New organic metals based on vinylenedithio-annulated diselenadithiafulvalene derivatives

Jun-ichi Yamada,*[a]† Shûji Satoki,[a] Hiroyuki Anzai,[a] Kenji Hagiya,[a] Masafumi Tamura,[b] Yutaka Nishio,[b] Koji Kajita,[b] Emiko Watanabe,[c] Michiko Konno,[c] Tatsuo Sato,[d] Hiroyuki Nishikawa[d] and Koichi Kikuchi[d]

[a] *Department of Material Science, Faculty of Science, Himeji Institute of Technology, 1479-1 Kanaji, Kamigori-cho, Ako-gun, Hyogo 678-12, Japan*
[b] *Department of Physics, Faculty of Science, Toho University, Miyama 2-2-1, Funabashi 274, Japan*
[c] *Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku Tokyo 112, Japan*
[d] *Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachiohji, Tokyo 192-03, Japan*

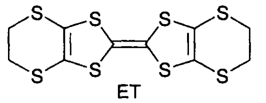
The synthesis of vinylenedithio-annulated DSDTF (diselenadithiafulvalene) derivatives 1–3 and their radical cation salts are investigated, several of which exhibit metallic conducting behaviour.

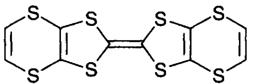
For ET‡-based superconductors, it has been reported that the π-electron system of the conducting component should be extended to its periphery to increase the T_c (superconducting transition temperature).[1] One synthetic strategy to extend the π-system in the ET molecule might be the replacement of the ethylene groups with vinylene groups, but investigations on the electrical conductivity and structural analysis of $(VT)_2PF_6$ have revealed that this salt exhibits a metal-insulator transition due to its one-dimensional metallic property.[2] In addition, the unsymmetrical donor EVT, which possesses structural moieties of both the ET and the VT frameworks, has produced semiconductive radical cation salts.[3] We have already reported the efficient synthesis of ethylenedithio-annulated DSDTFs, such as DMET and TMET-STF, by the Me_3Al-promoted reaction of the corresponding organotin thiolate or selenolate with esters.[4] The question of if the introduction of a vinylene group instead of an ethylene group into DSDTFs is recognized as a favoured strategy for the development of π-electron donors which lead to new organic metals has not been investigated. We now report the synthesis of vinylenedithio-annulated DSDTFs **1–3** *via* the Me_3Al-promoted reaction and their electrochemical properties and the electrical conductivities of their radical cation salts, and the crystal structure of $(\mathbf{2})_2PF_6$.

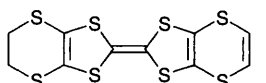
First, although the preparation of 4,5-vinylenedithio-1,3-dithiole-2-thione **5** is known,[5] we examined an alternative synthetic route to **5** (Scheme 1). Reaction of $(Bu_4N)_2[Zn(dmit)_2]$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) with 1,2-dibromoethyl ethyl ether in boiling THF gave thione **4** in 91% yield. Thione **5** was obtained by elimination of ethanol from **4** under basic conditions in 53% yield. The overall yield of **5** *via* these synthetic procedures was relatively improved in comparison with that described in the literature.[5] Treatment of **5** with $Hg(OAc)_2$ in THF–AcOH afforded ketone **6** in 82% yield.

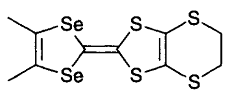
The results of the Me_3Al-promoted reaction of organotin selenolates **7a–c** or thiolate **7d** with esters **8a,b**§ are summarized in Table 1. Vinylenedithio-annulated DSDTFs **1–3**¶ were obtained by treating the corresponding tin selenolates **7a–c** with ester **8a**, respectively.|| Reaction of tin thiolate **7d** with ester **8b** also gave **2** in 25% yield.

