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Electrical Conductivities of the Complexes of Naphthaceno[5,6-*cd*:11,12-*c′d′*]-bis[1,2]dithiole and Its Analogs Obtained by Electrochemical Crystallization and Diffusion Method

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Electrochemical crystallizations of the complexes of naphthaceno[5,6-*cd*:11,12-*c′d′*]bis[1,2]dithiole (TTT), anthra[1,9-*cd*:4,10-*c′d′*]bis[1,2]dithiole (TTA), anthra[1,9-*cd*:4,10-*c′d′*]bis[1,2]diselenole (TSA), and naphtho[1,8-*cd*:4,5-*c′d′*]bis[1,2]dithiole (TTN) were made in 1,1,2-trichloroethane or tetrahydrofuran as a solvent. Most of the crystals were obtained with non-stoichiometric compositions, and they included the solvent. Some charge-transfer complexes including the above donors were also made by a diffusion method. The electrical conductivities of the crystals were measured by a two-probe or four-probe method. TTT-$(PF_6)_{0.61}$ was found to be the most conductive materials in the complexes studied. Its electrical conductivity was 762 $(\Omega\,cm)^{-1}$ at room temperature, and it showed metallic behavior above 220 K. The conductivities of the other complexes varied widely in the range 10^2—10^{-7} $(\Omega\,cm)^{-1}$

The studies on the highly conductive organic materials have progressed greatly in the past few years.[1] The first organic superconductors were discovered for complexes of tetramethyltetraselenafulvalene (TMTSF).[2] Another organic superconductor has recently been reported for the complex of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), (BEDT-TTF)$_4$(ReO$_4$)$_2$.[3] The crystals of these organic superconductors were grown by an electrochemical method.[4] However, most of the electrochemical crystallizations have been conducted on the complexes of tetrathiafulvalene (TTF) and its analogs. Naphthaceno[5,6-*cd*: 11,12-*c′d′*]bis[1,2]dithiole (TTT) is known to give highly conductive organic complexes.[5] The TTT analogs are planar molecules with four chalcogen atoms stretched out from the aromatic ring. Interchain coupling through chalcogen atoms is expected for the complexes of TTT analogs; this might suppress Peierls transitions. Thus, these complexes are expected to be highly conductive down to low temperatures. We have made electrochemical crystallizations of TTT, anthra[1,9-*cd*: 4,10-*c′d′*]bis[1,2]diselenole (TSA), anthra[1,9-*cd*: 4,10-*c′d′*]bis[1,2]dithiole (TTA), and naphtho[1,8-*cd*: 4,5-*c′d′*]bis[1,2]dithiole (TTN). We have also made some charge-transfer complexes by use of these donor molecules by diffusion method. Their electrical conductivities were measured by a two-probe or four-probe method. We have also measured the half-wave oxidation potentials and electronic absorption spectra of the above donor molecules to get their basic data.

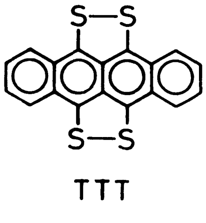
Experimental

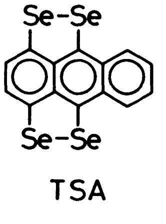
Materials. TTT,[6] TSA,[7] TTA,[8] and TTN[9] were synthesized by the procedures reported. Tetrabutylammonium perchlorate was recrystallized from ethanol. Tetrabutylammonium hexafluorophosphate was synthesized according to the reported procedures.[10] Tetrabutylammonium hexafluoroarsenate was synthesized by mixing equimolar amounts of aqueous solutions of tetrabutylammonium bromide with potassium hexafluoroarsenate. The white powder was filtered, dried in vacuum, and recrystallized twice from the mixed solution of ethyl acetate and hexane (7:3). Tetrabutylammonium hexafluoroantimonate was synthesized by the reported procedures.[11] Tetrabutylammonium tetrafluoroborate was obtained by mixing equimolar amounts of aqueous tetrabutylammonium bromide with tetrafluoroboric acid (40%) at 0 °C in a polyethylene vessel. The crude product was recrystallized from ethyl acetate in the polyethylene vessel. Tetrabutylammonium triiodide was synthesized by the procedures reported.[12] 1,1,2-Trichloroethane was purified by refluxing it over phosphorus pentaoxide, followed by distillation. Tetrahydrofuran was purified by refluxing it over calcium hydride, followed by distillation. Benzonitrile was steam distilled, the organic layer was shaken with aqueous sodium carbonate, and the solution was mixed with diethyl ether. The organic solution was shaken with water, and the resulting mixture was dried over calcium chloride overnight. Diethyl ether was then distilled out, and the remaining liquid was distilled in vacuum.

