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Emiko Ojima^{a b}, Hideki Fujiwara^c, Hayao Kobayashi^c, Madoka Tokumoto^{a b} & Akiko Kobayashi^d

^a Institute for Molecular Science, Myodaiji, Ozaki, 444-8585, Japan

^b Electrotechnical Laboratory, Umezono, Tsukuba, 305-0045, Japan

^c Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

^d The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan

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NEW ORGANIC CONDUCTORS BASED ON TELLURIUM-CONTAINING DONOR MOLECULES

Emiko Ojima

*Institute for Molecular Science, Myodaiji, Ozaki 444-8585,
Japan*

*Electrotechnical Laboratory, Umezono, Tsukuba 305-0045,
Japan*

*Hideki Fujiwara and Hayao Kobayashi**

*Institute for Molecular Science, Myodaiji, Okazaki 444-8585,
Japan*

Madoka Tokumoto

*Institute for Molecular Science, Myodaiji, Ozaki 444-8585,
Japan*

*Electrotechnical Laboratory, Umezono, Tsukuba 305-0045,
Japan*

Akiko Kobayashi

*The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033,
Japan*

Trimethyleneditelluro- and trimethyleneoxaditelluro-substituted dimethyl-TTF derivatives were prepared. The CV result of the trimethyleneditelluro-substituted dimethyl-TTF derivative shows characteristic multi-redox behavior and the trimethyleneoxaditelluro-substituted dimethyl-TTF derivative exhibits two pairs of reversible redox waves. The structures and physical properties of conducting salts based on their donors are also clarified.

Keywords: organic conductor; Tellurium; TTF derivative

*Corresponding author. E-mail: hayao@ims.ac.jp

INTRODUCTION

Radical cation salts of tetrathiafulvalene (TTF) derivatives have been attracted a great deal of attention because they show high electrical conductivity and sometimes superconductivity. Among them, the tellurium-containing TTF derivatives have drawn much attention as superior electron donors for organic conductors, because the introduced tellurium atoms are expected to produce a novel metallic system in which wide bandwidth and high dimensionality may be realized due to the large van der Waals radii and electron density of tellurium atoms. Furthermore conducting salts based on tellurium-containing donor molecules are interesting because the tellurium network in the crystal is dominant for the construction of whole the crystal structure [1]. Recently, several tellurocycle-fused donor molecules **1–4** have been reported [2]. Several studies have been made on their 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,5-difluoro-TCNQ (TCNQF₂) complexes, however no cation radical salt has been reported. Therefore we prepared new trimethyleneditelluro- and trimethyleneoxaditelluro-substituted dimethyl-TTF derivatives **5–6**. Herein we report the synthesis of new tellurium-containing donors **5–6** and their electrochemical properties. Furthermore electrical properties and crystal structures of the TCNQ complex and cation radical salts, which were prepared from donor **5**, are described.

1: R₁ = -Te(CH₂)₃Te-, R₂ = -(CH₂)₃-

2: R₁ = -TeCH₂CH(CH₃)CH₂Te-, R₂ = -CH₂CH(CH₃)CH₂-

3: R₁ = -H, R₂ = -(CH₂)₃-

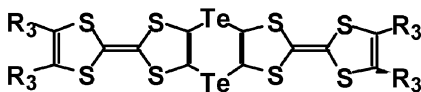
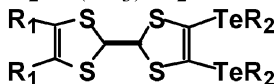
4: R₁ = -SCH₃, R₂ = -(CH₂)₃-

5: R₁ = -CH₃, R₂ = -(CH₂)₃-

6: R₁ = -CH₃, R₂ = -CH₂OCH₂-

7: R₃ = -SCH₃

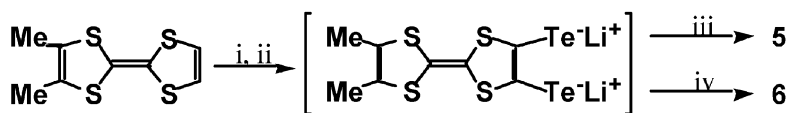
8: R₃ = -CH₃



RESULTS AND DISCUSSION

Syntheses and Electrochemical Properties of Donors **5–6**

Synthesis of the tellurocycle-fused donor **5** has been already reported [3]. The trimethyleneoxaditelluro-substituted TTF derivatives **6** was synthesized by the method similar to the synthesis of donor **5** as shown in Scheme 1. The donor **6** was prepared as air-stable reddish orange crystals in the yield of 12%. The measurement of the cyclic voltammetry data was performed in benzonitrile containing 0.1 M tetra-*n*-butylammonium