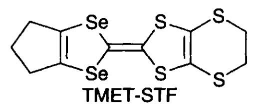
Cyclic voltammograms (CVs) of **1** and **2** showed two pairs of reversible redox waves in MeCN [**1**; E_1 = +0.59 V, E_2 = +0.91 V, **2**; E_1 = +0.60 V, E_2 = +0.91 V (0.1 mol dm^{-3} Bu_4NClO_4, Pt electrode, room temperature, scan rate 50 mV s^{-1}, V *vs.* SCE.)], whereas a satisfactory CV of **3** was not obtained due to

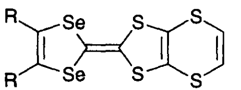

ET


VT

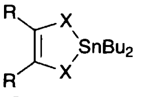

EVT

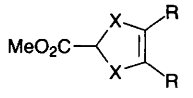

DMET

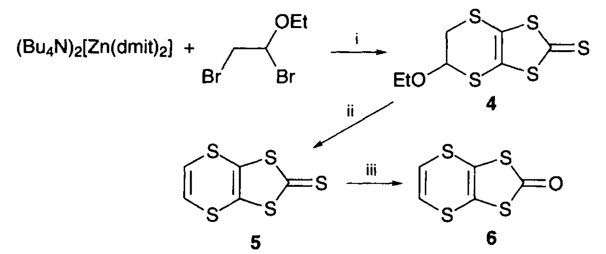

TMET-STF


DME T

1 DMVT; R = R = Me
2 TMVT; R–R = $(CH_2)_3$
3 EDVT; R–R = $S(CH_2)_2S$


7a X = Se, R =R = Me
b X = Se, R–R = $(CH_2)_3$
c X = Se, R–R = $S(CH_2)_2S$
d X = S, R–R = S(CH=CH)S


8a X = S, R–R = S(CH=CH)S
b X = Se, R–R = $(CH_2)_3$



Scheme 1 *Reagents and conditions*: i, THF, reflux, 1 h; ii, LDA (3.2 equiv.) in THF, −78 °C, 30 min, room temp., 1.5 h; iii, $Hg(OAc)_2$ (1.6 equiv.) in THF–AcOH, room temp., 30 min

Table 1 Synthesis of vinylenedithio-annulated DSDTFs

Organotin compound 7	Ester 8	Reaction temp.	Reaction time	Product	Isolated yield (%)[a]
a	**a**	rt[b]	overnight	**1**	40
b	**a**	rt	2 d	**2**	28
c	**a**	rt	overnight	**3**	13
d	**b**	rt	overnight	**2**	25

[a] After column chromatography on silica gel followed by recrystallization. [b] Room temp.

its insolubility in MeCN. The E_1 value of **1** is higher by 0.18 V compared with that of DMET (E_1 = +0.41 V), and the E_1 value of **2** is also higher than that of TMET-STF (E_1 = +0.48 V).

Preparation of the radical cation salts listed in Table 2 was carried out by electrochemical oxidation with a controlled current[6] in chlorobenzene or 1,1,2-trichloroethane (TCE) containing the corresponding tetrabutylammonium salt. Although all of the radical cation salts derived from DMVT **1** exhibited semiconductive behaviour, some TMVT **2**-based salts were metallic at room temperature. Particularly, $(TMVT)_2PF_6$ exhibited metallic behaviour down to 4.2 K with a high room temperature conductivity (σ_{rt} = 620 S cm^{-1}). Also, whilst the I_3^- salt of EDVT **3** showed semiconducting behaviour with small activation energy (34 meV), the PF_6^- salt of **3** was metallic down to 4.2 K.

