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SYNTHESIS AND PROPERTIES OF 7,10-DITHIAFLUOROANTHENES AND THEIR 8,9-DIHYDRO DERIVATIVES WITH CHALCOGEN SUBSTITUENTS

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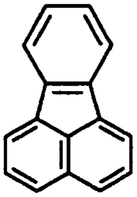
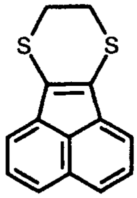
Abstract 3,4-Bis(methylthio)- and 3,4-dichalcogeno-8,9-dihydro-7,10-dithiafluoroanthene and 3,4-bis(methylthio)- and 3,4-dithio-7,10-dithiafluoroanthene were synthesized as novel donor components for organic conductors. These donors showed low oxidation potentials, and intermolecular van der Waals interaction between the sulfur atoms was observed by X-ray crystallographic analysis. The radical cation salts and charge transfer complexes of the donors with various inorganic and organic acceptors were prepared either by electrocrystallization in the presence of tetraalkylammonium salts or by recrystallization of the mixture of donors and acceptors. Some of these radical cation salts showed good electrical conductivities.

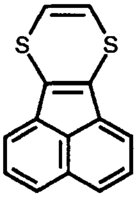
Keywords: Organic donor, radical cation salt, charge transfer complex, X-ray crystallographic analysis, electrical conductivity

INTRODUCTION

Simple arenes such as naphthalene, fluoroanthene (**1**), perylene, and pyrene give electrically conducting radical cation salts, represented approximately as $[Aryl_2]X_{1+x}(Solv.)$, by anodic oxidation.[1] These radical cation salts represent a very interesting class of organic metals with electrical conductivites up to a few thousands Scm^{-1} at room temperature. However they are generally unstable and the conductivities lose quickly. Replacement of the sp^2 carbon atoms by sulfur atoms or introduction of sulfur substituents at the periphery in these arenes generally brings about remarkable improvement in stability of their radical cation salts and charge transfer complexes.[2-4] In addition, it is known that their electrical conductivities are improved by the construction of S···S networks through strong van der Waals interaction in the crystals.[2-5] Introduction of peri-dichalcogen bridges into such polycyclic arenes also supplies superior π-electron donors.[2,5] We have recently synthesized 7,10-dithiafluoroanthene (**3**) as a new donor, which has produced stable metallic cation radical salts.[6] In order to improve the donor abilities of **3** and its dihydro derivative (**2**), the introduction of further sulfur (or chalcogen) at the aromatic periphery has been attempted. In this paper we report the synthesis, structures, and electrochemical properties of new donors **7** - **11**, which have a peri-dicalcogen bridge or two methylthio groups. Furthermore, the conducting properties of their radical cation salts and charge transfer salts are described.







