Design, Syntheses and Properties of Novel Organic Electron Donors

Kazuo Takimiya

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Industrial Chemistry, Graduate School of Engineering,
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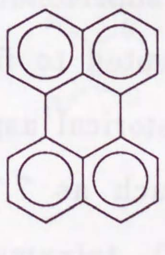
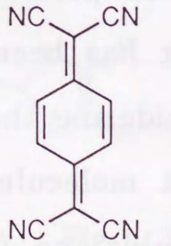
General Introduction

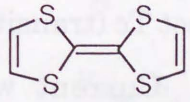
In the past three decades, there has been considerable interest in organic materials showing unique electronic, magnetic, and optical properties. The motivation of the research for such materials is based on not only their potential of practical applications but also on their own scientific interests, that is, the origins how organic materials show such properties. In particular, electrical conducting organic solids including superconductors have aroused wide interests, so they have been investigated actively by both chemists and physicists. Most of organic molecules are generally electrical insulators, because they have usually closed shell electronic structures. On the other hand, organic conductors possess conducting charge carriers which are generated by charge transfer between π-electron donors and π-electron acceptors. Up to now, many kinds of electron donors and acceptors have been synthesized, and a number of charge-transfer (CT) complexes and radical ion salts have been derived from them. Table 1 lists major landmarks in the progress of organic conductors in chronological order.



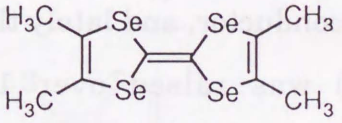
Perylene



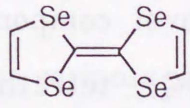
TCNQ



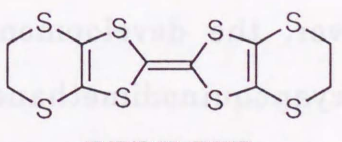
TTF



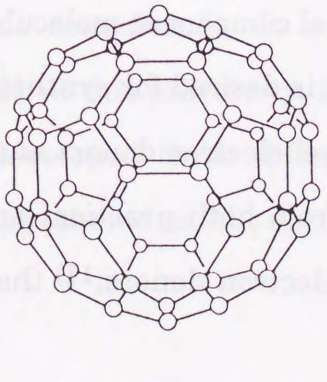
TMTSF



TSF



BEDT-TTF



C_{60} (Buckminsterfullerene)

Table 1.

Year	Material	Property	Reference
1954	Perylene-bromine	σ=ca 1.0 Scm^{-1} (Semiconductive)	1
1962	TCNQ	Semiconductive metal salts.	2
1970	TTF	First reported synthesis.	3
1973	TTF-TCNQ	σ_{rt}=500 Scm^{-1} (The first metallic CT-complex, $T_{M\text{-}I}$=53K)	4
1974	TSF-TCNQ	σ_{rt}=700-800 Scm^{-1} ($T_{M\text{-}I}$=30K)	5
1980	$(TMTSF)_2PF_6$	The first organic superconductor (Tc=0.9K, under 9Kbar)	6
	$(TMTSF)_2ClO_4$	The first ambient pressure superconductor (Tc=1.3K)	7
1983	$(ET)_2ReO_4$	The first superconductor based on ET (BEDT-TTF) (Tc=1.4K at 4Kbar)	8
1986	β-$(ET)_2I_3$	Tc=8K	9
1990	κ-$(ET)_2Cu(NCS)_2$	Tc=11.6K	10
1992	K_3C_{60}	Tc=19K	11

As can be seen in Table 1, the field of organic conductive materials starting with semiconducting perylene-bromine[1)] salt in 1950's has been developed so far to give a superconductor, and lately the highest Tc (transition temperature to superconducting state) was raised over 10K.[10)] Current work has been devoted to find a superconductor with a further higher Tc. Considering the historical aspects, however, the development of novel component molecules, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), tetrathiafulvalene (TTF), tetramethyltetraselenafulvalene (TMTSF), bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), and C_{60} (Buckminsterfullerene), has made dramatic progress in the field of organic conductive materials. Providing such novel component molecules is thus essential for the progress of organic conductors, and it is desired for synthetic organic chemists to actively contribute to the syntheses of novel electron donors and/or acceptors.

The knowledge hitherto obtained from both practical and theoretical studies provides several concepts on designing electron donors,[11)] that is, construction of a multistage redox system, high planarity and symmetry of the molecule, or introduction of heteroatoms. TTF is the prototype of such electron donors. Since the discovery of the metallic conductivity of TTF-TCNQ complex, TTF-type molecules have been a center of research for new conductive materials. The synthetic flexibility of this class of compounds has permitted a wide variety of systematic chemical modifications (Fig. 1); replacement of sulfur with heavier chalcogen atoms derived tetraselenafulvalene (TSF)5) or its tellurium isologue (TTeF).13) And also introduction of various substituent groups, such as alkyl-,14) alkylthio-,14) benzo-15) *etc.*, or insertion of a spacer moiety between two dithiole rings16) afforded a lot of TTF derivatives, of which complexes and radical salts showed a wide range of electrical conductivities from insulating to superconducting.

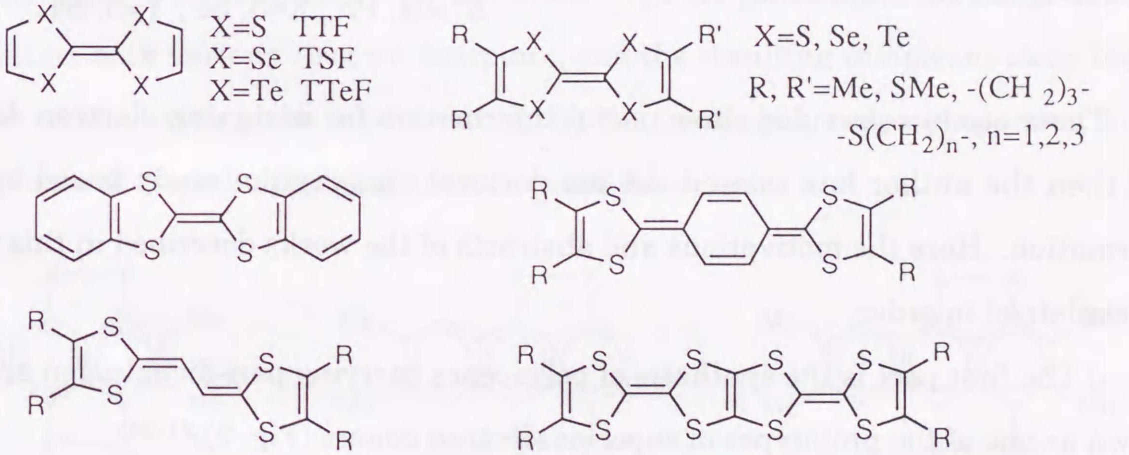
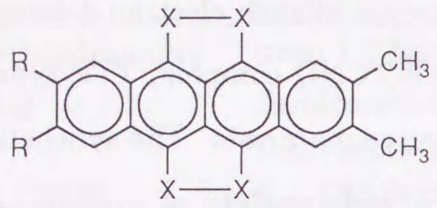


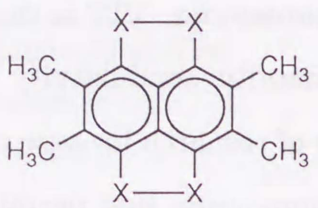
Fig.1. Some variants of TTF.

In contrast to a wide variety of TTF type donors, investigations of the other types have been little considered. In order to enrich the varieties of organic conductors, Ogura *et al.* in this university, from the viewpoint of synthetic chemistry, have designed and developed three different types of novel electron donors not belonging to TTF system shown as follows.

i) Polyacenes bearing dichalcogenide bridges[17, 18)]

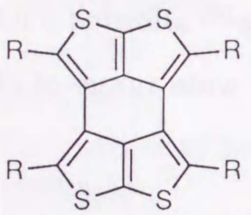

X—X
R
R
CH3
CH3
X—X

R=H or CH_3
X=S, Se


X—X
H3C
H3C
CH3
CH3
X—X

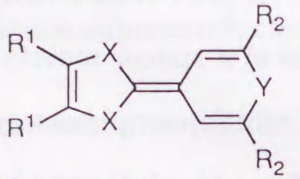
X=S, Se, Te

ii) heteroarenes[19)]



R=H (BTT), CH_3 , SCH_3

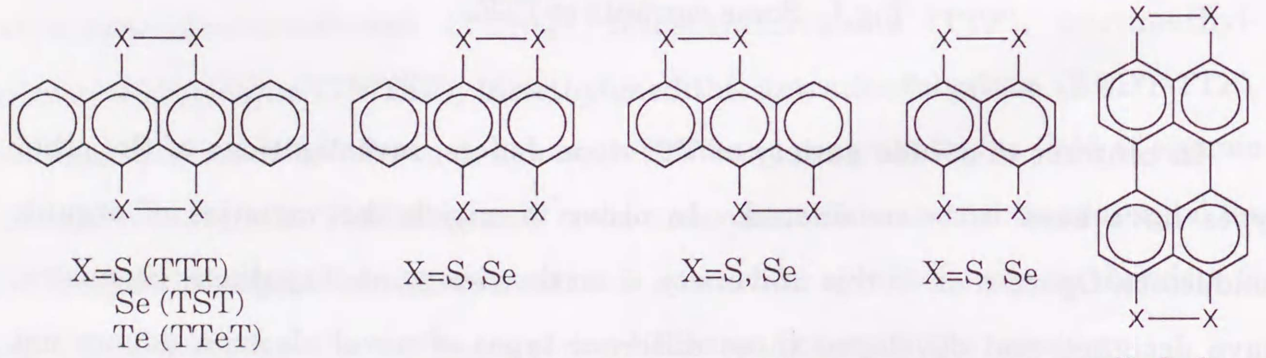
iii) hybrid TPDT system[20)]


R2
R1
X
X
Y
R1
X
X
R2

R^1, R^2 =H, X=Y=S (TPDT)
R^1 =H, CH_3, SCH_3, $S(CH_2)_2S$, Ph
R^2 =H, Ph ; X=S, Se ; Y=S, Se

These studies provided some useful information for designing electron donors, and then the author has carried out his doctoral dissertation study based on this information. Here the motivations and abstracts of the works described in this paper are explained in order.

i) The first part is the synthesis of polyacenes carrying peri-dichalcogen bridges, known as one of the prototypes of superior electron donors (Fig. 2).[21-24)]


X—X
X—X
X—X
X—X
X—X
X—X
X—X
X—X
X—X
X—X

X=S (TTT)
Se (TST)
Te (TTeT)

X=S, Se

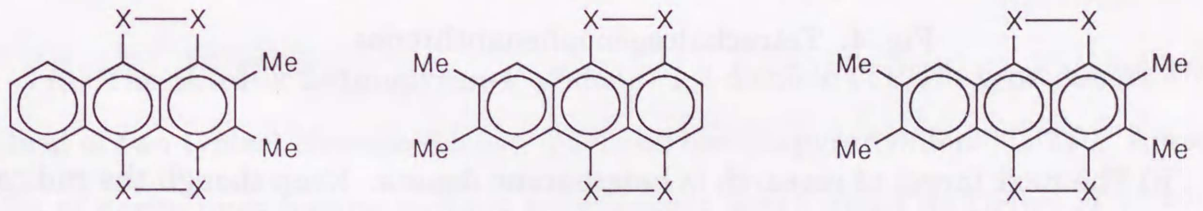
X=S, Se

X=S, Se

X=S, Se

Fig. 2. Peri-chalcogen bridged polyacenes.

Naphthaceno[5,6-cd:11,12-c'd']bis[1,2]dithiole, abbreviated as tetrathiotetracene or TTT is a representative member of this class and possesses stronger electron donating ability than does TTF. Although TTT and its selenium isologue (TST) afforded high conductive iodine salts and CT-complex with TCNQ,23) only limited synthetic investigation as well as complexation studies of TTT-type donors have been reported. This is due to their synthetic difficulty, except for TTT, compared with TTF-type donors, and particularly their poor solubilities make handling and purification of these materials difficult. Our strategy to overcome the solubility problem was introduction of methyl groups, that already afforded good results in naphthalene17) and tetracene series.18) Thus, the same modification was conducted to anthracene isologues (Fig. 3). Introduction of methyl groups served to enhance donor strength and solubility in common organic solvents, enabling ready complexation with various electron acceptors, and the resulting complexes show high electrical conductivities. In the first chapter, the syntheses, redox properties, and CT-complexes of tetrachalcogenoanthracenes are described.



2,3-DMTTA, X=S
2,3-DMTSA, X=Se
2,3-DMTTeA, X=Te

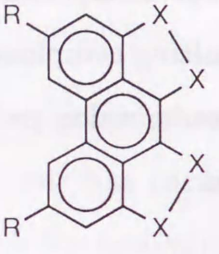
6,7-DMTTA, X=S
6,7-DMTSA, X=Se

TMTTA, X=S
TMTSA, X=Se
TMTTeA, X=Te

Fig. 3. Tetrachalcogenoanthracenes.

In addition, improved solubilities of anthracene series also enabled us electrocrystallization, offering some highly conductive radical cation salts. Among them, NO_3 and BF_4 salts of 2,3-dimethyl derivatives had 1:1 stoichiometry, but showed high conductivities of 440 and 450 Scm^{-1} at room temperature, respectively, and metallic behavior down to ca.200K. In chapter 2, this unusual results are discussed in detail with the combined results of X-ray crystal structure analyses and solid electronic spectra.

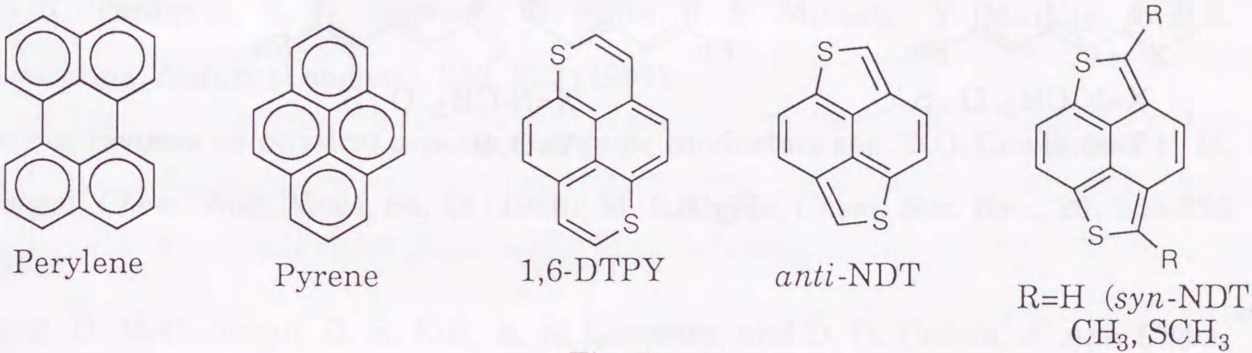
Although peri-dichalcogenides of naphthalene,21) anthracene,22) naphthacene,23) and perylene24) had been synthesized (Fig. 2), phenanthrene isologue has been remained unknown. In addition, the interesting results of the anthracene series have prompted us to investigate the synthesis of phenanthrene series. In chapter 3, the syntheses and properties of tetrachalcogenophenanthrenes (Fig. 4), their charger-transfer complexes, and radical cation salts are described. They were weaker electron donors than the anthracene counterparts, but several CT-complexes and radical cation salts showed high conductivities at room temperature.



TTPh	R=H ,	X=S
TSPh	R=H ,	X=Se
DMTTPh	$R=CH_3$,	X=S
DMTSPh	$R=CH_3$,	X=Se
MTTTPh	$R=CH_3$,	X=S
MTTSPh	$R=CH_3$,	X=Se

Fig. 4. Tetrachalcogenophenanthrenes.

ii) The next target of research is heteroarene donors. Even though the radical cation salts of parent hydrocarbons, perylene or pyrene, showed high conductivity,1,25) their electron donating abilities were rather low. For improving their donor strengths, introduction of sulfur atoms into their frameworks is one of the potential modifications, and that modification might be also favorable for organic conducting materials due to enabling intermolecular interaction through sulfur atoms in crystal structure. Ogura and coworkers already synthesized BTT, isoelectronic heteroarene with perylene, and reported its donor property and conducting complexes.19) As concerned to heteroarenes related to pyrene, Nakasuji (Osaka university) and his coworkwes designed to replace two sp^2 carbons of pyrene with sulfur atoms, affording 1,6-DTPY, which is isoelectronic with pyrene in dicationic state, accordingly behaving as a good electron donor.[26] Alternative manner to introduction of sulfur atoms into pyrene is substitution of two C=C bonds with two sulfur atoms. This modification derives two kinds of naphthodithiophene skeleton, which are isoelectronic with pyrene in the neutral state. In chapter 4, the synthesis of one of the isomers, *syn*-NDT and its derivatives is described (Fig. 5). They possessed better electron donating abilities than pyrene, and also afford high conductive complexes. In addition, an X-ray crystallographic analysis revealed that the crystal structure of *syn*-NDT is quite different from that of pyrene.



Perylene Pyrene 1,6-DTPY *anti*-NDT R=H (*syn*-NDT) CH_3, SCH_3

Fig. 5

iii) The third is 2-(thiopyran-4'-ylidene)-1,3-dithiole (TPDT) type donors,[27] a hybrid of two typical electron donors, TTF and bis(thiopyranylidene) (BTP). Among a lot of derivatives having various substituents synthesized by Ogura *et al.*,[20] a series of compounds bearing phenyl groups at 2- and 6-position of thiopyranylidene moiety was generally more stable than the other derivatives, and afforded some high conductive CT complexes. In addition, the X-ray crystallographic analysis of 4,5,2',6'-tetraphenyl-TPDT indicated that the 2'- and 6'-phenyl groups attached on the thiopyrane ring take a coplanar conformation with the TPDT skeleton, whereas 4,5-congeners on dithiole ring deviate from the plane. This indicates the phenyl groups on thiopyrane ring can conjugate well with thiopyranylidene moiety, as also supported by the UV spectroscopic studies of the TPDTs. Diphenylthiopyranylidene moiety is consequently regarded as an useful building block for constructing extended π electron systems. Combination of the moiety or its oxygen counterpart, 2,6-diphenylpyranylidene, with heteroaromatics, such as *N*-methylpyrrole, furan and thiophene affords novel electron donors with extended π electron structures (Fig. 6). In chapter 5, their syntheses and electrochemical properties are discussed and, in addition, their third-order nonlinear optical (NLO) properties, which is of current interest in the field of material science, are also studied.

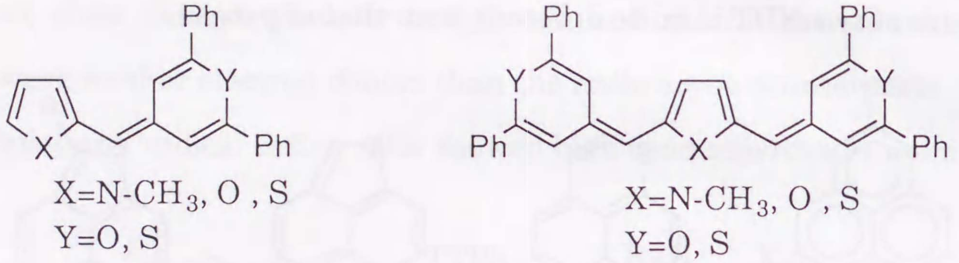


Fig. 6.

References

1) H. Akamatu, H. Inokuchi, and Y. Matsunaga, *Nature (London)*, **173**, 168 (1954); *Bull. Chem. Soc. Jpn.*, **29**, 3170 (1956).

2) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, B. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

3) F. Wudl, G. M. Smith, and E. Hufnagel, *J. Chem. Soc., Chem. Commun*, **1970**, 1453.

4) J. Ferraris, D. O. Cowan, V. V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).

5) E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974).

6) K. Bechgaard, C. S. Jacobsen, K. Mortenson, H. J. Pedersen, and N. Thorup, *Solid State Commun.*, **33**, 1119 (1980).

7) D. Jérome, A. Mazand, M. Ribault, and K. Bechgaard, *J. Phys. Lett.*, **41**, L95 (1980).

8) S. S. P. Parkin, E. M. Engler, R. R. Schumaker, V. Y. Lee, J. C. Scott, and R. L. Green, , *Phys. Rev. Lett.*, **50**, 270 (1983).

9) J. E. Schirber, L. J. Azevedo, J. K. Kwak, E. L. Venturini, P. C. W. Leung, M. A. Beno, H. H. Wang, and J. M. Williams, *Phys. Rev.* B, **33**, 1987 (1986).

10) A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoot, J. E. Thompson, D. L. Stupka, D. Jung, and M. H.-H. Whangbo, *Inorg. Chem.*,**29**, 2555 (1990).

11) K. Tanigaki, T. W. Ebbesen, S. Saito, J. S. Mizurki, Y. Murthy, and S. Kuroshima, *Nature* (Londone), **352**, 222 (1991).

12) For reviews on physical aspects of organic conductors see: D.O. Cowan and F. M. Wiygul, *Chem. Eng. News*, **64**, 28 (1986); M. R. Bryce, *Chem. Soc. Rev.*, **20**, 355-390 (1991).

13) R. D. McCullough, G. B. Kok, K. A. Lerstrup, and D. O. Cowan, *J. Am. Chem. Soc.*, **109**, 4115 (1987); R. D. McCullough, M. D. Ways, A. R. Bailey, and D. O. Cowan, *Synth. Metals*, **28**, B487 (1987).

14) J. S. Miller, and A. J. Epstein, eds. "Synthesis and Properties of Low-Dimensional Materials", *Ann. N. Y. Acad. Sci.* **313**, 1-828 (1978).

15) J. Nakayama, E. Seki, and M. Hoshino, *J. Chem. Soc.,Perkin Trans. 1*, **1978**, 468.

16) Y. Yamashita, Y. Kobayashi, and T. Miyashi, *Angew. Chem. Int. Ed. Engl.*, **29**, 1450 (1990).

17) T. Otsubo, N. Sukenobe, Y. Aso, and F. Ogura, *Chem. Lett.*, **1987**, 315; *Synth. Met.*, **27**, B509 (1988).

18) H. Miyamoto, Doctoral dissertation, Hiroshima University, 1991.

19) Y. Kono, H. Miyamoto, Y. Aso. T. Otsubo, F. Ogura, T. Tanaka, and M. Sawada, *Angew. Chem., Int. Ed. Engl.*, **28**, 1222 (1989); T. Otsubo, Y. Kono, N. Hozo, H.

Miyamoto, Y. Aso, F. Ogura, T. Tanaka, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **66**, 2033 (1993).

20) Y. Shiomi, Y. Aso, T. Otsbo, and F. Ogura, *J. Chem. Soc., Chem. Commun.*, **1988**, 822; F. Ogura, T. Otsubo, and Y. Aso, *Pure & Appl. Chem.*, **65**, 683 (1993); T. Otsubo, Y. Shiomi, M. Imamura, R. Kittaka, A. Ohnishi, H. Tagawa, Y. Aso,, and F. Ogura, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 1815.

21) F. Wudl, D. E. Schafer, and B. Miller, *J. Am. Chem. Soc.*, **98**, 252 (1976); A. Yamahira, T. Nogami, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, **1983**, 904; J. C. Stark, R. Reed, L. A. Acampora, D. J. Sandman, S. Jansen, M. T. Jones, and B. M. Foxman, *Organometallics*, **3**, 732 (1984)..

22) H. Endres, H. J. Keller, J. Queckborner, J. Veigel, and D. Schweitzer, *Mol. Cryst. Liq. Cryst.*, **86**, 111 (1982); H. Endres, H. J. Keller, J. Queckborner, D. Schweitzer, and J. Veigel, *Acta Crystallogr.*, **B38**, 2855 (1982); S. Ohnishi, T. Nogami, and H. Mikawa, *Tetrahedron Lett.*, **1983**, 2401; S. Ohnishi, T. Nogami, and H. Mikawa, *Chem. Lett.*, **1982**, 1841.

23) I. F. Shchegolev and E. B. Yagubskii,"Extended linear chain compounds" ed by J. S. Miller, New York Plenum Press, 1982, Vol. 2, pp. 385-434.

24) C. W. Mayer, *Eur. Pat.* O 10685A1 (1982).

25) J. Kommandeur and E. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961).

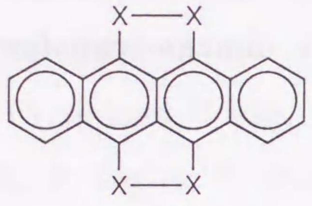
26) K. Nakasuji, H. Kubota, T. Kotani. I. Murata, G. Saito, T. Enoki, K. Imaeda, H. Inokuchi, M. Honda, C. Katayama, and J. Tanaka, *J. Am. Chem. Soc.*, **108**, 3460 (1986); K. Nakasuji, M. Sasaki, T. Kotani. I. Murata, T. Enoki, K. Imaeda, H. Inokuchi, A. Kawamoto, and J. Tanaka, *J. Am. Chem. Soc.*, **109**, 6970 (1987).

27) D. J. Sandman, A. P. Fisher,III, T. J. Holmes, and A. J. Epstein, *J. Chem. Soc., Chem. Commun.*, **1977**, 688; D. J. Sandman, G. P. Ceasar, A. P. Fisher,III, D. D. Titus, and A. D. Baker, *Chem. Materials*, **1**, 427 (1989).

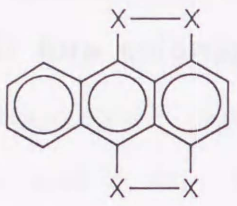
Chapter 1. Syntheses and properties of dimethyl and tetramethyl anthra[1,9-cd:4,10-c'd']bis[1,2]dichalcogenoles and their charge-transfer complexes.

Introduction

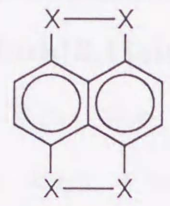
Polyacenes bearing peri-dichalcogen bridges are known as prototypes of superior electron donors. A representative is naphthaceno[5,6-cd:11,12-c'd']bis[1,2]dithiole, abbreviated as tetrathiotetracene or TTT; it has stronger electron donating ability than does tetrathiafulvalene (TTF).1) However, it has the very low solubility in common solvents, limiting any wide study concerning its molecular complexes. Although the selenium isologue (TST)1) and the tellurium isologue (TTeT)2) have also aroused interest concerning the introduction of interactive heavy chalcogens, they are intractable because of their poorer solubilities. The lower polyacene homologues (anthra[1,9-cd:4,10-c'd']bis[1,2]dithiole (tetrathioanthracene or TTA)3), naphtho[1,8-cd:4,5-c'd']bis[1,2]dithiole (tetrathionaphthalene or TTN)4), and their selenium isologues (TSA5) and TSN6))), have thus been studied as more tractable materials. However, their donor characters considerably decrease, and their solubilities are not so much improved as expected. In addition, their tellurium isologues still remain unknown. Sukenobe in Ogura's group previously investigated the 2,3,6,7-tetramethyl derivatives of tetrachalcogenonaphthalenes.7) This structural modification allowed the formation of all of the chalcogen derivatives (TMTTN, TMTSN, and TMTTeN) involving the tellurium isologue. In addition, the introduced methyl groups served to enhance not only the donor strength, but also the solubility, enabling a detailed study of their complexes. We have further designed the same modification in other peri-dichalcogenide polyacenes. We here report on the syntheses and properties of 2,3-dimethyl, 6,7-dimethyl, and 2,3,6,7-tetramethyl derivatives of tetrachalcogenoanthracenes and their charge-transfer complexes.



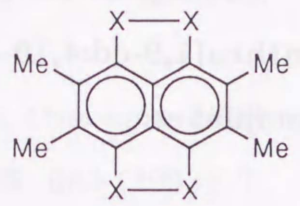
TTT, X=S
TST, X=Se
TTeT, X=Te



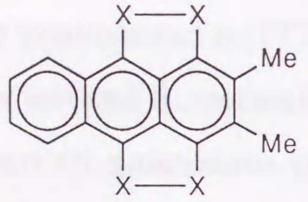
TTA, X=S
TSA, X=Se



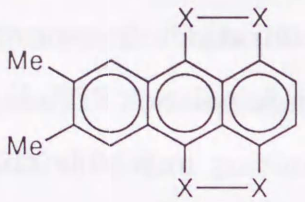
TTN, X=S
TSN, X=Se



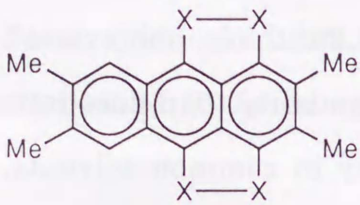
TMTTN, X=S
TMTSN, X=Se
TMTTeN, X=Te



2,3-DMTTA, X=S
2,3-DMTSA, X=Se
2,3-DMTTeA, X=Te



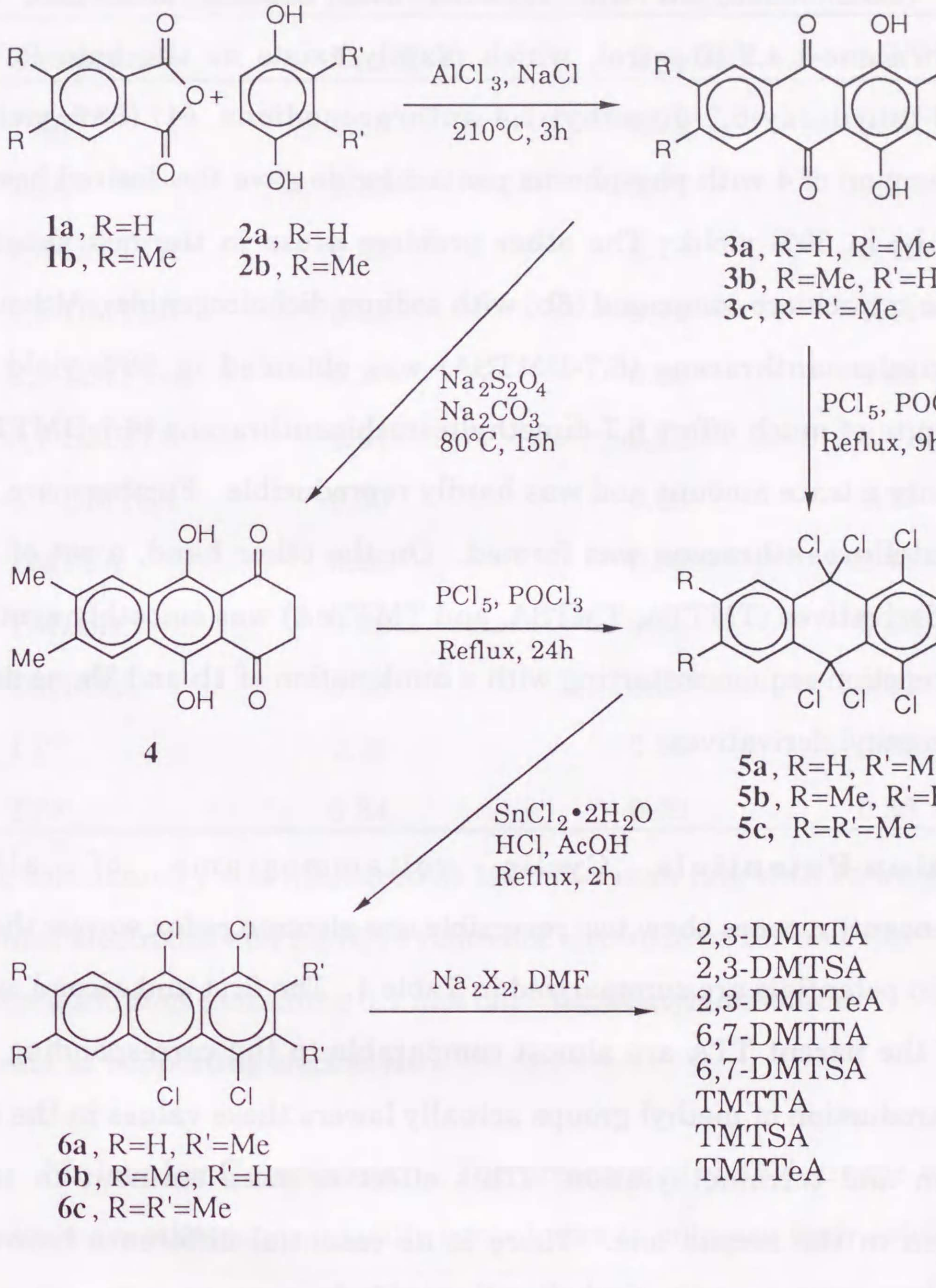
6,7-DMTTA, X=S
6,7-DMTSA, X=Se



TMTTA, X=S
TMTSA, X=Se
TMTTeA, X=Te

Results and Discussion

Syntheses. Syntheses of dimethyl and tetramethyl tetrachalcogenoanthracenes were carried out according to Scheme 1. Thus 1,4-dihydroxy-2,3-dimethylanthraquinone (**3a**), prepared from a one-step condensation of phthalic anhydride (**1a**) with 2,3-dimethylhydroquinone (**2b**),8) was allowed to react with phosphorus pentachloride to give 1,4,9,9,10,10-hexachloro-2,3-dimethyl-9,10-dihydroanthracene (**5a**) in 59% yield which, upon subsequent dechlorination with tin (II) chloride dihydrate, afforded 1,4,9,10-tetrachloro-2,3-dimethylanthracene (**6a**) in 75% yield. Treatment of **6a** with sodium disulfide, freshly prepared from sodium and sulfur, in refluxing *N,N*-dimethylformamide gave 2,3-dimethyltetrathioanthracene (2,3-DMTTA) in 43% yield. A similar reaction of 6a with sodium diselenide gave the selenium isologue (2,3-DMTSA) in 31% yield. In contrast to the unsuccessful synthesis of the parent tetratelluro-anthracene (TTeA), the tellurium isologue (2,3-DMTTeA) was obtained in 15% yield from a reaction of **6a** with sodium ditelluride at a lower temperature of 100 °C.