Table 2 Electrical conductivities of radical cation salts based on **1–3**

Donor	Anion	Solvent	D:A^a	σ_{rt}/S cm$^{-1\,b}$
1	I_3	PhCl	2:1	$1.9 \times 10^{-1\,d}$ (Ea = 0.070 eV)
1	$AuCl_2$	PhCl	1:1	$6.4 \times 10^{-1\,d}$ (Ea = 0.061 eV)
1	AuI_2	TCE^c	3:2	3.2^d (Ea = 0.11 eV)
1	ClO_4	PhCl	—^{e}	$6.1 \times 10^{-4\,d}$ (Ea = 0.41 eV)
1	PF_6	PhCl	5:2	$1.2 \times 10^{-2\,d}$ (Ea = 0.18 eV)
2	I_3	PhCl	5:2	13^f (metallic down to 260 K)
2	AuI_2	TCE^c	2:1	21^f (metallic down to 220 K)
2	ClO_4	TCE^c	—^{e}	43^f (metallic down to 280 K)
2	PF_6	PhCl	2:1	620^d (metallic down to 4.2 K)
3	I_3	PhCl	9:2	$1.7 \times 10^{-1\,d}$ (Ea = 0.039 eV)
3	PF_6	PhCl	5:2	13^d (metallic down to 4.2 K)

^{a} Determined by elemental analysis. ^{b} Room temp. conductivity measured by a four-probe technique. ^{c} 1,1,2-Trichloroethane. ^{d} Measured on a single crystal. ^{e} Not determined because this complex may explode during analysis. ^{f} Measured on a compressed pellet.

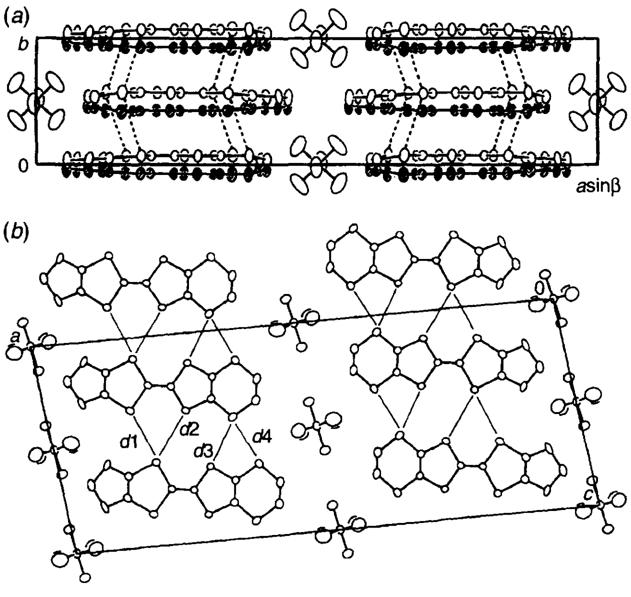


Fig. 1 Crystal structure of $(TMVT)_2PF_6$, viewed along the *c* axis (*a*) and the *b* axis (*b*); (*a*) interstack shorter Se···S contacts (< 3.85 Å) between the front molecules, which are drawn by open circles, shown by the dotted lines, (*b*) interstack shorter Se···Se contact (<4.00 Å): *d*1 = 3.7022(9) Å, Se···S contact (<3.85 Å): *d*2 = 3.787(2) Å, S···S contacts (<3.70 Å): *d*3 = 3.506(2) Å, *d*4 = 3.457(2) Å

The crystal structure of the $(TMVT)_2PF_6$ salt was determined by X-ray diffraction.** The TMVT molecules stack head-to-tail along the *b*-axis, as shown in Fig. 1(*a*). The interplanar distance [3.5869(3) Å] is exactly equal to *b*/2 due to the symmetry restriction, so there is no dimerization within a stack. As illustrated in Fig. 1(*b*), there exist also several chalcogen–chalcogen contacts shorter than the sum of the van der Waals radii between stacks. These interstack contacts are responsible for the metallic conductivity of this salt down to low temperatures.

Footnotes

† E-mail: yamada@sci.himeji-tech.ac.jp

‡ *Abbreviations*: ET = bis(ethylenedithio)tetrathiafulvalene; VT = bis(vinylenedithio)tetrathiafulvalene; EVT = 4,5-ethylenedithio-4′,5′-vinylenedithiotetrathiafulvalene; DMET = dimethyl(ethylenedithio)diselenadithiafulvalene; TMET-STF = trimethylene(ethylenedithio)diselenadithiafulvalene; DMVT = dimethyl(vinylenedithio)diselenadithiafulvalene; TMVT = trimethylene(vinylenedithio)diselenadithiafulvalene; EDVT = ethylenedithio(vinylenedithio)diselenadithiafulvalene.

