DA	DA
Spacing	Uniform	Uniform	Uniform	Uniform
/Å	3.45	3.51	3.49	3.57
Molecular structure	n-Form[b]	p-Form	n-Form	p-Form
Mode of DA overlap	n-Mode[b]	p-Mode	n-Mode	p-Mode
γ (X-ray)	0.04	0.29	0.50	0.33
γ (IR)	0.30	0.34	0.25	0.48
E_{CT}/cm^{-1}	6100	4700	4700	4200
$\rho_{RT}/\Omega\,\mathrm{cm}$	3.6×10^7	3.5×10^3	2.3×10^5	$5.0\ (\sim10^{2c})$
E_a/eV	0.35	0.09	0.29	0.06
Melting point/°C	108—109	108—109	107—108	151—154

n = 3

	X=T (Sulfur)[a]	X=Se[a]	X=Te[a]
D:A	1:1	1:1	1:1
Stacking	DA	DA	DA
Spacing	Uniform	Uniform	Uniform
/Å	3.44	3.43	3.47
Molecular structure	p-Form	n-Form	n-Form
Mode of DA overlap	p-Mode	n-Mode	p-Mode
γ (X-ray)	0.13	0.42	0.71
γ (IR)	0.30	0.30	0.52
E_{CT}/cm^{-1}	5200	4600	3900
$\rho_{RT}/\Omega\,\mathrm{cm}$	1.2×10^6	2.2×10^6	7.5×10^3
E_a/eV	0.33	0.39	0.18
Melting point/°C	95—96	100—101	87—89

a) The first redox potential $(E^1_{1/2})$ vs. SCE 0.1 M TBA·BF₄/CH₂ClCH₂Cl, Pt electrode: 0.64 V (TTCₙ-TTF), 0.58 V (TSeCₙ-TTF), 0.51 V (TTeCₙ-TTF). b) The abbreviation is described in the text. c) The value reported by Aharon-Shalom et al. (Ref. 21).

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