AlCl$_3$, NaCl
210°C, 3h
1a, R=H
1b, R=Me
2a, R=H
2b, R=Me
3a, R=H, R'=Me
3b, R=Me, R'=H
3c, R=R'=Me
Na$_2$S$_2$O$_4$
Na$_2$CO$_3$
80°C, 15h
PCl$_5$, POCl$_3$
Reflux, 9h
4
PCl$_5$, POCl$_3$
Reflux, 24h
5a, R=H, R'=Me
5b, R=Me, R'=H
5c, R=R'=Me
SnCl$_2$•2H$_2$O
HCl, AcOH
Reflux, 2h
Na$_2$X$_2$, DMF
2,3-DMTTA
2,3-DMTSA
2,3-DMTTeA
6,7-DMTTA
6,7-DMTSA
TMTTA
TMTSA
TMTTeA
6a, R=H, R'=Me
6b, R=Me, R'=H
6c, R=R'=Me

Scheme 1

The same approach to 6,7-dimethyl isomers from a combination of 4,5-dimethylphthalic anhydride (**1b**) and hydroquinone (**2a**) was confronted with unexpected trouble regarding the following two steps. The first problem was that treatment of 1,4-dihydroxy-6,7-dimethylanthraquinone (**3b**) with phosphorus pentachloride afford no 1,4,9,9,10,10-hexachloro-6,7-dimethyl-9,10-dihydroanthracene (**5b**). Then, **3b** was reduced with sodium dithionite to 6,7-dimethylanthracene-1,4,9,10-tetrol, which mainly exists as the keto form, 2,3-dihydro-9,10-dihydroxy-6,7-dimethyl-1,4-anthracenedione (**4**) (88% yield). An alternative reaction of **4** with phosphorus pentachloride gave the desired hexachloro compound (**5b**) in 30% yield. The other problem arose in the last substitution reaction of the tetrachloro compound (**6b**) with sodium dichalcogenide. Although 6,7-dimethyltetraselenoanthracene (6,7-DMTSA) was obtained in 38% yield by the reaction, in spite of much effort 6,7-dimethyltetrathioanthracene (6,7-DMTTA) was obtained in only a trace amount and was hardly reproducible. Furthermore, no 6,7-dimethyltetratelluroanthracene was formed. On the other hand, a set of 2,3,6,7-tetramethyl derivatives (TMTTA, TMTSA, and TMTTeA) was smoothly synthesized by the same reaction sequence starting with a combination of **1b** and **2b**, as described for the 2,3-dimethyl derivatives.

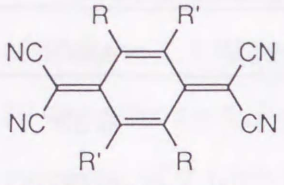
Oxidation Potentials. Cyclic voltammograms of all the tetrachalcogenoanthracenes show two reversible one-electron redox waves; their half-wave oxidation potentials are summarized in Table 1. The first and second oxidation potentials of the parent TTA are almost comparable to the corresponding ones of TTF. The introduction of methyl groups actually lowers these values in the order of dimethylation and tetramethylation. This effect is more eminent in the first oxidation than in the second one. There is no essential difference between the enhanced effects due to dimethylation at the 2,3-positions and at the 6,7-positions. Substitution of selenium for sulfur in any series of the parent, dimethyl, and tetramethyl derivatives has little influence on the oxidation potentials. However, substitution of tellurium results in a considerable lowering of both the first and second potentials. As a result, 2,3-DMTTeA and TMTTeA have very strong donating abilities which are either comparable or superior to that of TTT.

Table 1. Half-wave oxidation potentials of peri-dichalcogenide donors[a)]

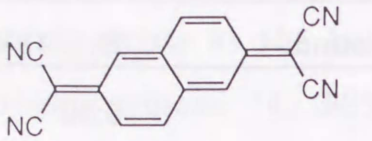
Compound	$E_{1/2}(1)$/V	$E_{1/2}(2)$/V	ΔE/V
TTA	0.36	0.75	0.39
TSA	0.35	0.71	0.36
2,3-DMTTA	0.32	0.73	0.41
2,3-DMTSA	0.31	0.72	0.41
2,3-DMTTeA	0.20	0.63	0.43
6,7-DMTTA	0.31	0.72	0.41
6,7-DMTSA	0.30	0.68	0.38
TMTTA	0.26	0.69	0.43
TMTSA	0.26	0.68	0.42
TMTTeA	0.16	0.55	0.39
TTT	0.19	0.56	0.37
TTF	0.34	0.72	0.38

a) Cyclic voltammetry was measured at 100 mV/s scan rate with Pt working and counter electrodes and Ag/AgCl reference electrode in 10^{-3} mol dm^{-3} benzonitrile solution containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.

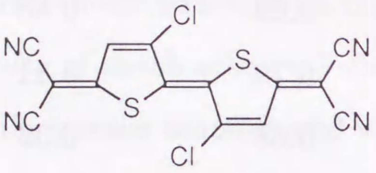
Molecular Complexes. The presence of methyl groups in the present tetrachalcogenoanthracenes actually contributes to enhance their solubilities. This effect, however, is more remarkable in dimethylation than in tetramethylation. For example, the molar solubilities of a series of tetraselenoanthracenes in chloroform are as follows: TSA 2.1 x 10^{-4} mol dm^{-3}, 2,3-DMTSA 3.1 x 10^{-3} mol dm^{-3}, 6,7-DMTSA 8.5 x 10^{-4} mol dm^{-3}, and TMTSA 3.2 x 10^{-4} mol dm^{-3}. The stronger donating abilitiy and better solubility of the dimethyl and tetramethyl derivatives than parent tetrachalcogenoanthracenes facilitated a study of their complexation.



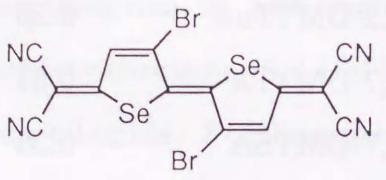
TCNQ: R=R'=H
TCNQF$_4$: R=R'=F
DMTCNQ: R=Me, R'=H
DMOTCNQ: R=MeO, R'=H



TNAP



DCBT



DBBS

Table 3. Half-wave reduction potentials[a)] and nitrile vibrational frequencies of electron acceptors

Acceptor	$E_{1/2}(1)$/V	$E_{1/2}(2)$/V	ΔE/V	ν_{CN}/cm^{-1}
TCNQ	0.19	-0.43	0.62	2232
TCNQF$_4$	0.60	-0.05	0.65	2234
DMTCNQ	0.12	-0.42	0.54	2230
DMOTCNQ	0.01	-0.52	0.53	2225
TNAP	0.21	-0.21	0.42	2225
DCBT	0.16	-0.09	0.25	2217
DBBS	0.12	-0.10	0.22	2220

a) Cyclic voltammetry was measured at 100 mV/s scan rate with Pt working and counter electrodes and Ag/AgCl reference electrode in 10^{-3} mol dm^{-3} benzonitrile solution containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.

Thus, they gave a number of charge-transfer complexes, as summarized in Table 2. The acceptors used in this experiment involve not only those of well-known classes such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), its 2,3,5,6-tetrafluoro derivative

Table 2. Charge-Transfer complexes of peri-dichalcogenide anthracenes

Complex	D:A	Appearance[a)]	Dp	Found (Calcd)[b)]/%			ν_{CN}	CT Band[c)]	ΔE_{redox}[d)]	σ[e)]
			°C	C	H	N	cm^{-1}	X 10^3 cm^{-1}	V	Scm^{-1}
2,3-DMTTA•TCNQ	2:3	Black needles	214	64.66	2.56	13.92	2206	3.1, 10.1	0.13	9.6 X 10^{-1}
				(64.13	2.57	13.20)				
2,3-DMTSA•TCNQ	1:2	Black needles	238	52.56	1.95	11.40	2203	2.8, 9.9, 11.4	0.12	1.2
				(51.85	1.96	12.09)				
2,3-DMTTeA•TCNQ	1:1	Black needles	>300	36.58	1.49	5.55	2186	10.2	0.01	5.3 X 10^{-6}
				(36.68	1.54	6.11)				
6,7-DMTSA•TCNQ	1:1	Blue-black powder	245	47.49	1.95	7.31	2202	3.2, 11.5	0.11	2.0
				(46.56	1.95	7.75)				
TMTTA•TCNQ	1:2	Black needles	220	65.50	3.10	13.81	2204	3.3, 11.5, 13.0	0.07	5.0 X 10^{-2}
				(65.78	2.89	14.61)				
TMTSA•TCNQ	1:2	Black needles	237	53.32	2.58	11.00	2207	6.1, 10.0, 11.5	0.07	2.7 X 10^{-1}
				(53.03	2.11	10.71)				
TMTTeA•TCNQ	1:1	Black fine needles	>300	39.04	2.11	5.33	2187	10.0	-0.03	1.8 X 10^{-6}
				(38.13	1.92	5.93)				
2,3-DMTTA•$TCNQF_4$	1:1	Black powder	>300	55.78	1.55	9.31	2200	11.2	-0.28	2.2 X 10^{-6}
				(55.44	1.66	9.24)				

Table 2. (continued No. 1)

2,3-DMTSA•TCNQF$_4$	1:1	Purple powder	>300	42.05	1.17	7.00	2199	11.2	-0.29	5.4 X 10^{-6}
				(42.34	1.27	7.05)				
2,3-DMTTeA•TCNQF$_4$	1:1	Black powder	>300	34.80	1.02	6.11	2198	10.5	-0.40	1.8 X 10^{-7}
				(34.01	1.02	5.67)				
6,7-DMTSA•TCNQF$_4$	1:1	Black needles	>300	42.17	1.33	6.06	2200	11.0	-0.30	8.8 X 10^{-5}
				(42.34	1.27	7.05)				
TMTTA•TCNQF$_4$	1:1	Purple powder	240	56.53	2.00	9.72	2202	11.3	-0.34	5.0 X 10^{-7}
				(56.77	2.22	8.83)				
TMTSA•TCNQF$_4$	1:1	Purple powder	270	43.52	1.62	6.82	2201	11.1	-0.34	5.2 X 10^{-7}
				(43.82	1.72	6.81)				
TMTTeA•TCNQF$_4$	1:1	Dark blue powder	>300	35.43	1.41	5.43	2201	11.4	-0.44	4.4 X 10^{-6}
				(35.44	1.39	5.51)				
2,3-DMTTA•DMTCNQ	2:1	Black needles	219	62.37	3.41	6.49	2198	3.3, 11.2	0.20	9.5 X 10^{-1}
				(61.85	3.16	6.27)				
2,3-DMTSA•DMTCNQ	2:1	Black needles	236	44.25	2.32	4.49	2172	4.6, 11.3, 12.6	0.19	5.3 X 10^{-1}
				(43.56	2.22	4.42)				
2,3-DMTTeA•DMTCNQ	2:1	Black needles	>300	33.29	2.29	3.85	2186	10.2	0.08	1.2 X 10^{-3}
				(33.13	1.70	3.58)				

Table 2. (continued No. 2)

6,7-DMTSA•DMTCNQ	2:1	Black needles	262	44.09	2.18	4.25	2190	5.4, 11.6	0.18	2.7 X 10^{-8}
				(43.55	2.22	4.42)				
TMTTA•DMTCNQ	2:1	Black needles	241	63.72	3.88	6.57	2214	non	0.14	7.4 X 10^{-7}
				(63.26	3.82	5.90)				
TMTSA•DMTCNQ	2:1	Black needles	>300	46.29	2.94	4.25	2210	11.5	0.14	1.2 X 10^{-5}
				(45.34	2.74	4.23)				
TMTTeA•DMTCNQ	2:1	Black powder	>300	35.56	2.37	3.68	2183	10.2	0.04	4.6 X 10^{-2}
				(35.04	2.12	3.26)				
2,3-DMTTA•DMOTCNQ	1:1	Black needles	266	46.17	2.80	6.74	2204	3.7, 10.3	0.31	2.2
				(46.06	2.32	7.16)				
2,3-DMTSA•DMOTCNQ	1:1	Black needles	269	60.91	3.43	9.32	2208	6.9	0.32	5.0 X 10^{-7}
				(60.59	3.05	9.42)				
2,3-DMTTeA•DMOTCNQ	1:1	Black needles	>300	37.18	1.86	5.57	2190	10.3	0.19	3.2 X 10^{-2}
				(36.89	1.86	5.74)				
6,7-DMTSA•DMOTCNQ	2:1	Black needles	270	43.12	2.03	4.33	2222	non	0.29	1.9 X 10^{-9}
				(42.49	2.17	4.31)				
TMTTA•DMOTCNQ	2:1	Brown needles	283	61.36	4.08	6.52	2220	non	0.25	4.0 X 10^{-9}
				(61.20	3.70	5.71)				

Table 2. (continued No. 3)

TMTSA•DMOTCNQ	2:1	Black needles	295	45.18	2.60	4.12	2219	non	0.25	1.0×10^{-8}
				(44.27	2.67	4.13)				
TMTTeA•DMOTCNQ	2:1	Black powder	>300	35.00	2.10	3.13	2183	non	0.15	1.1×10^{-7}
				(34.40	2.07	3.21)				
2,3-DMTTA•TNAP	1:1	Black fine needles	232	66.05	2.64	9.42	2200	2.3, 8.8	0.11	7.9
				(65.73	2.76	9.58)				
2,3-DMTSA•TNAP	1:1	Black fine needles	250	49.93	2.16	7.30	2205	3.5, 8.9	0.10	2.6×10^{-2}
				(49.76	2.09	7.25)				
2,3-DMTTeA•TNAP	1:1	Black powder	>300	40.40	1.63	5.55	2187	8.5, 10.2	-0.01	4.9×10^{-2}
				(39.75	1.67	5.79)				
TMTTA•TNAP	1:1	Black powder	231	66.88	3.23	8.90	2202	2.4, 8.8	0.05	1.7
				(66.64	3.29	9.14)				
TMTSA•TNAP	1:1	Purple plates	>300	50.02	2.59	6.73	2184	8.8, 10.0	0.05	9.2×10^{-3}
				(51.02	2.52	7.00)				
TMTTeA•TNAP	1:1	Black powder	>300	41.59	2.03	5.70	2190	8.8, 10.3	-0.05	6.0×10^{-1}
				(41.04	2.03	5.63)				
2,3-DMTTA•DCBT	1:1	Dark green	>300	51.17	2.02	7.86	2216	5.9	0.16	1.5×10^{-6}
		fine needles		(52.09	1.75	8.10)				

Table 2. (continued No. 4)

2,3-DMTSA•DCBT	1:1	Dark green	>300	40.94	1.41	6.32	2206	3.6	0.15	3.7
		fine needles		(40.98	1.38	6.37)				
2,3-DMTTeA•DCBT	1:1	Dark green	>300	33.51	1.21	5.03	2196	3.5, 10.1	0.04	6.0
		fine needles		(33.55	1.13	5.22)				
TMTTA•DCBT	1:1	Green fine needles	254	54.09	2.16	6.78	2201	5.1, 8.7	0.10	6.0 X 10^{-3}
				(53.40	2.24	7.78)				
TMTSA•DCBT	1:1	Green needles	280	42.18	1.91	5.94	2208	5.5, 8.7	0.10	3.1 X 10^{-3}
				(42.36	1.78	6.17)				
TMTTeA•DCBT	1:1	Black powder	>300	34.46	1.51	4.80	2199	3.5, 8.5, 10.1	0	2.3
				(34.88	1.46	5.08)				
2,3-DMTTA•DBBS	1:1	Dark green	>300	42.16	1.62	6.20	2216	3.5, 8.3	0.20	7.1 X 10^{-1}
		fine needles		(41.21	1.38	6.41)				
2,3-DMTSA•DBBS	1:1	Dark green plates	>300	33.95	1.29	5.23	2198	3.4, 8.3	0.19	8.0
				(33.93	1.14	5.27)				
2,3-DMTTeA•DBBS	1:1	Dark green powder	>300	28.81	1.19	4.40	2200	3.4, 10.0	0.08	5.8
				(28.68	0.96	4.46)				
TMTTA•DBBS	1:1	Dark green needles	>300	42.94	2.17	5.48	2212	5.0, 8.7	0.14	1.0 X 10^{-3}
				(42.59	1.79	6.21)				

Table 2. (continued No. 5)

TMTSA•DBBS	1:1	Dark green needles	>300	35.71	1.45	4.38	2208	5.5, 8.7	0.14	8.1 X 10^{-4}
				(35.26	1.48	5.14)				
TMTTeA•DBBS	1:1	Black powder	>300	30.08	1.25	4.34	2202	3.3, 9.9	0.04	3.6
				(29.92	1.26	4.36)				

a) Obtained from chlorobenzene.

b) Calculated as stoichiometry indicated for the complex.

c) Measured with a KBr disk method.

d) $\Delta E_{redox}=E_{1/2}(D)-E_{1/2}(A)$.

e) Measured on compressed pellets at room temperature with a two-probe or four-probe method.

($TCNQF_4$), 2,5-dimethyl derivative (DMTCNQ), 2,5-dimethoxy derivative (DMOTCNQ), and 2,6-bis(dicyanomethylene)-2,6-dihydronaphthalene (a common name: 9,9,10,10-tetracyano-2,6-naphthoquinodimethane or TNAP), but also those of new types such as 3,3'-dichloro-5,5'-bis(dicyanomethylene)-$\Delta^{2,2'}$-bi(3-thiolene) (DCBT)[9] and 3,3'-dibromo-5,5'-bis(dicyanomethylene)-$\Delta^{2,2'}$-bi(3-selenolene) (DBBS).[10] The half-wave reduction potentials and nitrile stretching frequencies of these acceptors in infrared spectra are given in Table 3. The reduction potentials, except for that of $TCNQF_4$, are just appropriate to form conductive complexes with the present donors; the differences ΔE_{redox} between the oxidation potentials of the donors and the reduction potentials of the acceptors are in the range from -0.05 V to 0.32 V, which has a high probability of being organic metals.[11] The resulting complexes are mostly 1:1 stoichiometrical, but some complexes favor a composition rich in either donors or acceptors, even when both components are mixed in equimolar amounts. In addition, their electrical conductivities widely range from 8 to 10^{-9} Scm^{-1}, being independent of the stoichiometry. The stoichiometry and conductivities are apparently dependent on appropriate combinations of the donors and acceptors, but can be somewhat systematized according to the used acceptors rather than the donors, as follows. The TCNQ complexes of the TTA and TSA derivatives tend to favor a composition rich in acceptor species, and the electrical conductivities measured on compressed pellets at room temperature are in the high range of 0.05-2.0 Scm^{-1}. These complexes, except for the TMTSA complex, show a broad electron absorption in the infrared region, being characteristic of a segregated stacked structure in a mixed valence state.[12] The incomplete charge transfer was also supported by nitrile vibrational frequencies, which are intermediate between those of neutral TCNQ (2232 cm^{-1}) and Na^+TCNQ^- (2174 cm^{-1}).[13] In contrast, the TCNQ complexes of stronger tellurium-containing donors, DMTTeA and TMTTeA, have the 1:1 composition and low conductivities. All of the complexes with a stronger acceptor, $TCNQF_4$, are also 1:1 stoichiometrical and exhibit a low conductivity.

These complexes with low conductivities must correspond to Mott insulators, since the increasing donor or acceptor character causes a complete charge transfer, as indicated by the low frequencies of the infrared nitrile vibrations. On the other hand, a weaker acceptor DMTCNQ forms complexes of a 2:1 composition, reflecting increasing bulkiness of the acceptor. These complexes mostly exhibit low conductivities, and the electronic spectra indicate segregated stacking only for a complex with 2,3-DMTTA. A similar result was observed for the DMOTCNQ complexes. Some of the DMTCNQ complexes were actually confirmed by X-ray crystallographic analyses to be mixed stacking, which is further discussed later in connection with their conductivities. The other acceptors (TNAP, DCBT, and DBBS) are strong electron acceptors comparable to TCNQ and have additional advantages of high polarization and reduced Coulomb repulsion due to their extensive conjugation. Their complexes are all 1:1 stoichiometrical and mostly high-conductive, indicating mutual fitness of the donors and the acceptors. The enhanced intermolecular interactions of the individual components due to the extended π-systems as well as interactive heteroatoms are considered to lead to a ready formation of segregated columns. In particular, it is worth noting that the tellurium-containing donors can form highly conductive complexes with these acceptors.

Crystal structures of DMTCNQ complexes. The four DMTCNQ complexes with 2,3-DMTSA, 6,7-DMTSA, TMTSA, and TMTTA offered good single crystals for X-ray analysis. Table 4 shows their crystal data, in which all crystals belong to the monoclinic space group. Of these complexes, only the 2,3-DMTSA complex has a high conductivity (0.53 Scm^{-1}) and an electronic absorption band at 4.6 kcm^{-1}. Although it is expected to have a different crystal structure, all of the DMTCNQ complexes are isostructural with mixed stacked columns of a donor-donor-acceptor sequence along the c-axis (Fig. 1).

Table 4. Crystal data of DMTCNQ complexes

	2,3-DMTSA	6,7-DMTSA	TMTSA	TMTTA
formura	$C_{46}H_{28}N_4Se_8$	$C_{46}H_{28}N_4Se_8$	$C_{50}H_{36}N_4Se_8$	$C_{50}H_{36}N_4Se$
formula wt	1268.44	1268.44	1324.54	949.37
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\,2_1/n$	$P\,2_1/n$	$P\,2_1/n$	$P\,2_1/n$
a/Å	8.869(1)	16.561(4)	10.027(1)	9.942(1)
b/Å	20.322(2)	11.532(3)	20.852(2)	20.542(2)
c/Å	11.132(2)	10.901(3)	10.613(1)	10.500(1)
β/°	91.14(1)	99.22(2)	99.06(1)	98.65(1)
V/Å^3	2005.9(4)	2054.9(9)	2191.4(4)	2120.1(4)
Z	2	2	2	2
No.of data	2423	2538	2333	2623
R	0.045	0.068	0.070	0.069

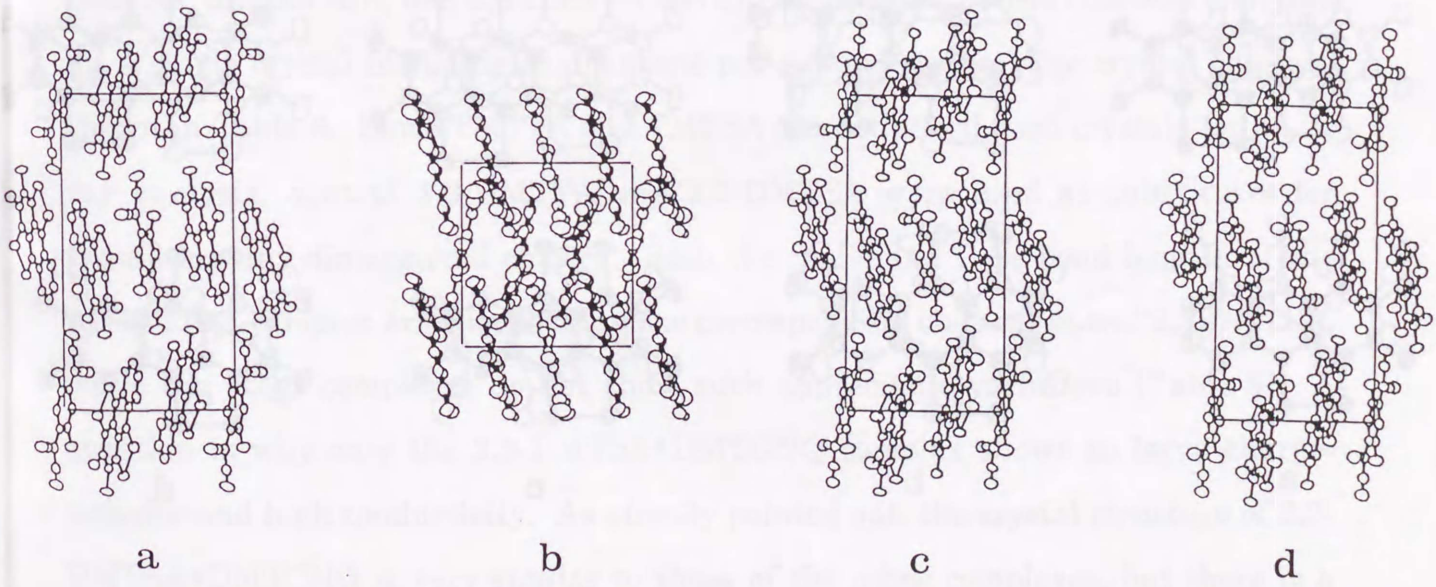


Fig. 1. Crystal structures of DMTCNQ complexes with 2,3-DMTSA (a), 6,7-DMTSA (b), TMTSA (c), and TMTTA (d) projected along the a axis.

In addition, overlapping modes for donor-donor and donor-acceptor are quite similar (Fig. 2). Their infrared nitrile vibrations as compared with that (2230 cm^{-1}) of neutral DMTCNQ indicate complete charge-transfer for the 2,3-DMTSA complex (2172 cm^{-1}) but some charge-transfer for the 6,7-DMTSA complex (2190 cm^{-1}), the TMTTA complex (2214 cm^{-1}), and the TMTSA complex (2210 cm^{-1}). The actual charge-transfer of the 2,3-DMTSA complex is also supported by a detailed examination of the molecular structures of the components. The molecular geometry of DMTCNQ becomes more benzenoid in character for the 2,3-DMTSA•DMTCNQ complex (Table 5), supporting the complete charge transfer.[14] Because the strong donating character of the peri-dichalcogenide polyacenes is based on aromatization of the heterocyclic ring in the resulting cationic species, the charge-transfer in their complexes might bring about a change in the ring dimensions: that is, a shortening of the Se-Se and Se-C bond lengths.[15]

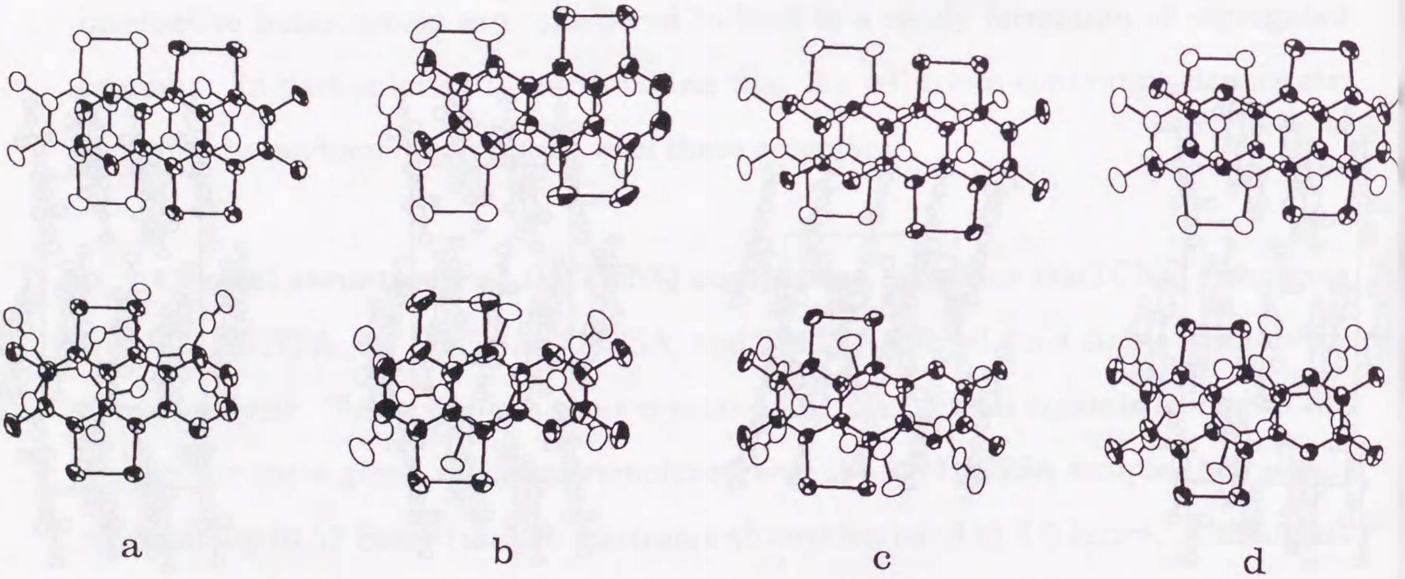


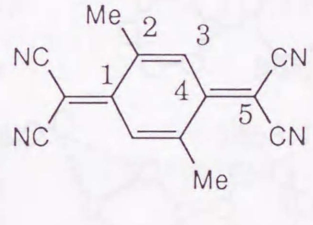
Fig. 2. Molecular overlapping modes of DMTCNQ complexes with 2,3-DMTSA (a), 6,7-DMTSA (b), TMTSA (c), and TMTTA (d) viewed perpendicular to the molecular planes.

Table 5. Selected bond distances (Å) of DMTCNQ complexes

		2,3-DMTSA	6,7-DMTSA	TMTSA	TMTTA
DMTCNQ	C1-C2	1.420(10)	1.445(11)	1.489(15)	1.448(8)
	C2-C3	1.367(10)	1.357(11)	1.340(15)	1.341(8)
	C3-C4	1.406(10)	1.460(11)	1.435(15)	1.432(8)
	C4-C5	1.437(10)	1.347(11)	1.386(15)	1.383(8)
Donor	X-X[a]	2.323(1)	2.348(2)	2.333(2)	2.091(2)
	C-X[a,b]	1.895(7)	1.900(9)	1.920(10)	1.756(5)

a) Neutral 2,3-DMTSA; Se-Se 2.340(1), C-Se 1.915(6)Å. 6,7-DMTSA; Se-Se 2.341(1), C-Se 1.904(6)Å. 2,3-DMTTA; S-S 2.096(3), C-S 1.756(5)Å

b) Average distance.



For a comparison of the molecular geometry, the molecular structures of neutral 2,3-DMTSA, 6,7-DMTSA, and 2,3-DMTTA were determined. 2,3-DMTSA was analyzed for a single crystal including one benzene per two molecules. The crystal data are shown in Table 6. Since TMTTA and TMTSA did not afford good crystals for an X-ray analysis, neutral 2,3-DMTTA and 2,3-DMTSA were used as substitutes for examining any dimensional change. Both the Se-Se and C-Se bond lengths of the 2,3-DMTSA complex are shorter than the corresponding ones of neutral 2,3-DMTSA, while the other complexes do not show such appreciable variations (Table 5). A question is why only the 2,3-DMTSA•DMTCNQ complex shows so large charge-transfer and high conductivity. As already pointed out, the crystal structure of 2,3-DMTSA•DMTCNQ is very similar to those of the other complexes, but there is a small difference in overlapping distances. Thus, the 2,3-DMTSA•DMTCNQ complex has a rather longer interplanar distance between the donor and acceptor than do the other complexes, being in conflict with the actual degree of charge transfer. On the other hand, the interplanar distance between paired donors is shorter, and a short Se-Se contact (3.62 Å) is observed. In addition, some intercolumnar Se-N contacts between 2,3-DMTSA and neighboring DMTCNQ, constituting a net-work sheet are also obserbed (Fig. 3). It is thus concluded that the large charge transfer and high conductivity of the 2,3-DMTSA•DMTCNQ complex are induced by strong heteroatomic interactions of Se-Se and Se-N.