Electrochemical Crystallization. Electrochemical crystallization was conducted under galvanostatic conditions (1—5 μA). The detailed procedures were described before.[13]

Crystal Growth by Diffusion Method. The single crystals of TCNQ complexes and iodine complexes of TTT and its analogs were grown by diffusion method in organic solvents. For the crystal growths of iodine complexes, tetrabutylammonium triiodide was used instead of iodine. The detailed procedures are similar to those of the literature.[14]

Cyclic Voltammetry. Cyclic voltammetry was made by a Potentiostat/Galvanostat (Hokuto Denko, HA-501), and by


TTT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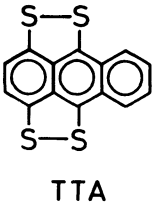
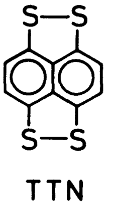

TTA


TTN

a Function Generator (Hokuto Denko, HB-104).

Measurement of Electrical Conductivity. Electrical conductivities of the crystals were measured by a two-probe or four-probe method. Temperature dependence of the electrical conductivity was measured by a Type D Cryo Mini (Osaka Sanso Co. Ltd).

Results and Discussion

Cyclic Voltammetries of Donor Molecules. The electrochemical half-wave potentials were measured *vs.* SCE at a platinum electrode in benzonitrile-Bu_4NAsF_6 (0.1 mol dm^{-3}). Table 1 summarizes the first and second half-wave oxidation potentials and their differences ($E_{1/2}(2)-E_{1/2}(1)$) of TTT, TTA, and TSA, together with the reported values of TTN, TSN, TTF, TMTTF, TMTSF, and HMTTeF for comparison.[15] Here, TSN, TMTTF, and HMTTeF denote naphtho[1,8-*cd*:4,5-*c′d′*]bis[1,2]diselenole,[16] tetramethyltetrathiafulvalene, and bis(trimethylene)tetratellurafulvalene, respectively. The first oxidation potentials increase in the order: TTT≃TMTTF<TTF<TSA≃TTA≃TMTSF≃HMTTeF<TSN<TTN.

Electronic Absorption Spectra of Donor Molecules. The electronic absorption spectra of a series of TTT analogs were measured in several solvents at room temperature. Figure 1 shows the electronic absorption spectra of TTT, TSA, TTA, TTN, and TSN.[16] Table 2 summarizes the absorption peak positions and logarithms of extinction coefficients. The absorption peak positions of the lowest energy transition of selenium derivatives showed bathochromic shifts relative to the corresponding sulfur derivatives.

Electrochemical Crystallization. Electrochemical crystallization was conducted for the donor molecules TTT, TSA, TTA, and TTN. The counter anions were Cl^-, Br^-, I^-, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, and SbF_6^-. Table 3 summarizes the complexes obtained, their decomposition temperatures, elemental analyses, solvents, appearances, and electrical conductivities at room temperature. Since the elemental analyses of chalcogen atoms and halogen atoms could not be made when they coexist in the same sample, elemental analyses were made only for carbon and hydrogen. The content of the solvent was estimated from the analyses by the least-squares method. Most of the complexes contained the solvent in non-stoichiometric ratios. The solvent could not be removed merely by drying the complex *in vacuo* at room temperature. The ratio of the donor molecule and the counter anion was also non-stoichiometric. The reason why $TTT(ClO_4)_{0.56}$, $TTT(PF_6)_{0.61}$, and $TTT(SbF_6)_{0.64}$ do not contain the solvent, 1,1,2-trichloethane, is not clear.