SCHEME 1 Reagents and conditions: i) LDA (2.2 equiv.), dry THF, -78°C , 2.5 h; ii) Te (2.0 equiv.), -78 to 0°C , 6 h; iii) $\text{Br}(\text{CH}_2)_3\text{Br}$ (1.0 equiv.), -78°C to room temperature, overnight; iv) $\text{ClCH}_2\text{OCH}_2\text{Cl}$ (1.0 equiv.), -78°C to room temperature, overnight.

perchlorate at 20°C (Table 1). The donor molecule **5** showed three pairs of reversible redox waves at +0.37, +0.76 and +0.88 V. On the other hand, the donor molecule **6** showed two pairs of reversible redox waves at +0.38 and +0.77, and one irreversible wave at +0.92 V. The first redox potentials are slightly high compared to that of dimethyl-TTF (+0.34 V under the identical conditions), suggesting that the electron-donating abilities of donors **5–6** are lower than that of dimethyl-TTF by the substitution of trimethyleneditelluro and trimethyleneoxaditelluro groups. Their third redox process at +0.88 and 0.92 V, respectively, probably occur at the tellurium atoms because the first and second redox waves are equal to the oxidation of the TTF moiety. When we repeated sweeping cycles between 0 and +1.2 V, all the three redox waves of **5** displayed no change. In the meantime, repeated cycling between 0 and +1.5 V (higher than a shoulder peak around +1.4 V) gradually extinguished only the third redox waves, which were completely disappeared after 20 cycles (Figure 1). These results suggest that further oxidation derived from the application of high potential (+1.5 V) would not affect the ditellurium substituted TTF skeleton but cause some structural transformation to only the trimethyleneditelluro ring.

TABLE 1 Oxidation Potentials of Tellurocycle-Fused Donors and their Related Compound^a

Donors	Oxidation potential/V ^b		
	$E_{1/2}$ (1)	$E_{1/2}$ (2)	$E_{1/2}$ (3)
5	0.37	0.76	0.88
6	0.38	0.77	0.92 ^c
dimethyl-TTF	0.34	0.77	

^a0.1 M *n*-Bu₄N⁺ ClO₄⁻ in benzonitrile, Pt electrode, scan rate 50 mV · s⁻¹, 20 °C, V vs. Ag/AgCl.

^bReversible steps.

^cIrreversible step.

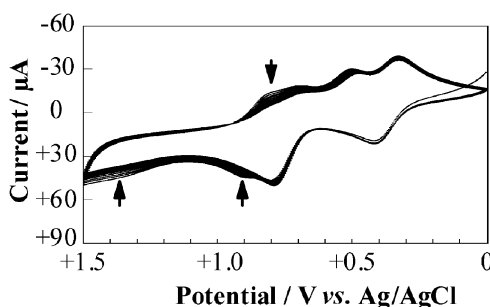


FIGURE 1 Cyclic voltammogram of **5** swept repeatedly in the potential range of 0 to +1.5 V.

Preparation of the TCNQ Complex and the Cation Radical Salts

The TCNQ complex was obtained by diffusion method using the carbon disulfide solutions of donor **5** and the acetonitrile solution of TCNQ for 1–2 months. Single crystals of cation radical salts were prepared by electrochemical oxidation of donors **5** in the presence of the corresponding tetra-*n*-butylammonium salts at a constant current of $0.2\text{--}0.3\ \mu\text{A}\cdot\text{cm}^{-2}$ in tetrahydrofuran or monochlorobenzene solution with a small amount of ethanol (10%, v/v) for 3–4 weeks (Table 2).