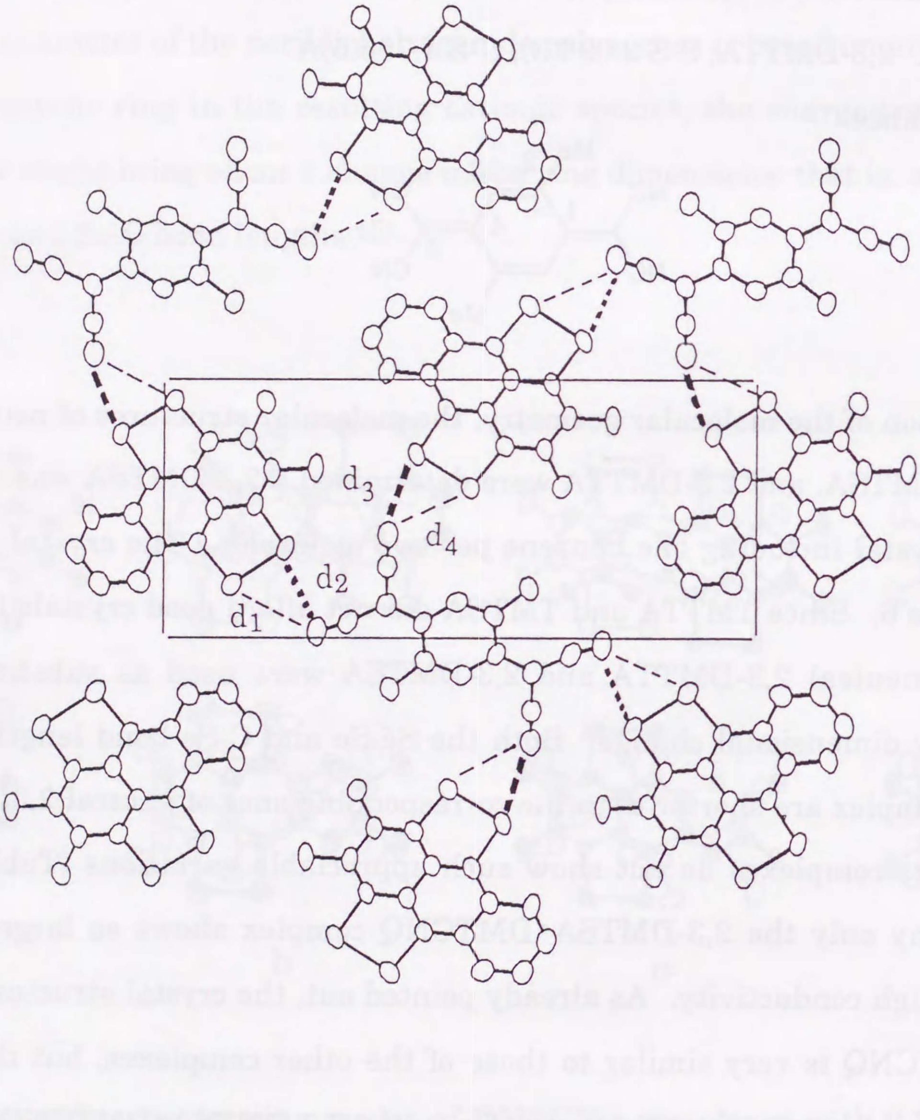


Fig. 3. Crystal structure of 2,3-DMTSA•DMTCNQ projected along the *c* axis. (d_1=3.38Å, d_2=3.20Å, d_3=3.23Å, d_4=3.29Å)

Table 6. Crystal data of 2,3-DMTSA, 6,7-DMTSA, and 2,3-DMTTA

	$(2,3\text{-DMTSA})_2C_6H_6$	6,7-DMTSA	2,3-DMTTA
formura	$C_{38}H_{26}Se_8$	$C_{16}H_{10}Se_4$	$C_{16}H_{10}S_4$
formula wt	1114.30	518.10	330.51
cryst system	monoclinic	monoclinic	triclinic
space group	$P\,2_1/n$	$P\,2_1/c$	$P\,1$
a/Å	18.354(1)	7.509(1)	10.343(2)
b/Å	16.199(2)	22.028(2)	12.496(2)
c/Å	5.679(1)	9.471(1)	7.456(2)
α/°	90.0	90.0	90.15(2)
β/°	93.51(1)	111.41(1)	108.14(2)
γ/°	90.0	90.0	129.37(1)
V/Å^3	1685.3(4)	1458.4(3)	681.2(3)
Z	2	4	2
No.of data	2274	1874	1853
R	0.041	0.041	0.059

Experimental

General. Melting points are uncorrected. All chemicals and solvents are of reagent grade. Elemental analyses were measured by Mr. Hideaki Iwatani, Microanalytical Laboratory in the Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. NMR spectra were recorded on a JEOL PMX-60 spectrometer (60 MHz) using deuteriochloroform as a solvent and tetramethylsilane as an internal standard. IR spectra were taken on a Hitachi 260-30 spectrophotometer with a KBr disk method. MS spectra were measured at 70 eV on a Shimadzu QP-1000A spectrometer using a direct insertion technique. Electronic spectra were recorded on a Shimadzu UV-160 spectrometer or on a Hitachi 330 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

1,4-Dihydroxy-2,3-dimethylanthraquinone (3a) 8)

A mixture of anhydrous aluminium chloride (50 g) and sodium chloride (10 g) was well ground together in a mortor, and heated at 210°C to melt. Into the stirred solution was added a mixture of phthalic anhydride (**1a**)(7.4 g, 50 mmol) and 2,3-dimethylhydroquinone (**2b**)(6.9 g, 50 mmol); heating at the temperature was continued for further 4 h. Concd hydrochloric acid (50 cm^3) and water (200 cm^3) were successively added into a mixture cooled to ca. 100°C, which was then gently boiled for 2 h. The resulting solid, while still hot, was collected by filtration and dissolved in chloroform (2 dm^3). After the solution was filtered, the filtrate was concentrated to ca. 200 cm^3 and purified by column chromatography on silica gel using chloroform as an eluent to give a reddish-orange solid of 3a (11.3 g, 84.6%). An analytical sample was obtained as reddish-orange needles upon recrystallization from benzene-hexane: mp 259-260°C (lit.,9) mp 252-253 °C); ^{1}H NMR δ=2.40 (s, 6H, CH_3), 7.73 (AA'BB' m, 2H, ArH), 8.24 (AA'BB' m, 2H, ArH), and 13.48 (s, 2H, OH); IR 1590 cm^{-1}

(C=O); MS *m*/*z* 268 (M^+); Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51%. Found: C, 71.63; H, 4.51%.

1,4-Dihydroxy-6,7-dimethylanthraquinone (3b): 74% yield; reddish orange needles from chloroform; mp 228°C; ^{1}H NMR δ=2.30 (s, 6H, CH_3), 7.20 (s, 2H, ArH), 7.95 (s, 2H, ArH), and 12.75 (s, 2H, OH); IR 1630 and 1590 cm^{-1} (C=O); MS *m*/*z* 268 (M^+); Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51%. Found: C, 71.60; H, 4.49%.

1,4-Dihydroxy-2,3,6,7-tetramethylanthraquinone (3c): 69% yield; reddish orange needles from chloroform; mp 276°C; ^{1}H NMR δ=2.25 (s, 6H, CH_3), 2.40 (s, 6H, CH_3), 7.96 (s, 2H, ArH), and 13.40 (s, 2H, OH); IR 1580 cm^{-1} (C=O); MS *m*/*z* 296 (M^+); Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44%. Found: C, 72.84; H, 5.40%.

2,3-Dihydro-9,10-dihydroxy-6,7-dimethyl-1,4-anthracenedione (4)

Into a suspension of **3b** (5.3 g, 19.8 mmol) and anhyd. sodium carbonate (5 g) in water (100 cm^3) was added sodium dithionite (10 g); the mixture was heated at 80°C for 15 h. After cooling, the resulting yellow solid was collected by filtration and dried. Chromatography on silica gel using dichloromethane as an eluent followed by recrystallization from benzene-hexane gave yellow needles of **4** (4.8 g, 88%): mp 182°C; ^{1}H NMR δ=2.45 (s, 6H, CH_3), 2.96 (s, 4H, CH_2), 8.00 (s, 2H, ArH), and 13.60 (s, 2H, OH); IR 1610 cm^{-1} (C=O); MS *m*/*z* 270 (M^+); Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.11; H, 5.22%. Found: C, 71.40: H, 5.05%.

1,4,9,9,10,10-Hexachloro-2,3-dimethyl-9,10-dihydroanthracene (5a)

A mixture of **3a** (4.2 g, 15.7 mmol), phosphorus pentachloride (23 g, 110 mmol), and phosphoryl chloride (40 cm^3) was refluxed for 9 h. Concentration under reduced pressure followed by thorough washing of the residue with hexane and then with methanol left a white solid of **5a** (3.8 g, 59%): mp 140°C (dec); ^{1}H NMR δ=2.55 (s, 6H,

CH_3), 7.42 (AA'BB' m, 2H, ArH), and 7.95 (AA'BB' m, ArH); IR 710 cm^{-1} (C-Cl); MS m/z 414 (M^+) with an isotopic pattern hexachlorine; Anal. Calcd for $C_{16}H_{10}Cl_6$: C, 46.31; H, 2.43%. Found; C, 45.71; H, 2.36%.

1,4,9,9,10,10-Hexachloro-6,7-dimethyl-9,10-dihydroanthracene (5b): 30% yield from **4**; a white solid; mp 232°C (dec); ^1H NMR δ=2.45 (s, 6H, CH_3), 7.52 (s, 2H, ArH), and 7.73 (s, 2H, ArH); IR 740 cm^{-1} (C-Cl); MS m/z 414 (M^+) with an isotopic pattern of hexachlorine; Anal. Calcd for $C_{16}H_{10}Cl_6$; C, 46.31; H, 2.43%. Found: C, 45.72; H, 2.24%.

1,4,9,9,10,10-Hexachloro-2,3,6,7-tetramethyl-9,10-dihydroanthracene (5c): 44% yield from **3c**; a white solid; mp 139°C (dec); ^1H NMR δ=2.37 (s, 6H, CH_3), 2.58 (s, 6H, CH_3), and 7.73 (s, 2H, ArH); IR 750 cm^{-1} (C-Cl); MS m/z 440 (M^+) with an isotopic pattern of hexachlorine; Anal. Calcd for $C_{18}H_{14}Cl_6$: C, 48.80; H, 3.19%. Found: C, 48.37; H, 3.00%.

1,4,9,10-Tetrachloro-2,3-dimethylanthracene (6a)

A mixture of **5a** (3.8 g, 9.2 mmol), tin (II) chloride dihydrate (29.2 g), acetic acid (40 cm^3), and concd hydrochloric acid (36 cm^3) was refluxed for 1.5 h. After cooling, the resulting yellow solid of 6a was collected by filtration, washed, and purified by column chromatography on active alumina using benzene as eluent (2.4 g, 75%). An analytical sample was obtained as yellow needles by recrystallization from chloroform-hexane; mp 119-120°C (dec); ^1H NMR δ=2.56 (s, 6H, CH_3), 7.52 (AA'BB' m, 2H, ArH), and 8.45 (AA'BB' m, 2H, ArH); IR 660 cm^{-1} (C-Cl); MS m/z 344 (M^+) with an isotopic pattern of tetrachlorine; Anal. Calcd for $C_{16}H_{10}Cl_4$: C, 55.85; H, 2.93%. Found: C, 55.84; H, 2.89%.

1,4,9,10-Tetrachloro-6,7-dimethylanthracene (6b): 80% yield; yellow needles from chloroform-hexane; mp 172°C; ^{1}H NMR δ=2.48 (s, 6H, CH_3), 7.32 (s, 2H, ArH), and 8.45 (s, 2H, ArH); IR 810 and 605 cm^{-1}; MS *m/z* 344 (M^+) with an isotopic pattern of tetrachlorine; Anal. Calcd for $C_{16}H_{10}Cl_4$: C, 55.85; H, 2.93%. Found: C, 55.82; H, 3.06%.

1,4,9,10-Tetrachloro-2,3,6,7-tetramethylanthracene (6c): 75% yield; yellow needles from benzene; mp 187-188.5°C; ^{1}H NMR δ=2.47 (s, 6H, CH_3), 2.53 (s, 6H, CH_3), and 8.23 (s, 2H, ArH); IR 670 cm^{-1} (C-Cl); MS *m/z* 370 (M^+) with an isotopic pattern of tetrachlorine; Anal. Calcd for $C_{18}H_{14}Cl_4$: C, 58.10; H, 3.79%. Found: C, 58.07; H, 3.58%.

3,4-Dimethylanthra[1,9-cd:4,10-c'd']dithiole (2,3-DMTTA)

In a nitrogen atmosphere, sodium metal (165 mg, 7.2 mmol) was allowed to react with sulfur (236 mg, 7.2 mmol) in dry DMF (30 cm^3) at 100°C for 2 h, forming fresh sodium disulfide. Into the mixture was added a solution of **6a** (516 mg, 1.5 mmol) in dry DMF (30 cm^3). It was refluxed for 8 h, stirred overnight at room temperature with exposure to air, and then poured into brine (200 cm^3). The resulting brown solid was collected by filtration, dried, and extracted with hexane and then with carbon disulfide by use of a Soxhlet apparatus. The carbon disulfide extract was recrystallized from benzene to give black purple needles of 2,3-DMTTA (211 mg, 43%); mp 271°C; IR 1610, 1300, and 740 cm^{-1}; MS *m/z* 330 (M^+); UV (CS_2) 450.5 (log ε 3.79), 531 (3.87), and 566.5 nm (3.90); Anal. Calcd for $C_{16}H_{10}S_4$: C, 58.15; H, 3.05%. Found: C, 58.41; H, 2.87%.

3,4-Dimethylanthra[1,9-cd:4,10-c'd']diselenole (2,3-DMTSA)

2,3-DMTSA was prepared from a similar reaction of **6a** with sodium diselenide at 150°C and recrystallized from benzene to give black crystals. The elemental analysis and X-ray crystallographic analysis showed that it consists of 2,3-DMTSA and benzene of 2:1 ratio. Its heating at 150°C under a reduced pressure left the free 2,3-DMTSA: 31% yield; mp 289°C; IR 1270 and 740 cm^{-1}; MS *m/z* 520 (M$^+$); UV (CS$_2$) 439.5 (log ε 3.75) and 568.5 nm (4.09); Anal. Calcd for $C_{16}H_{10}Se_4$: C; 37.09; H, 1.95%. Found: C, 37.21; H, 1.93%.

3,4-Dimethylanthra[1,9-cd:4,10-c'd']ditellurole (2,3-DMTTeA)

2,3-DMTTeA was prepared from a similar reaction of **6a** with sodium ditelluride at 100°C. Recrystallization from chlorobenzene gave black needles; 15% yield; mp>300°C; IR 1250 cm^{-1}; MS *m/z* 714 (M$^+$); UV (CS$_2$) 598.5 nm (log ε 4.05); Anal. Calcd for $C_{16}H_{10}Te_4$: C, 26.97; H, 1.41%. Found: C, 26.96; H, 1.40%.

8,9-Dimethylanthra[1,9-cd;4,10-c'd']dithiole (6,7-DMTTA): 2% yield; black purple powder; mp>300°C; IR 1340, 1290, 1165, and 790 cm^{-1}; MS *m/z* 330 (M$^+$); UV (CS$_2$) 451 (log ε 3.66), 529 (3.92), and 562 nm (3.98); Anal. Calcd for $C_{16}H_{10}S_4$: C, 58.14; H, 3.05%. Found: C, 58.08; H, 3.04%.

8,9-Dimethylanthra[1,9-cd:4,10-c'd']diselenole (6,7-DMTSA): 38% yield; black plates from chlorobenzene; mp>300°C; IR 1320, 1280, 1150, and 795 cm^{-1}; MS *m/z* 520 (M$^+$); UV (CS$_2$) 446.5 (log ε 3.66) and 568.5 nm (log ε 4.10); Anal. Calcd for $C_{16}H_{10}Se_4$: C, 37.09; H, 1.95%. Found: C, 37.19; H, 1.95%.

3,4,8,9-Tetramethylanthra[1,9-cd:4,10-c'd']dithiole (TMTTA): 41% yield; mp>300°C; IR 2990, 2850, and 1310 cm^{-1}; MS *m/z* 358 (M$^+$); UV (CS$_2$) 447.5 (log ε 3.82), 525.5 (3.89), and 557 nm (3.94); Anal. Calcd for $C_{18}H_{14}S_4$: C, 60.29; H, 3.94%. Found: C, 60.23; H, 3.85%.

3,4,8,9-Tetramethylanthra[1,9-cd:4,10-c'd']diselenole (TMTSA): 29% yield; black powder from gradient sublimation; mp>300°C; IR 3000, 2930, and 1290 cm^{-1}; MS m/z 548 (M^+); UV (CS_2) 559 nm (log ε 4.11); Anal. Calcd for $C_{18}H_{14}Se_4$: C, 39.59; H, 2.58%. Found: C, 39.55; H, 2.51%.

3,4,8,9-Tetramethylanthra[1,9-cd:4,10-c'd']ditellurole (TMTTeA): 14% yield; black powder from carbon disulfide; mp>300°C; MS m/z 740 (M^+); UV (CS_2) 586.5 nm (log ε 4.07); Anal. Calcd for $C_{18}H_{14}Te_4$: C, 29.19; H, 1.91%. Found: C, 29.48; H, 1.82%.

Charge-Transfer Complexes. All of the complexes described in this report were prepared by mixing two hot saturated solutions of the donor and acceptor in chlorobenzene. The resulting complexes precipitated out upon cooling, which were collected by filtration, washed with cold dichloromethane, and dried.

Crystal Structures. The X-ray diffraction data were collected with a Rigaku automated diffractometer using Cu $K\alpha$ radiation monochromatized with a graphite plate. Independent reflections within $2\theta=126°$ ($|F_o| \geq 3.0\sigma(F_o)$) were used for analyses. The structures were solved by a direct method combined with the Monte-Carlo method for the selection of the initial set of phase,16) and refined by a full-matrix least squares method.17) Atomic scattering factors were taken from International Tables for X-ray Crystallography.18) The anisotropic temperature factors were used for the refinement; hydrogen atoms were not included in the refinement.

References

1) For an excellent review on TTT and TST, see I. F. Shchegolev and E. B. Yagubskii,"Extended linear chain compounds" ed by J. S. Miller, New York Plenum Press, 1982, Vol. 2, pp. 385-434.

2) D. J. Sandman and J. C. Stark, *Organometallics*, **1**, 739 (1982).

3) S. Ohnishi, T. Nogami, and H. Mikawa, *Tetrahedron Lett.*, **1983**, 2401; T. Nogami, H. Tanaka, S. Ohnishi, Y. Tasaka, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **57**, 22 (1983).

4) F. Wudl, D. E. Schafer, and B. Miller, *J. Am. Chem. Soc.*, **98**, 252 (1976).

5) S. Ohnishi, T. Nogami, and H. Mikawa, *Chem. Lett.*, **1982**, 1841.

6) A. Yamahira, T. Nogami, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, **1983**, 904; J. C. Stark, R. Reed, L. A. Acampora, D. J. Sandman, S. Jansen, M. T. Jones, and B. M. Foxman, *Organometallics.*, **3**, 732 (1984).

7) T. Otsubo, N. Sukenobe, Y. Aso, and F. Ogura, *Chem. Lett.*, **1987**, 315; *Synth. Met.*, **27**, B509 (1988).

8) F. A. J. Kerdesky and M. P. Cava, *J. Am. Chem. Soc.*, **100**, 3635 (1978); F. A. J. Kerdesky, R. J. Ardecky, M. V. Lakshmikantham, and M. P. Cava, *ibid.*, **103**, 1992 (1981).

9) K. Yui, Y. Aso, T. Otsubo, and F. Ogura, *Bull. Chem. Soc. Jpn.*, **62**, 1539 (1989).

10) K. Yui, Y. Aso, T. Otsubo, and F. Ogura, *Chem. Lett.*, **1988**, 1179.

11) J. B. Torrance, *Acc. Chem. Res.*, **12**, 79 (1979); G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, **53**, 2141 (1980).

12) J. B. Torrance, B. A. Scott, and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975); J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, *Bull. Chem. Soc. Jpn.*, **49**, 2358 (1976); E. M. Engler, V. V. Patel, J. R. Andersen, R. R. Schumaker, and A. A. Fukushima, *J. Am. Chem. Soc.*, **100**, 3769 (1978); K. Nakasuji and I. Murata, *Synth. Metals*, **27**, B289 (1988).

13) J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, *J. Am. Chem. Soc.*, **103**, 2442 (1981).

14) T. J. Kristenmacher, T. J. Emge, A. N. Bloch, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **38**, 1193 (1982).

15) R. P. Shibaeva, "Extended linear chain compounds," ed by J. S. Miller, New York, Plenum Press, 1982, Vol. 2, pp. 435-467.

16) A. Furusaki, *Acta Crystallogr., Sect. A*, 35, 220 (1979).

17) C. Katayama, N. Sakabe, and K. Sakabe, *Acta Crystallogr., Sect. A*, **28**, S207 (1972).

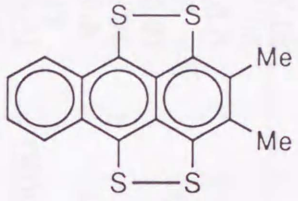
18) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. IV.

Chapter 2. Syntheses, crystal structures and properties of radical cation salts of 2,3-dimethyltetrathioanthracene (2,3-DMTTA) and 2,3-dimetyltetraselenoanthracene (2,3-DMTSA).

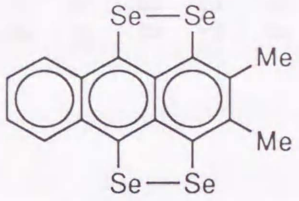
Introduction

Electrocrystallization was first used by Chiang *et al.* to prepare electrically conductive radical cation salts of aromatic hydrocarbons such as pyrene and perylene.1) Since then, a lot of reports on radical salts synthesized with this technique has been published, and most of the salts showed high conductivities or metallic properties. For example, Bechgaard *et al.* reported the conducting properties of $(TMTSF)_2 \bullet X$ complexes ($X=PF_6$, ClO_4, ReO_4 •••), which showed the first organic superconductivity at low temperature (about 1K).2) In addition, a series of organic conductors with much higher transition temperature to superconducting state have been prepared from multi-sulfur donor, BEDT-TTF (ET) by electrocrystallization.2) One of the superiorties of this technique is to offer easily single crystals of a radical salt. Consequently, this method is enable us to study its properties in detail. Although there have been so many reports on electrocrystallization of tetrachalcogenofulvalenes (TXF, X=S, Se) and their derivatives, only a few studies about electrocrystallization of peri-chalcogen bridged arenes have been known. Nogami *et al.* reported that electrocrystallization of tetrathiotetracene (TTT) afforded highly conductive radical cation salts ($TTT \bullet PF_6$; $\sigma=762$ Scm^{-1}, $TTT \bullet SbF_6$; $\sigma=40$ Scm^{-1}, $TTT \bullet I$; $\sigma=158$ Scm^{-1} *etc.*).3) However, this paper described no structural aspects; the crystal structures of the TTT salts have not been revealed by an X-ray structural analysis up to date. In addition, they mentioned the poor solubility of the donor, that made difficult to prepare radical salts with this technique.

In this context, our new donors, tetrachalcogenoanthracenes, whose syntheses are mentioned in the previous chapter, seem to be suitable for electrocrystallization, because of their better solubilities and strong donor abilities. Indeed, the electrocrystallization of two of them, 2,3-DMTTA and 2,3-DMTSA, gave good crystals of radical salts with highly electrical conductivities. In this chapter, the properties and crystal structures of radical cation salts of 2,3-DMTTA and 2,3-DMTSA are described.



2,3-DMTTA



2,3-DMTSA

Results and Discussion.

Syntheses and Physical Properties. In preliminary experiments, electrocrystallization of 2,3-dimethyl, 6,7-dimethyl and tetramethyl TTA and TSA donors in various solvents (1,1,2-trichloroethane, chlorobenzene, benzonitrile, or tetrahydrofuran) was examined. Among them 6,7-dimethyl and tetramethyl donors gave a small amount of black solid radical salts, but the reproducibility was poor, probably due to their low solubilities. On the other hand, 2,3-DMTTA and TSA afforded needle-shaped crystals of radical cation salts in 1,1,2-trichloroethane as solvent. Depending on a supporting electrolyte employed on electrochemical oxidation, radical cation salts with various counter anions were obtained. Table 1 lists physical properties of the salts. The ratios of donor molecules to the anions were determined by C, H, N elemental analyses, within an error of 1.02%. These stoichiometries were also confirmed by X-ray crystallographic analyses as described later. In contrast to the usual tendency to produce radical cation salts with 2:1 stoichiometry by electrocrystallization, 2,3-DMTXA afforded radical salts with both 1:1 and 2:1 stoichiometries. As shown in Table 1, small anions such as NO_3^-, BF_4^-, ClO_4^- or Br^- produce the salts with 1:1 ratio, whereas a large AsF_6^- anion gives the salt with 2:1 ratio. The PF_6^- anion is on the borderline, that is, the 2,3-DMTTA salt consists of 2:1 ratio, while the 2,3-DMTSA salt consists of 1:1 ratio. It is obvious that a dominative factor to determine the donor/anion ratio might be the volume of a counter anion.

Table 1. Radical cation salts of 2,3-DMTTA and 2,3-DMTSA

Radical Salt [a)]	D : A	Appearance	Dp	Found (Calcd) [b)]/%			σ [c)]	E_{act}	$h\nu_{CT}$ [d)]
			°C	C	H	N	Scm^{-1}	eV	$X10^3cm^{-1}$ (eV)
2,3-DMTTA•NO_3	1 : 1	Black needles	239	48.80	2.69	2.55	4.4	0.065	5.2, 9.7
				(48.96	2.57	3.57)			17.5, 22.7
2,3-DMTTA•BF_4	1 : 1	Black needles	253	46.90	2.89	0	7.0	0.063	5.2, 9.8
				(46.05	2.42	0)			17.2, 22.5
2,3-DMTTA•ClO_4	1 : 1	Black needles	285	45.24	2.38	0	0.50	0.072	5.1 10.0
				(44.70	2.34	0)			17.6, 23.1
2,3-DMTTA•PF_6	2 : 1	Black needles	249	46.17	2.33	0	0.12	0.072	3.3, 10.5,17.5
				(46.84	2.41	0)			20.7, 23.8
2,3-DMTTA•AsF_6	2 : 1	Black needles	276	45.32	2.37	0	0.19	0.079	3.5, 10.5,17.5
				(45.22	2.37	0)			20.7, 23.8
2,3-DMTTA•Br	1 : 1	Black micro crystals	229	46.17	2.33	0	$3.2 X 10^{-3}$ [e)]	0.106 [e)]	5.5, 11.7
				(46.82	2.46	0)			16.5, 22.5
2,3-DMTSA•NO_3	1 : 1	Black needles	>300	33.46	1.72	1.62	$4.4 X 10^2$	metallic	4.6, 9.5
				(33.13	1.74	2.41)		(down to 220K)	16.6, 23.0
2,3-DMTSA•BF_4	1 : 1	Black needles	253	31.70	1.63	0	$4.5 X 10^2$	metallic	4.5, 9.5
				(31.77	1.67	0)		(down to 180K)	16.6, 23.0

Table 1. (continued)

2,3-DMTSA•ClO$_4$	1 : 1	Black needles	285	32.06	1.89	0	40	0.020	4.6, 9.1
				(31.12	1.63	0)			16.5, 23.8
2,3-DMTSA•PF$_6$	1 : 1	Black needles	249	28.98	1.52	0	0.65	0.092	4.8, 9.4
				(29.04	1.51	0)			16.5, 23.8
2,3-DMTSA•AsF$_6$	2 : 1	Black crystals	274	31.04	1.58	0	0.10 e)	0.117 e)	3.5, 10.1, 16.9
				(31.37	1.65	0)			20.7, 23.5

a) Obtained from 1,1,2-trichloroethane.

b) Calculated from stoichiometry indicated for the salt.

c) Measured on single crystals with four-probe method.

d) Measured with a KBr disk method.

e) Measured on a compressed pellet with four-probe method.

In the case of 1:1 salt with a closed shell anion species, each of donor molecules carries a net positive charge, so the salt should be a complete charge-transfer salt, which is known as a Mott insulator with a large energy gap of transferring an electron to a neighboring site. The present 1:1 salts, however, has relatively high electrical conductivities. In particular, 2,3-DMTSA•NO_3 and BF_4 salts show remarkably high conductivities of 440 and 450Scm^{-1} at room temperature and *metallic* behavior down to 230K and 180K, respectively (Fig. 1).[7)]

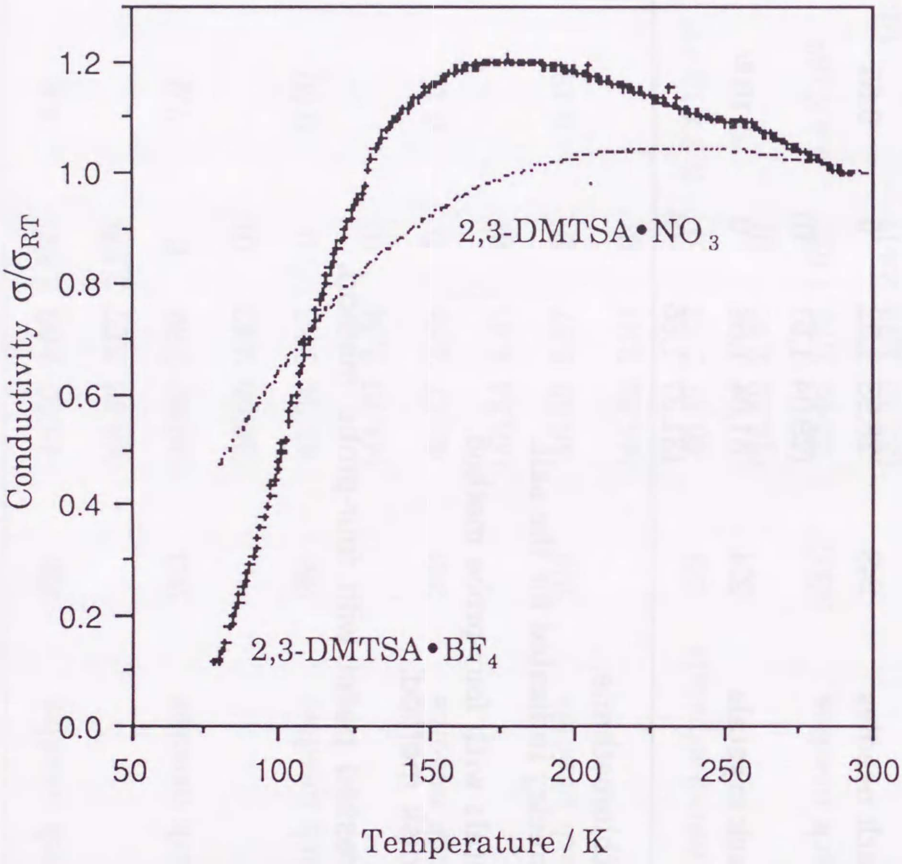


Fig. 1. Temperature dependences of conductivities of 2,3-DMTSA•NO_3 and 2,3-DMTSA•BF_4.

In marked contrast to the present two salts, other 1:1 salts have been showen to be semiconductors with very low activation energies. The 2:1 salts were also conductive, but the conductivities were somewhat lower than those of 1:1 salts. This is unusual for organic conductors since the 2:1 salts constitute mixed valence state in which an unpaired electron can be transfered with no coulombic energy among the donor molecules. In addition, Table 1 also indicates that 2,3-DMTSA salts are more conductive than 2,3-DMTTA salts with the same counter anions.

Crystal structures. In order to elucidate these unusual results, X-ray crystallographic analyses were examined. All the salts except for 2,3-DMTTA•Br and 2,3-DMTSA•AsF_6 gave good single crystals suitable for X-ray analyses. The crystal data and final R values are listed in Table 2-4. The crystal structures are mainly classified into three main types. The first one (Type I) comprises the NO_3 and BF_4 salts of 2,3-DMTTA and 2,3-DMTSA. All the Type I salts belong to orthorhombic with similar unit-cell parameters. Figure 2 shows crystal structure of 2,3-DMTSA•NO_3 salt as a representative of Type I. In agreement with the results of the elemental analyses, the crystals are composed of one donor molecule and one inorganic anion.