Electrical Conductivities of the Complexes. Electrical conductivities of the complexes were measured by a two-probe or four-probe method. Table 3 summarizes

Table 1. Electrochemical half-wave oxidation potentials of donor molecules in benzonitrile

Molecules	(Oxidation potentials *vs.* SCE)/V $E_{1/2}(1)$	$E_{1/2}(2)$	ΔE
TTT	0.24	0.67	0.43
TTA	0.41	0.85	0.44
TSA	0.42	0.84	0.42
TTN[a]	0.55	0.93	0.38
TSN[b]	0.40	—	—
TTF[a]	0.34	0.71	0.37
TMTTF[a]	0.24	0.73	0.49
TMTSF[a]	0.42	0.81	0.39
HMTTeF[a]	0.40	0.69	0.29

a) Ref 15; b) Ref 16. We could not measure $E_{1/2}(2)$ of TSN because of the irreversible chemical reaction.

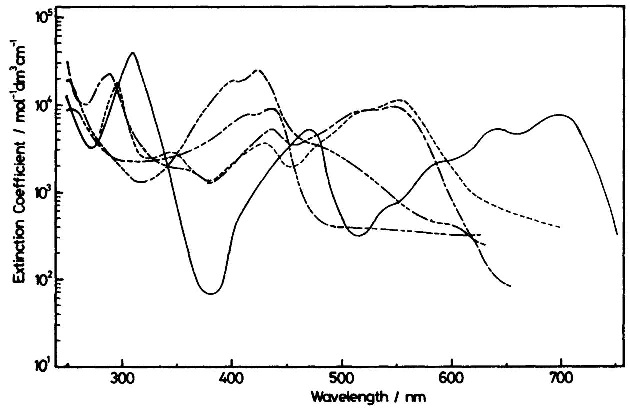
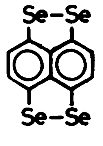


Fig. 1. Electronic absorption spectra of donor molecules.
—— TTT, ---- TSA, — — — TTA, — — — — TSN, — — — — — TTN

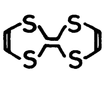
Table 2. Electronic absorption peak positions and extinction coefficients of donor molecules

Molecules	λ_{max}/nm (log ε)
TTT[a]	316 (4.62), 462 (4.0), 596 (2.67), 649 (3.45)
TST[b]	321 (4.13), 465 (3.29), 598 (1.73), 656 (2.75)
TTA[a]	288 (4.36), 437 (3.71), 520 (3.93), 548 (3.98)
TSA[a]	297 (4.20), 430 (3.57), 520 (3.93), 552 (4.05)
TTN[c]	251 (4.16), 420 (4.26)
TSN[d]	256 (3.94), 415 (3.88), 436 (3.96)

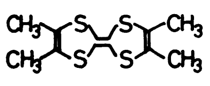
a) Solvent: chloroform; b) TST denotes naphthaceno[5,6-*cd*:11,12-*c′d′*]bis[1,2]diselenole. Solvent: 1,2,4-trichlorobenzene (Ref. 6). c) Solvent: acetonitrile; d) Solvent: 1,2-dichloroethane.



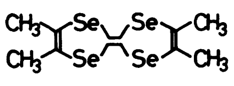
TSN



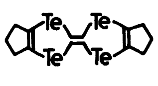
TTF



TMTTF



TMTSF



HMTTeF

TABLE 3. THE COMPLEXES OBTAINED, AND THEIR ELEMENTAL ANALYSES, DECOMPOSITION TEMPERATURES, SOLVENTS, APPEARANCES, AND ELECTRICAL CONDUTIVITIES AT ROOM TEMPERATURE

