A New Organic Metal Based on the DHTTF (Dihydrotetrathiafulvalene) Derivative, $(MDHT)_2AuI_2$

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Electrochemical properties of various DHTTF derivatives and electrical conductivities of their radical cation salts have been investigated. Among their radical cation salts, the electrical resistance of $(MDHT)_2AuI_2$ [MDHT = methylenedithio(dihydro)-tetrathiafulvalene] on a single crystal exhibited the metallic temperature dependence.

Despite the progress in development of organic metals based on TTFs (tetrathiafulvalenes),[1] no investigation has been reported on the electrical properties of DHTTF derivatives which belong to a class of TTFs.[2] The results of such investigations are versatile for the design of novel organic conductors derived from DHTTFs. We have recently reported the synthesis of a series of DHTTF derivatives (**1a**-**c** and **2a**,**b**, Figure 1) via the Me_3Al-promoted noncoupling reaction of tin thiolates (**3a**-**c**) or tin selenolates (**4a**,**b**) with ester (**5**).[3] Here we disclose (i) an alternative synthetic route to a new tin thiolate **3d**, (ii) the cyclic voltammograms (CVs) of the DHTTFs, including new ones (**1d** and **2c**), and (iii) the electrical conductivities of their radical cation salts.

We have established the synthetic method for preparation of tin thiolates (**3a**-**c**) and selenolates (**4a**,**b**) from the corresponding magnesium thiolates and selenolate or lithium selenolate.[3] For the preparation of tin selenolate **4c**, the synthetic procedure via the dilithium thiolate was used. Treatment of the dilithium salt of 5,6-dihydro-1,4-dithiin-2,3-diselenol[4] with Cl_2SnBu_2 enabled us to obtain **4c** in 60% yield. On the other hand, tin thiolate **3d** could not be prepared by the synthetic method via Grignard reaction of ketone form **6**. Accordingly, we examined the synthetic route to **3d** from the disodium salt of the corresponding dithiol. Basic cleavage of **6** with NaOMe (2 equiv) / MeOH followed by treatment with Cl_2SnBu_2 / THF at - 78 °C gave **3d**.[5] Noncoupling reaction of both **3d** and **4c** with ester **5** in the presence of Me_3Al gave new DHTTFs **1d** (26% from **6**) and **2c** (42%), respectively.[6]

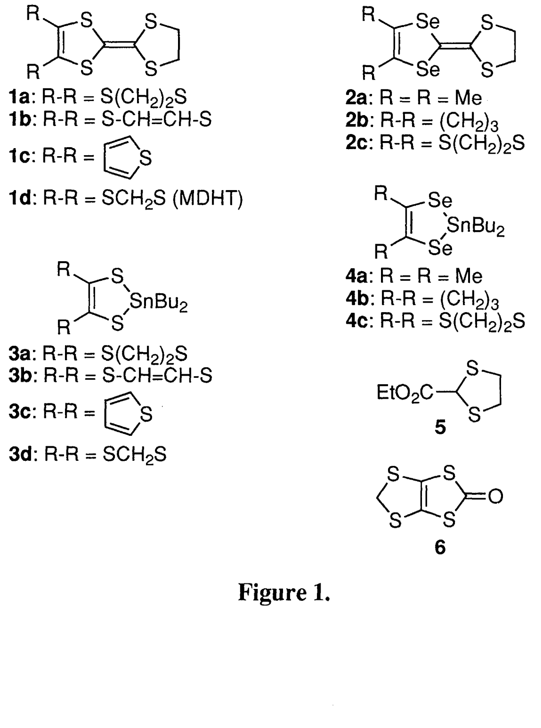

Figure 1.

Table 1. Oxidation potentials of DHTTF derivatives [a]

Compound	E_1	E_2	E_3	ΔE (E_2-E_1)
1a	0.63	1.02		0.39
1b	0.69	1.05		0.36
1c	0.75	1.17		0.42
1d	0.60	1.00	1.14 [b]	0.40
MDT-TTF	0.49	0.78		0.29
2a	0.56	0.97		0.41
2b	0.56	0.98		0.42
2c	0.73 [c]	—	—	—

[a] V vs. standard calomel electrode (SCE), 0.1 M $n\text{-}Bu_4NClO_4$ in CH_3CN, Pt electrode, at room temperature, under nitrogen, scan rate 50 mV s^{-1}. [b] Irreversible anodic peak potential. [c] Four other poorly-defined peaks exist at more anodic potential.