Table 2. Crystal data of 2,3-DMTXA•NO_3 and BF_4 (Type I)

	2,3-DMTTA•NO_3	2,3-DMTTA•BF_4	2,3-DMTSA•NO_3	2,3-DMTSA•BF_4
formula	$C_{16}H_{10}S_4N_1O_3$	$C_{16}H_{10}S_4B_1F_4$	$C_{16}H_{10}Se_4N_1O_3$	$C_{16}H_{10}Se_4B_1F_4$
formula wt.	392.50	417.32	580.08	604.90
cryst system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$Cmc2_1$	$Cmcm$	$Cmc2_1$	$Cmcm$
a/Å	13.787(1)	13.922(1)	14.036(2)	14.214(1)
b/Å	16.331(1)	16.454(1)	16.585(2)	16.620(1)
c/Å	6.677(1)	6.7087(6)	6.737(1)	6.770(1)
V/Å^3	1503.2(4)	1536.8(2)	1568.3(3)	1599.3(2)
Z	4	4	4	4
No.of data	650	648	656	705
R	0.081	0.075	0.041	0.048

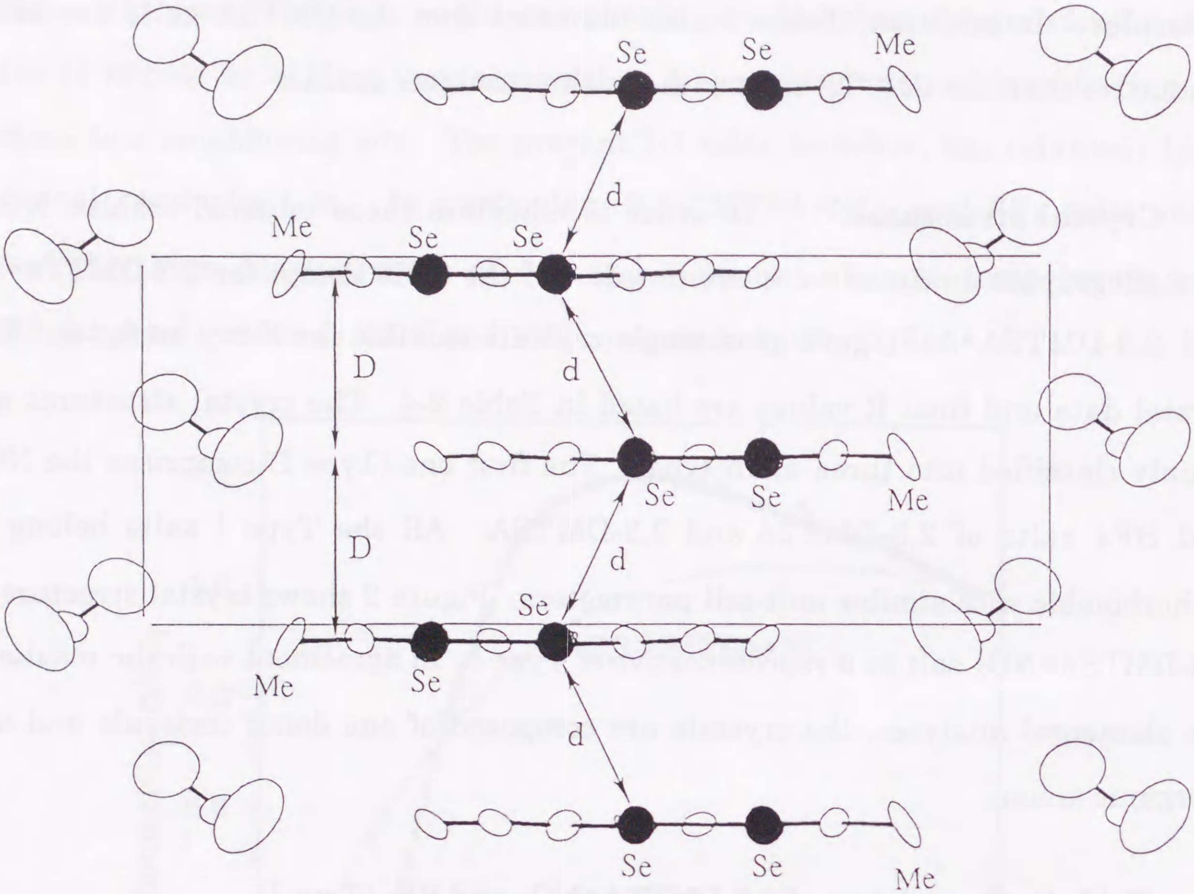

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Fig. 2. Crystal structures of 2,3-DMTSA•NO_3 viewed along *a*-axis. (D=3.37Å, d=3.67Å)

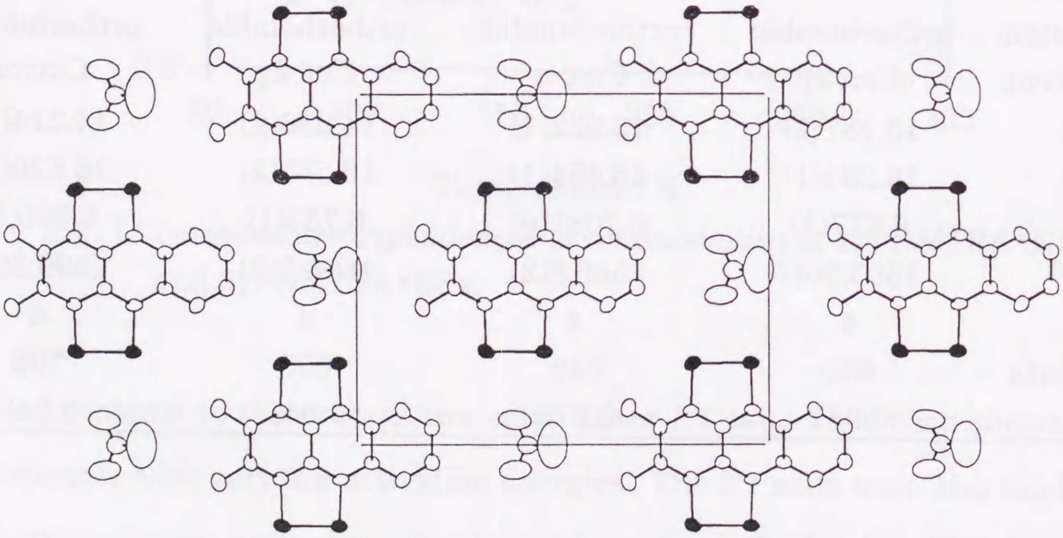


Fig. 3. Crystal structures of 2,3-DMTSA•NO_3 viewed along *c*-axis.

The thermal parameters of O atoms are large, suggesting an orientational disorder of anion parts. No positional disorder is, however, found, since the thermal parameters of central N atoms are normal. The geometry of the 2,3-DMTSA molecule is somewhat different from that of neutral 2,3-DMTSA owing to carrying positive charge. The most different point from the neutral molecule is the bond length (2.321Å) of Se-Se bridge, which is fairly shorter than that of the neutral one (2.366Å). The donor molecules stack uniformly along the *c* axis with the alternate arrangement of two methyl groups in the opposite directions in order to reduce their intermolecular steric repulsion. The direction of this donor stacking accords with the long crystal axis, in which the high conductivity of the salt was observed. Each donor column is separated by the anion columns along both *a* and *b* directions, indicating that the salt is essentially one-dimensional conductor (Fig. 3). The interstack distances are $c/2$, that is 3.37Å, indicating the presence of a strong π-electron interaction. In addition, the shortest nonbonded Se-Se distance is 3.67Å, which is much shorter than the van der Waals contact distance (3.80Å).[8)] These strong intrastack interactions through π-π and Se-Se contacts presumably serve to make a conduction band wider and decrease an energy gap between the conduction band and

Table 3. Crystal data (Type II)

	2,3-DMTTA•ClO$_4$	2,3-DMSTA•ClO$_4$	2,3-DMTSA•PF$_6$
formula	$C_{16}H_{10}S_4Cl_1O_4$	$C_{16}H_{10}Se_4Cl_1O_4$	$C_{16}H_{10}Se_4P_1F_6$
formula wt	429.94	617.52	663.06
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/c$	$P2_1/c$
a/Å	19.804(2)	7.166(1)	7.262(6)
b/Å	11.798(1)	11.837(1)	12.220(1)
c/Å	7.023(1)	20.203(2)	20.611(2)
β/°	94.72(1)	93.81(1)	95.65(8)
V/Å^3	1635.4(3)	1709.9(3)	1820(3)
Z	4	4	4
No.of data	2224	1685	1980
R	0.091	0.081	0.080

the valence state, resulting in the high conduction with metallic behavior around room temperature. Bonded and nonbonded heteroatom distances and interstack distances of radical cation salts are listed in Table 5, which indicates that 2,3-DMTSA•BF_4 is completely the same situation as 2,3-DMTSA•NO_3 salt. On the other hand, 2,3-DMTTA•NO_3 and BF_4 salts are in a different situation; the interstack distances are slightly shorter than those of 2,3-DMTSA salts (3.34-3.35Å), whereas the nonbonded intermolecular S-S distances are 3.69Å for 2,3-DMTTA•NO_3 and 3.72Å for 2,3-DMTTA•BF_4, that are rather longer than the van der Waals contact distance (3.60Å). This is responsible for lower conductivities (4-7 Scm^{-1}) of the 2,3-DMTTA salts as compared with the selenium salts.

The second type of the crystal structure consists of the other 1:1 salts, 2,3-DMTTA•ClO_4, 2,3-DMTSA•ClO_4 and 2,3-DMTSA•PF_6. As shown in Table 3, the crystal data of all these salts are very similar to each other and they all belong to monoclinic space group. Since the structures of these salts are essentially the same, the crystal structure of 2,3-DMTTA•ClO_4 is shown in Fig. 4 as a representative of Type II.

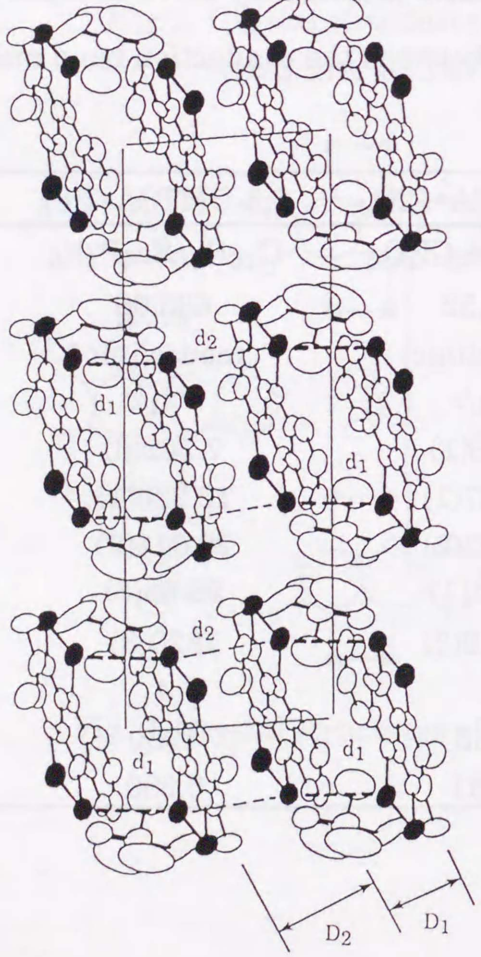


Fig. 4.
Crystal structures of 2,3-DMTTA•ClO_4 viewed along *b*-axis.
(D_1=3.29Å, D_2=3.44Å, d_1=3.37Å, d_2=3.75Å)

The crystals are composed of one donor and one inorganic anion, according with the results of the elemental analyses. The crystal structure of 2,3-DMTTA•ClO_4 is, however, quite different from that of Type I. In this case, the component molecules lie in inversion centers and the donor molecules stack with alternate spaces of 3.29 and 3.44Å, making stacking columns with sliding along the *c* axis. The nonbonded S-S distances in two spaces are 3.37 and 3.75Å. As a result, the alternation of donor stacking in Type II salts reflects their lower conductivities than those of Type I salts and semiconducting behavior.

The 2:1 salts, 2,3-DMTTA•PF_6 and 2,3-DMTTA•AsF_6, are classified as Type III salts. The crystal data of these two salts quite resemble (Table 4). Since their crystal structures are completely isomorphous, only the structure of 2,3-DMTTA•PF_6 is shown in Fig. 5. The donor molecules stack with alternate spaces of 3.39 and 3.55Å like Type II salts, making a columnar structure parallel to the high conductive *c* axis. One PF_6^- anion is located by sulfur bridges of the donor pairs, thus the crystal composition is two donor molecules par one anion. The bonded S-S length (2.083Å) is just in the middle of those of neutral 2,3-DMTTA (2.102Å) and the 1:1 salts (2.066-2.077Å), supporting a half formal charge on each donor molecule (Table 5).[9]

Table 4. Crystal data of 2,3-DMTTA•PF_6 and AsF_6 salts (Type III)

	(2,3-DMTTA)$_2$•PF_6	(2,3-DMTTA)$_2$•AsF_6
formula	$C_{32}H_{20}S_8P_1F_6$	$C_{32}H_{20}S_8As_1F_6$
formula wt	805.96	849.94
cryst system	orthorhombic	orthorhombic
space group	*Pnmn*	*Pnmn*
a/Å	14.987(1)	15.180(2)
b/Å	14.247(1)	14.275(1)
c/Å	7.219(1)	7.211(1)
V/Å^3	1541.4(3)	1546.7(3)
Z	2	2
No.of data	1046	1002
R	0.059	0.057

Although the 2:1 salts take advantage of a mixed valence state of donor molecules, stacking alternation prevents metallic conduction in the salts of Type III.

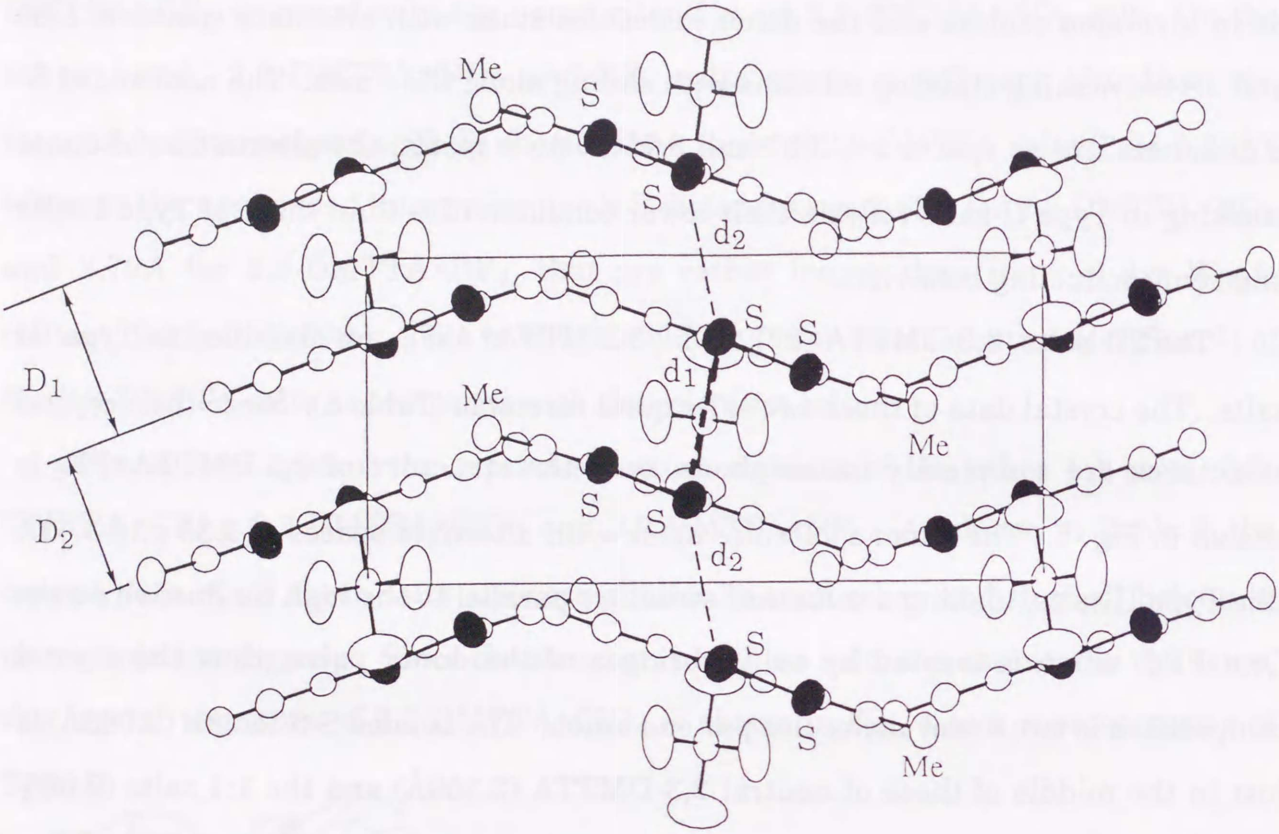


Fig. 5. Crystal structures of 2,3-DMTTA•PF_6 viewed along (a) *a*-axis (b) *c*-axis. (D_1=3.55Å, D_2=3.39Å, d_1=3.65Å, d_2=3.69Å)

Table 5. Bonded and nonbonded heteroatomic distances and interstack distances of radical cation salts

Salt	Formal charge	bonded X-X distance / Å	Nonbonded X-X distance / Å	Interstack distance / Å
2,3-DMTTA•NO_3	1	2.070	3.69	3.34
2,3-DMTTA•BF_4	1	2.077	3.72	3.35
2,3-DMTTA•ClO_4	1	2.066	3.37, 3.75	3.29, 3.44
2,3-DMTTA•PF_6	1/2	2.083	3.65, 3.69	3.39, 3.55
2,3-DMTTA•AsF_6	1/2	2.085	3.66, 3.69	3.39, 3.56
2,3-DMTSA•NO_3	1	2.321	3.67	3.37
2,3-DMTSA•BF_4	1	2.325	3.69	3.39
2,3-DMTSA•ClO_4	1	2.319	3.32, 3.88	3.32 3.49
2,3-DMTSA•PF_6	1	2.319	3.42, 3.95	3.33, 3.42

Electronic spectra The electronic absorption spectra of the radical cation salts taken on a compressed pellet with KBr give some information on their electronic states. The absorption maxima are summarized in Table 1, and the spectral shapes of the representative salts of Types I-III are illustrated in Fig. 6. The 1:1 salts of Types I-II exhibit absorption bands at around 5, 10, 17, 24 kcm^{-1}, and there is no apparent difference between both types. The latter three bands are ascribable to intramolecular transition of the radical cation species, because the corresponding absorption bands are observed in the solution spectrum of 2,3-DMTTA•Br. Thus the 5 Kcm^{-1} band might be assigned to an intermolecular electronic transition in the solid state.

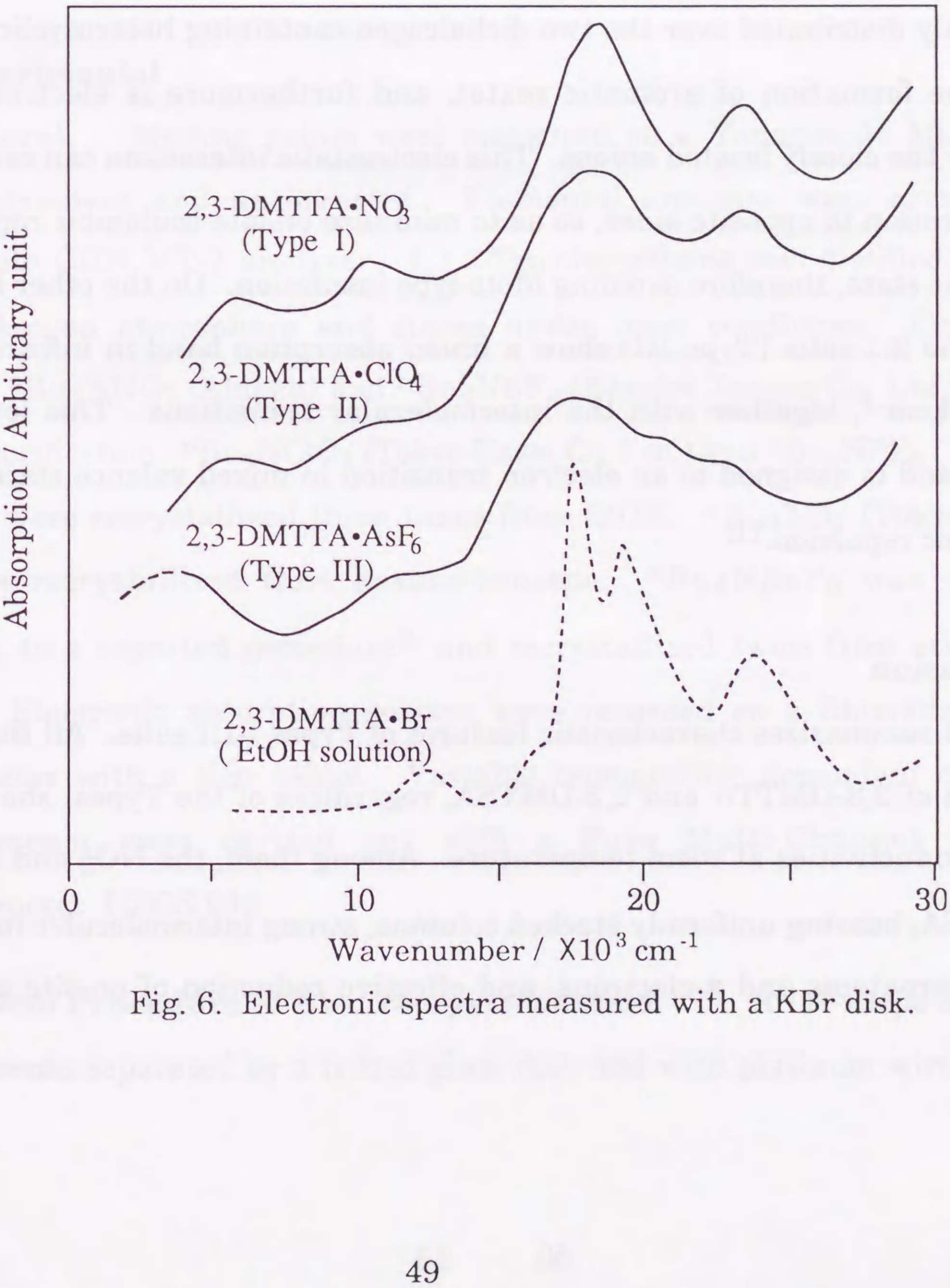


Fig. 6. Electronic spectra measured with a KBr disk.

This transition energy is too small compared with typical complete charge-transfer salts derived from tetrathiafulvalene (TTF),10) of which spectra show the bands at around 10 kcm^{-1}. This low-energy transition indicate marked reduction of coulombic repulsion in dicationic state of 2,3-DMTTA and TSA. The half-wave oxidation potentials of 2,3-DMTTA are 0.32 and 0.73 V vs. Ag/AgCl in benzonitrile, and those of 2,3-DMTSA are 0.31 and 0.72 V, being almost comparable to those of TTF (0.34 and 0.72 V). This indicate that 2,3-DMTTA and TSA as a single component have the same degree of on-site coulombic repulsion as that of TTF. Thus the origin of the small on-site coulombic repulsion in the 2,3-DMTTA and TSA salts is considered to be present in the solid state and ascribable to an electrostatic interaction with the neighboring counter anions as a possibility. The cationic charge of 2,3-DMTTA and TSA is mainly distributed over the two dichalcogen-containing heterocyclic moieties owing to the formation of aromatic sextet, and furthermore is electrostatically stabilized by the closely located anions. This electrostatic interaction can cause much charge separation to opposite sides, so as to minimize on-site coulombic repulsion in the dicationic state, therefore avoiding Mott-type insulation. On the other hand, the spectra of the 2:1 salts (Type III) show a broad absorption band in infrared region around 3.5 kcm^{-1}, together with the intermolecular transitions. This low energy transition band is assigned to an electron transition in mixed valence state without any coulombic repulsion.11)

Conclusion

Table 6 summarizes characteristic features of Types I-III salts. All the present radical salts of 2,3-DMTTA and 2,3-DMTSA, regardless of the Types, showed high electrical conductivities at room temperature. Among them, the NO_3 and BF_4 salts of 2,3-DMTSA, bearing uniformly stacked columns, strong intermoleculer interaction through heteroatoms and π-electrons, and effective reduction of on-site coulombic repulsion in the crystalline states, showed high room-temperature conductivities and also behaved metallically down to ca. 200K.

Table 6. Classification of 2,3-DMTXA salts

	Type I	Type II	Type III
D : A	1 : 1 (ionic)	1 : 1 (ionic)	2 : 1 (mixed valence)
structure	uniform	alternative	alternative
$h\nu_{CT}$	5.0 Kcm^{-1}	5.0 Kcm^{-1}	3.5 Kcm^{-1}
2,3-DMTTA salt	NO_3 , BF_4	ClO_4, Br	PF_6, AsF_6
2,3-DMTSA salt	NO_3 , BF_4	ClO_4 , PF_6	AsF_6

Experimental

General. Melting points were measured on a Yanagimoto Micro melting point instrument and uncorrected. Elemental analyses were carried out on Yanagimoto CHN MT-2 analyzer. 1,1,2-Trichloroethane was distilled from CaH_2 under nitrogen atmosphere and stored under inert conditions. Commercially available $^nBu_4NNO_3$ (Aldlich) and $^nBu_4NBF_4$ (Nacalei Tesque Co. Ltd.) were used without purification. $^nBu_4NClO_4$ (Tokyo Kasei Co. Ltd.) and $^nBu_4NPF_6$ (Tokyo Kasei Co. Ltd.) were recrystallized three times from EtOH. $^nBu_4NBr$ (Tokyo Kasei Co. Ltd.) was recrystallized from hexane-benzene. $^nBu_4NAsF_6$ was synthesized according to a reported procedure[3)] and recrystallized twice from ethyl acetate-hexane. Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrometer with a KBr tablet. Variable temperature dependent conductivity measurements were carried out with a Fuso Multi-Channel 4-Terminal Conductometer HECS 994.

Typical Procedure of Electrocrystallization. An H-shape cell with two compartments separated by a fritted glass disk and with platinum wire electrodes, was used. About 30ml of 1,1,2-trichloroethane containing ${}^{n}BuNBF_4$ (200mg) was placed in the cell, and 2,3-DMTSA (5mg) was added to the anode compartment. The solution was degassed by passing nitrogen stream, and electrolyzed at room temperature under a constant current of 2μA. Black lustrous needles of 2,3-DMTSA•BF_4 salt were harvested on the anode electrode within several days. The crystals were collected by filtration, washed with cold methylene chloride and dried.

Crystal Structure Analyses. The X-ray diffraction data were collected with a Rigaku automated four-circle diffractometer with Cu *Ka* radiation monochromatized by a graphite plate. Independent reflections within 2θ=126° ($|F_o| \geq 1.0\sigma(F_o)$) were used for analyses, except for 2,3-DMTSA•AsF_6, and 2,3-DMTSA•ClO_4, where independent reflections ($|F_o| \geq 3.0\sigma(F_o)$) were used for analyses. The structures were solved by a direct method combined with the Monte-Carlo method for the selection of the initial set of phase,[4] and refined by a full-matrix least squares method.[5] Atomic scattering factors were taken from International Tables for X-ray Crystallography.[6] The anisotropic temperature factors were used for the refinement. Hydrogen atoms were included in the refinement of 2,3-DMTTA•PF_6 and AsF_6, and not included in the other salts.

References

1) T. C. Chiang, A. H. Reddoch, and D. F. Willams, *J. Phys. Chem.*, **54**, 2051 (1971).

2) J. R. Ferraro and J. M. Williams, "Introduction to Synthetic Electrical Conductors", Academic Press, 1987, pp.1-80.

3) P. Kathirgamanathan and D. R. Rosseinsky, *J. Chem. Soc., Chem. Commun.*, **1980**, 356; H. Tanaka, T. Nogami, and H. Mikawa, *Chem. Lett.*, **1982**, 727; T. Nogami, H, Tanaka, S. Ohnishi, Y. Tasaka, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **57**, 22 (1983).

4) A. Furusaki, *Acta Crystallogr., Sect. A*, **35**, 220 (1979).

5) C. Katayama, N. Sakabe, and K. Sakabe, *Acta Crystallogr., Sect. A*, **28**, S207 (1972).

6) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. IV.

7) δ-(BEDT-TTF)$I_3(C_2H_3Cl_3)_{0.333}$ is, to the best our knowledge, the only examples of 1:1 stoichiometrical metallic salt, but no detailed study has been reported except for its crystal structure: R. P. Shibaeva, V. F. Kaminskii, and E. B. Yagubskii, *Mol. Liq. Cryst, Liq.*, **119**, 361 (1985);R. P. Shibaeva, R. M. Lobkovskaya, V. F. Kaminskii, S. V. Lindeman, and E. B. Yagubskii, *Kristallographiya*, **31**, 920 (1986).

8) A. Bondi, *J.Phys. Chem.*, **68**, 441 (1967).

9) R. P. Shibaeva, "Extended linear chain compounds," ed by J. S. Miller, New York, Plenum Press, 1982, Vol. 2, pp. 435-467.

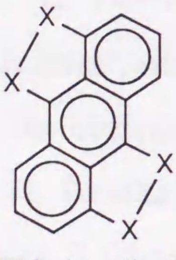
10) B. A. Scott, S. J. La Placa, J. B. Torrance, B. D. Silverman, and B. Welber, J. Am. Chem. Soc., **99**, 6631 (1977); C. Garrigou-Lagrange, E. Dupart, J. P. Morand, and P. Delhaés, *Synth. Metals*, **27**, B537 (1988).

11) J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, *Phys. Rev. B*, **19**, 730 (1979).

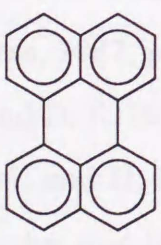
Chapter 3. Syntheses and properties of peri-dichalcogen bridged phenanthrene donors.

Introduction

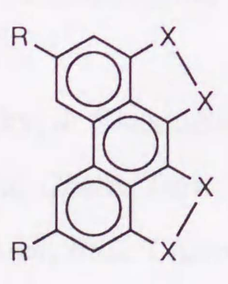
As described in the previous chapters, anthra[1,9-*cd*:4,10-*c'd'*]bis[1,2] dichalcogenoles were superior electron donors with good solubilities, and afforded highly conductive CT-complexes and also metallic radical cation salts. In addition, another anthracene-based donors, anthra[9,1-*cd*:10,5-*c'd'*]bis[1,2]dichalcogenoles have been already studied by Endres *et al.*, who reported that the iodine salt of the selenium donor (TSA) showed a high conductivity (σ_{rt}=300 Scm^{-1}).[1] These results demonstrate the importance of solubility in a detailed complexation study. In the peri-bridged polyacene system, the solubility is correlated with the number of aromatic rings, that is, it reduces as the number of the ring increases.[2] These studies of peri-bridged anthracene analogues have driven our interest to another tricyclic arene, phenanthrene, and hence we have designed the synthesis of phenanthro[1,10-*cd*:8,9-*c'd'*]bis[1,2]dichalcogenoles as novel electron donors. These novel hetrocyclic compounds might be isoelectronic with perylene upon two-electron oxidation. However, the close arrangement of the two heterocyclic rings as compared with the peri-dichalcogen anthracenes is expected to lead different solid-state properties. Furthermore, we have also tried to synthesize 3,6-dimethyl and -bis(methylthio) derivatives. Since no example of alkylthio substituted peri-dichalcogen arene have been reported to date, it must be interesting to study how



TTA (anti), X=S
TSA (anti), X=Se



Perylene

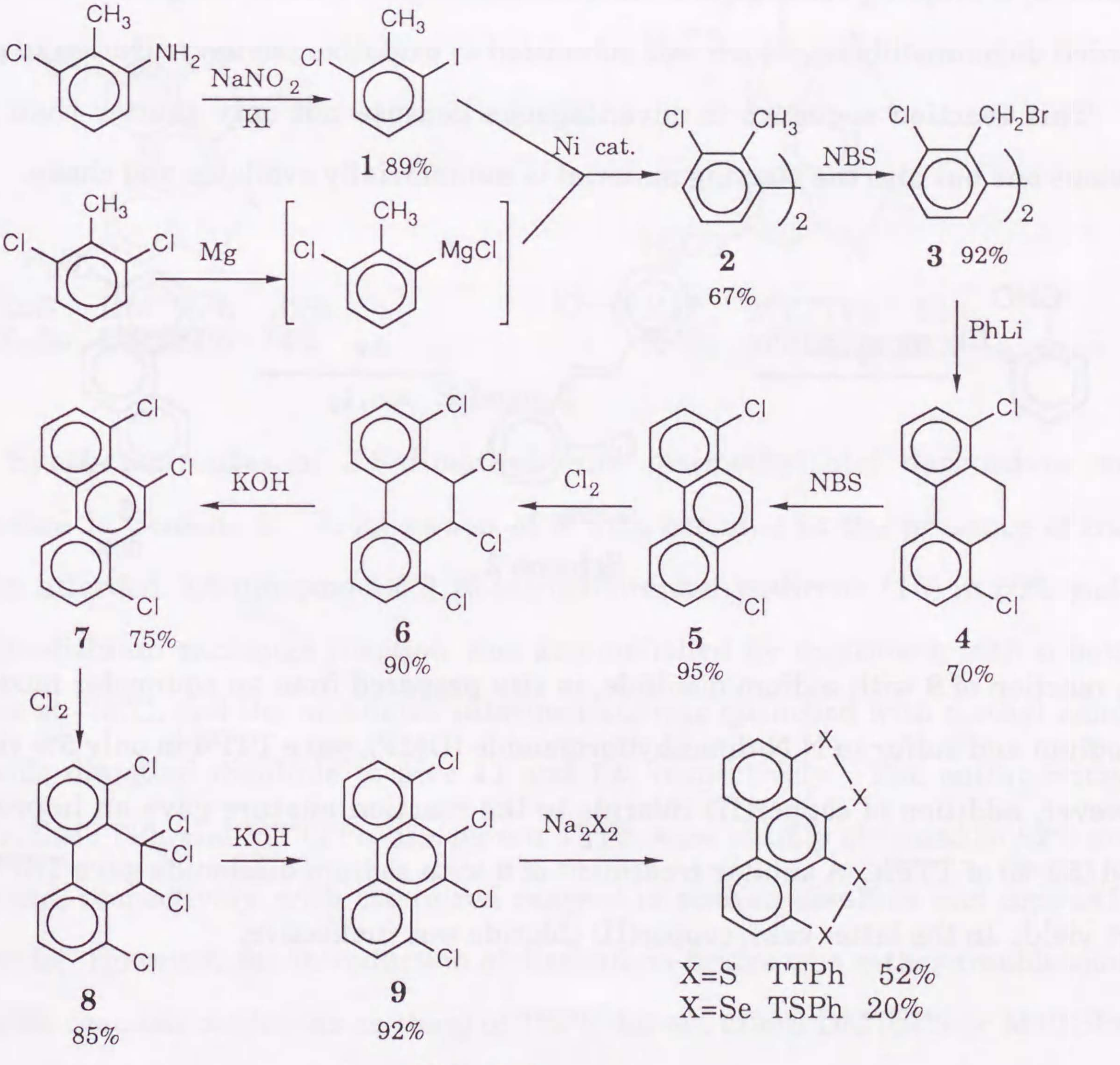


TTPh : R=H , X=S
TSPh : R=H , X=Se
DMTTPh : R=CH_3 , X=S
DMTSPh : R=CH_3 , X=Se
MTTTPh : R=SCH_3 , X=S
MTTSPh : R=SCH_3 , X=Se

the introduced methylthio groups affect their electron donating properties and the solid-state properties of their complexes. In this chapter, the syntheses and properties of these new donors are described.

