HETEROCYCLES, Vol. 67, No. 2, 2006, pp. 655 - 663. © The Japan Institute of Heterocyclic Chemistry
Received, 28th July, 2005, Accepted, 29th September, 2005, Published online, 30th September, 2005. COM-05-S(T)48

SYNTHESIS AND PROPERTIES OF ETHYLENETHIOTETRASELENAFULVALENE (ET-TSF) AND ITS CONDUCTIVE RADICAL CATION SALTS

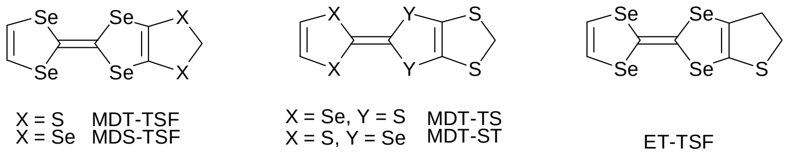
Kazuo Takimiya,[†]* Mie Kodani,[†] Satoshi Murakami,[†] Tetsuo Otsubo,[†] and Yoshio Aso[‡]

[†]Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan and [‡]The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-8479, Japan

Abstract – The title heterocycle-fused tetraselenafulvalene derivative, ET-TSF (ethylenethiotetraselenafulvalene) has been synthesized as a novel electron donor. Electrocrystallization of ET-TSF gave highly conductive radical cation salts with I_3^-, Cl^-, Br^-, and AuI_2^- counter anions. Among them, the AuI_2 salt isostructural with the organic superconductor (MDT-TSF)-AuI_2 (MDT-TSF = methylenedithiotetraselenafulvalene) was highly conductive (1600 S cm^{-1}) and metallic down to 1.8 K with no superconducting transition.

INTRODUCTION

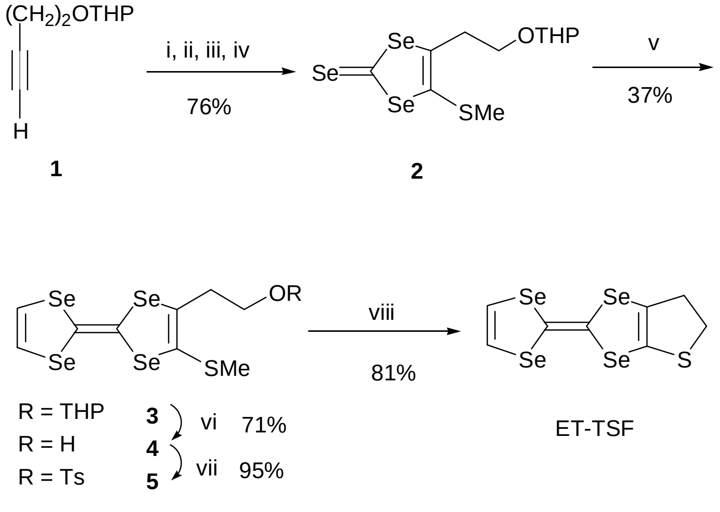
Synthesis and characterization of novel molecular conductors and superconductors based on organic electron donors have been actively investigated in the last three decades.[1] Although a great number of electron donors, in particular, tetrathiafulvalene (TTF)-type electron donors have been developed,[2] the donor molecules capable of affording superconducting salts are still limited.[1] Recently we have developed a new electron donor, methylenedithiotetraselenafulvalene (MDT-TSF) forming unique superconductors.[3] The AuI_2 salt of MDT-TSF, showing a superconducting transition at 4.5 K under ambient pressure, has characteristic features both in conductive and structural properties. First, the salt shows very high conductivity of 2000 S cm^{-1} at room temperature, which is higher by two orders of magnitude than those of usual organic superconductors.[1] Second, the salt consists of uniform donor stacks along the conducting direction, which is very rare for organic superconductors so far reported.[4] These intriguing aspects of the MDT-TSF-based superconductor led us to successfully develop three new donors possessing the related molecular structures, MDT-TS,[5] MDT-ST,[6] and MDS-TSF,[7] which gave a series of superconducting radical salts. Note that all these donors have the same carbon/chalcogen framework with C_2 symmetry (Scheme 1). We then focus on a new TSF donor, ethylenethiotetraselenafulvalene (ET-TSF). Owing to replacement of one of two sulfur atoms in the attached five membered-ring in MDT-TSF by a methylene (CH_2) moiety, ET-TSF has lower symmetry (C_S) than does MDT-TSF. This structure change might give helpful information on the contribution of the chalcogen atoms in the outer five-membered ring to the superconductive property of the salts derived from MDT-TSF and related electron donors. In this paper, we report on the synthesis of ET-TSF and the properties of its radical cation salts including the AuI_2 salt isostrucural with the superconducting (MDT-TSF)-AuI_2 and discuss the effect of low symmetry of the donor in the AuI_2 salts.