SYNTHESIS AND PHYSICAL PROPERTIES OF THE DONORS

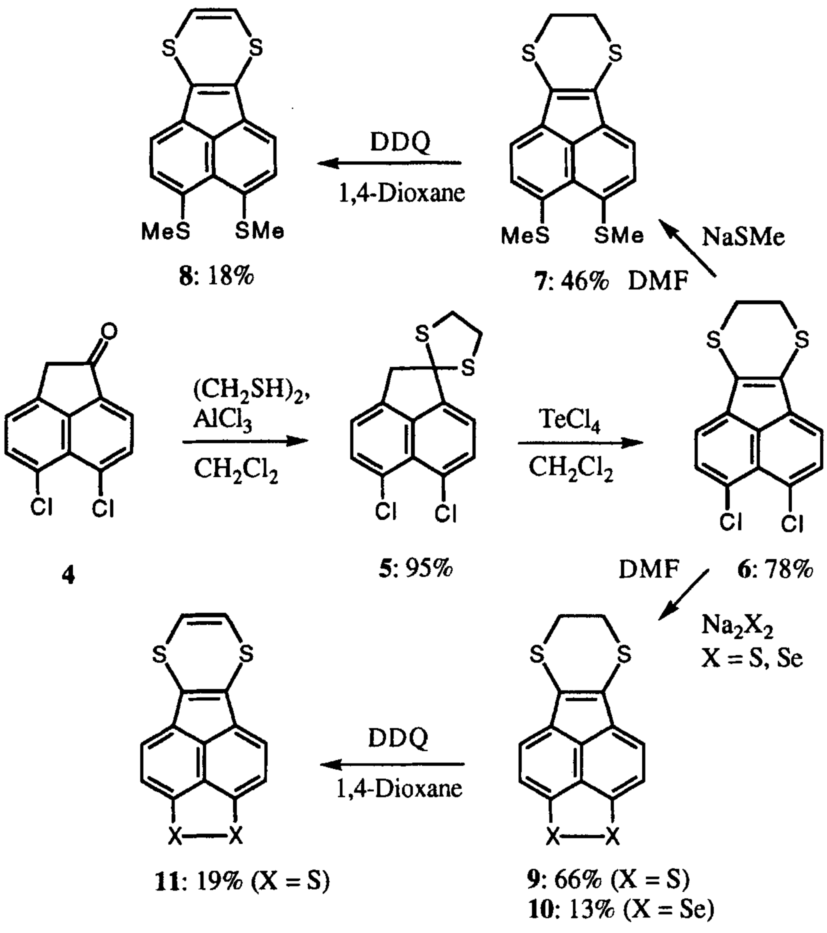
The synthetic approach to the novel donors is illustrated in SCHEME 1. These donors were synthesized starting with 5,6-dichloroacenaphthenone (**4**) in four steps. 1,2-Ethylenedithio-5,6-dichloroacenaphthylene (**6**) was prepared by the ring expansion reaction of 5,6-dichloroacenaphthenone ethylenedithioacetal (**5**), which was easily available from **4** by dithioacetalization, with tellurium tetrachloride in dichloromethane. 5,6-Bis(methylthio)- (**7**) and 5,6-dithia-1,2-ethylenedithio-acenaphthylene (**9**) were prepared by the reaction of **6** with sodium thiomethoxide or sodium sulfide in DMF in 46 and 66% yields, respectively. 5,6-diselena-1,2-ethylenedithio-acenaphthylene (**10**) was obtained in 13% yield by using sodium diselenide instead of sodium disulfide in the above reaction condition. The subsequent dehydrogenation of **7** and **9** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave **8** and **11** in 18 and 19% yields, respectively. The cyclic voltammetric data of the new donors (**7** - **11**) prepared in this study, are summarized in TABLE I along with those of **2** and **3**.

TABLE I Redox Potentials (V vs. SCE) of **2**, **3**, and **7** - **11**

Compound	First (E_1/V)	Second (E_2/V)	ΔE(/V)=E_2 -E_1
2	0.89	1.39	0.50
3	0.68	1.42	0.74
7	0.65	1.19	0.54
8	0.49	0.83	0.34
9	0.71	0.86	0.15
10	0.70	1.05	0.35
11	0.51	0.92	0.41

[platinum electrode versus SCE; tetrabutylammonium perchlorate (0.1 M) in acetonitrile, scan rate 50 mV s^{-1}]; E_1: Reversible; E_2: Irreversible, anodic peak potential

First redox potentials of the donors with two methylthio or dithio substituents at 5,6-positions are generally lower by about 0.2 V than those of the parent compounds. And the change of ethylenedithio to vinylenedithio substituents at 1,2-positions further lowers the first redox potentials by about 0.2 V, which is due to the extended conjugation (see compounds **2** –> **3**, **7** –> **8**, **9** –> **11**). But the substitution of sulfur atoms of **9** by heavier chalcogen atoms (Se and Te) resulted in the rise of second oxidation potentials.



SCHEME 1. The synthetic approach to the donors[7]

PREPARATION AND CRYSTAL STRUCTURE OF THE RADICAL CATION SALTS

The preparation of the radical cation salts of the donors (**7** - **11**) was carried out by electrocrystallization in the presence of various tetraalkylammonium salts. When **7** - **11** were electrooxidized in dichloromethane by platinum electrodes in the presence of various tetrabutylammonium salts as a supporting electrolyte, black crystals of their charge transfer salts grew on the anode.[8] The compositions of these salts were determined by elemental analysis (TABLE IV). These salts are stable and the electrical conductivities of the salts has not been changed after more than several months at room temperature.