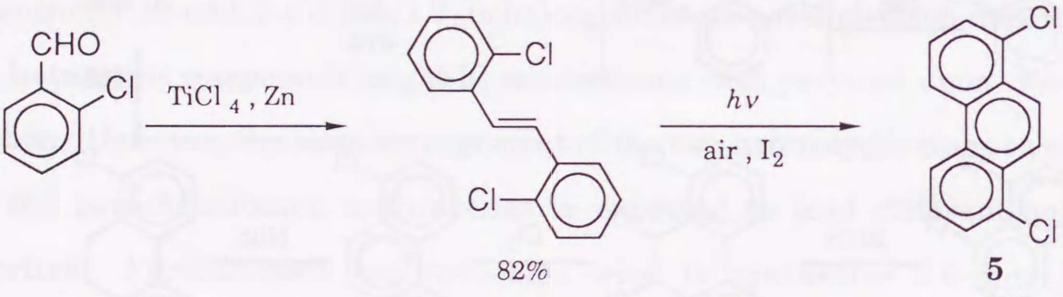
Results and Discussion

Syntheses. Tetrachalcogeno polyacenes are accessible by a general method that involves a reaction of tetrachloroaromatic compounds with an alkali metal dichalcogenide in aprotic polar solvent.[2),3)] We therefore regarded 1,8,9,10-tetrachlorophenanthrene (**9**) as the most promising precursor for approaching tetrachalcogenophenanthrene (TXPh), and **9** was synthesized in the following manner (Scheme 1).


CH3
Cl
NH2
NaNO2
KI
Cl
I
1 89%
Ni cat.
Cl
CH3
2
67%
NBS
Cl
CH2Br
2
3 92%
Cl
Cl
Mg
MgCl
PhLi
Cl
4
70%
NBS
5
95%
Cl2
6
90%
KOH
7 75%
Cl2
8
85%
KOH
9
92%
Na2X2
X
X=S TTPh 52%
X=Se TSPh 20%

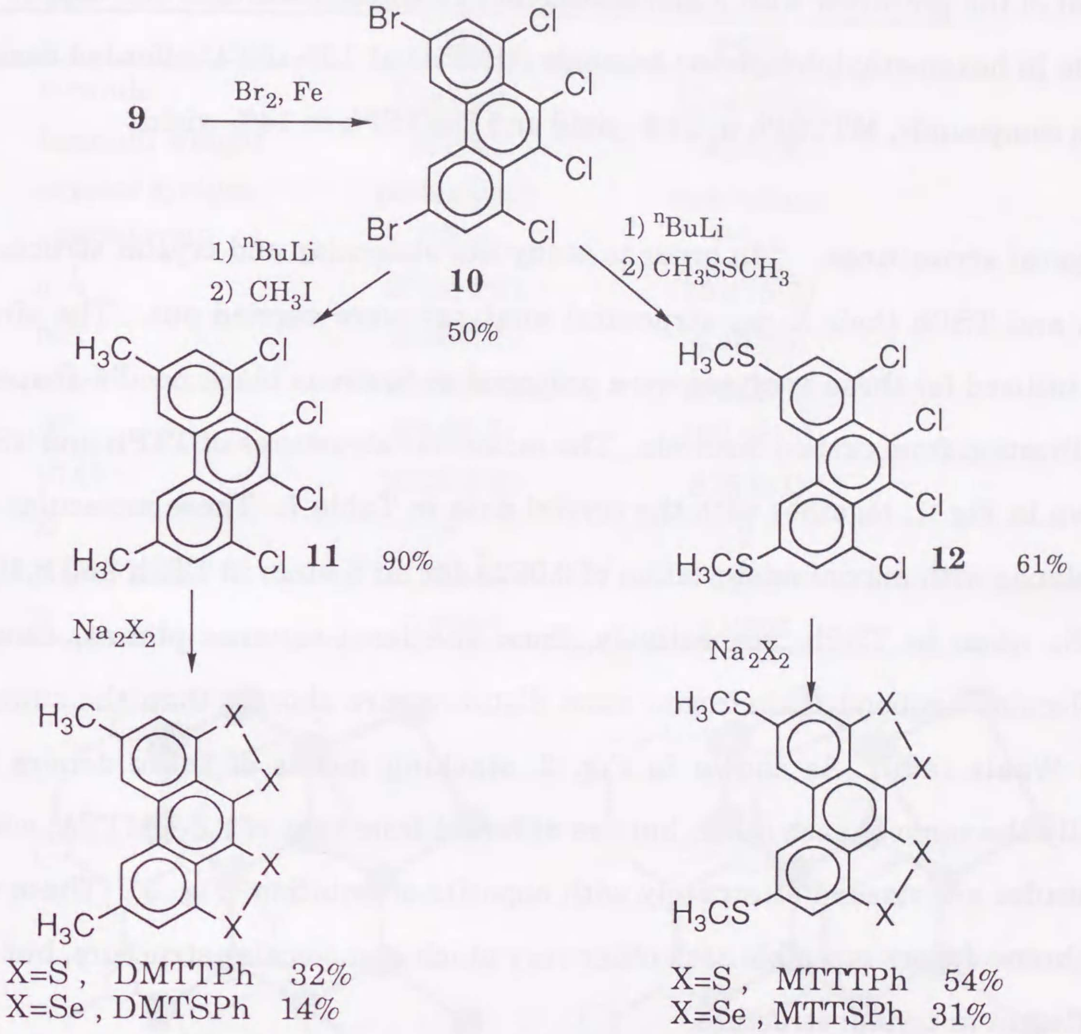
Scheme 1

A cross coupling reaction between 2-chloro-6-iodotoluene (**1**)[4] and 3-chloro-2-methylphenylmagnesium chloride afforded biphenyl derivatives (**2**)[5] in 67% yield, which was readily converted into dibromide **3** by a treatment with N-bromosuccinimide (NBS). Intramolecular coupling reaction of **3** was carried out with phenyllithium in tetrahydrofuran (THF) to give dihydrophenanthrene (**4**) in 70% yield, and then dehydrogenation reaction with NBS gave 1,8-dichlorophenanthrene (**5**). A sequence of the reactions that consist of an addition reaction of chlorine and an elimination reaction of hydrogen chloride was repeated twice to afford the precursor, 1,8,9,10-tetrachlorophenanthrene (**9**). This synthesis of **9**, however, needs multistep, and then an alternative synthetic method was examined. As shown in Scheme 2, a coupling reaction of *o*-chlorobenzaldehyde with low-valent titanium[6] afforded dichlorostilbene, which was submitted to oxidative photo-cyclization to give **5**.[7] This reaction sequence is advantageous because not only shorter than the previous one but also the starting material is commercially available and cheap.



Scheme 2

The reaction of **9** with sodium disulfide, *in situ* prepared from an equimolar mixture of sodium and sulfur in N,N-dimethylformamide (DMF), gave TTPh in only 5% yield. However, addition of copper(II) chloride to the reaction mixture gave an improved yield (52 %) of TTPh. A similar treatment of **9** with sodium diselenide gave TSPh in 20 % yield. In the latter case, copper(II) chloride was ineffective.


9
Br₂, Fe
Br
Cl
Cl
Cl
Br
Cl
10
50%
1) ⁿBuLi
2) CH₃I
1) ⁿBuLi
2) CH₃SSCH₃
H₃C
Cl
Cl
Cl
H₃C
Cl
11
90%
H₃CS
Cl
Cl
Cl
H₃CS
Cl
12
61%
Na₂X₂
Na₂X₂
H₃C
X
X
X
H₃C
X
H₃CS
X
X
X
H₃CS
X
X=S , DMTTPh 32%
X=Se , DMTSPh 14%
X=S , MTTTPh 54%
X=Se , MTTSPh 31%

Scheme 3

Synthetic routes of 3,6-dimethyl- and bis(methylthio) derivatives are illustrated in Scheme 3. Bromination of **9** with bromine in the presence of iron powder afforded 3,6-dibromo-1,4,9,10-tetrachlorophenanthrene (**10**) in 50% yield. Bromine-lithium exchange reaction was accomplished by treatment with n-butyl lithium at -78°C, and the metalated intermediate was quenched with methyl iodide and with dimethyl disulfide to give **11** and **12**, respectively. The sulfur-bridged donors, DMTTPh and MTTTPh like parent TTPh were readily obtained in 32% and 54% yield, respectively, with the mixed reagent of sodium disulfide and copper(II) dichloride. However, the introduction of diselenium bridge was rather troublesome. The same reaction conditions as those of TSPh did not afford DMTSPh or MTTSPh. After several preliminary experiments, we could optimize the reaction conditions;

treatment of the precursor with a mixed reagent of sodium diselenide and copper (II) dichloride in hexamethylphosphoric triamide (HMPA) at 155-160°C afforded desired selenium compounds, MTTSPh in 31% yield and DMTSPh in 14% yield.

Crystal structures. In order to study the molecular and crystal structures of TTPh and TSPh their X-ray structural analyses were carried out. The single crystals utilized for these analyses were prepared as lustrous black needle-shape by recrystallization from carbon disulfide. The molecular structures of TTPh and TSPh are shown in Fig. 1, together with the crystal data in Table 1. These molecules are almost planar with maximum deviation of 0.092Å for an S atom in TTPh and 0.101Å for an Se atom in TSPh, respectively, from the least-squares planes, though intramolecular nonbonded chalcogen atom distances are shorter than the sums of van der Waals radii. As shown in Fig. 2, stacking modes of these donors are essentially the same to each other, but are different from that of 2,3-DMTTA, where the molecules are stacked alternately with opposite orientation (Fig. 3). These two phenanthrene donors resemble each other very much in molecular structure, but are quite different in crystal structure.

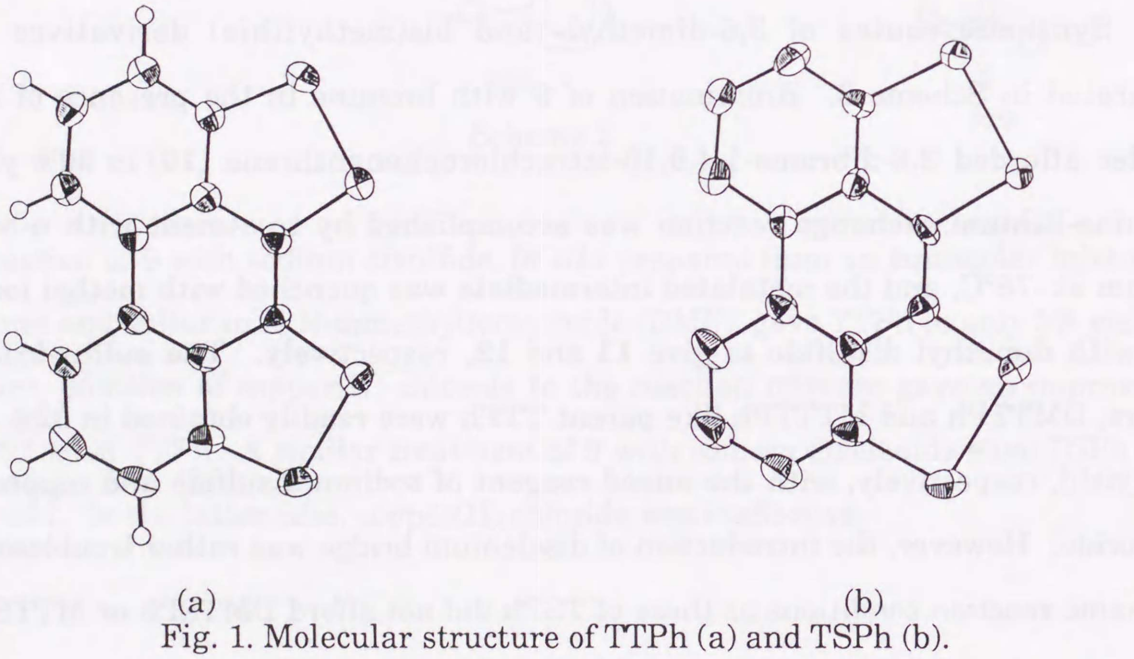

(a) (b)

Fig. 1. Molecular structure of TTPh (a) and TSPh (b).

Table 1. Crystal data of TTPh and TSPh

	TTPh	TSPh
formula	$C_{14}H_6S_4$	$C_{14}H_6Se_4$
formula weight	302.47	490.04
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a/Å	20.154(2)	10.475(2)
b/Å	3.960(2)	4.103(5)
c/Å	29.302(2)	15.253(2)
β/°	96.48(7)	109.78(9)
V/Å^3	2323.8(6)	616.9(1)
Z	8	2
No. of data	2734	1148
R	0.0507	0.0395

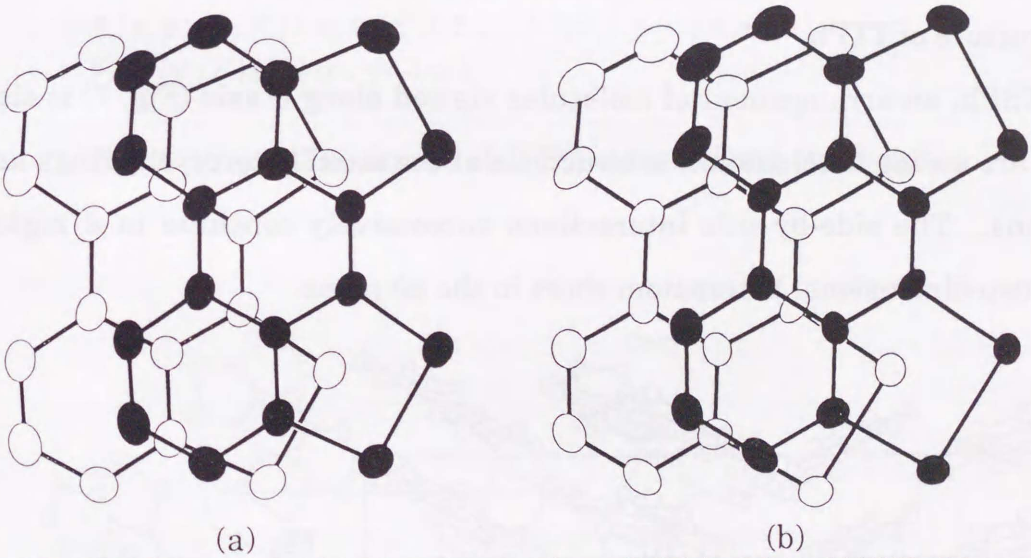

(a) (b)

Fig. 2. The modes of molecular overlap of TTPh (a) and TSPh (b).

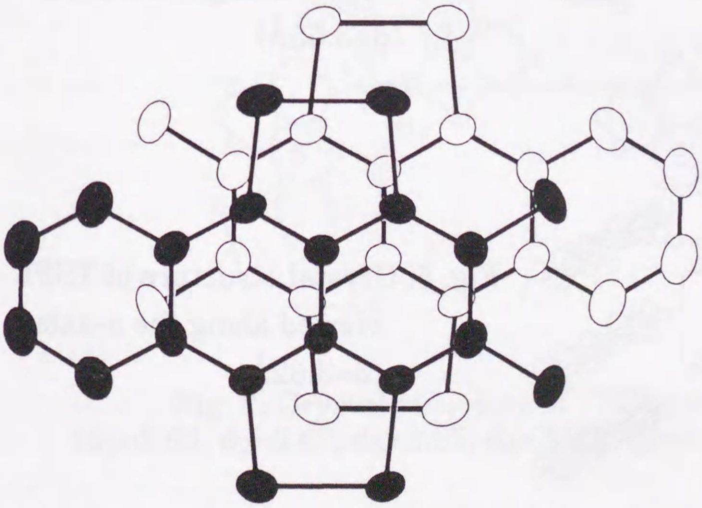


Fig. 3.
The mode of molecular overlap of neutral 2,3-DMTTA.

In the crystal of TTPh, there exist two crystallographically independent molecules, and each of them forms stacking columns, respectively, along *b* axis with a separation of 3.55Å (Fig. 4). On the other hand, the crystal structure of TSPh consists of stacking columns in which unique molecule of TSPh stacks uniformly along *b* axis with an intermolecular distance of 3.62Å (Fig. 5). In the both crystal structures, the neighboring stacks are tilted in opposite directions to form a typical herring-bone pattern. Fig. 6 shows projections of the molecules along *b* axis. For TTPh, the orientation of molecule A differs from that of molecular B, which might be favorable to pack closely. There are many S-S contacts shorter than the sum of van der Waals radii among the stacking columns not only in the *ab* plane but in the *bc* plane, consequently suggesting existence of a three dimensional S-S network in the crystal structure of TTPh.

For TSPh, an arrangement of molecules viewed along *b* axis (Fig. 7) is simple, and there are strong heteroatomic interactions of the faced heterocyclic rings among the columns. The side-by-side interactions successively continue in a zigzag to achieve a two-dimensional heteroatom sheet in the *ab* plane.

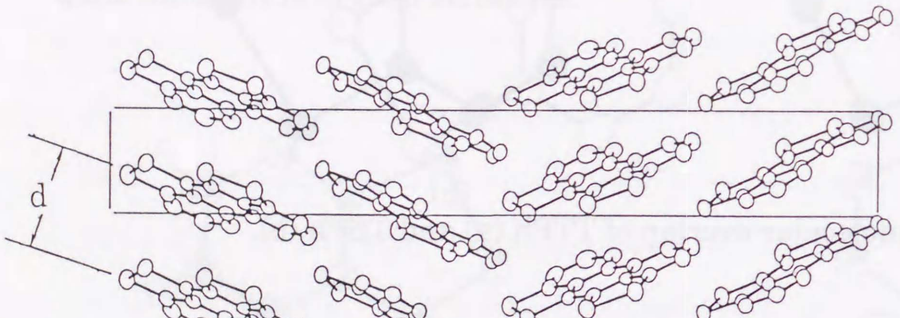


Fig. 4
Crystal structure of TTPh
viewed along the *a*-axis.
(d=3.55Å)

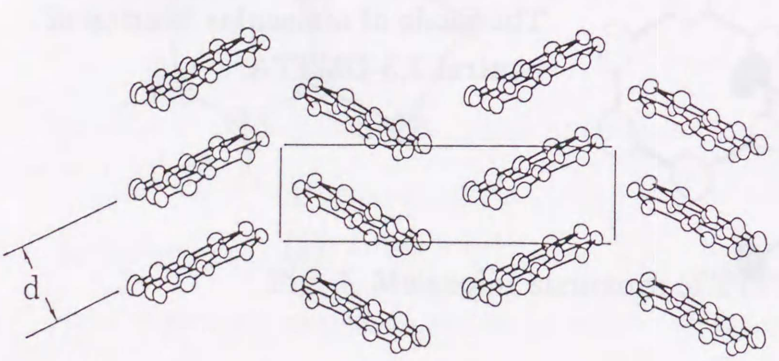
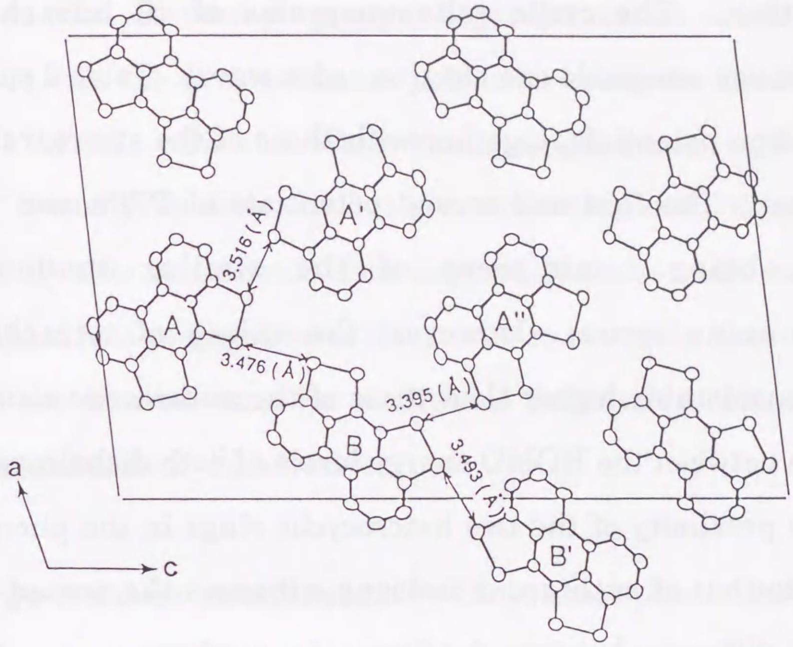


Fig. 5. Crystal structure of TSPh
viewed along the *a*-axis.
(d=3.62Å)


A'
3.516 (Å)
A
A''
3.476 (Å)
3.395 (Å)
B
3.493 (Å)
B'
a
c

The symmetry operations are the following ;
A (x , y , z) , A' (1-x , 0.5-y , 0.5-z) , A'' (x , 1.5-y , 0.5+z)
B (x' , y' , z') , B' (-x' , -y' , 1-z')

Fig. 6. Crystal structure of TTPh viewed along the *b*-axis.

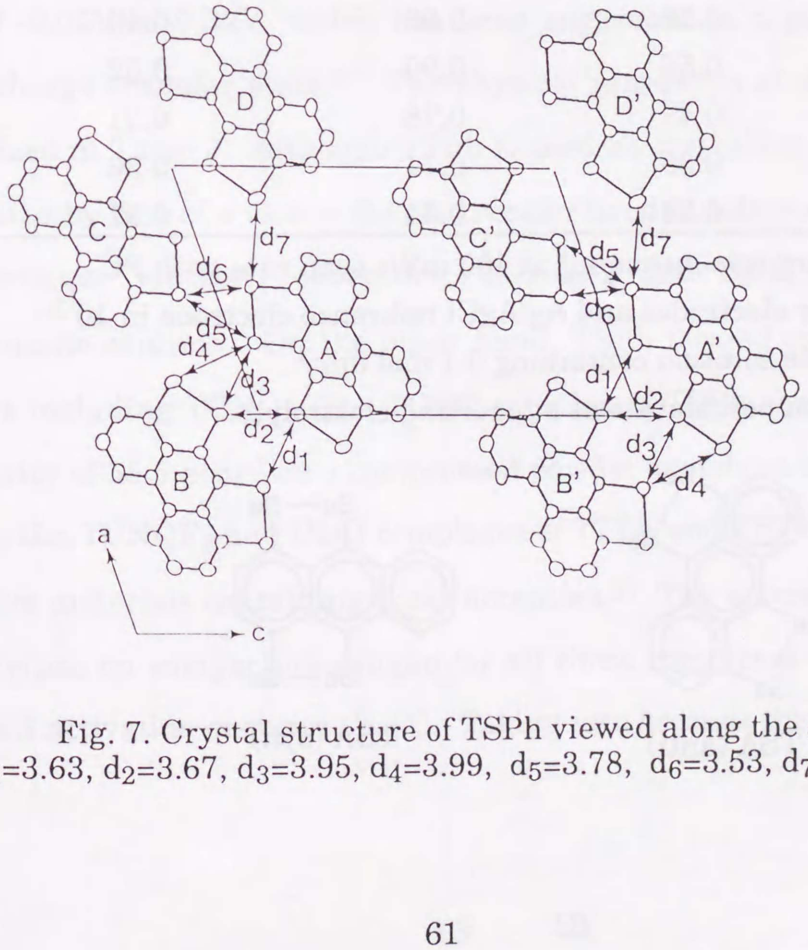

D
D'
C
C'
d7
d6
d5
d4
d3
d2
d1
A
A'
B
B'
d7
d5
d6
d1
d2
d3
d4
a
c

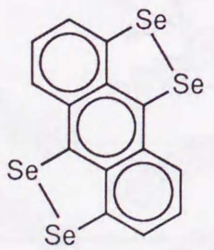
Fig. 7. Crystal structure of TSPh viewed along the *b*-axis.
(d_1=3.63, d_2=3.67, d_3=3.95, d_4=3.99, d_5=3.78, d_6=3.53, d_7=3.51Å.)

Redox properties. The cyclic voltammograms of all tetrachalcogenophenanthrenes exhibit two reversible one-electron redox waves. Table 2 summarizes their half-wave oxidation potentials, together with those of the structural isomers, tetraselenoanthracenes. The first and second potentials of TTPh and TSPh are almost the same, being reminiscent of the similar tendency with tetrachalcogenoanthracene series. However, the values of tetrachalcogenophenanthrenes are considerably higher than those of the anthracene counterparts, reflecting a difference between the HOMO energy levels of both dichalcogen arenes. In addition, the close proximity of the two heterocyclic rings in the phenanthrene donors as compared to that of anthracene isologue enhances the second oxidation potential, increasing a difference between the first and second ones.

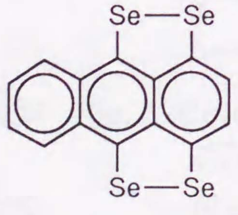
Table 2. Half-wave oxidation potentials a)

Donor	$E_{1/2}(1)$	$E_{1/2}(2)$	ΔE
TTPh	0.65	1.02	0.37
DMTTPh	0.59	1.00	0.41
MTTTPh	0.58	0.91	0.33
TSPh	0.64	1.02	0.38
DMTSPh	0.58	0.98	0.40
MTTSPh	0.58	0.90	0.32
TSA (anti)	0.47	0.78	0.31
TSA (syn)	0.35	0.71	0.36
TTF	0.34	0.71	0.37

a) Cyclic voltammetry was measured at 100 mV/s scan rate with Pt working and counter electrodes and Ag/AgCl reference electrode in 10^{-3} mol dm^{-3} benzonitrile solution containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.



TSA (anti)



TSA (syn)

Introduction of methyl groups, regarded as an electron donating group, somewhat lowers the first oxidation potential, being the same as that observed in anthracene series. On the other hand, modification with methylthio groups decreases_ not only the first one but also the second one, resulting in the small ΔE value of methylthio derivatives. This suggests that the additional methylthio groups can participate in a conjugation of the parent heterocycle; thus charge delocalization is ready in the dication state for methylthio derivatives, compared with the parent compounds and dimethyl derivatives.

Charge-transfer complexes. Since these phenanthrene donors had weak electron donating abilities, several strong electron acceptors, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$), and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) were employed for preparation of charge-transfer (CT) complexes. In the complexation with $TCNQF_4$ and DDQ, the ΔE_{redox} values, the difference between the oxidation potential of donors and the reduction potential of acceptors, are in the range of -0.05V to 0.32V, which has been suggested as a guide line to realize a partial charge transfer state.8) The physical properties of the CT complexes are summarized in Table 3. Although TTPh formed no crystalline complex with TCNQ, as indicated by lack of a visible charge-transfer band in solution, the solid complexes with stronger electron acceptors, $TCNQF_4$ and DDQ were isolated from chlorobenzene solution. On the other hand, TSPh formed complexes with all the acceptors including TCNQ. The TCNQ complex of TSPh showed a high electrical conductivity of 55.5 Scm^{-1} on a compressed powder sample at room temperature. In addition, the $TCNQF_4$ and DDQ complexes of TTPh and TSPh are rare examples of conductive materials containing these acceptors.9) The temperature dependence of conductivities on compaction sample for all these complexes were semiconducting with small activation energies (E_{act}). Taking into account their conductivities were

Table 3. Charge -Transfer complexes of TTPh and TSPh

Complex	D : A	Appearance [a)]	Dp °C	Found(Calcd) [b)]/% C	 H	 N	ν_{CN} cm^{-1}	$h\nu_{CT}$ [c)] X10^{3}cm^{-1}	σ [d)] Scm^{-1}	ΔE_{redox} [e)] V	E_{act} [d)] eV
TTPh • TCNQF$_4$	2 : 1	black fine needles	296	54.53	1.35	6.26	2208	2.2, 6.4	2.0	0.05	0.033
				(54.53	1.37	6.36)		9.3			
TTPh • DDQ	1 : 1	brown powder	228	49.74	1.22	5.27	-	5.0, 10.5	0.1	0.13	0.12
				(49.91	1.14	5.29)					
TSPh • TCNQ	1 : 1	black powder	276	45.02	1.46	7.92	2204	2.5, 9.5	55.5	0.45	0.010
				(44.98	1.45	8.07)					
TSPh • TCNQF$_4$	2 : 1	black powder	>300	38.10	0.88	4.46	2218	2.4, 6.2	8.0	0.04	0.018
				(38.24	0.96	4.46)	2208	8.7			
TSPh • DDQ	1 : 1	brown powder	249	36.83	0.85	3.86	-	4.5, 9.5	0.07	0.12	0.14
				(36.85	0.84	3.91)					

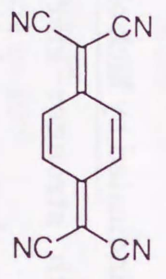
a) Obtained from chlorobenzene.

b) Calculated from stoichiometry indicated for the complex.

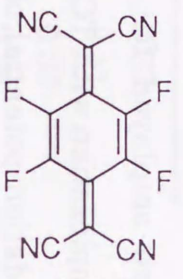
c) Measured with a KBr disk method.

d) Measured on compressed pellets with four-probed method.

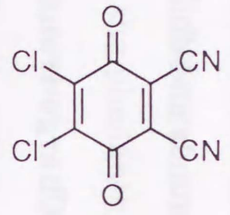
e) $\Delta E_{redox} = E_{1/2}(D) - E_{1/2}(A)$.