Crystal Structures of the TCNQ Complex and the Cation Radical Salts

A single crystal X-ray structure analyses were performed for a black plate-like crystal of the TCNQ complex and a black stick-like crystal of the $\text{Au}(\text{CN})_2^-$ salt. The crystal data for **5**·(TCNQ): Monoclinic, space group

TABLE 2 Electrical Properties of the TCNQ Complex and the Cation Radical Salts^a

Donors	Acceptor or anion	Crystal form	$\sigma_{\text{rt}}/\text{S}\cdot\text{cm}^{-1}$	Conducting behavior
5 ^b	TCNQ	Stick	1.1×10^{-3}	$E_a = 0.286\ \text{eV}$
8 ^b	$\text{Au}(\text{CN})_2^-$	Plate	13	$E_a = 0.037\ \text{eV}$
8 ^c	ClO_4^-	Plate	6.6	$E_a = 0.057\ \text{eV}$
8 ^c	PF_6^-	Plate	3.3	$E_a = 0.053\ \text{eV}$

^a Measured on a single crystal using four-probe method.

^b Determined by X-ray structure analysis.

^c Determined by EPMA measurement from the existence ratio of sulfur and tellurium atoms.

$P2_1/a$, the lattice constants $a = 16.064(2)$, $b = 6.698(4)$, $c = 23.971(1)$ Å, $\beta = 101.570(7)^\circ$, $V = 2526(1)$ Å³, $Z = 4$. The final $R(R_w)$ value was 0.061 (0.064) for the independent 2869 reflections [$I > 3.00\sigma(I)$]. The crystal data for **8**·[Au(CN)₂]_{0.42}: Monoclinic, space group $C2/c$, the lattice constants $a = 40.76(4)$, $b = 4.0853(8)$, $c = 15.165(9)$ Å, $\beta = 107.98(5)^\circ$, $V = 2402(2)$ Å³, $Z = 4$. The final $R(R_w)$ value was 0.079 (0.090) for the independent 1368 reflections ($I > 5.00\sigma(I)$). As Figure 2(a) indicates, the crystal structure of **5**·(TCNQ) comprises donor-acceptor (DA) type stacking columns and is different from that of the earlier reported TCNQF₂ complex of **4**, which has DDAA type stacking columns [2]. There are several contacts less than the sum of the van der Waals radii [$S \cdots Te$ (3.86 Å) and $Te \cdots Te$ (4.12 Å)], suggesting one-dimensional (1D) conductor along the side-by-side direction of the donor molecule Figure 2(b). The crystal structure analysis of the Au(CN)₂[−] salt revealed that the tellurocycle-fused donor **5** has been transformed into the symmetrical donor **8** Figure 3(a). The electron probe microanalysis (EPMA) measurements on all the cation radical salts suggested that they are composed of the symmetrically dimerized donor **8**, as determined from the ratio of sulfur and tellurium atoms. We consider that such a dimerization could occur by the high oxidation state produced during the electrochemical oxidation, which gives rise to the structural change of the trimethyleneditelluro moiety mentioned in the cyclic voltammetry study. Donors containing two TTF units fused to 1,4-ditellurine ring (**7**[4]–**8**[5]) are already known, however, no cation radical salt has been reported so far because of their poor solubility in most common organic solvents. The composition of the Au(CN)₂[−] salt was determined to be **8**·(anion)_{0.42} by the population refinement. As shown in