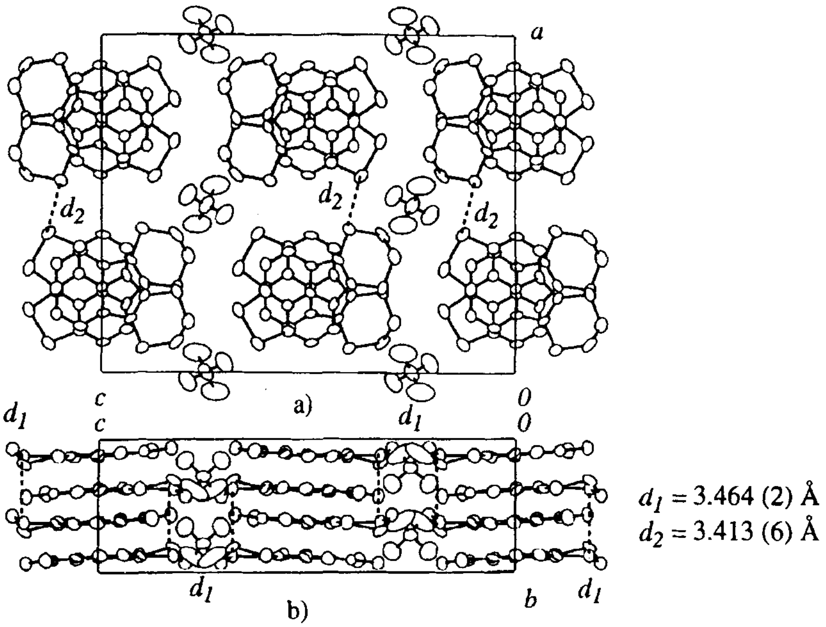


FIGURE 1 Crystal structure of $(\mathbf{9})_2BF_4$ viewed along a) the *b* axis and b) the *a* axis. (The hydrogen atoms are omitted.)

The radical cation salts of **9** and **10** with tetrafluoroborate (BF_4^-) were obtained in single crystals suitable for an X-ray crystallographic analysis.[9] Crystal data, and selected bond lengths and angles of these radical cation salts were shown in TABLE II and III, respectively, together with those of neutral **9** and **10**.

Although the crystal structures of neutral **9** and **10** were quite different from each other, both donors afforded the radical cation salts with BF_4^- anion which were the identical orthorhombic space group *Pbcn* having the same composition (donor : anion = 2 : 1) and similar cell dimension, i.e. isomorphous (TABLE II). The BF_4^- anion was on 2-fold rotation axis and there was only one crystallographically independent donor molecule, accodingly, which led to a half of positive charge on each donor. There was observed no systematic difference between the bond distances of the donors **9** and **10** and the correspondings in their BF_4 salts. The molecular packings are shown in FIGURE 1 and 2. The columnar stack of the donors was found along the *b* axis in the both radical cation salts. By the replacement of sulfur atoms to selenium atoms at the 3,4-positions of the donors, improvement of dimensionality from pseudo two- to three-dimensional heteroatom van der Waals connectivities was found (Figure 1 and 2). In $(\mathbf{9})_2BF_4$, short S···S van der Waals interactions (d_1 = 3.464(2) and d_2 = 3.413(6) Å) are observed along the *b* and *a* axes, respectively. In $(\mathbf{10})_2BF_4$, a substantial interaction due to a S···Se contact (d_3 = 3.650(3) Å) appeared along the *c* axis other than the *a* and *b* directions (d_1 = 3.479(1) and d_2 = 3.421(3) Å).