TCNQ



TCNQF$_4$



DDQ

Table 4. Radical cation salts of TTPh and TSPh

Radical Salt a)	D : A	Appearance	Dp	Found (Calcd) b)/%			σ c)	$h\nu_{CT}$ d)
			°C	C	H	N	Scm^{-1}	X $10^3 cm^{-1}$(eV)
$TTPh \bullet BF_4$	2 : 1	Brown powder	229	48.61	1.75	0	0.35	5.0 , 10.7
				(48.62	1.75	0)		
$TTPh \bullet ClO_4$	2 : 1	Brown powder	241	47.86	1.68	0	0.08	4.7 , 10.4
				(47.75	1.72	0)		
$TTPh \bullet I_3$ e)	4 : 3	Golden powder	161	28.53	1.09	0	3.0	3.1 , 9.3
				(28.60	1.09	0)		
$TSPh \bullet BF_4$	2 : 1	Black fine	264	31.50	1.17	0	1.0	5.5 , 9.1
		crystals		(31.52	1.13	0)		
$TSPh \bullet ClO_4$	2 : 1	Black fine	246	30.96	1.18	0	2.1	5.4 , 9.0
		crystals		(31.15	1.12	0)		
$TSPh \bullet PF_6$	2 : 1	Black fine	270	29.88	1.06	0	3.6	5.0 , 8.7
		crystals		(29.89	1.07	0)		
$TSPh \bullet AsF_6$	2 : 1	Black micro	>300	28.51	1.21	0	0.57	5.0 , 8.7
		crystals		(28.77	1.21	0)		
$TSPh \bullet I_3$ e)	4 : 3	Golden powder	262	21.68	0.78	0	33.9	3.1 , 9.2
				(21.68	0.78	0)		

a) Solvent ; 1,1,2-trichloroethane or chlorobenzene.

b) Calculated from stoichiometry indicated for the complex.

c) Measured on compressed pellets with four-probed method at room temperature.

d) Measured with a KBr disk method.

e) Solvent ; N,N-dimethylformamide (DMF).

measured on compaction samples under the condition difficult to exclude the influence of contact resistivity, the small activation energies of TCNQ and $TCNQF_4$ complexes imply the intrinsic metallic nature of their single crystals.10) The shifts of stretching vibrations of a nitrile group of TCNQ and $TCNQF_4$ complexes from the position of those of the corresponding neutral acceptors (TCNQ ; 2232cm^{-1}, $TCNQF_4$; 2234cm^{-1}) in the infrared spectra, are moderate, suggesting that these complexes are in a mixed valence state. In addition, these complexes showed a broad electron absorption in the infrared region, indicating the presence of segregated columnar structures with incomplete charge transfer, which are related to the high conductivities.11)

Radical cation salts. Electrocrystallization is one of the most useful technique for making metallic radical salts. Electrocrystallization of TTPh and TSPh was carried out under galvanostatic conditions (1-5μA), in the presence of $^nBu_4NX$ ($X=BF_4$, ClO_4, PF_6, AsF_6 and I_3) as the supporting electrolyte. 1,1,2-Trichloroethane or chlorobenzene containing about 10% ethanol was used as the suitable solvent, though for I_3 salts, N,N-dimethylformamide (DMF) was preferred. Table 4 lists the physical properties of the radical cation salts of TTPh and TSPh. Electrocrystallization of TTPh with $^nBu_4NPF_6$ or $^nBu_4NAsF_6$ gave no crystalline radical salts. All the radical salts involved 2:1 stoichiometry except for the I_3 salts and were highly conductive, suggesting that the donor molecule might be in a mixed valence state. The salts derived from TSPh were more conductive than TTPh salts as observed in 2,3-DMTXA salts. Unfortunately, all TXPh salts were formed as a powder or micro crystals, that prevented a precise investigation of their crystal structures by an X-ray analysis. However, they showed an electron absorption in infrared region (3.0-5.0 kcm^{-1}), suggesting the presence of the stacking columnar structure of donor molecules in their mixed valence state.10)

Conclusion

Present tetrachalcogenophenanthrenes are weak electron donors as compared with their structural isomer, tetrachalcogenoanthracenes. However, introduction of methyl or methylthio groups enhanced electron donating ability. In particular, those of methylthio derivatives, which were the first examples of peri-bridged polyacene donor containing alkylthio substituents, were significantly improved. The solubilities are generally better than those of anthracene series, and their complexation and electrocrystallization were readily examined. Most CT-complexes and radical cation salts derived from these donors were electrically highly conductive, and the conductivities of TSA•TCNQ and TSA•I_3 complex were determined to be 55.5 Scm^{-1} and 33.9 Scm^{-1}, respectively at room temperature, even when the compressed powder samples were used. These high conductive CT-complexes and radical cation salts showed a broad electronic absorption in the infrared region, attributed to a segregated stacking structure in a mixed valence state.

Experimental

General. Melting points are uncorrected. All chemicals and solvents are of reagent grade. Elemental analyses were measured by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. ^{1}H-NMR spectra were recorded on a Hitachi R-1200 (60 MHz) , a JEOL EX-270 (270 MHz) , or a Bruker AMX-400wb (400MHz) spectrometer using tetramethylsilane as an internal standard. IR spectra were taken on a Hitachi 260-30 spectrophotometer with a KBr disk method. MS spectra were measured at 70 eV on a Shimadzu QP-1000A spectrometer using a direct insertion technique. Electronic spectra were recorded on a Shimadzu UV-160 spectrometer or on a Shimadzu UV-3100 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-

104 function generator. Variable temperature dependent conductivity were measured with a Fuso Multi-Channel 4-Terminal Conductometer HECS 994.

2-Chloro-6-iodotoluene (1) [4)]

A mixture of 3-chloro-2-methylaniline (29.6g, 0.209mol), concentrated hydrochloric acid (54ml), and water (42ml) was cooled to 0-5°C. Keeping this temperature with an ice-bath, a solution of sodium nitrate ($NaNO_2$, 15g, 0.21mol) was added slowly over 5 min, and the mixture was further stirred for 10 min. To the resulting diazonium solution, an aqueous solution (200ml) of potassium iodide (70g , 0.42mol) was added at once and allowed to stand at room temperature for 30 min. Liberating iodine and nitrogen gas, then the mixture was heated to 90°C till evolution of nitrogen gas was complete (ca. 1.5 h). After cooling, sodium hydrogen sulfite (2g) was added, and the resulting brown oil was separated and the water layer was extracted with dichloromethane (50ml X 3). The combined organic layer was dried over anhydrous $MgSO_4$ and consentrated *in vacuo*. The residue was distilled to give a colorless oil (46g, 89%); bp 92.0-93.0/3mmHg. (lit.[4)] 132-133°C /25mmHg) ^{1}H-NMR (CCl_4, 60MHz) δ 2.56 (s, 3H, CH_3), 6.72 (t, J=8.0Hz, 1H, ArH), 7.28 (dd, J=8.0, 1.0Hz, 1H, ArH), and 7.67 (dd, J=8.0, 1.0Hz, 1H, ArH).

3,3'-Dichloro-2,2'-dimethylbiphenyl (2) [5)]

To a mixture of magnesium (17.7g, 0.73mol) and dry tetrahydrofuran (THF, 15ml) was added dropwise a solution of 2,6-dichlorotoluene (118g, 0.73mol) in THF (40ml) during 3h, and the reaction mixture was refluxed for an additional 2h. The Grignard reagent was added to a solution of 2-chloro-6-iodotoluene (**1**, 129g, 0.51mol) and bis(triphenylphosphine)nickel dichloride ($NiCl_2(PPh_3)_2$, 2g, 3mmol) in 140ml of THF during 2h at 55-60°C. After cooling, the mixture was poured onto ice containing diluted hydrochloric acid. The organic layer was separated, and the water layer was extracted with ether (100ml X 3). The combined organic layer was washed successively with aqueous sodium hydrogen sulfite, water, and brine, and dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by distillation afforded the biphenyl (**2**) as white solid (bp 130-140°C/0.7mmHg, 89g, 67%). Compound **2** was recrystallized from hexane-methanol: colorless prisms; mp 74.5-75.5°C (lit.[5]) 74.3- 75°C). ^{1}H-NMR (CCl_4, 60MHz) δ 2.08 (s, 6H, CH_3) and 7.31 (m, 6H, ArH). MS m/z 250(M^+). Anal. Calcd for $C_{14}H_{12}Cl_2$: C, 66.95; H, 4.82%. Found: C, 66.92; H, 4.82% .

3,3'-Dichloro-2,2'-bis(bromomethyl)biphenyl (3)

A mixture of biphenyl (**2**, 16g, 64mmol) and N-bromosuccinimide (NBS, 24g, 0.13mol) in carbon tetrachloride (CCl_4, 500ml) was refluxed for 2h while irradiated with sun light. After cooling, the resulting solid was filtered off, and the filtrate was concentrated under reduced pressure. The oily residue was dissolved in chloroform and reprecipitated with hexane to give white powder of the dibromide (24g , 92%). Compound **3** was recrystallized as colorless prisms from hexane-chloroform; mp 122-124.0°C. ^{1}H-NMR (CCl_4, 60MHz) δ 4.15 (d ,2H, J=10.1Hz, CH_2), 4.38 (d,2H,J=10.1Hz , CH_2), and 7.20-7.47 (m , 6H , ArH). MS m/z 406, 408, 410(M^+). Anal. Calcd for $C_{14}H_{10}Cl_2Br_2$: C, 41.12; H, 2.46%. Found: C, 41.11; H, 2.32%.

1,8-Dichloro-9,10-dihydrophenanthrene (4)

To a solution of dibromide (**3**, 20g, 48.8mmol) in THF (200ml) was added 50ml of phenyllithium solution (1.0N in ether/cyclohexane, 1:1) under nitrogen atmosphere at 0°C. After stirring for an additional 2h at room temperature, the mixture was poured onto ice (100g), acidified with diluted hydrochloric acid (1N, 100ml) and extracted with benzene (100ml X 3). The extract was washed with water, dried over $MgSO_4$, and evaporated *in vacuo*. The resulting oil was taken up with chloroform, adsorbed to the top of silica-gel column, and then eluted with hexane to afford crude **4** as white solid. Recrystallization from hexane gave colorless needles

(8.4g, 70%). mp 88.0-88.5°C. ^{1}H-NMR (CCl_4, 60MHz) δ 3.01 (s, 4H, CH_2), 7.15-7.40 (m, 4H, ArH), and 7.60 (dd, J=7.0, 2.0Hz, 2H, ArH). MS m/z 248,250 (M^+). Anal. Calcd for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05%. Found: C, 67.44; H, 4.04%.

1,8-Dichlorophenanthrene (5)

A mixture of **4** (7.5g, 0.03mol) and NBS (5.65g, 0.032mol) in CCl_4 (150ml) was refluxed for 2h. After cooling, the mixture was concentrated under reduced pressure. The residue was washed with hot water, and fine crystals of **5** were collected by filtration (7.1g, 95%). The analytically pure sample was obtained by recrystallization from benzene; colorless prisms; mp 221-222.5°C. ^{1}H-NMR ($CDCl_3$, 60MHz) δ 7.68 (m, 4H, ArH), 8.35 (s, 2H, ArH) and 8.62 (dd, J=7.2, 2.0Hz, 2H, ArH). MS m/z 246,248(M^+). Anal. Calcd for $C_{14}H_8Cl_2$: C, 68.04; H, 3.26%. Found: C, 68.04; H, 3.16%.

1,8,9,10-tetrachloro-9,10-dihydrophenanthrene (6)

A solution of **5** (7.5g, 0.03mol) in CCl_4 (350ml) was refluxed with introduction of chlorine gas. The reaction was followed by ^{1}H-NMR, until the peaks of **5** disappeared; usually the reaction needed ca.4h to complete. Then, evaporation of the solvent *in vacuo* afforded a white solid of **6**, and recrystallization from chloroform-hexane gave colorless prisms (8.6g, 90%). mp 152-153.5°C. ^{1}H-NMR (CCl_4, 60MHz) δ 5.79 (s, 2H, CH), 7.35-7.45 (m, 4H, ArH) and 7.75 (dd, J=6.0, 3.5Hz, 2H, ArH). MS m/z 316, 318 320 (M^+). Anal. Calcd for $C_{14}H_8Cl_4$: C, 52.87; H, 2.54%. Found: C, 52.64; H, 2.47%.

1,8,9-Trichlorophenanthrene (7)

A mixture of **6** (11g, 0.034mol) and 85% potassium hydroxide (KOH, 4g, 0.07mol) in ethanol (150ml) was refluxed overnight. After cooling, the resulting precipitate was collected by filtration and dried *in vacuo*. Column chromatography on silica-gel using dichloromethane as eluent gave **7** (7.1g, 75%), which was recrystallized from chloroform-hexane; colorless needles, mp 154.5-156°C. ^{1}H-NMR ($CDCl_3$, 60MHz) δ 7.51-7.82 (m, 4H, ArH), 8.34 (s, 1H, ArH) and 8.54-8.70 (m, 2H, ArH). MS m/z 280, 282(M^+). Anal. Calcd for $C_{14}H_7Cl_3$: C, 59.72; H, 2.51%. Found: C, 59.50; H, 2.37%.

1,8,9,9,10-Pentachloro-9,10-dihydrophenanthrene (8)

Chlorination of **7** to **8** was carried out in a similar manner as described in the case of compound **5**; 85% yield. Colorless prisms (chloroform-hexane); mp 166.0-168.0°C. ^{1}H-NMR ($CDCl_3$, 60MHz) δ 6.02 (s, 1H, CH), and 7.30-7.90 (m, 6H, ArH). MS m/z 350, 352, 354(M^+). Anal. Calcd for $C_{14}H_7Cl_5$: C,47.71; H,2.00%. Found: C,47.70; H,200%.

1,8,9,10-Tetrachlorophenanthrene (9)

Dechlorination of **8** to **9** was similar to that of **6** to **7**. 92% yield; colorless needles (chloroform-hexane); mp 163.0°C. ^{1}H-NMR ($CDCl_3$, 60MHz) δ 7.30-7.85 (m, 4H, ArH), and 8.45 (dd, J=8.0, 2.0Hz, 2H, ArH). MS m/z 314 (M^+) with isotopic pattern of tetrachlorine. Anal. Calcd for $C_{14}H_6Cl_4$: C, 53.21; H, 1.91%. Found: C, 53.01; H, 2.05%.

1,8-Dichlorophenanthrene (5) from *o*-chlorobenzaldehyde.

o-Chlorobenzaldehyde (28.1g, 0.2mol) was added to an yellow suspension of $TiCl_4$ in THF, which was prepared by slow addition of $TiCl_4$ (58g, 0.3mol) to THF (500ml) with ice-cooling. The mixture was cooled with an ice-salt bath, then zinc powder (40g) was added by portions. The color of the suspension turned black, and the mixture was warmed to room temperature and refluxed for 4h. After cooling, the mixture was poured onto ice, hydrolyzed with saturated aqueous $NaHCO_3$ (500ml), and extracted with CH_2Cl_2 (500ml). The extract was dried ($MgSO_4$) and concentrated. The crude residue was passed through a short column of silca-gel using CH_2Cl_2 as eluent to afford colorless prisms of dichlorostilbene (20.3g, 82%). mp 95.0-96.0°C (from chloroform-hexane). ^{1}H-NMR ($CDCl_3$, 60MHz) δ 7.51 (s, 2H, olefinic) and 7.10-7.85 (m, 8H, ArH).

The crude stilbene was used without further purification for photocyclization. A mixture of 20.3g of dichlorostilbene and 0.5g of iodine in benzene (3l) was irradiated with a high pressure mercury lamp with bubbling air at 20°C. The progress of the reaction was followed by ^{1}H-NMR. After the reaction was complete, the solvent was evavorated and resulting crystals of **5** were collected by filteration and washed with acetone. (13.1g, 65%).

Phenanthro[1,10-cd:8,9-c'd']bis[1,2]dithiole (TTPh)

A mixture of sodium (1.32g, 57.5mmol) and sulfur (1.84g, 57.5mmol) was heated at 130°C in N,N-dimethylformamide (DMF, 70ml) for 2h under nitrogen atmosphere, and further sulfur (0.92g, 28.75mmol) and DMF (20ml) were added. To the resulting suspension was added a solution of tetrachloride **9** (474mg, 1.5mmol) and cupric chloride ($CuCl_2$, 402mg, 3mmol) in DMF (70ml), and the mixture was heated at 140°C for 48h. After cooling, it was exposed to air for 2h, and poured into brine (200ml). The resulting precipitate was collected by filteration, washed with water, and dried. The crude TTPh was purified by gradient sublimation (twice), chromatography on silica-gel using cabon disulfide as eluent, and recrystallization from carbon disulfide to give black needles of TTPh (950mg, 52%); mp 256.0-257°C (decomp.). ^{1}H-NMR (CS_2-acetone-d_6, 270MHz) δ 7.33 (d, J=7.9Hz, 2H, ArH), 7.39 (t, J=7.9Hz, 2H, ArH), and 8.03 (d, J=7.9Hz, 2H, ArH). MS m/z 302 (M^+) with isotopic pattern of tetrasulfur. Anal. Calcd for $C_{14}H_6S_4$: C, 55.60; H, 2.00%. Found: C, 55.60; H, 1.98%. UV (Chloroform) 320.0 (log ε 4.22) and 395.0 (4.21) nm.

Phenanthro[1,10-cd:8,9-c'd']bis[1,2]diselenole (TSPh)

A mixtur of sodium (276mg, 12mmol) and selenium (945mg, 12mmol) was heated at 120°C in N,N-dimethylformamide (DMF, 10ml) for 5h under nitrogen atmospher. To the resulting sodium diselenide solution was added tetrachloride **9** (474mg, 1.5mmol) and DMF (20ml). The mixture was heated at 140°C for additional 48h and allowed to cool to room temperature. Then it was exposed to air for overnight, and poured into brine (100ml). The resulting precipitate was collected by filtration, washed with water, and dried. Gradient sublimation of the crude product gave a black solid showing metallic luster, which contained TSPh and elemental selenium. The solid was extracted with carbon disulfide, chromatographed on silica-gel using cabon disulfide as eluent, and recrystallized from carbon disulfide to give black needles of TSPh (132mg, 18%); mp 273.0-274.0°C(decomp.). ^{1}H-NMR (CS_2-Acetone-d_6, 270MHz) δ 7.35 (t, J=7.9Hz, 2H, ArH), 7.46 (d, J=7.9Hz, 2H, ArH), and 8.19 (d, J=7.9Hz, 2H, ArH). MS m/z 490 (M^+) with isotopic pattern of tetraselenium. Anal. Calcd for $C_{14}H_6Se_4$: C, 34.31; H, 1.23%. Found: C, 34.31; H, 1.19%. UV (Chloroform) 289.0 (log ε 3.90), 333.0 (4.18) and 401.0 (4.14) nm.

3,6-Dibromo-1,4,9,10-tetrachlorophenanthrene(10)

To a refluxing mixture of **9** (948mg, 3.0mmol) and iron powder (0.2g, 3.7mmol) in 150ml of CCl_4 was added dropwise a solution of bromine (0.37ml, 7.2mmol) in CCl_4 (20ml), and the mixture was refluxed for an additional 30min. Iron powder was filtered off, and the solvent was evaporated in vacuo. The residue was dissolved in benzene (50ml), and the solution was washed with aqueous $NaHSO_3$ (20ml) and water, and dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by recrystallization from benzene gave colorless needles of **10** (710mg, 50%). mp 215.5°C. ^{1}H-NMR ($CDCl_3$, 60MHz) δ 7.91 (d, J=1.6Hz, 2H, ArH), and 8.56 (d, J=1.6Hz, 2H, ArH). MS m/z 474(M^+) with isotopic pattern of dibromine and tetrachlorine. Anal. Calcd for $C_{14}H_4Cl_4Br_2$: C, 35.49; H, 0.85%. Found: C, 35.46; H, 0.82%.

3,6-Dimethyl-1,4,9,10-tetrachlorophenanthrene(11)

Under nitrogen atmosphere, to a solution of **10** (474mg, 1mmol) in 50ml of THF was added 1.5ml of n-BuLi solution (1.5N, in hexane) at -80°C, and the mixture was stirred for 30min at the same temperature. To this solution methyl iodide (0.5ml) was added, and the resulting mixture was allowed to warm up to room temperature and stirred overnight at room temperature. The mixture was poured into 1N hydrochloric acid (30ml), and extracted with dichloromethane (20ml X 3). The extract was washed with water, dried and evaporated *in vacuo*. Recrystallization of the obtained pale yellow solid from hexane-chloroform afforded colorless needles of **11** (309mg, 90%). mp 119-121°C. ^{1}H-NMR ($CDCl_3$, 60MHz) δ 2.54 (s, 6H, CH_3), 7.53 (s, 2H, ArH), and 8.21 (s, 2H, ArH). MS m/z 344 (M^+) with isotopic pattern of tetrachloride. Anal. Calcd for $C_{16}H_{10}Cl_4$: C, 55.85; H, 2.93%. Found: C, 55.73; H, 2.83%.

3,6-Bis(methylthio)-1,4,9,10-tetrachlorophenanthrene(12)

To a solution of dilithiated **10**, prepared as described above, dimethyl disulfide was added. The mixture was stirred for 30min at -30°C and then worked up in a similar manner as described in the case of **11**. yield; 61%. colorless fine needles from hexane-chloroform. mp 163.5-165°C. ^{1}H-NMR($CDCl_3$, 60MHz) δ 2.63 (s, 6H, CH_3), 7.55 (d, J=1.6Hz, 2H, ArH), and 8.12 (d, J=1.6Hz, 2H, ArH). MS m/z 408 (M^+) with isotopic pattern of tetrachlorine and disulfur. Anal. Calcd for $C_{16}H_{10}Cl_4S_2$: C, 47.08; H, 2.47%. Found: C, 47.05; H, 2.47%.

3,6-Dimethylphenanthro[1,10-cd:8,9-c'd']bis[1,2]dithiole (DMTTPh)

Preparation of DMTTPh from **11** was similar to that of TTPh from **9**. 32% yield; mp 231-232.5°C (decomp.) (from benzene-hexane). ^{1}H-NMR (CS_2-acetone-d_6, 270MHz) δ 2.49 (s, 6H, CH_3), 7.09 (s, 2H, ArH), and 7.74 (s, ArH). MS m/z 330(M^+). Anal. Calcd for $C_{16}H_{10}S_4$: C, 58.15; H, 3.05%. Found: C, 58.10; H, 3.05%. UV (Chloroform) 315.6 (log ε 4.31) and 389.8 (4.30) nm.

3,6-Dimethylphenanthro[1,10-cd:8,9-c'd']bis[1,2]diselenole (DMTSPh)

A mixture of sodium (110mg, 4.8mmol) and selenium (380mg, 4.8mmol) was heated at 140°C in hexamethylphosphoric triamide (HMPA, 18ml) for 5h under nitrogen atmosphere. To the resulting suspension was added tetrachloride **11** (137mg, 0.4mmol), cupric chloride ($CuCl_2$, 215mg, 1.6mmol) and HMPA (12ml), and the mixture was heated at 160°C for 48h. After cooling, it was exposed to air for 2h, and poured into brine (40ml). The resulting precipitate was collected by filtration, washed with water, and dried. The crude DMTSPh was purified by chromatographed on silica-gel using cabon disulfide as eluent and gradient sublimation, and then recrystallization from carbon disulfide-hexane to give black needles of DMTSPh (28mg, 14%); mp 300-302°C (decomp.). ^{1}H-NMR (CS_2-acetone-d_6, 400MHz) δ 2.49 (s, 6H, CH_3), 7.30 (s, 2H, ArH), and 8.02 (s, 2H, ArH). MS m/z 518 (M^+) with isotopic pattern of tetraselenium. Anal. Calcd for $C_{16}H_{10}Se_4$: C, 37.09; H, 1.94%. Found: C, 37.08; H, 1.94%. UV (Chloroform) 331.0 (log ε 4.05) and 393.8 (3.97) nm.

3,6-Bis(methylthio)phenanthro[1,10-cd:8,9-c'd']bis[1,2]dithiole (MTTTPh)

Preparation of MTTTPh from **12** was similar to that of TTPh from **9**. Silica-gel column chromatography (carbon disulfide as eluent) was employed in purification step instead of gradient sublimation method. 32% yield; mp 212.0-214.0°C (decomp.)

(from carbon disulfide). ^{1}H-NMR (CS_2-acetone-d_6, 270MHz) δ 2.57 (s, 6H, CH_3), 7.12 (d, J=1.3Hz, 2H, ArH), and 7.12 (d, J=1.3Hz, 2H, ArH). MS m/z 394 (M^+) with isotopic pattern of hexasulfur. Anal. Calcd for $C_{16}H_{10}S_6$: C, 48.70; H, 2.55%. Found: C, 48.68; H, 2.51%. UV (Chloroform) 321.5 (log ε 4.46) and 407.0 (4.32) nm.

3,6-Bis(methylthio)phenanthro[1,10-cd:8,9-c'd']bis[1,2]diselenole (MTSTPh)

A mixtur of sodium (69mg, 3.0mmol) and selenium (237g, 3.0mmol) was heated at 140°C in HMPA (10ml) for 5h under nitrogen atmosphere. To the resulting suspension was added tetrachloride **12** (204mg, 0.5mmol), cupric chloride ($CuCl_2$, 134mg, 1.0mmol) and HMPA (8ml), and the mixture was heated at 155°C for 48h. After cooling, it was exposed to air, and poured into brine (50ml). The resulting precipitate was collected by filteration, washed with water, and dried. The crude MTTSPh was purified by silica-gel chromatography using cabon disulfide as eluent, and recrystallization from chlorobenzene to give black needles of MTTSPh (87mg, 31%); mp 265.0-266.0°C (decomp.). ^{1}H-NMR (CS_2-acetone-d_6, 400MHz) δ 2.60 (s, 6H, CH_3), 7.41 (d, J=1.2Hz, 2H, ArH), and 7.98 (d, J=1.2Hz, 2H, ArH). MS m/z 582 (M^+) with isotopic pattern of tetraselenium and disulfur. Anal. Calcd for $C_{16}H_{10}S_2Se_4$: C, 33.01; H, 1.73%. Found: C, 32.90; H, 1.74%. UV (Chloroform) 335.5 (log ε 4.35) and 410.0 (4.15) nm.

Crystal Structure Analyses. The X-ray diffraction data were collected with a Rigaku automated four-circle diffractometer with Cu $K\alpha$ radiation monochromatized by a graphite plate. Independent reflections within 2θ=126° were used for analyses. The structure of TTPh was solved by a direct method combined with the Monte-Carlo method for the selection of the initial set of phase,$^{12)}$ and refined by the full-matrix least squares method.$^{13)}$ The positions of four selenium atoms of TSPh were located by using Patterson techniques (SHELXS-86), and subsequent Fourier syntheses revealed the remaining carbon atoms. The structure of TSPh refined by the full-matrix least squares method.[13] Atomic scattering factors were taken from International Tables for X-ray Crystallography.[14] The anisotropic temperature factors were used for the refinement and hydrogen atoms were not included in the refinement.

References

1) H. Endres, H. J. Keller, J. Queckborner, J. Veigel, and D. Schweitzer, *Mol. Cryst. Liq. Cryst.*, **86**, 111 (1982); H. Endres, H. J. Keller, J. Queckborner, D. Schweitzer, and J. Veigel, *Acta Cryst.*, **B38**, 2855 (1982).

2) H. Miyamoto, Doctral dissertation, Hiroshima University, 1991.

3) A. Yamahira, T. Nogami, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, **1983**, 904; S. Ohnishi, T. Nogami, and H. Mikawa, *Chem. Lett.*, **1982**, 1841; S. Ohnishi, T. Nogami, and H. Mikawa, *Tetrahedron Lett.*, **1983**, 2401; J. C. Stark, R. Reed, L. A. Acampora, D. J. Sandman, S. Jansen, M. T. Jones, and B. M. Foxman, *Organomet.*, **3**, 732 (1984); T. Otsubo, N. Sukenobe, Y. Aso, and F. Ogura, *Chem. Lett.*, **1987**, 315; *Synth. Met.*, **27**, B509 (1988); H. Miyamoto, Y. Aso, T. Otsbo, and F. Ogura, *Bull. Chem. Soc. Jpn.*, **63**, 2441 (1990).

4) J. B. Cohen and J. Miller, *J. Chem. Soc.*, **85**, 1622 (1904).

5) Y. Ikoma, F. Taya, E. Ozaki, S. Higuchi, Y. Naoi, and K, Fuji-i, *Synthesis*, **1990**, 147.

6) T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, **1973**, 1041.

7) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Am. Chem. Soc.*, **84**, 4361 (1962).

8) G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, **53**, 2141 (1980).

9) J. J. Mayerle and J. B. Torrance, *Bull. Chem. Soc. Jpn.*, **54**, 3170 (1981); K. Nakasuji, H. Kubota, T. Kotani, I. Murata, G. Saito, T. Enoki, K. Imaeda, H.

Inokuchi, M. Honda, C. Katayama, and J. Tanaka, *J. Am. Chem. Soc.*, **108**, 3460 (1986); H. -J. Räder, U. Scherer, P. Wolf, and K. Müllen, *Synth. Metals.*, **32**, 15 (1985).

10) It is well-known that a single crystal of TTF-TCNQ complex shows metallic behavior down to ca 50K with high conductivity of 500 $\mathrm{Scm^{-1}}$ at room temperature. However, in the case of measurement using the compressed powder sample in our laboratory, the conductivity at room temperature was 20 $\mathrm{Scm^{-1}}$ and the temperature dependence of conductivity was semiconductive with activation energy of 0.02eV.

11) J. B. Torrance, B. A. Scott, and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975).

12) A. Furusaki, *Acta Crystallogr., Sect. A*, **35**, 220 (1979).

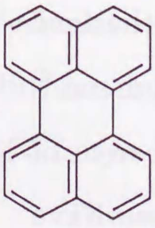
13) C. Katayama, N. Sakabe, and K. Sakabe, *Acta Crystallogr., Sect. A*, **28**, S207 (1972).

14) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. IV.

Chapter 4. Syntheses, crystal structures and physical properties of novel heteroarene donors.

Introduction

Polynuclear arenes such as perylene and pyrene have been known for a long time to possess relatively low ionization potentials and to form highly conductive halogen complexes1),2) or radical salts.3) Their donor strengths are, however, weaker than common Weitz-type donors such as tetrathiafulvalene (TTF), tetrathiatetracene (TTT), and bithiopyranylidene (BTP). In order to improve their donor characters, substitution of C=C double bond by sulfur seems to be the effective modifications. Moreover, this is desirable for conductive materials because sulfur atoms serve for the enhancement of intermolecular interactions. In this context, Wudl *et al.* and Ogura *et al.* previously reported the isoelectronic heterocyclic analogs of perylene, 3,4:3',4'-bibenzo[*b*]thiophene (BBT)4) and 3,3':4,4'-bis(thieno[2,3-*b*]thiophene) (BTT)5), respectively. There are two isomers, naphtho[1,8-*bc*:4,5-*b,'c',*]dithiophene (*syn*-NDT) and naphtho[1,8-*b,c*;5,4-*b',c'*]dithiophene (*anti*-NDT), as isoelectronic heteroarene of pyrene, and the author has interested in their synthetic study. Watanabe in Ogura's group succeeded in the synthesis of *syn*-NDT.6) recently. The synthetic method, however, required a multistep, and the total yield was very low. For the purpose of studies on the properties of *syn*-NDT in detail and extension of the research to its derivatives, it is necessary to develop an alternative easily accessible approach.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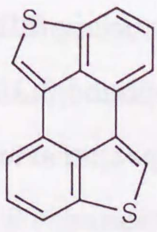
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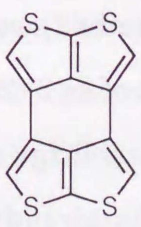
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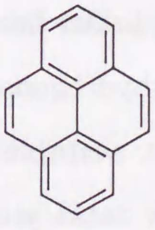
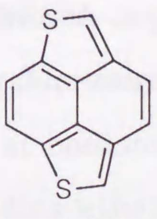
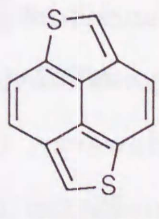

Pyrene

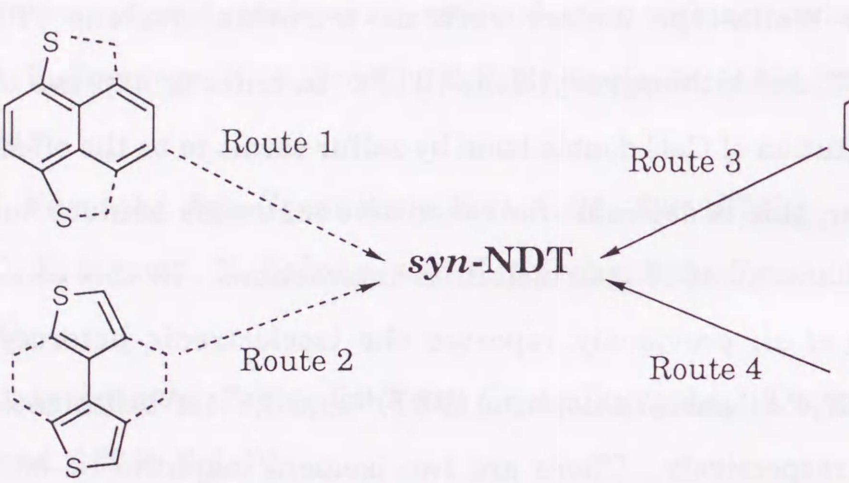

syn-NDT


anti-NDT

In this chapter, a novel and facile synthesis of *syn*-NDT and the conversion to its derivatives are described. Furthermore, their structures, redox properties, and complexations are also discussed.