Complex	Found(Calcd) (%)		Dp/°C$^{a)}$	Solvent	Appearance	Conductivity (Ω cm)$^{-1}$
TTT $Cl_{0.75}(TCE)_{0.52}$	50.78 (51.00)	2.56 (2.17)	220	TCE	Dark brown needles	1.47
TTT $Br_{0.70}(TCE)_{0.16}$	51.27 (51.24)	2.25 (2.00)	259	TCE	Dark brown needles	45
TTT $I_{0.90}(TCE)_{0.20}$	44.78 (44.79)	1.74 (1.76)	274	TCE	Black needles	158
$TTT(ClO_4)_{0.56}$	52.86 (52.98)	2.20 (1.98)	259	TCE	Dark brown needles	6 ×10^{-3}
$TTT(BF_4)_{0.25}(TCE)_{0.20}$	55.49 (55.20)	2.25 (2.17)	283	TCE	Black needles	2.5 ×10^{-2}
$TTT(PF_6)_{0.61}$	49.33 (49.13)	2.28 (2.53)	>300	TCE	Black needles	762
$TTT(SbF_6)_{0.64}$	42.85 (42.60)	2.16 (2.42)	264	TCE	Black needles	40
$TTT(PF_6)_{0.58}(THF)_{0.66}$	51.22 (51.20)	2.74 (2.76)	>300	THF	Black needles	5
$TTT(AsF_6)_{0.68}(THF)_{1.1}$	48.03 (48.02)	3.00 (3.02)	210	THF	Black needles	8.4
$TTT(SbF_6)_{0.47}(THF)_{0.64}$	48.48 (48.47)	2.63 (2.59)	263	THF	Black needles	4.9
$TTT(ClO_4)_{0.61}(THF)_{0.48}$	53.45 (53.43)	2.69 (2.67)	273	THF	Black needles	0.31
$TTT(BF_4)_{0.55}(THF)_{0.16}$	54.40 (54.37)	2.25 (2.27)	300	THF	Black needles	0.12
$TTA(PF_6)_{0.33}(TCE)_{0.96}$	39.99 (39.99)	1.88 (1.87)	—	TCE	Dark green needles	2.3 ×10^{-4}
$TSA(PF_6)_{0.41}(TCE)_{1.97}$	26.23 (26.53)	1.45 (1.48)	260	TCE	Violet plate	2.5 ×10^{-5}
$TSA(ClO_4)_{0.61}(TCE)_{1.12}$	27.86 (27.86)	1.35 (1.35)	143	TCE	Dark brown powder	1.7 ×10^{-5}
$TTN(PF_6)_{0.39}(TCE)_{1.07}$	32.28 (32.28)	1.61 (1.61)	205	TCE	Dark green powder	1.25×10^{-7}
$TTN(ClO_4)_{0.86}(TCE)_{0.27}$	33.85 (33.85)	1.31 (1.30)	269	TCE	Dark green powder	2.56×10^{-7}
$TTN(SbF_6)_{0.88}(TCE)_{0.84}$	24.53 (24.53)	1.15 (1.15)	262	TCE	Dark green powder	7.69×10^{-7}
$TTN(AsF_6)_{0.55}(TCE)_{0.94}$	29.62 (29.62)	1.43 (1.43)	280	TCE	Dark green powder	1.92×10^{-7}
$TTN(PF_6)_{0.81}(THF)_{0.41}$	35.02 (35.01)	1.84 (1.84)	232	THF	Dark green needles	1.40×10^{-7}
$TTN(ClO_4)_{0.99}(THF)_{0.14}$	35.13 (35.14)	1.43 (1.43)	272	THF	Dark green needles	1.58×10^{-7}
$TTN(AsF_6)_{0.69}(THF)_{0.68}$	35.39 (35.38)	2.21 (2.21)	261	THF	Dark green needles	3.22×10^{-6}
$TTA{\cdot}I_{1.2}$	36.62 (36.98)	1.30 (1.33)	225	$CH_3CN^{b)}$ $C_6H_5NO_2^{b)}$	Dark green needles	4.2
TSA·TCNQ	45.38 (44.98)	1.61 (1.45)	250	$C_6H_5CN^{c)}$	Black needles	15
$TTN{\cdot}I_{2.4}$	21.51 (21.57)	0.73 (0.71)	187	$CH_3CN^{b)}$ $C_6H_5NO_2^{b)}$	Dark green needles	1.45×10^{-2}

a) Decomposition temperature. b) Diffusion method: the solvents of Bu_4NI_3 and donor molecule are acetonitrile and nitrobenzene, respectively. c) Diffusion method: the solvent is benzonitrile.

the observed results. Roughly speaking, the order of the electrical conductivities obtained by electrochemical method is as follows: TTT complexes (10^{-3}—10^{3}(Ω cm)$^{-1}$)>TTA complexes (10^{-4}(Ω cm)$^{-1}$)>TSA complexes (10^{-5}(Ω cm)$^{-1}$)>TTN complexes (10^{-6}—10^{-7}(Ω cm)$^{-1}$). That is to say, the larger the aromatic ring is, the higher is the conductivity. The charge carrier in these complexes is considered to be a hole. The above orders of the conductivities arise partly from the weaker on-site Coulomb repulsion energy between holes for large aromatic systems than that for small aromatic systems, because the average distance between the holes becomes larger in going from TTN to TTT.[17] The electrical conductivities of the complexes which do not