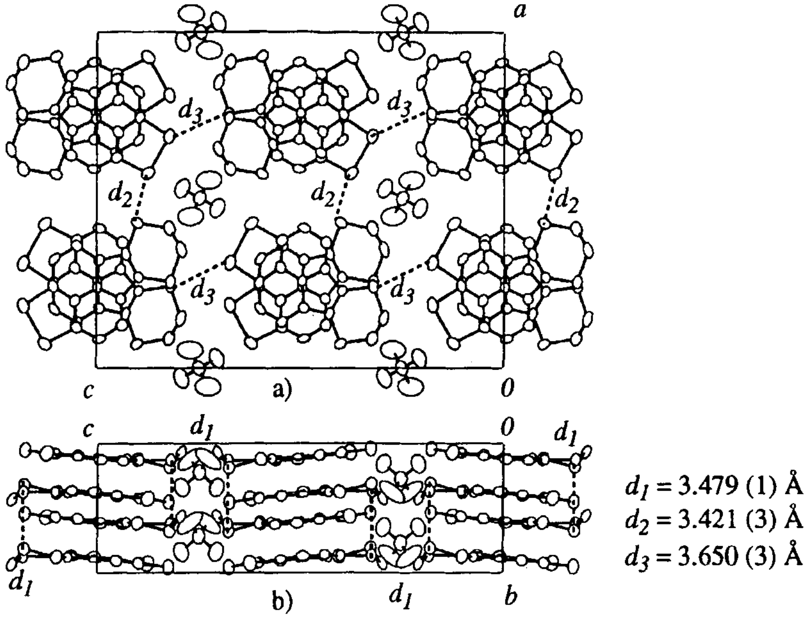


FIGURE 2 Crystal structure of $(\mathbf{10})_2BF_4$ viewed along a) the *b* axis and b) the *a* axis. (The hydrogen atoms are omitted.)

TABLE II Crystal data of **9**, **10**, and their BF_4 salts.

	9	$(\mathbf{9})_2BF_4$	**10**	$(\mathbf{10})_2BF_4$
Formula	$C_{14}H_8S_4$	$C_{28}H_{16}S_8BF_4$	$C_{14}H_8S_2Se_2$	$C_{28}H_{16}S_4Se_4BF_4$
F_w	304.46	695.72	398.26	883.32
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	*P*2₁/*n*	*Pbcn*	*Pbca*	*Pbcn*
a / Å	7.1651(6)	17.628(6)	12.543(2)	17.813(6)
b / Å	14.538(2)	6.912(4)	21.427(3)	6.941(2)
c / Å	12.134(1)	21.905(5)	9.484(2)	22.142(6)
α / °	90	90	90	90
β / °	100.875(8)	90	90	90
γ / °	90	90	90	90

(Continued)

V / Å^3	1241.2(2)	2669(3)	2548.8(8)	2738(3)
Z	4	4	8	4
D_{calc}	1.629	1.731	2.076	2.143
No. of unique reflections	2974	3500	3336	3592
R, R_w	0.041, 0.047	0.072, 0.079	0.045, 0.042	0.049, 0.050

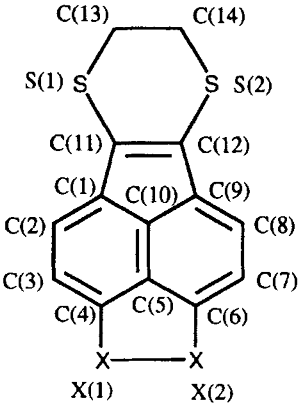


FIGURE 3 Atomic numbering scheme for neutral **9**, **10**, **9** in $(\mathbf{9})_2BF_4$, and **10** in $(\mathbf{10})_2BF_4$

TABLE III Selected Bond lengths and angles of **9**, **10**, and their BF_4 salts.

	9	$(\mathbf{9})_2BF_4$	**10**	$(\mathbf{10})_2BF_4$
Bond length / Å				
S(1)-C(11)	1.740(3)	1.71(1)	1.73(1)	1.73(1)
S(1)-C(13)	1.783(5)	1.79(2)	1.80(1)	1.81(1)
S(2)-C(12)	1.736(3)	1.72(1)	1.73(1)	1.72(1)
S(2)-C(14)	1.799(5)	1.86(2)	1.80(1)	1.72(1)
C(1)-C(2)	1.372(4)	1.39(2)	1.35(2)	1.38(4)
C(1)-C(10)	1.407(4)	1.41(2)	1.40(2)	1.40(1)
C(1)-C(11)	1.471(4)	1.45(2)	1.50(2)	1.48(1)
C(2)-C(3)	1.418(4)	1.41(2)	1.42(1)	1.42(1)
C(3)-C(4)	1.382(4)	1.38(2)	1.37(1)	1.38(1)
C(4)-C(5)	1.400(4)	1.42(2)	1.40(2)	1.40(1)
C(5)-C(6)	1.409(4)	1.41(2)	1.41(2)	1.40(1)
C(5)-C(10)	1.370(4)	1.38(2)	1.37(1)	1.39(1)
C(6)-C(7)	1.378(4)	1.39(2)	1.35(2)	1.39(1)
C(7)-C(8)	1.425(4)	1.40(2)	1.44(2)	1.39(1)
C(8)-C(9)	1.380(4)	1.39(2)	1.37(1)	1.39(1)
C(9)-C(10)	1.405(4)	1.40(2)	1.38(1)	1.41(1)
C(9)-C(12)	1.474(4)	1.47(2)	1.47(1)	1.46(1)
C(11)-C(12)	1.376(4)	1.42(2)	1.38(2)	1.38(1)
C(13)-C(14)	1.372(7)	1.51(2)	1.50(2)	1.48(2)
C(4)-X(1)	1.754(3)	1.754(3)	1.90(3)	1.90(1)
C(6)-X(2)	1.761(3)	1.76(1)	1.91(1)	1.893(9)
X(1)-X(2)	2.094(1)	2.099(6)	2.357(2)	2.337(2)