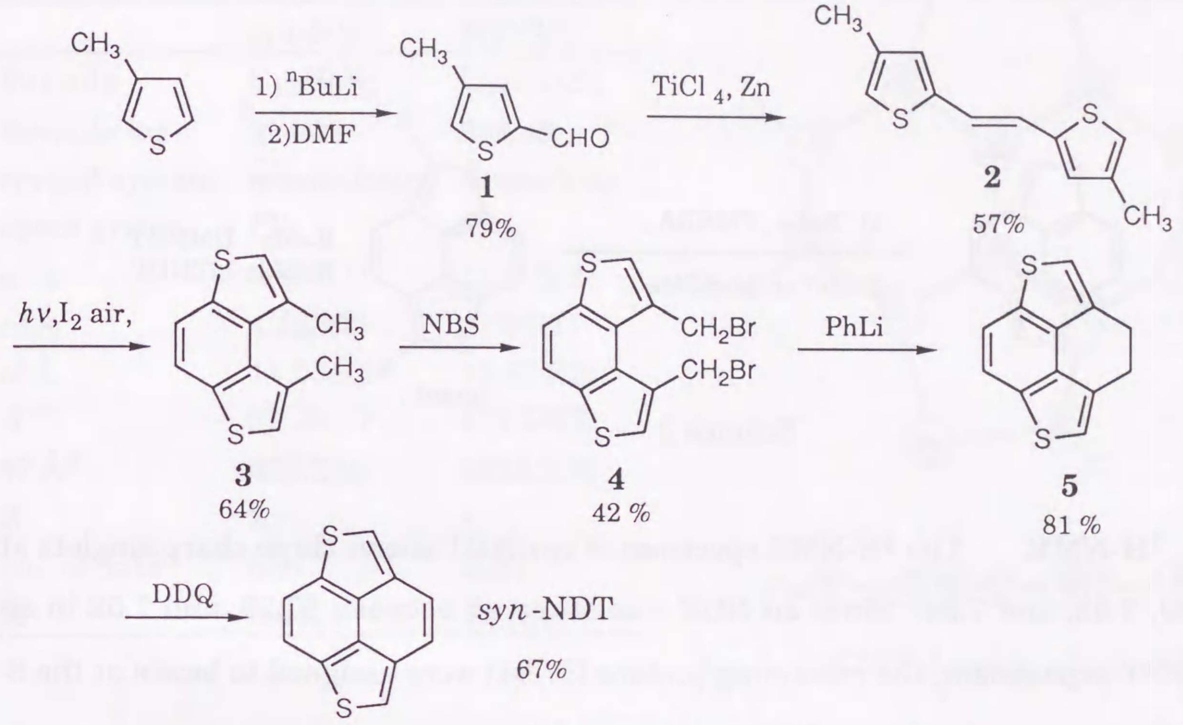
Results and Discussion

Syntheses Since *syn*-NDT consists of a naphthalene and two thiophene rings, various synthetic pathways might be proposed as illustrated in Scheme 1.



Scheme 1. Synthetic strategies.

The first strategy is based on a double thiophene ring closure reaction on naphthalene. However, a preliminary experiment found that the ring closure reaction in this route is a difficult step. The basic concept of the second and the third one is to construct the central naphthalene ring starting from bithienyl derivative or thiophenophane, respectively. The second strategy, however, has difficulty in synthesizing desired bithiophene derivative bearing appropriate functional groups. According to the third method, we have successfully synthesized *syn*-NDT via transannular dehydrogenation of [2.2](2,4)thiophenophane-1,8-diene.6) However, the method is not suitable for a large scale preparation because of multistep synthesis and low total yield as already mentioned. Then we have examined the fourth route which involves annulation of benzo[1,2-*b*:4,3-*b'*]dithiophene as illustrated in Scheme 2.

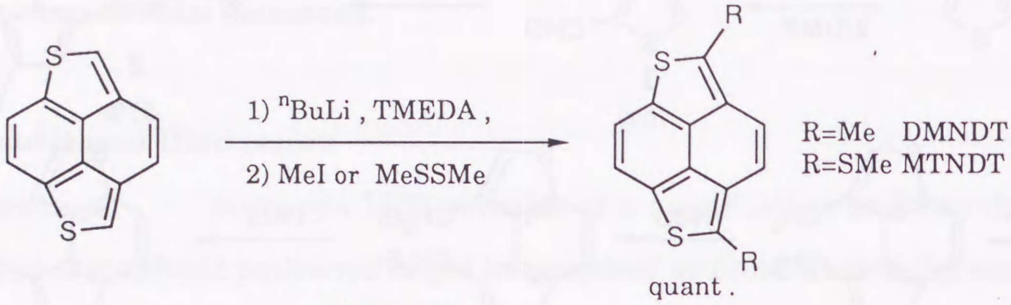


Scheme 2

4-Methyl-2-thiophenecarboxyaldehyde(**1**) was prepared according to the procedure reported in the literature,$^{7)}$ but it was found that the product was contaminated with a significant amount of 3-methyl isomer, which was difficult to remove by fractional distillation. The isomeric mixture was directly used in the next step, reductive coupling reaction with low-valent titanium.$^{8)}$ From the several products of this reaction, desired *trans*-1,2-bis(4-methyl-2-thienyl)ethene (**2**) could be separated by fractional recrystallization from hexane. The pure **2** was utilized in photocyclization$^{9)}$ to afford 1,8-dimethylbenzo[1,2-*b*:4,3-*b'*]dithiophene (**3**) in 64% yield. The reaction of **3** with *N*-bromosuccinimide gave 1,8-bis(bromomethyl) derivative **4** in 42% yield, which was then treated with phenyllithium to afford 3,4-dihydronaphtho[1,8-*bc*:4,5-*b'c'*]dithiophene (**5**) in 81% yield. The dehydrogenation of **5** to *syn*-NDT was performed with DDQ in 67% yield.

The easy preparation of parent *syn*-NDT enabled to extend the study on its derivatives. Treatment of *syn*-NDT with excess butyllithium followed by methyl iodide and by dimethyl disulfide gave 2,5-dimethyl derivative (DMNDT) and 2,5-

bis(methylthio) derivative (MTNDT), respectively, in quantitative yields (Scheme 3).



Scheme 3

^{1}H-NMR The ^{1}H-NMR spectrum of *syn*-NDT shows three sharp singlets at δ7.29, 7.52, and 7.94. Since an NOE was observed between δ7.29, and 7.52 in an NOESY experiment, the remaining protons (δ7.94) were assigned to locate at the 8- and 9-positions. In the ^{1}H-NMR spectrum of 2,5-dimethyl derivative, protons at the 3- and 4-positions showed resonances at the highest field (δ7.07). Thus, the singlet peak of δ7.29 in the spectrum of *syn*-NDT was assigned to protons at the 3- and 4-positions.

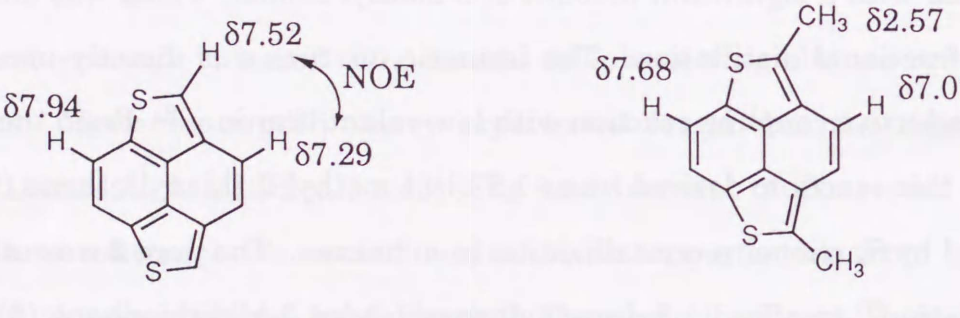


Fig.1 . ^{1}H-NMR assignments.

Crystal structure Recrystrallization of *syn*-NDT from chloroform-hexane provided a good single crystal that was subjected to an X-ray crystallographic analysis. As shown in Fig. 2, the molecular structure is perfectly planar. Both bond lengths and bond angles are, however, strained.[10, 11)

Table 1. Crystal data

	syn-NDT	MTNDT
formula	$C_{12}H_6S_2$	$C_{14}H_{10}S_4$
formula wt	214.31	306.49
crystal system	*momoclinic*	*monoclinic*
space group	$P2_1$	$P2_1$
a/ Å	7.837(1)	15.275(2)
b/ Å	4.128(2)	4.694(1)
c/ Å	14.035(2)	19.874(2)
β/ °	93.29(1)	111.12(3)
V/ Å^3	453.2(2)	1329.3(3)
Z	2	4
No. of data	836	2081
R	0.0424	0.0634

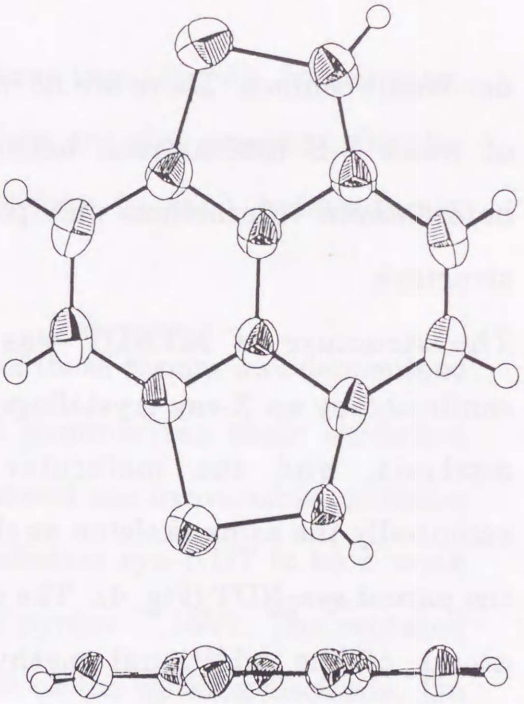


Fig. 2. ORTEP drawing of *syn*-NDT.

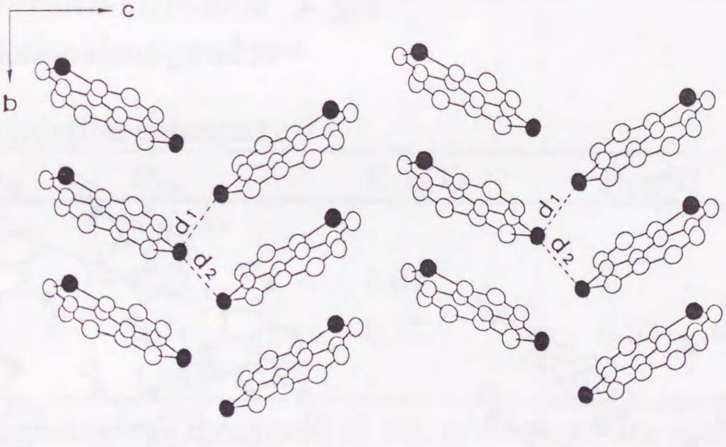


Fig. 3. Crystal structures of *syn*-NDT viewed along a-axis. (S-S contacts d_1 =3.767Å , d_2=3.768Å)

In the crystal structure of pyrene, the molecules are grouped in stacked pairs about the symmetry centers, and the pair units are packed so as to avoid any direct overlap.[11)] On the other hand, that of *syn*-NDT consists of a herringbone type of uniform stacking columns (Fig. 3). The molecules are stacked face-to-face with van der Waals contact. There are no indications of close S-S contacts in the columns but of weak S-S interactions between the adjacent columns. This nonbonded heteroatomic interactions may possibly facilitate the herringbone type of crystal structure.

The structure of MTNDT was also confirmed by an X-ray crystallographic analysis, and the molecular has essentially the same skeleton as that of the parent *syn*-NDT (Fig. 4). The sulfur atoms of the additional methylthio groups are on the same plane of the framework of NDT, and one methyl group lies parallel with the plane, but another one lies perpendicular to it.

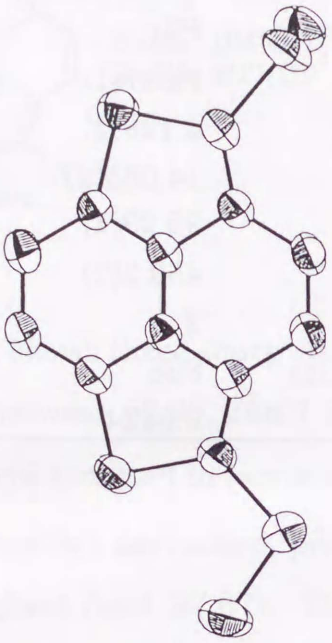


Fig. 4. Molecular structures of MTNDT.
(The hydrogen atoms are omitted.)

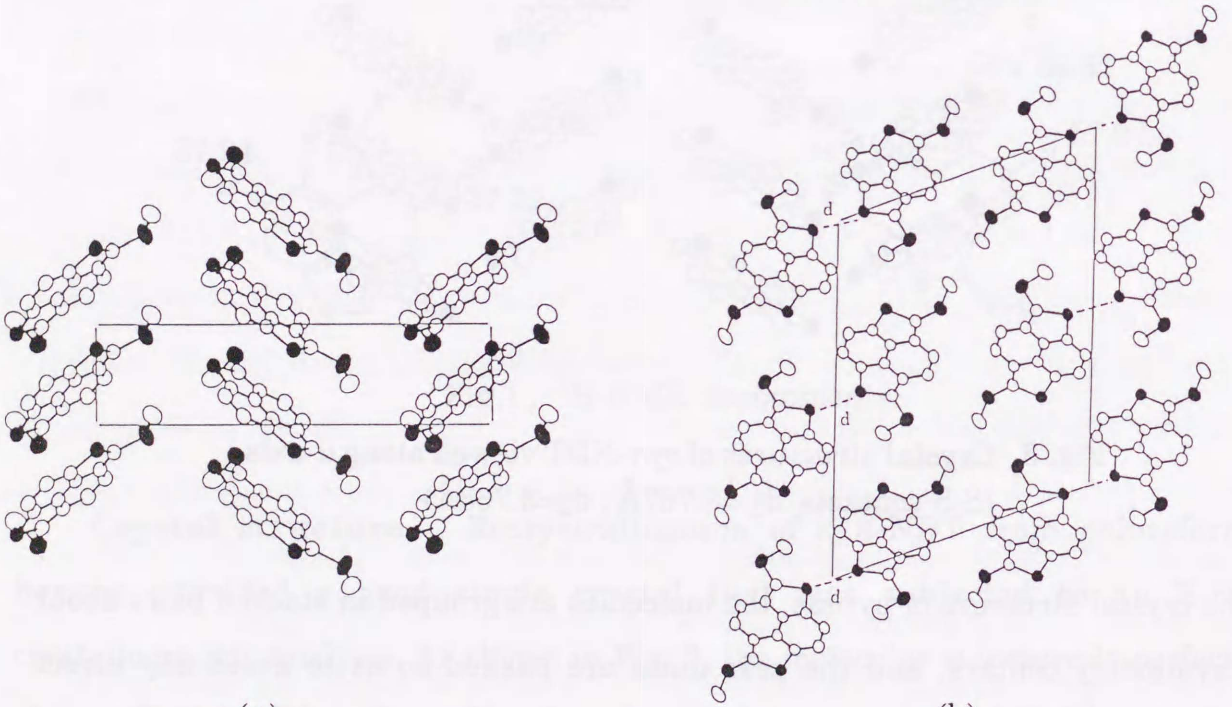


Fig. 5. Crystal structures of MTNDT viewed along *a*-axis (a) and *b*-axis (b).
(S-S contacts d=3.79Å)

The crystal structure of MTNDT is also of a herringbone type (Fig. 5). In this case, the intercolumnar interactions of the skeletal sulfurs are also present. On the other hand, the functional sulfurs do not participate in such heteroatomic interactions.

Redox properties . The redox behavior of these donors was determined by cyclic voltammetry in benzonitrile. Table 2 summarizes their oxidation potentials together with that of pyrene. *syn*-NDT showed one irreversible oxidation wave at +1.01 V. This value is rather high and indicates *syn*-NDT to be a weak electron donor, but is remarkably lower than that of pyrene (1.35V). The repeated cycles induced polymerization, forming a black deposit on the working electrode. On the other hand, the two derivatives showed reversible cyclic voltammograms because of blocking the active α-sites of the thiophene rings. The oxidation potentials of these derivatives are much lower owing to conjugation of the substituent groups than that of *syn*-NDT, and MTNDT shows not only the first oxidation wave but also the second one.

Table 2. Oxidation potentials a)

Donor	E_{ox}	$E_{1/2}(1)$	$E_{1/2}(2)$	ΔE
NDT	1.01 b)	-		
DMNDT	0.92	0.84		
MTNDT	0.77	0.71	0.97	0.26
pyrene	1.35 b)	-		

a) Cyclic voltammetry was measured at 100 mV/s scan rate with Pt working and counter electrodes and Ag/AgCl reference electrode in 10^{-3} mol dm^{-3} benzonitrile solution containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.

b) Irreversible wave.

Charge-transfer complexes. These novel donors formed some complexes with iodine, DDQ, and $TCNQF_4$. All complexes were prepared by mixing the acetonitrile solution of donor and acceptor. The physical properties of the complexes

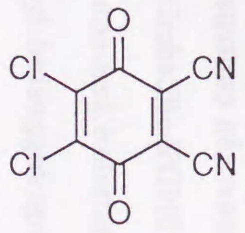
Table 3. Charge -Transfer complexes and radical cation salts of *syn*- NDT and its derivatives

Complex	D : A	Appearance	Dp	Found(Calcd) a)/%			$h\nu_{CT}$ b)	σ c)
			°C	C	H	N	X 10^3 cm^{-1}	Scm^{-1}
syn-NDT • DDQ d)	2 : 1	black powder	>300	58.45	1.83	3.32	6.5	2.1
				(58.63	1.84	4.27)		
syn-NDT• I_2 d)	1 : 0.83	black powder	>300	33.83	1.47	0	6.6	0.92
				(36.89	1.42	0)		
DMNDT • DDQ d)	1 : 2	black powder	>300	52.18	1.71	7.07	10.1	1.2 X 10^{-8}
				(51.75	1.45	8.04)	8.0	
DMNDT • I_2 d)	1 : 0.5	dark green powder	180	45.56	2.50	0	10.0	3.6 X 10^{-9}
				(45.54	2.73	0)		
MTNDT• DDQ d)	1 : 1	black powder	156	49.36	1.81	5.58	5.4	5.5 X 10^{-2}
				(49.53	1.89	5.27)		
MTNDT• $TCNQF_4$ d)	1 : 1	black fine needles	169	51.67	1.86	9.74	7.3	1.3 X 10^{-4}
				(51.60	1.80	10.03)		
MTNDT • I_2 d)	1 : 2	dark green powder	128	20.65	1.26	0	3.0	1.3
				(20.66	1.24	0)		
MTNDT• BF_4 e)	1 : 1	black solid	192	42.93	2.39	0	6.5	1.1 X 10^{-5}
				(42.76	2.56	0)		

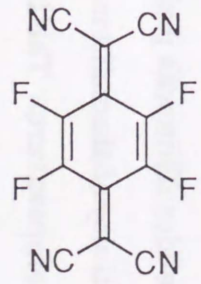
Table 3. (Continued)

MTNDT• ClO_4 e)	1 : 1	black solid	181	41.21 2.43 0	7.1	1.6×10^{-6}
				(41.43 2.48 0)		
MTNDT • PF_6 e)	1 : 1	black solid	175	37.28 2.21 0	7.7	3.6×10^{-7}
				(37.25 2.23 0)		
MTNDT • I_3 f)	1 : 1.33	dark green	90	21.08 1.44 0	3.1	26.7 g)
		needles		(20.66 1.24 0)		

a) Calculated from stoichiometry indicated for the complex.
b) Measured with a KBr disk method.
c) Measured on compressed pellets with two or four-probe method at room temperature..
d) Direct combination of the solutions of donor and acceptor: the solvent is acetonitrile.
e) Electrocrystallization : the solvent is tetrahydrofuran.
f) Electrocrystallization : the solvent is acetonitrile.
g) Measured on a single crystal with four-probe method at room temperature.



DDQ



$TCNQF_4$

are shown in Table 3. *syn*-NDT formed highly conductive complexes with DDQ and with iodine, whose conductivities were 2.1 and 0.92 Scm^{-1}, respectively. The conductivity of the iodine complex is approximately two orders of magnitude higher than that reported for pyrene-iodine2) complex (0.013Scm^{-1}), supporting the potential of *syn*-NDT as an electron donor for conductive materials. Both complexes of methylthio derivative are also conductive. However, it is not the case with those of the methyl derivative, DMNDT. The introduced methyl groups, though they serve to enhance the donor ability, may sterically hinder the formation of conductive complexes. A galvanostatic electrochemical oxidation of parent *syn*-NDT in the presence of $^{n}Bu_4NClO_4$ as supported electrolyte in THF afforded a black solid on the platinum anode. This was probably an oligomer of *syn*-NDT doped with ClO_4 anion. The conductivity of the solid material measured on compaction sample was 24.5 Scm^{-1} at room temperature. The temperature dependence of the conductivity showed a semiconducting behavior with a small activation energy of 0.010 eV. The room temperature conductivity is rather higher than that of doped poly(3-methylthiophene), indicating the potential of *syn*-NDT as a monomer for conducting organic polymer. In contrast, DMNDT gave no crystalline salt on electrochemical oxidation. MTNDT afforded radical cation salts as shown in Table 3, but BF_4^-, ClO_4^- and PF_6^- salts were low conductive and might be insulators with complete charge transfer, being suggested by 1:1 stoichiometry. Only the I_3^- salt prepared in an acetonitrile solution showed a high conductivity of 26.7 Scm^{-1} at room temperature on a single crystal measurement, though the crystal growth of the salt showed poor reproducibility.

Conclusion

The new synthetic route of *syn*-NDT described in this chapter has superior advantages to the previous route in terms of its short synthetic sequence, high total yield, and large scale preparation. This made the extention to its derivatives possible. An X-ray crystallographic analysis reveals that *syn*-NDT has a planer molecular structure and uniform columnar crystal structure. The fact that the donor molecule prefers to make a columnar structure indicates that the donor is useful as a component of organic conductor. The electron donating ability of present donors are apparently improved as compared with that of pyrene. Some of their CT-complexes and radical salts are highly conductive.

Experimental

General. Melting points are uncorrected. All chemicals and solvents are of reagent grade. Elemental analyses were measured by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. ^{1}H-NMR spectra were recorded on a Hitachi R-1200 (60 MHz) or a Bruker AMX-400wb (400MHz) spectrometer using tetramethylsilane as an internal standard. ^{13}C-NMR spectra were recorded on a Bruker AMX-400wb (100MHz) spectrometer using deuteriochloroform as a solvent and tetramethylsilane as an internal standard. IR spectra were taken on a Hitachi 260-30 spectrophotometer with a KBr disk method. MS spectra were measured at 70 eV on a Shimadzu QP-1000A spectrometer using a direct insertion technique. Electronic spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator. Variable temperature dependent conductivity measurements were carried out with a Fuso Multi-Channel 4-Terminal Conductometer HECS 994.

4-Methyl-2-thiophenecarbaldehyde (1) [7)]

To a solution of n-butyllithium (365ml,1.5N hexane solution) in ether (600ml) was added dropwise 3-methylthiophene (49g, 0.5mol) at room temperature. The mixture was stirred for 2h, and slowly added to an ice-cooled solution of N,N-dimethylformamide (DMF, 50ml) in ether (100ml). After stirring overnight, the resulting solution was poured onto ice, and the mixture was acidified with 1N hydrochloric acid, and the ethereal layer was separated, washed with aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). After evaporation of the solvent, distillation of the residue afforded a yellow oil (50g, 79%). bp 92-95°C/10mmHg (lit.[7] 84-86°C/ 8mmHg). This distillate contained approximately 30% of **1**. ^1H-NMR ($CDCl_3$ 60MHz) δ2.33 (s 3H, CH_3), 7.40 (s, 1H, ArH), 7.62 (d, J=0.8Hz, 1H, ArH) and 9.93 (d, J=0.8Hz, 1H, CHO).

***trans*-1,2-Di(4-methyl-2-thienyl)ethene (2)** [8]

4-Methyl-2-thiophenecarboxyaldehyde (**1**) was added to an yellow suspension of $TiCl_4$ in THF, which was prepared by slow addition of $TiCl_4$ (74.4g, 0.39mol) to THF (600ml) with ice-cooling. The mixture was cooled with an ice-salt bath, and then zinc powder (50g) was added by portions with care. The color of the suspension turned black, and the mixture was warmed to room temperature and refluxed for 9h. After cooling, the mixture was poured onto ice, hydrolyzed with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated. The crude residue was passed through a short column of silca-gel using hexane as eluent and recrystallized from hexane to afford colorless prisms of **2** (9.0g, 49%). mp 132°C. ^1H-NMR($CDCl_3$, 60MHz) δ 2.22 (d, J=0.8Hz, 6H, CH_3), 6.75 (brs, 2H, ArH), 6.84 (s, 2H, ArH) and 6.95 (s, 2H, olefin). MS m/z 220(M^+). Anal. Calcd for $C_{12}H_{12}S_2$: C, 65.41; H, 5.49%. Found: C, 65.40; H, 5.42%.

1,8-Dimethylbenzo [1,2-b : 4,3-b'] dithiophene (3) [9]

2 (1.1g, 0.05mmol) was dissolved in benzene (350ml) and irradiated with a high pressure mercury lamp with bubbling air at 20°C. The progress of the reaction was followed by ^1H-NMR, until peaks of **2** disappeared. The solution was washed with aqueous $NaHSO_3$ and water, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by silca-gel chromatography using hexane. Recrystallization from hexane-benzene gave colorless prisms of **3** (0.7g, 64%). mp 114-116.5°C. ^{1}H-NMR($CDCl_3$, 400MHz) δ 2.79 (s, 6H, CH_3), 7.16 (s, 2H, ArH), and 7.73 (s, 2H, ArH). ^{13}C-NMR($CDCl_3$, 100MHz) δ 21.63, 119.35, and 123.56. MS m/z 218(M^+). Anal. Calcd for $C_{12}H_{10}S_2$: C, 66.01; H, 4.62%. Found: C, 65.88; H, 4.58%.

1,8-Bis(bromomethyl)benzo [1,2-b:4,3-b'] dithiophene (4)

To a refluxing mixture of N-bromosuccinimide (NBS, 1.06g, 5.95mmol) and benzoyl peroxide (10mg) in carbon tetrachloride (25ml) was added 3 (545mg, 2.5mmol), and the mixture was refluxed for 30 minute. After cooling, the solvent was evaporated and the resulting residue was washed with hot water and crude **4** was collected by filtration. The pure **4** was obtained by recrystallization from chloroform as colorless needles (394mg, 42%). mp 130-132°C(decomp). ^{1}H-NMR ($CDCl_3$, 400MHz) δ 5.36 (s, 4H, CH_2), 7.72 (s, 2H, ArH), and 7.83 (s, 2H, ArH). ^{13}C-NMR ($CDCl_3$, 100MHz) δ 32.44, 120.32, and 129.52. MS m/z 374, 376, 378(M^+). Anal. Calcd for $C_{12}H_8S_2Br_2$: C, 38.32; H,2.14%. Found: C, 38.45; H,2.22%.

3,4-Dihydronaphtho [1,8-bc : 4,5-b'c'] dithiophene (5)

To a solution of **4** (376mg, 1mmol) in THF (15ml) was added 1.2ml of phenyllithium solution (1.2N in cyclohexane) under nitrogen atmosphere. After additional stirring for 30 minutes at room temperature, it was poured onto ice, acidified with diluted hydrochloric acid, and extracted with dichloromethane. The extract was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Silica-gel chromatography eluted with hexane afforded colorless crystals of **5** (176mg , 81.5%). Recrystallization from hexane-benzene gave colorless prisms. mp 109-109.5°C. ^{1}H-NMR($CDCl_3$, 400MHz) δ 3.17 (s, 4H, CH_2), 7.10 (s, 2H, ArH), and 7.72 (s, 2H, ArH). ^{13}C-NMR($CDCl_3$, 100MHz) δ 24.12, 118.37, and 119.74. MS m/z 216 (M^+). Anal. Calcd for $C_{12}H_8S_2$: C, 66.63; H, 3.73%. Found: C, 66.60; H, 3.73%.

Naphtho [1,8-bc:4,5-b'c'] dithiophene (*syn*-NDT)

Under nitrogen atmosphere, a mixture of **5** (80mg, 0.37mmol) and DDQ (83.7mg, 0.37mmom) in toluene (10ml) was refluxed for 4 hours. After cooling, resulting black precipitate was filtered off, and the filtrate was washed successively with 10% aqueous NaOH solution, water, and brine, and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded brown solid (73mg), and the crude product was purified by liquid chromatography (LC-908); *syn*-NDT, VR=255ml, 47mg (67%), orange needles from chloroform-hexane. mp 187-188°C (decomp.). ^{1}H-NMR($CDCl_3$, 400MHz) δ 7.29 (s, 2H), 7.52 (s, 2H), and 7.94 (s, 2H). ^{13}C-NMR($CDCl_3$, 100MHz) δ 119.21, 119.54, and 122.30. MS m/z 214 (M^+). Anal. Calcd for $C_{12}H_6S_2$: C, 67.25; H, 2.82%. Found: C, 67.23; H, 3.03%. UV (cyclohexane) λ_{max} 239 (log ε 4.25), 287 (3.85), 299 (3.98), 336 (4.49) and 353 (4.46) nm.

2,5-Dimethylnaphtho[1,8-bc:4,5-b'c']dithiophene (DMNDT)

To a mixture of n-butyllithium (1.6N solution in hexane, 1.45ml, 2.3mmol) and tetramethylethylenediamine (TMEDA, 0.92ml) in THF (8ml) was added a solution of 130mg (0.607mmol) of *syn*-NDT in THF (10ml) at -78°C. The mixture was stirred for 1.5h at -30°C, then cooled to -78°C and added methyl iodide (0.7ml).The resulting mixture was allowed to stand to room temperature for overnight. After treatment with diluted hydrochloric acid, the mixture was extracted with benzene. The extract was dried over $MgSO_4$ and evaporated *in vacuo* to afford brown crystals of DMNDT (146mg, quant.). The crude product was purified by column chromatography on silica-gel (eluted with benzene-hexane 1:1) followed by recrystallization from hexane to give pure DMNDT as faint yellow needles. mp 96-97°C. ^{1}H-NMR ($CDCl_3$, 400MHz) δ 2.74 (s, 3H, CH_3), 7.07 (s, 2H, ArH), and 7.68 (s, 2H, ArH). ^{13}C-NMR($CDCl_3$, 100MHz) δ 13.49, 118.09, 119.82, 127.49, 130.64, 133.57, and 135.11.

MS m/z 242(M+). Anal. Calcd for $C_{14}H_{10}S_2$: C, 69.38 ; H, 4.16%. Found: C, 69.35; H, 4.16%. UV (cyclohexane) λ_{max} 242 (log ε 4.23), 288 (3.92), 300 (4.09), 334 (4.27), 349 (4.42) and 366 (4.32) nm.

2,5-Bis(methylthio)naphtho[1,8-bc:4,5-b'c']dithiophene (MTNDT)

To a solution of dilithiated *syn*-NDT, prepared as described above, dimethyldisulfide was added. The mixture was stirred for 1.5h at -30°C and then worked up in usual manner: quantitative yield. yellow needles from hexane. mp 80°C. ^{1}H-NMR($CDCl_3$, 400MHz) δ 2.61 (s, 3H, CH_3), 7.37 (s, 2H, ArH), and 7.76 (s, 2H, ArH). ^{13}C-NMR($CDCl_3$, 100MHz) δ 22.20, 119.04, 121.20, 132.47, 132.97, 133.46 and 134.14. MS m/z 306 (M+). Anal. Calcd for $C_{14}H_{10}S_4$: C, 54.86 ; H, 3.29%. Found : C, 54.82; H, 3.25%. UV (cyclohexane) λ_{max} 250 (log ε 4.07), 306 (3.89), 320 (3.97), 369 (4.48) and 385 (4.55) nm.

Crystal Structure Analyses. The X-ray diffraction data were collected with a Rigaku automated four-circle diffractometer with Cu *Kα* radiation monochromatized by a graphite plate. Independent reflections within 2θ=126° were used for analyses. The structures were solved by a direct method combined with the Monte-Carlo method for the selection of the initial set of phase,12) and refined by a full-matrix least squares method.13) Atomic scattering factors were taken from International Tables for X-ray Crystallography.14) The anisotropic temperature factors were used for the refinement.

References

1) H. Akamatu, H. Inokuchi, and Y. Matsunaga, *Nature (London)*, **173**, 168 (1954); *Bull. Chem. Soc. Jpn.*, **29**, 3170 (1956).

2) J. Kommandeur and E. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961).

3) C. Kröhnke, V. Enkelmann, and G. Wegner, *Angew. Chem., Int. Ed. Engl.*, **19**,912 (1980).