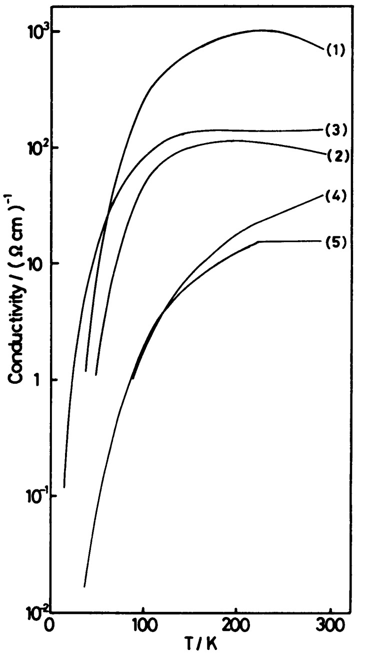


Fig. 2. Temperature dependences of the electrical conductivities of the complexes.
(1) TTT(PF$_6$)$_{0.61}$ (crystal 1), (2) TTT(PF$_6$)$_{0.61}$ (crystal 2), (3) TTT I$_{0.90}$(TCE)$_{0.20}$, (4) TTT(SbF$_6$)$_{0.64}$, (5) TSA·TCNQ.

contain the solvents were high in general. The steric effect of the solvent prevents the overlap of the π-electron clouds between adjacent donor molecules; this leads to the low conductivity. Thus, we must select a proper solvent or a special condition of electrocrystallization in order to prevent the coordination of the solvent to the complex. Electrochemical crystallizations of TTT complexes were conducted both in 1,1,2-trichloroethane (TCE) and in tetrahydrofuran (THF). Most of the TTT complexes obtained in the former solvent were more conductive than those obtained in the latter solvent. Temperature dependences of the electrical conductivities of TTT(PF$_6$)$_{0.61}$, TTT·I$_{0.90}$(TCE)$_{0.20}$, and TTT(SbF$_6$)$_{0.64}$ are shown in Fig. 2. TTT(PF$_6$)$_{0.61}$ gave two kinds of crystals, which could be distinguished from the appearances. The thin crystal (crystal 1 in Fig. 2) was more conductive than the thick one (crystal 2 in Fig. 2). TTT(PF$_6$)$_{0.61}$ (crystal 1) was the most conductive material, and its electrical conductivity was 762(Ω cm)$^{-1}$ at room temperature. The conductivity increased gradually with lowering the temperature which is a characteristic behavior of metallic conductivity, and showed the maximum value of 1050(Ω cm)$^{-1}$ at 220 K. TTT(PF$_6$)$_{0.61}$ (crystal 2) also showed metallic behavior above 190 K. TTT·I$_{0.90}$(TCE)$_{0.20}$ showed almost no activation energy of the conductivity above 160 K. The conductivities of TTT(PF$_6$)$_{0.61}$ and TTT·I$_{0.90}$(TCE)$_{0.20}$ decreased gradually at the lower temperature range due to a phase transition, like many low-dimensional conductors.

The complexes obtained by the diffusion method showed higher conductivities than those obtained by the electrochemical method, especially in TTA-, TSA-, and TTN-complexes; *e.g.*, TTA·I$_{1.2}$, 4.2(Ω cm)$^{-1}$; TSA·TCNQ, 15(Ω cm)$^{-1}$; TTN·I$_{2.4}$, 1.45×10^{-2}(Ω cm)$^{-1}$. Temperature dependence of the electrical conductivity of TSA·TCNQ is shown in Fig. 2. The conductivity was almost constant above 220 K, at which temperature the phase transition gave rise to a low conductive phase. In view of the high electrical conductivities of the following complexes,[18] we can get highly conductive complexes more easily by the diffusion method than by the electrochemical method if we use TTT and its analogs as donor molecules: TTT$_2$I$_3$, 10^3(Ω cm)$^{-1}$; TTT(TCNQ)$_2$, 10^2(Ω cm)$^{-1}$; TTN·TCNQ, 40(Ω cm)$^{-1}$.

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