Scheme 1. Structures of molecules

RESULTS AND DISCUSSION

Synthesis. The synthetic route to ET-TSF is shown in Scheme 2. 1,3-Diselenole-2-selone derivative (**2**), easily prepared from commercially available tetrahydropyranyl (THP)-protected 3-butyn-1-ol (**1**),[8] was employed as a key intermediate. By the conventional cross-coupling reaction with 1,3-diselenole-2-selone,[9] the desired cross coupling product (**3**) was obtained in 37% yield. The THP-protecting group of **3** was then removed by treatment with dilute hydrochloric acid (71% yield), and



Scheme 2. Synthesis of ET-TSF. *Reagents and conditions*: i, n-BuLi, TMEDA, THF, –78 °C, 0.5 h; ii, Se, 0 °C, 3 h; iii, CSe_2, –90 °C, 3 min; iv, MeSCN, rt, 1 h; v, 1,3-diselenole-2-selone, $P(OMe)_3$, benzene, reflux, 2 h; vi, 1.0 M HCl, THF–MeOH, rt, 12 h; vii, TsCl, pyridine, 0 °C, 12 h; viii, NaI, DMF, 80 °C, 1 h.

the resulting alcohol (**4**) was converted into the tosylate (**5**) (95% yield). The formation at the outer five-membered ring was achieved by transalkylation reaction on the sulfur atom promoted by sodium iodide in DMF, giving rise to the desired ET-TSF in 81% yield.

In the cyclic voltammogram (CV), ET-TSF showed two reversible redox waves. The first half-wave oxidation potential (+0.47 V vs. Ag/AgCl) is almost the same as that of MDT-TSF (+0.52 V), indicating that the replacement of a sulfur atom in the outer five-membered ring by a methylene does not significantly affect the electron donating ability. The crystal structure of the neutral ET-TSF was determined by means of an X-Ray analysis. As shown in Figure 1, one ET-TSF molecule is crystallographically independent, and no disorder on the position of the sulfur (S1) and carbon atoms (C5) in the outer five-membered ring is observed.

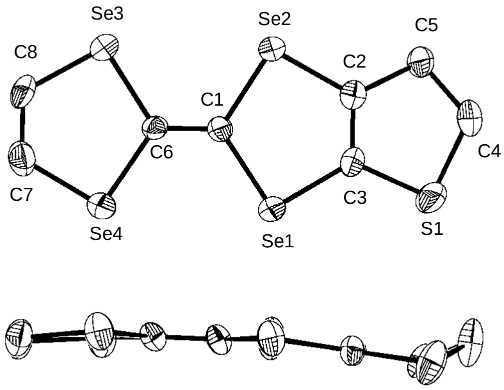


Figure 1. Molecular structure of neutral ET-TSF (hydrogen atoms are omitted).

Radical cation salts Electrocrystallization in chlorobenzene containing an appropriate tetrabutylammonium salt gave corresponding radical cation salts with I_3^-, Cl^-, Br^-, and AuI_2^-counter anions. Table 1 summarizes the appearances, donor : anoin (D:A) ratios, and conducting properties of these salts, and Figure 2 demonstrates the temperature dependence of resistivity of the metallic Cl, Br, and AuI_2 salts.