(Continued)

Bond angles / °				
C(11)-S(1)-C(13)	99.6(2)	102.9(7)	101.0(6)	100.6(5)
C(12)-S(2)-C(14)	102.5(2)	101.0(7)	100.4(6)	100.8(5)
C(2)-C(1)-C(10)	117.6(3)	118(1)	119(1)	119(1)
C(2)-C(1)-C(11)	137.9(3)	138(1)	137(1)	137(1)
C(10)-C(1)-C(11)	104.5(3)	104(1)	104(1)	103.9(9)
C(1)-C(2)-C(3)	120.3(3)	119(1)	119(1)	118(1)
C(2)-C(3)-C(4)	120.6(3)	123(1)	122(1)	121.5(9)
C(3)-C(4)-C(5)	119.5(3)	119(1)	119(1)	121(1)
C(4)-C(5)-C(6)	122.9(3)	124(2)	125(1)	127(1)
C(4)-C(5)-C(10)	118.7(3)	118(1)	119(1)	117(1)
C(6)-C(5)-C(10)	118.4(3)	118(1)	116(1)	115.9(9)
C(5)-C(6)-C(7)	119.4(3)	121(1)	121(1)	121.4(9)
C(6)-C(7)-C(8)	120.8(3)	119(1)	121(1)	121.5(9)
C(7)-C(8)-C(9)	120.3(3)	121(1)	119(1)	119.0(9)
C(8)-C(9)-C(10)	117.0(3)	119(1)	118(1)	118.3(9)
C(8)-C(9)-C(12)	138.4(3)	137(1)	135(1)	136(1)
C(10)-C(9)-C(12)	104.6(3)	104(1)	107(1)	105.4(9)
C(1)-C(10)-C(5)	123.3(3)	124(1)	123(1)	123.6(9)
C(1)-C(10)-C(9)	112.7(3)	114(1)	112(1)	112.6(9)
C(5)-C(10)-C(9)	124.0(3)	122(1)	125(1)	123.8(9)
S(1)-C(11)-C(1)	122.4(2)	123(1)	122.6(9)	122.1(8)
S(1)-C(11)-C(12)	128.4(2)	123(1)	128(1)	127.9(8)
C(1)-C(11)-C(12)	109.2(2)	109(1)	109(1)	110.0(8)
S(2)-C(12)-C(9)	123.2(2)	122(1)	123.3(9)	122.7(8)
S(2)-C(12)-C(11)	127.7(2)	129(1)	129.2(9)	129.3(8)
C(9)-C(12)-C(11)	109.0(2)	109(1)	107(1)	108.0(9)
S(1)-C(13)-C(14)	121.7(4)	114(1)	114.7(9)	114.3(9)
S(2)-C(14)-C(13)	124.6(4)	113(1)	115.3(9)	113.0(9)
X(1)-C(4)-C(5)	112.9(2)	111(1)	115.9(9)	113.7(8)
C(4)-X(1)-X(2)	95.9(1)	96.5(6)	91.7(4)	92.6(3)
X(1)-X(2)-C(6)	96.3(1)	96.4(6)	92.1(4)	92.7(3)
X(2)-C(6)-C(5)	112.0(2)	112(1)	114.7(9)	113.7(8)

ELECTRICAL CONDUCTIVITIES OF RADICAL CATION SALTS AND CHARGE TRANSFER COMPLEXES

Compounds **7** - **11** produced radical cation salts with various kinds of inorganic acceptors and charge transfer complexes with organic acceptors. Physical properties and compositions, and electrical conductivites of the radical cation salts and charge transfer complexes are summarized in TABLE IV. Electrical conductivities of the salts and complexes were measured using compressed pellets by a four probe method.