Table 1 compares oxidation potentials of DHTTFs (**1a**-**d** and **2a**-**c**) with that of MDT-TTF[7,8] as a representative unsymmetrical TTF derivative. The CVs of **1a**-**c** and **2a**,**b** revealed two pairs of reversible redox waves, whereas those of **1d** and **2c** exhibited irreversible redox waves. The E_1 value of **1d** was higher by 0.11 V than that of MDT-TTF, and the ΔE (E_2 - E_1) value of **1d** were larger than that of MDT-TTF. These tendencies were also the case for the E_1 and ΔE values of other DHTTFs (**1a**-**c** and **2a**,**b**).

The DHTTFs (**1a**-**d** and **2a**,**b**) formed their charge-transfer (CT) salts with TCNQ (tetracyanoquinodimethane), but all of their electrical conductivities at room temperature on single crystals were < 10^{-6} S cm^{-1}. Thus we investigated preparation of their radical cation salts with inorganic acceptors by electrocrystallization in appropriate solvents with a controlled current.[9] As listed in Table 2, two different types of I_3^- salts of **1a** were probably formed by changing solvents employed in electrocrystallization. The electrical conductivities of them were 10^{-3} – $<10^{-6}$ S cm^{-1} at room temperature. The room temperature conductivities of radical cation salts of **1a** with tetrahedral anions (BF_4^-, ClO_4^-, and ReO_4^-) showed higher values than those of CT complexes of **1a** with octahedral anions (PF_6^- and AsF_6^-). Among CT complexes of other DHTTFs (**1b**, **d**, and **2a**-**c**) with tetrahedral anions, the conductivities of the ClO_4^- and ReO_4^- salts of **2c** on compressed pellets were relatively high values of 2.3 and 1.0 S cm^{-1}, respectively. However, these CT complexes

Table 2. Electrical conductivities of radical cation salts based on **1** and **2**

Donor	Anion	Solvent	D : A [a]	σ_{rt} / S cm^{-1} [b]
1a	I_3	TCE [c]	1 : 1	< 10^{-6} [d]
1a	I_3	o-$C_6H_4Cl_2$	10 : 9	1.2 × 10^{-3} [d]
1a	BF_4	o-$C_6H_4Cl_2$	3 : 2	7.8 × 10^{-2} [e]
1a	ClO_4	PhCl	3 : 2	1.4 × 10^{-2} [e]
1a	ReO_4	o-$C_6H_4Cl_2$	5 : 4	1.3 × 10^{-4} [e]
1a	PF_6	PhCl	2 : 1	< 10^{-6} [d]
1a	AsF_6	PhCl	1 : 1	< 10^{-6} [d]
1b	BF_4	o-$C_6H_4Cl_2$	4 : 3	5.2 × 10^{-3} [e]
1b	ClO_4	o-$C_6H_4Cl_2$	—[f]	3.4 × 10^{-3} [e]
1d	$AuCl_2$	TCE [c]	5 : 2	5.8 × 10^{-2} [e]
1d	AuI_2	CH_3CN	2 : 1	60 [d]
1d	BF_4	o-$C_6H_4Cl_2$	7 : 2	3.7 × 10^{-3} [e]
2a	ClO_4	PhCl	2 : 1	< 10^{-6} [e]
2b	ClO_4	PhCl	1 : 1	< 10^{-6} [e]
2c	BF_4	o-$C_6H_4Cl_2$	3 : 2	8.9 × 10^{-2} [e]
2c	ClO_4	o-$C_6H_4Cl_2$	5 : 3	2.3 [e]
2c	ReO_4	o-$C_6H_4Cl_2$	3 : 2	1.0 [e]

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

exhibited semiconductor-type temperature dependances of conductivities (Ea: 0.15 eV for the ClO_4^- salt, and 0.22 eV for the ReO_4^- salt). Further, among AuX_2 (X = Cl, I) salts of **1d**, the AuI_2^- salt of **1d**[10] showed high room temperature conductivity (σ_{rt} = 60 S cm^{-1}) on a single crystal, and exhibited metallic conducting behavior down to 1.4 K essentially (Figure 2). Therefore, we are actively pursuing the preparation of a single crystal with higher quality suitable for X-ray diffractional analysis in order to clarify its crystal structure.