Table 1 Conductive radical cation salts of ET-TSF

Anion	Appearance	σ_{rt}/ S cm^{-1a}	D : A^b	Remark
I_3^-	black rods	10	2:1	E_{act} = 0.036 eV
Cl^-	black plates	270	-^{c}	metallic (4.2 K)
Br^-	black plates	480	2:1	metallic (4.2 K)
AuI_2^-	black needles	1600	ca. 2:1	metallic (4.2 K)

[a]Measured on a single crystal with a four-probe method. [b]Determined on the basis of microanalysis unless otherwise stated. [c]Can not be determined.

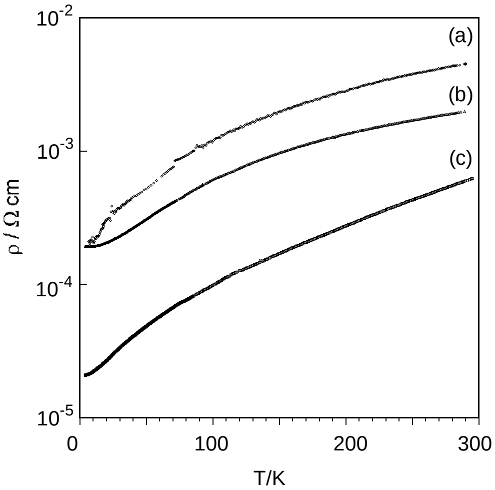


Figure 2 Temperature dependence of resistivity of ET-TSF salts: (a) Br, (b) Cl, and (c) AuI_2 salt.

Each salt has a typical crystal shape and a conducting behavior as follows. The I_3 salt with a rod-like shape showed a relatively high conductivity of 10 S cm^{-1} at room temperature and semiconductive temperature dependence with an activation energy of 0.036 eV. This is in sharp contrast to the superconducting I_3 salt of MDT-TSF,[3] which has a needle-like crystal shape. These differences are likely ascribed to the different crystal structures.

The Cl and Br salts with simple monoatomic anions crystallized in thin plate-like crystals, and their conductivities were fairly high, 270 S cm^{-1} for the Cl salt and 480 S cm^{-1} for Br salt. These salts showed similar temperature dependence of conductivity (Figure 2, traces (a) and (b)); stable metallic behavior down to the liquid helium temperature but no superconducting transition was observed.

Among all the ET-TSF salts, thin needle-like crystals of the AuI_2 salt showed the highest conductivity (1600 S cm^{-1}) and retained metallic down to 4.2 K (Figure 2, trace (c)). The conducting behavior of the AuI_2 salt is very similar to that of superconducting (MDT-TSF)-AuI_2; very high conductivity at room temperature (1600 S cm^{-1} for the ET-TSF, 2000 S cm^{-1} for the MDT-TSF salt) and strong temperature dependence of resistivity with $\rho_{rt}/\rho_{4.5K}$ = *ca.* 50. However, the ET-TSF salt showed no superconducting transition in the resistivity measurement. In addition, the Meissner effect (diamagnetic shielding) characteristic of superconductivity was not observed down to 1.8 K in magnetic susceptibility measurement with SQUID.

In order to understand the different conductive properties between the two AuI_2 salts, an X-Ray crystallographic analysis of ET-TSF–AuI_2 was carried out. As shown in Figure 3, the AuI_2 salt of ET-TSF is isostructural with the superconducting (MDT-TSF)-AuI_2.[3] The salt consists of uniform donor columns along the *a*-axis direction (Figure 3b), and the stacking columns interact with one another in the *b*-axis direction through Se–Se and Se–S contacts. In this crystal structure with *Pnma* space group, the donor molecules are located at the special positions with the mirror symmetry along the molecular long axis (Figure 3a). In other words, only the half of the donor molecule is crystallographically independent, and thus, the ET-TSF molecules with low symmetry are forced to adopt the disorder structure in the AuI$_2$ salt, whereas no such disorder in donor molecules exists in the MDT-TSF salt.