Among the various salts, (**9**)$_2$BF$_4$ showed the highest electrical conductivity of σ = 18 Scm^{-1} at room temperature. The temperature dependence of the single crystal conductivity of (**9**)$_2$BF$_4$ was measured along the needle (*b* direction) by a two probe method and exhibited metallic behavior down to 260 K. (**10**)$_2$BF$_4$ also showed high electrical conductivity of $\sigma = 9$ Scm^{-1} at room temperature. The temperature dependence of the single crystal conductivity of $(\mathbf{10})_2BF_4$ was measured along the needle (*b* direction) by a two probe method, because of the small size of the sample crystals, and exhibited metallic behavior down to 200 K.

Most of the radical cation salts of the donors (**7**, **9** - **11**) obtained by electrocrystallization with other inorganic anions also showed similar good electrical conductivities (TABLE IV), while the charge transfer complexes obtained from the solution of **7** - **11** with TCNQ (tetracyanoquinodimethane) were almost insulators or low electrical conductors. This result might be attributed to the low degree of charge transfer (ca. 0.2 – 0.3) estimated by the nitrile stretching frequency in infra red absorption spectra[10] and to the alternating mixed stacking of donor and acceptor in each crystal. The donors **9**, **10**, and **11** with $TCNQF_4$ (tetrafluorotetracyanoquinodimethane) or DDQ formed the charge transfer complexes which showed fairy good electrical conductivities (10^{-3} - 10^{-5} Scm^{-1}).

TABLE IV Physical properties, elemental analysis, and conductivities of radical cation and charge transfer complexes.

Salt or Complex Appearance	D.p. / °C	Found (Calcd.) / % C	 H	 N	σ / Scm$^{-1,a)}$
$(\mathbf{7})PF_6$ Black needles	170	40.12 (40.08)	2.94 (2.94)		3×10^{-3}
$(\mathbf{7})ClO_4$ Black needles	213	44.24 (44.28)	3.27 (3.27)		4×10^{-3}
$(\mathbf{7})BF_4$ Black needles	199	49.89 (45.61)	3.16 (3.35)		6×10^{-3}
$(\mathbf{7})(ReO_4)$ Black solids	>300	32.87 (32.87)	2.57 (2.41)		2×10^{-4}
$(\mathbf{7})$TCNQ Black needles	233	61.99 (62.43)	3.56 (3.37)	10.64 (10.40)	$<10^{-8}$
$(\mathbf{7})_2TCNQF_4$ Black needles	246	55.57 (55.07)	2.86 (2.31)	8.25 (9.17)	$<10^{-8}$
$(\mathbf{7})$DDQ Black needles	164	51.19 (51.34)	2.59 (2.51)	5.44 (4.99)	$<10^{-8}$
$(\mathbf{8})PF_6$ Black needles	225	40.52 (40.25)	2.59 (2.53)		$<10^{-8}$
$(\mathbf{8})ClO_4$ Black plates	215	—$^{b)}$ (—)	—$^{b)}$ (—)		$<10^{-8}$
$(\mathbf{8})BF_4$ Black powder	217	45.71 (45.83)	3.07 (2.88)		$<10^{-8}$
$(\mathbf{8})I_3$ Black powder	191	27.12 (26.94)	1.95 (1.70)		9×10^{-4}

(Continued)