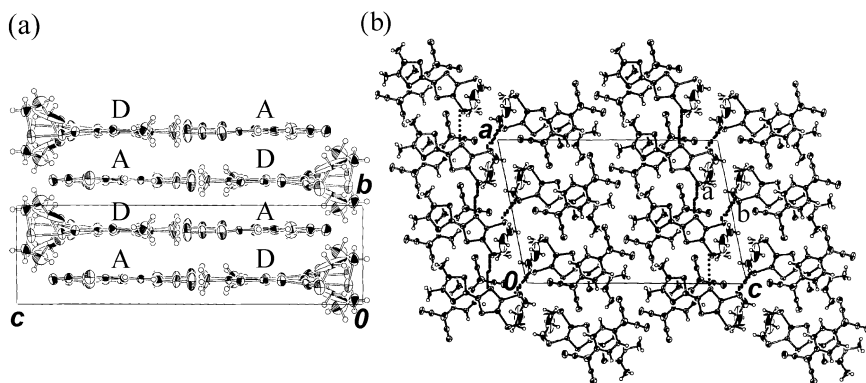


FIGURE 2 Mixed-stacking structure of **5**·(TCNQ). Intermolecular contacts (Å): $S \cdots Te$, $a = 3.86$; $Te \cdots Te$, $b = 4.12$.

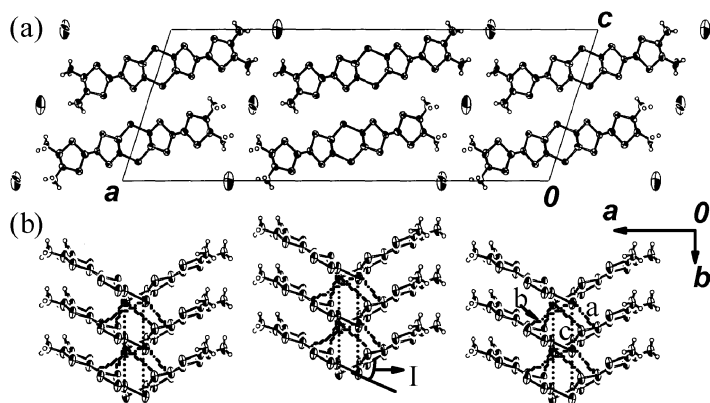


FIGURE 3 Crystal structure of **8** · [Au(CN)₂]_{0.42}. Dihedral angle (°): I = 59.1. The disordered anions are omitted in Figure III(b).

Figure 3(b), the donor molecule **8** adopts a V-letter shaped conformation with dihedral angle of 59.1° at the position of ditellurine ring. This molecular structure is quite different from that of the neutral one, which exhibits a 'bowed' nature of molecular conformation [5]. One crystallographically independent donor molecule forms a uniform column along the *b*-axis with an intermolecular interplane distance of 3.69 Å. The configuration of the donor molecules between neighboring columns is up-and-down type arrangement along the *c*-axis Figure 3(a). Therefore, no intermolecular contact exists between donor columns, however, there are several short intermolecular contacts mediated by the sulfur and tellurium atoms along stacking direction, suggesting 1D nature along the *b*-axis Figure 3(b). Overlap integrals are calculated for the Au(CN)₂[−] salt by the extended Hückel method. The overlap integral along the donor stacking direction (*b*) is very large (21.2×10^{-3}) in comparison with the others ($\leq 3.0 \times 10^{-3}$) owing to the 1D feature of the crystal structure.

Properties of the TCNQ Complex and the Cation Radical Salts

The electrical properties of the TCNQ complex and the cation radical salts are summarized in Table 2. The TCNQ complex of **5** is a semiconductor due to the DA type mixed-stacking structure. However, the room temperature conductivity ($10^{-3} \text{ S} \cdot \text{cm}^{-1}$) is relatively high for the mixed-stacking structure because of the strong intermolecular contacts along the side-by-side direction. The degree of charge transfer (*Z*) of the complex was estimated to be 0.74 from the infrared $\text{C} \equiv \text{N}$ stretching frequency of TCNQ

(2194 cm^{-1}). Consequently, we think that the chemical oxidation by TCNQ could not cause the dimerization of the donor **5** observed in the cases of the electrochemically prepared salts because general acceptors could not induce the very high oxidation state required for the dimerization of the donor. On the other hand, all the cation radical salts of **8** are semiconductors with a very small activation energy of 0.03–0.06 eV. The room temperature conductivities are comparatively high ($1\text{--}10\text{ S}\cdot\text{cm}^{-1}$) due to the tight 1D stacking along the donor stacking direction (the *b*-axis) concerning the $\text{Au}(\text{CN})_2^-$ salt.

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