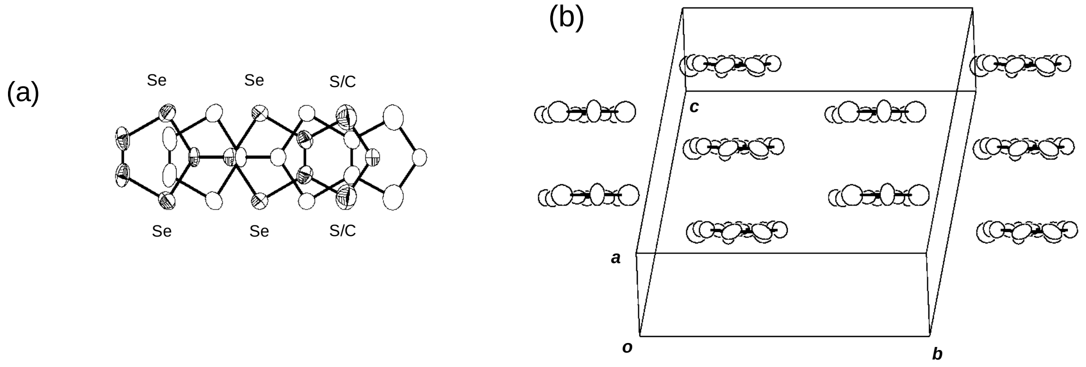


Figure 3 Crystal structure of (ET-TSF)$_2$AuI$_2$: (a) overlap of donor molecules, (b) a side view of the conducting donor sheet.

CONCLUSION

In conclusion, it has turned out that the newly synthesized electron donor ET-TSF is a good component for highly conductive organic metals with Cl$^-$, Br$^-$, and AuI$_2^-$ anions. Although the AuI$_2$ salt is isostructural with the superconducting (MDT-TSF)-AuI$_2$, it does not show superconducting transition down to 1.8 K. The X-Ray crystal structure analysis has revealed that the AuI$_2$ salt of ET-TSF unlike that of MDT-TSF has a disordering packing of the donor molecules owing to the lower symmetry. It is evident that the disordering packing does not affect metallic phase of the salt but deters the appearance of the superconducting phase at low temperature. Thus we can conclude that the two chalcogen atoms in the attached five-membered ring of MST-TSF and related electron donors with C$_2$ symmetry are requisite to the appearance of the superconducting phases of their radical cation salts.

EXPERIMENTAL

General. All chemicals and solvents are of reagent grade and used without further purification unless otherwise noted. All reactions were carried out in a nitrogen atmosphere. Tetrabutylammonium diiodoaurate was synthesized according to the literature procedure.[10] Tetrahydrofuran was distilled from benzophenone-sodium ketyl. Toluene was distilled from calcium hydride. Melting points are uncorrected. NMR spectra were obtained in deuteriated chloroform with a JEOL Lambda 400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C using tetramethylsilane as internal slandered; chemical shifts (δ) are reported in parts per million. IR spectra were taken on a Shimadzu FTIR 8100 spectrophotometer with a neat method. MS spectra were measured at 70 eV on a Shimadzu

GCMS-QP 2000 spectrometer using a direct injection technique. The molecular ion peaks of the selenium containing compounds showed a typical isotopic pattern, and all the mass peaks are reported for ^{80}Se. Cyclic voltammograms were measured at room temperature using a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