($\mathbf{8}$)NO_3 Black plates	219	52.14 (52.87)	3.54 (3.33)	1.75 (1.93)	$<10^{-8}$
($\mathbf{9}$)$_2PF_6$ Black needles	160	44.52 (44.61)	2.12 (2.14)		0.04
($\mathbf{9}$)$_2ClO_4$ Black needles	>300	47.15 (47.48)	2.22 (2.28)		5
($\mathbf{9}$)$_2BF_4$ Black needles	185	48.25 (48.34)	2.36 (2.32)		18c)
($\mathbf{9}$)$_4(ReO_4)_3$ Black needles	146	34.29 (34.17)	1.71 (1.64)		9×10^{-4}
($\mathbf{9}$)$I_{3.5}$ (from $C_2H_4Cl_2$) Black needles	118	22.21 (22.46)	0.99 (1.08)		1.5
($\mathbf{9}$)$I_{1.1}$ (from MeCN) Black powder	124	37.91 (37.89)	1.71 (1.82)		3×10^{-3}
($\mathbf{9}$)TCNQ Dark green needles	257	61.96 (61.40)	2.41 (2.38)	10.43 (11.01)	$<10^{-8}$
($\mathbf{9}$)$_2TCNQF_4$ Black prisms	>300	54.17 (53.79)	1.94 (1.39)	9.26 (9.65)	2×10^{-5}
($\mathbf{9}$)DDQ Black needles	>300	49.13 (49.72)	1.86 (1.52)	4.83 (5.27)	3×10^{-6}
($\mathbf{10}$)$_3(PF_6)_2$ Black needles	>300	34.04 (33.98)	2.24 (1.63)		0.1
($\mathbf{10}$)$_2ClO_4$ Black needles	>300	37.24 (37.54)	2.34 (1.80)		0.5
($\mathbf{10}$)$_2BF_4$ Black prisms	183	38.25 (38.07)	1.96 (1.83)		9c)
($\mathbf{10}$)ReO_4 Black solids	130	26.14 (25.93)	1.76 (1.24)		9×10^{-4}
($\mathbf{10}$)TCNQ Black needles	258	52.31 (51.84)	2.28 (2.01)	9.31 (9.30)	$<10^{-8}$
($\mathbf{10}$)$_2TCNQF_4$ Black needles	236	47.42 (46.31)	1.65 (1.20)	8.56 (8.31)	2×10^{-5}
($\mathbf{11}$)PF_6 Black plates	>300	37.17 (37.58)	1.90 (1.35)		4×10^{-4}
($\mathbf{11}$)$_3(ClO_4)_2$ Black needles	>300	45.12 (45.60)	1.86 (1.64)		3×10^{-3}
($\mathbf{11}$)$_3(BF_4)_2$ Black needles	242	46.51 (46.67)	2.05 (1.68)		0.06
($\mathbf{11}$)$_3(I_3)_2$ Black needles	211	30.21 (30.23)	1.32 (1.09)		0.1
($\mathbf{11}$)TCNQ Black needles	>300	61.22 (61.64)	2.20 (1.99)	10.83 (11.06)	$<10^{-8}$
($\mathbf{11}$)DDQ Black needles	>300	49.45 (49.91)	1.43 (1.14)	4.90 (5.29)	2×10^{-3}

a) Measured on compressed pellets by the van der Pauw method at room temperature.
b) Not determined. c) Measured on a single crystal by a two probe method.

DEDICATION

Dedicated to Professor F. Ogura of Hiroshima University for his outstanding contribution in synthesis of new organic conductors.

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7. Physical properties and spectral data of the new compounds:

7: ^{1}H NMR(CDCl$_3$) δ = 2.55(6H, s), 3.37(4H, s), 7.22(2H, d, J = 7.3 Hz), 7.39(2H, d, J = 7.3 Hz). ^{13}C NMR(CDCl$_3$) δ = 18.56, 26.76, 118.94, 122.05, 124.87, 126.48, 129.34, 136.60, 137.92. IR(KBr) 2908, 1574, 1474, 1304, 1284, 1268, 1198, 1170, 1132, 952, 790, 660, 488 cm^{-1}. MS(20 eV) m/z 334(M^{+}:100), 304(25), 276(51). HRMS(70 eV) Found: 333.9945. Calcd for C$_{16}$H$_{14}$S$_4$: 333.997838. UV(CH$_2$Cl$_2$) $\lambda(\varepsilon)$ = 500(2495), 404(18635), 345(5291), 266(30110), 226(21639) nm. Found: C, 57.34; H, 4.31%. Calcd for C$_{16}$H$_{14}$S$_4$: C, 57.45; H, 4.22%.

8: ^{1}H NMR(CDCl$_3$) δ = 2.63(6H, s), 6.29(2H, s), 7.23(2H, d, J = 7.3 Hz), 7.37(2H, d, J = 7.3 Hz). ^{13}C NMR(CDCl$_3$) δ = 18.38, 119.44, 120.54, 124.15, 125.04, 126.42, 131.12, 133.61, 140.06. IR(KBr) 2920, 1574, 1414, 1304, 1246, 1076, 954, 818, 784, 668, 490 cm^{-1}. MS(20 eV) m/z 332(M^{+}:94), 302(100), 270(71), 149(43). HRMS(70 eV) Found: 331.9815. Calcd for C$_{16}$H$_{12}$S$_4$: 331.9821876. UV(CH$_2$Cl$_2$) $\lambda(\varepsilon)$ = 430(22601), 413(22674), 347(6694), 246 (29698), 209(18801) nm. Found: C, 57.56; H, 3.61%. Calcd for C$_{16}$H$_{12}$S$_4$: C, 57.80; H, 3.64%.