§ Ester **8a** could be prepared by transmetallation of **7d** with butyllithium followed by treatment with methyl dichloroacetate in 47% yield from **6**.

¶ *Physical and spectroscopic* data for **1**: mp 208 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$-CS_2) δ 6.54 (s, 2 H) and 2.02 (s, 6 H); MS *m*/*z* (% relative intensity) 416 (100, M$^+$ + 2) and 414 (88, M$^+$); calcd for $C_{10}H_8S_4{}^{80}Se_2$ *m*/*z* 415.7839, found 415.7838. For **2**: mp 222 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$-CS_2) δ 6.54 (s, 2 H), 2.61 (m, 4 H), and 2.39 (m, 2 H); MS *m*/*z* (% relative intensity) 428 (100, M$^+$ + 2) and 426 (89, M$^+$); calcd for $C_{11}H_8S_4{}^{80}Se_2$ *m*/*z* 427.7839, found 427.7825. For **3**: mp 231 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$-CS_2) δ 6.55 (s, 2 H) and 3.32 (s, 4 H); MS *m*/*z* (% relative intensity) 478 (100, M$^+$ + 2) and 476 (83, M$^+$); calcd for $C_{10}H_6S_6{}^{80}Se_2$ *m*/*z* 477.7124, found 477.7127.

‖ The procedure of Me_3Al-promoted reactions is as follows. To a solution of tin selenolate (**7a**, **b**, **c**) in CH_2Cl_2 was added Me_3Al (2 equiv.) in hexane at room temp. under nitrogen. The solution was then stirred for the appropriate time (**7a**; 4 h, **7b**; 1 h, **7c**; 1 h) and then a solution of ester **8a** (1 equiv.) in CH_2Cl_2 was added. Work-up was carried out as reported previously.[4]

** *Crystal data* for $(TMVT)_2PF_6$: $(C_{11}H_8S_4Se_2)_2PF_6$, M = 997.69, monoclinic, space group $C2/c$, a = 32.119(6), b = 7.174(1), c = 13.084(2) Å, β = 97.30(1)°, V = 2990.4(8) Å^3, Z = 4, D_c = 2.216 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, μ = 55.0 cm^{-1}, $F(000)$ = 1924. The data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with graphite monochromated Mo-Kα radiation using the ω-2θ scan technique to a maximum 2θ of 60°. The structure was solved by direct methods and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to R = 0.066, R_w = 0.082 for 2805 observed ([$I \geqslant 3\sigma(I)$] reflections from 4353 unique data. All calculations were performed using the Molen structure determination system. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/171.

References

1 H. Yamochi, T. Komatsu, N. Matsukawa, G. Saito, T. Mori, M. Kusunoki and K. Sakaguchi, *J. Am. Chem. Soc.*, 1993, **115**, 11 319.
2 H. Kobayashi, A. Kobayashi, T. Nakamura, T. Nogami and Y. Shirota, *Chem. Lett.*, 1987, 559.
3 H. Nakano, K. Miyawaki, T. Nogami, Y. Shirota, S. Harada and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2604.
4 J. Yamada, Y. Amano, S. Takasaki, R. Nakanishi, K. Mastumoto, S. Satoki and H. Anzai, *J. Am. Chem. Soc.*, 1995, **117**, 1149.
5 T. Nakamura, T. Nogami and Y. Shirota, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3447.
6 H. Anzai, J. M. Delrieu, S. Takasaki, S. Nakatsuji and J. Yamada, *J. Cryst. Growth*, 1995, **154**, 145.

Received, 21st May 1996; Com. 6/03532I