2-Methylthio-3-[2-(tetrahydropyran-2-yloxy)ethyl]tetraselenafulvalene (3). To a refluxing mixture of 4-methylthio-5-[2-(tetrahydropyran-2-yloxy)ethyl]-1,3-diselenole-2-selone (**2**, 2.33 g, 5.6 mmol)), prepared from THP-protected 3-butyn-1-ol (**1**),[8] and 1,3-diselenole-2-selone[9] (1.51 g, 5.6 mmol) in benzene (50 mL) was added trimethyl phosphite (2.0 mL, 17 mmol), and the resulting mixture was refluxed for 2 h. Evaporation of the solvent and excess phosphite gave an oily residue, which was purified by column chromatography on silica gel with dichloromethane as an eluent; the second fraction (R_f = 0.6) consisting of the desired cross coupling product was collected. Red oil (1.20 g, 37% yield). ^{1}H NMR ($CDCl_3$) δ 1.4–2.0 (m, 6H, CH_2), 2.35 (s, 3H, CH_3), 2.88–3.06 (m, 2H, CH_2), 3.44−3.56 (m, 4H, CH_2), 3.82–3.89 (m, 2H, CH_2), 4.64 (m, 1H, CH), 7.26 (s, 2H, CH). ^{13}C NMR ($CDCl_3$) δ 19.14, 20.80, 25.33, 30.44, 33.28, 61.92, 66.15, 98.63, 104.48, 108.26, 122.49, 122.52, 125.30, 141.64. MS (EI, 70 eV) *m/z* 570 (M^+). Anal. Calcd for $C_{14}H_{18}O_2SSe_4$: C, 29.70; H, 3.20. Found: C, 29.69; H, 3.14.

2-Methylthio-3-(2-hydroxyethyl)tetraselenafulvalene (4). A mixture of **3** (1.2 g, 2.1 mmol), hydrochloric acid (1.0 M, 1.4 mL), methanol (40 mL), and THF (35 mL) was stirred at rt for 12 h. The mixture was diluted with water (50 mL) and extracted with dichloromethane (15 mL × 3). The extract was washed with water (20 mL) and brine (20 mL), and dried ($MgSO_4$). Evaporation of the solvent gave crude **4**, which was purified by silica gel column chromatography eluted with dichloromethane to give red oil (R_f = 0.4, 0.70 g, 71%). ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 1H, OH), 2.36 (s, 3H, CH_3), 2.92 (t, J = 6.0 Hz, 2H, CH_2), 3.78 (t, J = 6.0 Hz, 2H, CH_2), 7.22 (s, 2H, CH). ^{13}C NMR ($CDCl_3$) δ 20.85, 35.83, 61.92, 103.53, 109.17, 122.58, 122.63, 125.92, 140.76. IR ν 3200−3800 cm^{-1} (OH). MS (EI, 70 eV) *m/z* 486 (M^+). Anal. Calcd for $C_9H_{10}OSSe_4$: C, 22.42; H, 2.09. Found: C, 22.45; H, 2.09.

2-Methylthio-3-(2-tosyloxyethylthio)tetraselenafulvalene (5). To a solution of **4** (0.89 g, 1.8 mmol) in pyridine (12 mL) was added tosyl chloride (1.1 g, 5.5 mmol) at 0 °C. The mixture was stirred for 12 h at the same temperature, and then poured onto a mixture of ice and hydrochloric acid (1 M, 10 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (10 mL × 3). The combined dichloromethane solution was washed successively with hydrochloric acid (1 M, 10 mL × 4), water (40 mL), and saturated NaCl aqueous solution (40 mL) and dried ($MgSO_4$). Evaporation of the solvent gave crude **5**, which was purified by column chromatography on silica gel eluted with dichloromethane (R_f = 0.7), giving a practically pure **5** (1.1 g, 95%). Analytically pure sample was obtained by recrystallization from dichloromethane as red microcrystals. mp 103–104 °C. ^{1}H NMR

($CDCl_3$) δ 2.30 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.95 (t, *J* = 6.2 Hz, 2H, CH_2), 4.10 (t, *J* = 6.2 Hz, 2H, CH_2), 7.24 (s, 2H, CH). 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.78 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ 20.70, 21.65, 31.78, 68.36, 102.19, 109.42, 122.66, 122.72, 127.83, 128.04, 129.85, 132.32, 137.68, 144.89. Anal. Calcd for $C_{16}H_{16}O_3S_2Se_4$: C, 30.20; H, 2.53. Found: C, 30.04; H, 2.47.