4) F. Wudl, R. C. Haddon, E. T. Zellers, and F. B. Bramwell, *J. Org. Chem.*, **44**, 2491 (1979).

5) Y. Kono, H. Miyamoto. Y. Aso. T. Otsubo, F. Ogura, T. Tanaka, and M. Sawada, *Angew. Chem., Int. Ed. Engl.*, **28**, 1222 (1989); T. Otsubo, Y. Kono, N. Hozo, H. Miyamoto. Y. Aso. , F. Ogura, T. Tanaka, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **66**, 2033 (1993).

6) K. Watanabe, Y. Aso, T. Otsubo, and F. Ogura, *Chem. Lett.*, **1992**, 1233.

7) J. Sicé, *J. Org. Chem.*, **19**, 70 (1954).

8) T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, **1973**, 1041.

9) R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, **32**, 3093 (1967).

10) B. Back, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Molecular Spectroscopy*, **7**, 58 (1961).

11) R. Allmann, *Z. Kristallogr.*, **132**, 129 (1970).

12)A. Furusaki, *Acta Crystallogr., Sect. A*, **35**, 220 (1979).

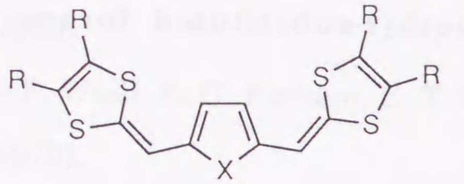
13) C. Katayama, N. Sakabe, and K. Sakabe, *Acta Crystallogr., Sect. A*, **28**, S207 (1972).

14) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. IV.

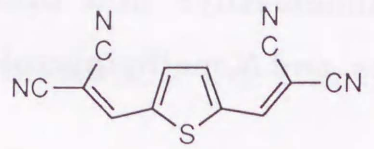
Chapter 5. Synthses, electrochemical, and optical properties of pyranylidenemethyl- and thiopyranylidenemethyl-substituted furans, thiophenes, and *N*-methylpyrroles.

Introduction

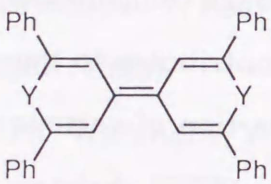
Recent attention in the field of organic metals has been directed towards the design of extensively conjugated electron donors and acceptors.1) Such components have the advantage of reduced on-site Coulomb repulsion, that contributes to the stability of the dication or dianion state. In this connection, insertion of various spacer groups between two 1,3-dithiole rings of tetrathiafulvalene (TTF) skeleton has been conducted, and recently TTF systems possessing heterocyclic spacer groups (**1a**) have been reported.2) As a new class of such extensively conjugated electron donors, the author has been interested in bipyranylidene and bithiopyranylidene systems (**2**) with a heterocyclic spacer group, since parent bipyranylidene (TPBP) and bithiopyranylidene (TPBTP) are strong electron donors and the incorporated heterocycles serve not only to decrease intramolecular coulombic repulsion but also to enhance intermolecular interactions.2) In addition, such conjugated heteroaromatics as **1b** are becoming of current interest in the development of organic materials showing nonlinear optical activities.3) Comparing the extensive researches conducted on the development of new compounds with second-order nonlinear optical, the study of third-order nonlinear optical has been relatively limited, and guidelines for molecular structural requirements for enhancing the third-order susceptibility have not been established yet.4) Recently, Cava *et al.* reported that 2,5-dicyanovinyl-substituted thiophenes showed the large third-order nonlinear optical responses.3) In this chapter, the syntheses, electrochemical properties, and third-order nonlinear optical properties of **2**, together with monopyranylidenemethyl- and thiopyranylidenemethyl-substituted heterocycles (**3**) are described.



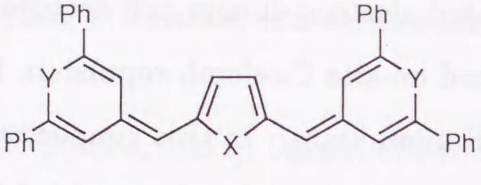
1a $X=N\text{-}CH_3$, O, S
$R=H, S(CH_2)_2S, CO_2CH_3, (CH=CH)_2$



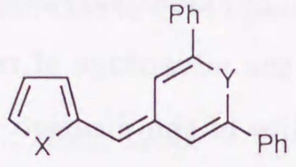
1b



TPBP Y=O
TPBTP Y=S



2 X=O , S, $N\text{-}CH_3$
Y=O, S

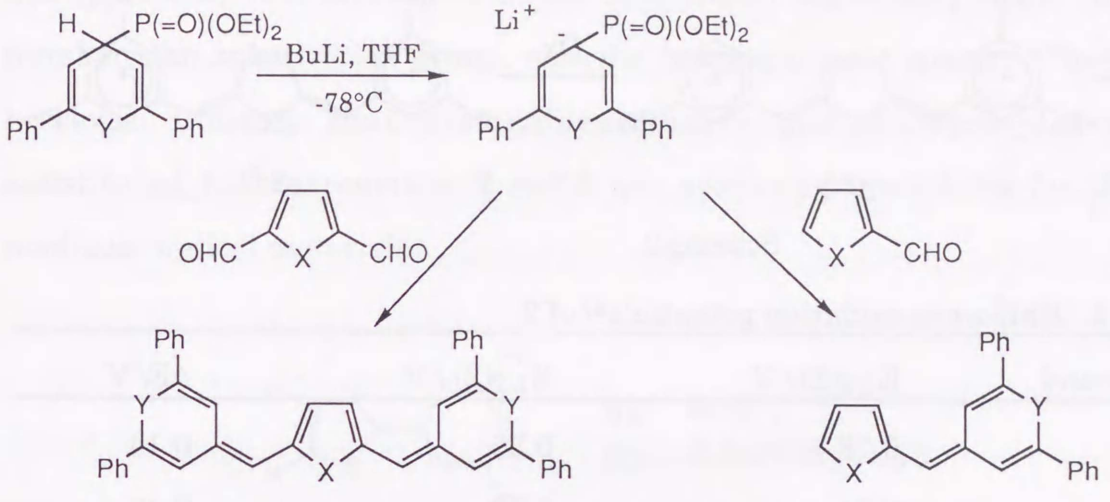


3 X=O , S, $N\text{-}CH_3$
Y=O, S

Results and discussion

Syntheses. A series of bispyranylidene and thiopyranylidene systems were synthesized by Wittig-Horner reactions between the appropriate heteroaromatic dialdehydes[5] and the corresponding ylides which were generated *in-situ* from treatment of diethyl 2,6-diphenyl-4H-pyran-4-ylphosphonate (**4a**)[6] or diethyl 2,6-diphenyl-4H-thiopyran-4-ylphosphonate (**4b**)[7] with butyllithium in dry tetrahydrofuran (THF). The mono-substituted derivatives **3** were similarly prepared using the corresponding 2-substituted heteroaromatic aldehydes (Scheme 1).

Electrochemical properties. The half-wave oxidation potentials of bis-substituted derivatives **2** measured with cyclic voltammetry are summarized in Table 1. All the compounds showed reversible redox waves. The central heteroaromatic rings of **2** might become less stable quinoid structures in the oxidation state (Scheme 2), suggesting to possess higher oxidation potentials than those of the corresponding parent TPBP and TPBTP.

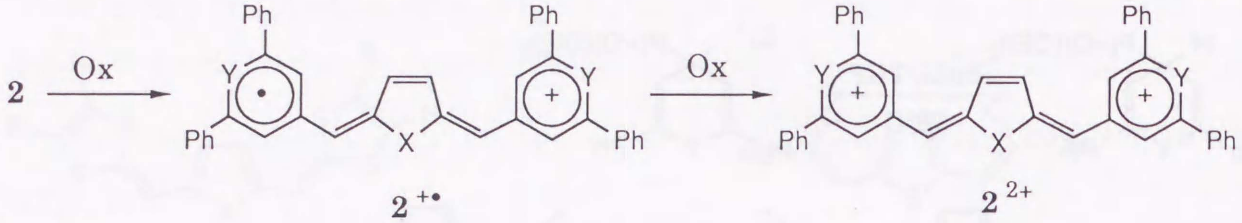


2a	X=Y=O	76%
2b	X=S, Y=O	91%
2c	X=NMe, Y=O	48%
2d	X=O, Y=S	79%
2e	X=Y=S	62%
2f	X=NMe, Y=S	79%

3a	X=Y=O	42%
3b	X=S, Y=O	39%
3c	X=NMe, Y=O	47%
3d	X=O, Y=S	58%
3e	X=Y=S	42%
3f	X=NMe, Y=S	41%

Scheme 1

Actually the furan and thiophene derivatives accord with this expectation, but the *N*-methylpyrrole derivatives showed reduced oxidation potentials than those of TPBP and TPBTP, and as the result, **2c** and **2f** became very strong electron donors. In addition, all the heteroaromatic spacers cause the decrease in the difference between the first and second oxidation potentials, confirming marked reduction of intramolecular coulombic repulsion as expected. In particular, introduction of the furan and thiophene spacers is very effective, as demonstrated by coalescence of two peaks for **2d** and **2e**. A preliminary examination revealed that strong electron donors **2c** and **2f** could form 1:2 charge transfer complexes with tetracyanoquinodimethane (TCNQ) and these complexes were highly conductive (**2c**•TCNQ 0.35Scm^{-1} and **2f**•TCNQ 1.0Scm^{-1}), indicating the potential of **2** as good electron donors.



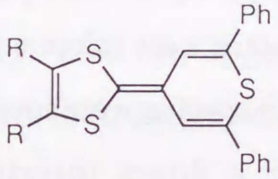
Scheme 2

Table 1. Half-wave oxidation potentials[a)] of **2**

Compound	$E_{1/2}(1)$ / V	$E_{1/2}(2)$ / V	ΔE/ V
2a	0.16	0.30	0.14
2b	0.24	0.36	0.12
2c	0.03	0.25	0.22
2d	0.25		0
2e	0.32		0
2f	0.11	0.30	0.19

a) Cyclic voltammetry was measured at 100 mV/s scan rate with Pt working and counter electrodes and Ag/AgCl reference electrode in 10^{-3} mol dm^{-3} benzonitrile solution containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.

Optical properties. The third-order nonlinearities of **2** and **3** except less soluble **2d** and labile **3c** were evaluated by the measurements of optical Kerr effects near the absorption edges of each compounds in 1% wt/vol % THF solution.[8)] The results are shown in Table 2, where the $\chi^{(3)}$ values of the sample solutions are calculated using that of carbon disulfide as the standard which was determined to be 1.0×10^{-12} esu and converted to the values of 100%. The observed susceptibilities are of the order of 10^{-12} esu, which are one or two orders of magnitude larger than those of various low-molecular compounds involving similar π-conjugated systems such as **5a** (30×10^{-12} esu) and **5b** (50×10^{-12}esu) previously screened by the same technique.[8)] These values are somewhat dependent on their molecular structures, but apparently it is difficult to decide comparative superiority of the substitution number, the substitution group, and the heteroaromatic spacer. These results, however, indicate that pyranylidenemethyl- and thiopyranylidenemethyl-substituted heteroaromatics **2** and **3** are promising candidates for third-order nonlinear optical materials.



5a R=H
5b R,R=SCH_2CH_2S

Table 2. Third-order nonlinear optical properties

Compound	$\chi^{(3)}[100\%]$ a)	$\alpha[100\%]$ a, b)	λ_{max}	$\lambda_{meas.}$ c)
	$\chi^{(3)}[CS_2]$	cm^{-1}	nm (log ε)	nm
2a	330	80	496.4 (4.56)	640.7
2b	300	100	500.8(4.60)	640.7
2c	260	70	480.4(4.71)	640.7
2f	280	55	526.0(4.66)	658.7
2e	77	90	501.0(4.69)	686.7
3a	440	100	382.4(4.51)	529.9
3b	530	115	384.0(4.51)	529.9
3d	470	110	387.2(4.48)	564.8
3e	110	40	393.6(4.50)	564.8
3f	290	110	396.8(4.39)	600

a) Measured with 1.0 wt/vol % solution in THF.

b) Absorption coefficients at $\lambda_{meas.}$ converted to the values of 100%.

c) Measurement wavelengths.

Experimental

General. Melting points are uncorrected. All chemicals and solvents are of reagent grade. Elemental analyses were measured by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. ^{1}H-NMR spectra were recorded on a Hitachi R-1200 (60 MHz) or a Bruker AMX-400wb (400MHz) spectrometer using tetramethylsilane as an internal standard. IR spectra were taken on a Hitachi 260-30 spectrophotometer with a KBr disk method. MS spectra were measured at 70 eV on a Shimadzu QP-2000A spectrometer using a direct insertion technique. Electronic spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator. Commercially available *N*-Methylpyrrole-2-carbaldehyde, furfural, and 2-thiphenecarbaldehyde were used without purification. *N*-Methylpyrrole-1), furan-2), and thiopene-2,5-dicarbaldehyde2) were prepared according to the reported procedures.

Diethyl(2,6-diphenyl-4H-thiopyrane-4-yl)phosphonate4)

Under nitrogen atmosphere, to a solution of 1.4g (4.0mmol) of 2,6-diphenylthiopyrylium perchlorate in 15ml of dry tetrahydrofurane (THF) was added a solution of sodium diethyl phosphonate, *in situ* prepared from 97mg (4.2 mmol) of sodium and 580mg (4.2mmol) of diethyl phosphonate in toluene (8 ml), at -78°C. The mixture was slowly warmed to room temperature overnight, and then poured into 30ml of saturated ammonium chloride (NH_4Cl) aqueous solution, and extracted with dichloromethane (CH_2Cl_2, 20mlX4). The extract was dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The red oily residue was chromatographed on silica-gel with ethyl acetate-hexane (5:1, v/v) as eluent, afforded pale yellow viscous oil (1.07g, 69%). (lit. 42%) ^{1}H-NMR ($CDCl_3$, 60MHz) δ 1.34 (t, J=7.2Hz, 6H, CH_3). 3.90 (dt, J_{PCH}=30Hz, J_{HH}=5.0Hz, 1H, methine), 4.07 (q, J=7.2Hz, 4H, CH_2), 5.9 (t, J_{PCCH}=5.2Hz, J_{HH}=5.2Hz, 2H, olefinic), 7.2-7.7 (m, 10H, ArH).

Diethyl(2,6-diphenyl-4H-pyrane-4-yl)phosphonate$^{4)}$

The synthesis was carried out as the same manner of that of thiopyran counterpart. Yield ; 81% as pale yellow oil. ^{1}H-NMR ($CDCl_3$, 60MHz) δ 1.31 (t, J=7.5Hz, 6H, CH_3). 3.69 (dt, J_{PCH}=27Hz, J_{HH}=4.1Hz, 1H, methine), 4.15 (q, J=7.25z, 4H, CH_2), 5.46 (t, J_{PCCH}=4.6Hz, J_{HH}=4.6Hz, 2H, olefinic), 7.2-7.8 (m, 10H, ArH).

Typical procedure of Wittig-Honer reaction with hetrocyclic aldehyde

To a solution of 1.05g (2.7mmol) of diethyl 2,6-diphenyl-*4H*-thiopyran-4-ylphosphonate in dry THF (30ml) was added ^{n}BuLi (1.5N hexane solution, 1.8ml, 2.7mmol) under nitrogen atmosphere at -78°C. After stirring 15 min, a solution of 150mg (1.09mmol) of *N*-methylpyrrole-2,5-dicarbaldehyde in dry THF (10ml) was slowly added. The mixture was slowly equilibrated to room temperature during overnight, and poured into 40ml of NH_4Cl aqueous solution, then extracted with CH_2Cl_2 (30mlX3). The extract was dried over anhydrous $MgSO_4$ and passed through a short column of silica-gel eluted with CH_2Cl_2 to give a purple solid. Recrystallization from hexane-benzene afforded reddish purple needles of **2f**. 520mg (79%). mp. 120°C (decomp.). ^{1}H-NMR ($CDCl_3$, 400MHz) δ 3.53 (s, 3H, CH_3), 5.94 (s, 2H, olefinic), 6.52 (s, 2H, pyrrole), 6.74 (s, 2H, thiopyrane), 7.34-7.45 (m, 2H, thiopyrane and 12H, Ph), and 7.57-7.65 (m, 8H, Ph). MS m/z 601 (M^+). Anal. Calcd for $C_{41}H_{31}N_1S_2$. C, 81.83 ; H, 5.19 ; N, 2.33%. Found. C, 81.78 ; H, 5.18 ; N, 2.26%. UV (THF) λ_{max} 501.0nm (log ε 4.69).

2a. 76% yield. reddish purple needles from hexane-benzene. mp. 221°C (decomp.). ^{1}H-NMR ($CDCl_3$, 400MHz) δ 5.71 (s, 2H, olefinic), 6.28 (d, J=1.8Hz, 2H, pyrane), 6.42 (s, 2H, furan), 7.16 (d, J=1.8Hz, 2H, pyrane), 7.35-7.50 (m, 12H, Ph), 7.70 (dd, J=8.0, 1.0Hz, 4H, Ph) and 7.77 (dd, J=8.0, 1.0Hz, 4H, Ph). MS m/z 556 (M^+). Anal. Calcd for $C_{40}H_{28}O_3$. C, 86.31 ; H, 5.07%. Found. C, 86.281 ; H, 4.90%. UV (THF) λ_{max} 496.4nm (log ε 4.56).

2b. 91% yield. reddish purple needles from hexane-benzene.. mp. 238°C (decomp.). ^{1}H-NMR ($CDCl_3$, 400MHz) δ 6.13 (s, 2H, olefinic), 6.43 (d, J=1.8Hz, 2H, pyrane), 6.88 (s, 2H, thiophene), 7.22 (d, J=1.8Hz, 2H, pyrane), 7.35-7.48 (m, 12H, Ph), 7.76 (dd, J=7.3, 1.6Hz, 4H, Ph) and 7.74 (dd, J=7.3, 1.6Hz, 4H, Ph). MS m/z 572 (M^+). Anal. Calcd for $C_{40}H_{28}O_2S_1$. C, 83.89; H, 4.93%. Found. C, 83.88 ; H, 4.80%. UV (THF) λ_{max} 500.8nm (log ε 4.60).

2c. 48% yield. reddish purple needles from hexane-benzene. mp. 245°C (decomp.). ^{1}H-NMR ($CDCl_3$, 400MHz) δ 3.55 (s, 3H, CH_3), 5.72 (s, 2H, olefinic), 6.43 (d, J=1.8Hz, 2H, pyrane), 6.51 (s, 2H, pyrrole), 7.07 (d, J=1.8Hz, 2H, pyrane), 7.34-7.50 (m, 12H, Ph), 7.76 (d, J=7.4Hz, 4H, Ph) and 7.74 (d, J=7.4Hz, 4H, Ph). MS m/z 569 (M^+). Anal. Calcd for $C_{41}H_{31}N_1O_2$. C, 86.44 ; H, 5.48 ; N, 2.46%. Found. C, 86.61 ; H, 5.35 ; N, 2.45%. UV (THF) λ_{max} 480.4nm (log ε 4.71).

2d. 79% yield. brown powder from hexane-benzene. mp. 214°C (decomp.). ^{1}H-NMR ($CDCl_3$, 400MHz) δ 5.90 (s, 2H, olefinic), 6.37 (s, 2H, furan), 6.71 (s, 2H, thiopyrane), 7.30-7.45 (m, 12H, Ph), 7.54-7.62 (m, 8H, Ph) and 7.76 (s, 1H, Ph). MS m/z 588 (M^+). Anal. Calcd for $C_{40}H_{28}O_1S_2$. C, 81.60 ; H, 4.79%. Found. C, 81.42 ; H, 4.79%. UV (THF) λ_{max} 513.8nm (log ε 4.59).

2e. 62% yield. black crystals from hexane-benzene. mp. 193-194°C (decomp.). ^{1}H-NMR ($CDCl_3$, 400MHz) δ 6.37 (s, 2H, olefinic), 6.75 (s, 2H, thiopyrane), 6.94 (s, 2H, thiophene), 7.20-7.46 (m, 12H, Ph), 7.53 (s, 1H, thiopyrane) and 7.57-7.65 (m, 8H, Ph).MS m/z 604 (M^+). Anal. Calcd for $C_{40}H_{28}S_3$. C, 79.43 ; H, 4.66%. Found. C, 79.46 ; H, 4.63%. UV (THF) λ_{max} 526.0nm (log ε 4.66).

3a. 42% yield. yellow needles from hexane. mp. 119°C. ^{1}H-NMR ($CDCl_3$, 400MHz) δ 5.69 (s, 1H, olefinic), 6.18 (d, J=3.1Hz, 1H, furan), 6.36 (d, J=1.8Hz, 1H, pyrane), 6.42 (dd. J=1.9, 3.1Hz, 1H, furan), 7.39-7.49 (m, furan 1H, pyrane 1H and Ph 6H), 7.74 (dd, J=1.4, 7.4Hz, 2H, Ph) and 7.82 (dd, J=1.5, 7.2Hz, 2H, Ph). MS m/z 312 (M^+). Anal. Calcd for $C_{22}H_{16}O_2$. C, 84.60 ; H, 5.16%. Found. C, 84.54 ; H, 5.13%. UV (THF) λ_{max} 382.4nm (log ε 4.51).

3b. 47% yield. orange needles from hexane. mp. 127°C. ^{1}H-NMR ($CDCl_3$, 400MHz) δ 6.12 (s, 1H, olefinic), 6.40 (d, J=1.8Hz, 1H, pyrane), 6.98 (d, J=3.5z, 1H, thiophene), 7.02 (dd. J=3.5, 5.0Hz, 1H, thiophene), 7.15 (d, J=1.8Hz, 1H, pyrane), 7.18 (dd, J=0.8, 5.0Hz, 1H, thiophene), 7.36-7.40 (m, 6H, Ph), 7.49 (dd, J=1.5, 7.2Hz, 2H, Ph) and 7.83 (dd, J=1.5, 7.0Hz, 2H, Ph). MS m/z 328 (M^+). Anal. Calcd for $C_{22}H_{16}O_1S_1$. C, 80.46; H, 4.91%. Found. C, 80.43 ; H, 4.84%. UV (THF) λ_{max} 384.0nm (log ε 4.51).

3c. 39% yield. yellow needles from hexane. mp. 185°C (decomp.). ^{1}H-NMR ($CDCl_3$, 400MHz) δ 3.60 (s, 3H, CH_3). 5.67 (s, 1H, olefinic), 6.20 (t, J=3.1z, 1H, pyrrole), 6.37 (brd, J=ca 2.8Hz, 1H, pyrrole), 6.40 (d. J=1.8Hz, 1H, pyrane), 6.61 (m, 1H, pyrrole), 7.02 (d, J=1.8Hz, 1H, pyrane), 7.35-7.46 (m, 6H, Ph) and 7.73-7.80 (m, 4H, Ph). MS m/z 325 (M^+). Anal. Calcd for $C_{23}H_{19}N_1O_1$. C, 84.89 ; H, 5.89 ; N, 4.30%. Found. C, 84.73 ; H, 5.59 ; N, 4.29%. UV (THF) λ_{max} 388.0nm (log ε 4.42).

3d. 58% yield. orange needles from hexane. mp. 105°C. ^{1}H-NMR ($CDCl_3$, 400MHz) δ 5.92 (s, 1H, olefinic), 6.27 (d, J=3.3z, 1H, furan), 6.42 (dd. J=1.8, 3.3Hz, 1H, furan), 6.69 (s, 1H, thiopyrane), 7.35-7.47 (m, furan,1H, pyrane, 1H,and Ph, 6H), 7.57 (dd, J=1.2, 7.9Hz, 2H, Ph) 7.64 (dd, J=1.2 7.9Hz, 2H, Ph) and 7.75 (s, 1H, thiopyrane). MS m/z 328 (M^+). Anal. Calcd for $C_{22}H_{16}O_1S_1$. C, 80.46 ; H, 4.91%. Found. C, 80.32 ; H, 4.80%. UV (THF) λ_{max} 387.2nm (log ε 4.48).

3e. 47% yield. orange needles from hexane. mp. 133-134°C. ^{1}H-NMR ($CDCl_3$, 400MHz) δ 6.37 (s, 1H, olefinic), 6.73 (s, 1H, thiopyrane),7.02 (m, 2H, thiophene), 7.22 (dd, J=2.1, 5.4Hz, 1H, thiophene), 7.35-7.48 (m, 6H, Ph), 7.50 (s, 1H, thiophene), 7.58 (dd, J=1.3, 8.2Hz, 2H, Ph) and 7.66 (dd, J=1.3, 8.2Hz, 2H, Ph). MS m/z 344 (M+). Anal. Calcd for $C_{22}H_{16}S_2$. C, 76.70; H, 4.68%. Found. C, 76.63 ; H, 4.62%. UV (THF) λ_{max} 393.6nm (log ε 4.50).

3f. 42% yield. orange needles from hexane. mp. 184-185°C . ^{1}H-NMR ($CDCl_3$, 400MHz) δ 3.60 (s, 3H, CH_3). 5.93 (s, 1H, olefinic), 6.18 (t, J=3.2z, 1H, pyrrole), 6.40 (d, J=3.2Hz, 1H, pyrrole), 6.64 (m, 1H, pyrrole), 6.72 (s, 1H, thiopyrane), 7.36-7.41 (m, Ph 6H and thiopyrane1H) and 7.57-7.60 (m, 4H, Ph). MS m/z 341 (M+). Anal. Calcd for $C_{23}H_{19}N_1S_1$. C, 80.90 ; H, 5.61 ; N, 4.10%. Found. C, 80.78 ; H, 5.61 ; N, 4.03%. UV (THF) λ_{max} 396.8nm (log ε 4.39).

Charge-Transfer Complexes. The hot solution of **2** and TCNQ in chlorobenzene was combined. The precipitated complexes upon standing were collected by filteration, washed with cold dichloromethane, and drid *in vacuo*.

2c•TCNQ; Anal. Calcd for $C_{65}H_{39}N_9O_2$. C, 79.82; H, 4.02; N, 12.89%. Found. C, 79.74; H, 4.09; N, 11.35%.

2f•TCNQ; Anal. Calcd for $C_{65}H_{39}N_9S_2$. C, 77.28 H, 3.89; N, 12.48%. Found. C, 76.23; H, 3.69; N, 12.48%.

Third-order Optical Nonlinearity. The measurement of third-order optical nonlinearities was carried out using as optical Kerr effect. The experiments were conducted in Chiba Research Laboratory of Ube Industries Ltd., and the detailed method was described in literature.[8)]

References

1) F. Ogura, T. Otsubo, and Y. Aso, *Sulfur Reports*, **11**, 439, (1992).

2) A. S. Benahmed-Gasmi, P. Frére, B. Garrigues, A. Gorgues, M. Jubault, R. Carlier, and Texier, *Tetrahedron Lett.*, **33**, 6457 (1992); T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. E. NIziurski-Mann, F. Jensen, and J. Becher, *J.*

Am. Chem. Soc.,**114**, 5035 (1992); K. Takahashi, T. Nihira, M. Yoshifuji, and K. Tomitani, *Bull. Chem. Soc. Jpn.*, **66**, 2330 (1993).

3) M. V. Joshi, M. P. Cava, M. V. Lakshmikantham, R. M. Metzger, H. Abdeldayem, M. Henry, and P. Venkateswarlu, *Synth. Metals*, **57**, 3974 (1993).

4) P. N. Prasad and J. Williams, "Introduction to Nonlinear Optical Effects in Molecules and Polymer", Wiley, New York ,1991, p.222; P. N. Presad and B. A. Reinhardt, Chem. Materials, **2**, 660 (1990).

5) C. E. Loader, G. H. Barnett and H. J. Anderson.,*Can. J. Chem.*, **60**, 383 (1982); B. L. Feringa, R. Hulst, R. Rikers and L. Brandsma, *Synthesis*, **1988**, 316.

6) C. H. Chen and G. A. Reynoldes, *J. Org. Chem.*, **45**, 2449 (1980).

7) C. H. Chen and G. A. Reynoldes, *J. Org. Chem.*, **45**, 2453 (1980).

8) K. Morita, T. Suehiro, Y. Yokoh, and H. Ashitaka, *J. Photopolym. Sci. Technol.*, **6**, 229 (1993).

Closing Remarks

In previous chapters, the author has discussed the syntheses, structures, and properties of various types of novel electron donors, involving not only a modification or an extention of known systems (Chapter 1 and 5), but also quite novel molecules (Chapter 3 and 4).

As mentioned in Chapters 1 and 2, the author indicated that even a simple modificationm, such as a methylation on tetrachalcogenoanthracenes, improved their properties dramatically; introduction of methyl groups served to enhance donor property and solubility, enabling ready formation of their CT-complexes with various electron acceptors. Furthermore, these donors on electrocrystallization formed highly conductive radical cation salts, and two of them showed metallic nature of conductivity. These results demonstrats that chemical modification is a useful method to obtain rather better electron donor.

Syntheses of novel heteroaromatics, tetrachalcogenophenanthrenes and naphtho-dithiophenes were also described in Chapters 3 and 4, respectively. The studies on the properties of these novel molecules showed that they behaved as good electron donors to give highly conductive CT-complexes and radical cation salts. The study of synthesizing such new compounds is particularly valuable for contributing the progress of this field.

As described in Chapter 5, extended pyranylidene and thiepyranylidene systems have been designed as new electron donors, and actually they behaved as good electron donors to form high conductive complexes. Moreover, the studies of optical properties revealed that these systems possessed reratively large third-order nonlinear susceptibilities, indicating that they might be promising candidates for third-order nonlinear optical materials.

In the field of material science, organic molecules possessing π-electron systems are recently regarded as a potential candidate for various functionalized materials, such as conductive materials, nonlinear optical materials, magnetic materials, and so on. Since all molecules synthesized in this thesis are classified as such π-electron system, the author anticipates that they will be further investigated from various points of view.

List of Publications

1) "2,3-Dimethyl and 2,3,6,7-Tetramethyl Derivatives of Anthra[1,9-cd:4,10-c'd']bis[1,2]dichalcogenoles as New Electron Donors" Kazuo Takimiya, Hisakazu Miyamoto, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura, *Chemistry Letters*, **1990**, 567-570

2) "Dimethyl and Tetramethyl Derivatives of Anthra[1,9-cd:4,10-c'd']- and Naphthaceno[5,6-c,d:11,12-c'd']-bis[1,2]dichalcogenoles" Hisakazu Miyamoto, Kazuo Takimiya, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura, *Synthetic Metals*, **41-43**, 2389-2392 (1991).

3) "Syntheses and Properties of Dimethyl and Tetramethyl Anthra[1,9-cd:4,10-c'd']bis[1,2]dichalcogenoles and Their Charge-Transfer Complexes" Kazuo Takimiya, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura, *Bulletin of The Chemical Society of Japan*, **64**, 2091-2102 (1991).

4) "Phenanthro[1,10-cd;8,9-c'd']bis[1,2]-dithiole and -diselenole as Novel Electron Donors" Kazuo Takimiya, Akiko Ohnishi, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura, *J .Chem. Soc., Chemical Communications*, **1992**, 278-280.

5) "Facile Preparation and Charge-Transfer Complexes of Naphtho[1,8-bc:4,5-b'c']dithiophene and 2,5-Dimethyl and Bis(methylthio) Derivatives" Kazuo Takimiya, Fumihiko Yashiki, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura, *Chemistry Letters*, **1993**, 365-368.

6) "Highly Conductive 1:1 Radical Cation Salts of Anthra[1,9-cd;4,10-c'd']bis[1,2]dichalcogenoles" Kazuo Takimiya, Akiko Ohnishi, Yoshio Aso, Tetsuo Otsubo, Fumio Ogura, Kazushige Kawabata, Keiji Tanaka, and Makoto Mizutani, *Bulletin of The Chemical Society of Japan*, **67**, (1994) *in press*.

7) "Pyranylidenemethyl- and Thiopyranylidenemethyl-substituted Furans, Thiophenes and *N*-Methylpyrroles as Precursors of Organic Metals and Thired-order Nonlinear Optical Materials" Kazuo Takimiya, Tetsuo Otsubo, Fumio Ogura, Hidetomo Ashitaka, Kazuhiro Morita, and Tsutomu Suehiro,
Chemistry Letters, **1994**, 255-258.

8) "Synthesis, Molecular Structure, and Properties of 1,9-Dithia[2.2] Metacyclophane" Kazuo Takimiya, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura, *Chem. Express*, **7**, 865-868 (1992).

9) "11,11,12,12-Tetracyano-2,6-anthraquinodimethane (TANT) as a Novel Extensive Electron Acceptor" Tetsuya Yanagimoto, Kazuo Takimiya, Tetsuo Otsubo, and Fumio Ogura, *J .Chem. Soc., Chemical Communications*, **1993**, 519-520.

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