9: ^{1}H NMR(CDCl$_3$) δ = 3.44(4H, s), 7.40(2H, d, J = 7.3 Hz), 7.56(2H, d, J = 7.3 Hz). ^{13}C NMR(CDCl$_3$) δ = 26.88, 115.83, 120.68, 120.99, 127.75, 130.02, 132.52, 142.24. IR(HBr) 2900, 1466, 1440, 1286, 1264, 1202, 1176, 1114, 884, 784, 440 cm^{-1}. MS(20 eV) m/z 304(M^{+}: 80), 276(100), 232(47). UV(CH$_2$Cl$_2$) $\lambda(\varepsilon)$ = 452(24061), 433(24774), 332(2463), 275(33637), 226(21271) nm. Found: C, 55.33; H, 2.61%. Calcd for C$_{14}$H$_8$S$_4$: C, 55.23; H, 2.65%.

10: ^{1}H NMR(CDCl$_3$) δ = 3.43(4H, s), 7.47(2H, d, J = 7.3 Hz), 7.55(2H, d, J = 7.3 Hz). ^{13}C NMR(CDCl$_3$) δ = 26.83, 119.16, 120.20, 120.26, 120.61, 120.70, 134.52, 140.83. IR(HBr) 2912, 1400, 1052 cm^{-1}. MS(20 eV) m/z 400([C$_{14}$H$_8$S$_2$Se$^{80}{}_2$]$^{+}$: 77), 398([C$_{14}$H$_8$S$_2$Se^{80}Se^{78}]$^{+}$: 67), 396([C$_{14}$H$_8$S$_2$Se$^{78}{}_2$]$^{+}$: 77), 372(100), 370(81), 352(52), 326(52), 324(84). UV(CH$_2$Cl$_2$) $\lambda(\varepsilon)$ = 452(22279), 280(21410), 227(20964), 208(19195) nm. Found: C, 41.90; H, 2.12%. Calcd for C$_{14}$H$_8$S$_2$Se$_2$: C, 42.22; H, 2.02%.

11: ^{1}H NMR(CDCl$_3$) δ = 6.33(2H, s), 7.48(2H, d, J = 6.8 Hz), 7.69(2H, d, J = 7.3 Hz). ^{13}C NMR(CDCl$_3$) δ = 115.96, 120.21, 122.35, 124.43, 129.53, 129.66, 130.21, 144.01. IR(KBr) 1394, 1374, 1120, 1052, 806 cm^{-1}. MS(20 eV) m/z 302(M$^+$:100), 270(40), 226(27). HRMS(70 eV) Found: 301.9331. Calcd for $C_{14}H_6S_4$: 301.935237. UV(CH$_2$Cl$_2$) $\lambda(\varepsilon)$ = 890(181), 876(175), 463(18347), 278(17996), 255(14251), 226(13810) nm. Found: C, 55.31; H, 2.14%. Calcd for $C_{14}H_6S_4$: C, 55.60; H, 2.00%.

8. General procedure for preparation of the cation radical salts is as follows: A solution of **7** - **11** (0.2 mmol) in dichloromethane (30 ml) containing tetra(*n*-butyl)ammonium salt (1.2 mmol) was cooled to –20 °C and electrolyzed using a divided electrolytic cell with platinum electrodes by constant low current density (2 µA cm^{-2}). Black long needles grew on the anode.
9. The X-ray diffraction data were collected on a Rigaku AFC-5R automated four-circle diffractometer with Mo Kα radiation monochromatized by graphite (λ(Mo Kα) = 0.71069 Å, 2θ-ω scans, $2\theta_{max}$ = 55°). The structures were solved by a direct method and refined by the full-matrix least-squares method on F with weight $w=1/\sigma^2(F)$. An empirical absorption correction with ψ-scan method was used. Anisotropic thermal parameters were used for the refinement of non-H atoms. The positions of H atoms were calculated from positions of non-H atoms. Calculations were done on a VAX station 3200 computer with the TEXSAN program[11] which used the atomic scattering factors taken from "International Tables for X-Ray Crystallography"[12] and took anomalous dispersion into account.
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