Ethylenethiotetraselenafulvalene (ET-TSF). A mixture of **5** (464 mg, 0.73 mmol) and sodium iodide (221 mg, 2.2 mmol) in DMF (5 mL) was stirred at 80 °C for 1 h. The reaction mixture was cooled, and diluted with water (10 mL) to precipitate a red solid, which was washed with water and dried. The crude solid was purified by recrystallization from toluene to afford ET-TSF as red needles (270 mg, 81%). mp 123–124 °C (melt with decomposition). ^{1}H NMR ($CDCl_3$) δ 2.89 (t, *J* = 8.2 Hz, 2H, CH_2), 3.68 (t, *J* = 8.2 Hz, 2H, CH_2), 7.26 (s, 2H, CH). MS (EI, 70 eV) *m/z* 454 (M^+). Anal. Calcd for $C_8H_6SSe_4$: C, 21.35; H, 1.34. Found: C, 21.38; H, 1.32.

Radical cation salts of ET-TSF. The radical cation salts of ET-TSF were prepared by a conventional electrochemical method. ET-TSF (3−5 mg) was placed in the anode compartment of a 20 mL H-shaped glass cell with a glass frit dividing the anode and cathode compartments, and 10−20 mg of the appropriate tetrabutylammonium salt (n-Bu_4NX, X = I_3, AuI_2,[10] Br or Cl) was placed in the cathode compartment. Chlorobenzene containing 10% of ethanol (*ca.* 18 ml) was added, and the resulting solution was deaerated with a dry nitrogen stream. Electrodes made of 1 mm platinum wires were set to the cell, and the constant current of 0.1−0.5 μA was applied. Within two weeks, crystals of the radical cation salts grew on the anode or on the glass frit. The crystals were collected by filtration, washed with dichloromethane, and dried in vacuo. The D : A ratios of the I_3 and Br salts were determined on the basis of microanalysis. $(ET\text{-}TSF)_2I_3$: Calcd for $C_{16}H_{12}I_3S_2Se_8$: C, 15.00; H, 0.94. Found: C, 15.42; H, 0.97; $(ET\text{-}TSF)_2Br$: Calcd for $C_{16}H_{12}BrS_2Se_8$: C, 19.61; H, 1.23. Found: C, 19.45; H, 1.30; $(ET\text{-}TSF)_2AuI_2$: Calcd for $C_{16}H_{12}AuI_2S_2Se_8$: C, 14.23; H, 0.90. Found: C, 14.29; H, 0.87.

Crystal structure determinations. A Rigaku AFC-7R diffractometer with graphite-monochromated Mo *Kα* radiation (λ = 0.7107 Å) was used and data collected at room temperature for all the crystals. Intensities were measured form continuous ω–2θ scans for the neutral ET-TSF and ω scans for the AuI_2 salt. All intensities were corrected for Lorenz polarization effects. The structures were solved by the direct methods (SIR92[11] or SHELXS86[12]). All non-hydrogen atoms were refined by a full matrix least-squares technique with anisotropic temperature factors. Structure solution and refinement were carried out using the TEXSAN program package.[13] For the refinement, the full-matrix least-squares (SHELEXL93)[14] was used.

In the case of structural analyses of the AuI_2 salt, the actual structural solution was obtained based on a model in which the donor is a symmetric $C_7H_4S_2Se_4$ (i.e. MDT-TSF), because the donor locates on the mirror symmetry and the half of the donor molecule is crystallographically independent. In addition, because of the disorder of the anion part, only Au atom was supposed to exist. Then the occupancies of S atom in the donor and Au atom in the anion were included in the refinement process and finally fixed to the certain value approximated by the atomic number and the multiplicity of the anion site as following; S: 0.687; Au: 0.585. Crystallographic data for ET-TSF: $C_8H_6SSe_4$, M = 450.04, orange plates, 0.38×0.20×0.13 mm^3, *monoclinic*, space group $P2_1/n$ (no. 14), a = 7.731(1), b = 12.180(1), c = 12.1478(8) Å, β = 103.133(7)°, V = 1113.9(2) Å^3, Z = 4, D_{calc} = 2.683 gcm^{-3}, R = 0.057 for 1521 observed reflections ($I > 3\sigma(I)$), R_w = 0.060 for all data. Crystallographic data for (ET-TSF)-AuI_2: $C_{16}H_{12}S_2Se_8AuI_2$, M = 1350.85, black needles, 0.40×0.03×0.01 mm^3, *orthorhombic*, space group *Pnma* (no. 62), a = 3.984(3), b = 12.640(4), c = 25.400(5) Å, V = 1279(1) Å^3, Z = 2, D_{calc} = 3.508 gcm^{-3}, R = 0.054 for 643 observed reflections ($I > 3\sigma(I)$), R_w = 0.057 for all data.