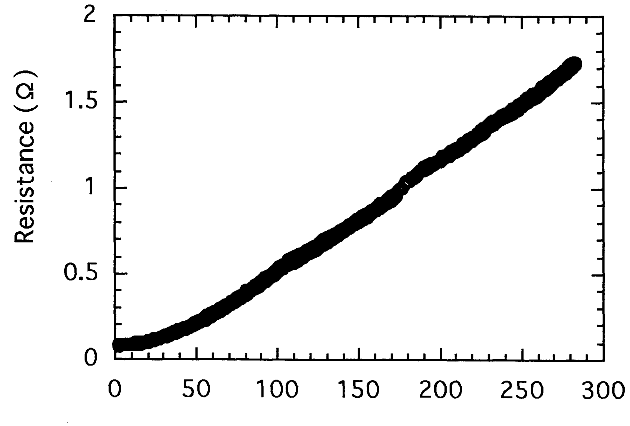

Figure 2. Temperature dependence of the resistances of $(MDHT)_2AuI_2$ on a single crystal.

In conclusion, although the π-electron system of DHTTFs is relatively less extended in comparison with those of the known organic π-donors [*e.g.*, TTFs, TTT (tetrathiatetracene), and TTN (tetrathianaphthalene)], one of cation radical salts based on DHTTFs showed the metallic temperature dependance of resistance. This finding breaks a way to the new class of organic metals.

References and Notes

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2 The electrochemistry of DHTTF itself was reported; D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971).

3 J. Yamada, Y. Amano, S. Takasaki, R. Nakanishi, K. Matsumoto, S. Satoki, and H. Anzai, *J. Am. Chem. Soc.*, **117**, 1149 (1995).

4 R. Kato, H. Kobayashi, and A. Kobayashi, *Synth. Met.*, **41-43**, 2093 (1991).

5 Tin thiolate **3d** tended to decompose through silica gel.

6 Compound **1d**: mp 129 °C (decomp); ^1H NMR (400MHz, $CDCl_3$) δ 3.47 (s, 4 H), 4.91 (s, 2 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 39.98, 44.77, 117.20, 117.33, 119.54; MS m/z (% relative intensity) 282 (100, M^+); HRMS m/z 281.8795. Calcd for $C_7H_6S_6$ m/z 281.8794; Anal. Found: C, 29.77; H, 2.08%. Calcd for $C_7H_6S_6$: C, 29.76; H, 2.14%. Compound **2c**: mp 201 °C (decomp); ^1H NMR (400MHz, $CDCl_3$) δ 3.29 (s, 4 H), 3.52 (s, 4 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 31.09, 40.90, 97.61, 114.03, 125.64; MS m/z (% relative intensity) 392 (100, M^++2), 390 (85, M^+); HRMS m/z 391.7812. Calcd for $C_8H_8S_4{}^{80}Se_2$ m/z 391.7839. Anal. Found: C, 24.53; H, 2.00%. Calcd for $C_8H_8S_4Se_2$: C, 24.61; H, 2.07%.

7 MDT-TTF = methylenedithiotetrathiafulvalene: G. C. Papavassiliou, G. A. Mousdis, J. S. Zameounis, A. Terzis, A. Hountas, B. Hilti, C. W. Mayer, and J. Pfeiffer, *Synth. Met.*, **27**, B379 (1988).

8 Preparation of MDT-TTF could also be carried out by the Me_3Al-mediated noncoupling reaction of tin thiolate **3d** with the corresponding ester in 16% overall yield from **6**.

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10 The AuI_2^- salt of **2c** could not be obtained under the similar electrochemical oxidation conditions. Preparation of the AuI_2^- salts based on other DHTTFs is in progress.