ACKNOWLEDGEMENTS

This work was partially supported by Grant-in-Aid for Scientific Research on Priority Areas of Molecular Conductors (No. 15073218). The authors also thank to the Cryogenic Center, Hiroshima University for supplying cryogen (liquid helium).

REFERENCES

1. For comprehensive reviews, see: J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M. -H. Whangbo, "Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties, and Theory," Prentice Hall, New Jersey, 1992; T. Ishiguro, K. Yamaji, and G. Saito, "Organic Superconductors” 2nd ed., Springer, Berlin, 1998.
2. G. Schukat, A. M. Richter, and E. Fanghanel, *Sul. Rep.*, 1987, **7**, 115; G. Schukat and E. Fanghanel, *Sul. Rep.*, 1993, **14**, 245; G. Schukat and E. Fanghanel, *Sul. Rep.*, 1996, **17**, 1.
3. K. Takimiya, Y. Kataoka, Y. Aso, T. Otsubo, H. Fukuoka, and S. Yamanaka, *Angew. Chem., Int. Ed.*, 2001, **40**, 1122; K. Takimiya, M. Kodani, Y. Kataoka, Y. Aso, T. Otsubo, T. Kawamoto, and T. Mori, *Chem. Mater.*, 2003, **15**, 3250.
4. T. Kawamoto, T. Mori, K. Takimiya, Y. Kataoka, Y. Aso, and T. Otsubo, *Phys. Rev. B,* 2002, **65**, 140508(R).
5. K. Takimiya, M. Kodani, N. Niihara, Y. Aso, T. Otsubo, Y. Bando, T. Kawamoto, and T. Mori, *Chem. Mater.*, 2004, **16**, 5120; T. Kawamoto, Y. Bando, T. Mori, K. Takimiya, and T. Otsubo, *Phys. Rev. B*, 2005, **71**, 052501.
6. K. Takimiya, A. Takamori, Y. Aso, T. Otsubo, T. Kawamoto, and T. Mori, *Chem. Mater.*, 2003, **15**, 1225; T. Kawamoto, T. Mori, S. Uji, J.-I. Yamaura, H. Kitagawa, A. Takamori, K. Takimiya, and T. Otsubo, *Phys. Rev. B,* 2005, **71**, 172503; T. Kawamoto, T. Mori, T. Terashima, S. Uji, A. Takamori,

K. Takimiya, and T. Otsubo, *J. Phys. Soc. Jpn.*, 2005, **74**, 1529.

7. M. Kodani, A. Takamori, K. Takimiya, Y. Aso, and T. Otsubo, *J. Solid State Chem.*, 2002, **168**, 582.
8. T. Jigami, K. Takimiya, T. Otsubo, and Y. Aso, *J. Org. Chem.*, 1998, **63**, 8865; M. Kodani, S. Murakami, T. Jigami, K. Takimiya, Y. Aso, and T. Otsubo, *Heterocycles*, 2001, **54**, 225.
9. K. Takimiya, A. Morikami, and T. Otsubo, *Synlett*, 1997, 319; T. Otsubo and K. Takimiya, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 43.
10. P. Braunstein, J. H. Clark, W. Ramsay, R. Foster, and C. Ingold, *J. Chem. Soc., Dalton Trans.*, 1973, 1845.
11. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
12. G. M. Sheldrick, SHELXS86: In *Crystallographic Computing 3*, ed. by G. M. Sheldrick, C. Kruger, and R. Goddard, Oxford University Press, Oxford, p. 175.
13. TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1992).
14. G. M. Sheldrick SHELEXL93: Programs for the Refinement of Crystal Structures. University of Goettingen, Germany, 1993.