Radical-cation salts based on TTF(s)–DHTTF (dihydrotetrathiafulvalene) fused donors: electrical conductivities and crystal structure

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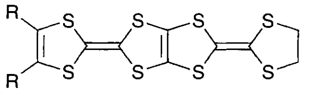
The electrochemical properties of TTF(s)–DHTTF fused donors, the electrical conductivities of their radical-cation salts, and the crystal structure of $(3)_2AuI_2$ are described.

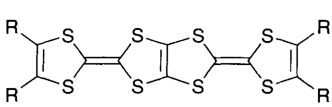
We have already reported the conducting behaviour of radical-cation salts based on DHTTF derivatives[1] and the efficient synthesis of TTF(s)–DHTTF fused donors **2**–**4**.[2] Of all the radical-cation salts composed of DHTTFs so far prepared, only $(MDHT†)_2AuI_2$ is metallic down to low temperatures.[1] On the other hand, recent investigations on the radical-cation salts prepared from TTF(s)–TTF(s) fused donors[3] have suggested that the insertion of a tetrathiapentalene unit into the central C=C bond of the TTF skeleton is one of the most promising molecular designs for new π-electron donors leading to two-demensional organic metals stable down to low temperatures. Therefore, it is interesting to reveal whether this molecular design is also applicable to the DHTTF skeleton or not. Here we disclose the oxidation potentials of TTF(s)–DHTTF fused donors **1**–**3** by cyclic voltammetry (CV), the electrical conductivities of radical-cation salts based on **1**–**4**, and the crystal structure of $(\mathbf{3})_2AuI_2$.

As shown in Scheme 1, the synthesis of **1**‡ was carried out according to a standard synthetic method *via* demethoxycarbonylation of **5**. Table 1 compares oxidation potentials (by CV) of **1**–**3** with that of EDHT **6**§ as a representative DHTTF derivative. A satisfactory CV of **4** could not be obtained because of its insolubility in the solvent used for the measurement. Although the CVs of **1** and **3** exhibited irreversible redox waves, that of **2** revealed three pairs of reversible single-electron redox waves. The E_1 value of **3** was lower by 0.05 V than that of **6**, and the ΔE $(E_2 - E_1)$ value of **3** was smaller by 0.22 V than that of **6**. These results suggest that both an enhancement in donating ability and a decrease in on-site coulombic repulsion in the dication state are achieved by the introduction of a tetrathiapentalene unit into the central C=C bond of EDHT.

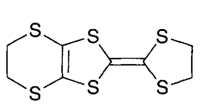


TTF(s)-DHTTF fused system

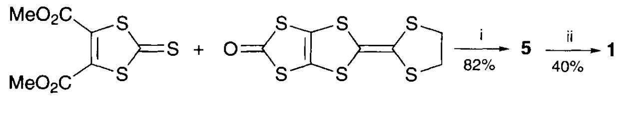
1 R = R = H (DTDH-TTP)
2 R = R = SMe (MTDH-TTP)
3 R-R = $S(CH_2)_2S$ (EDDH-TTP)
4 R-R = SCH_2S (MDDH-TTP)
5 R = R = CO_2Me



TTF(s)-TTF(s) fused donors



EDHT **6**



Scheme 1 *Reagents and conditions*: i, $(MeO)_3P$ in toluene, reflux, 2 h; ii, $LiBr{\cdot}H_2O$ (10 equiv.) in HMPA, 90 °C, 1 h, 110 °C, 1 h

Conducting behaviour of the radical-cation salts based on **1**–**4** is summarized in Table 2. Preparation of the TCNQ (tetracyanoquinodimethane) complex was carried out by reaction with TCNQ followed by recrystallization from thf upon slow cooling. The radical-cation salt with TCNQ was prepared by controlled-current electrochemical oxidation[4] in 1,1,2-trichloroethane (TCE) or thf containing the corresponding tetrabutylammonium salt. The parent DTDH–TTP **1**¶ produced metallic radical-cation salts with TCNQ and the anions

Table 1 Oxidation potentials of **1**–**3** and **6**[a]

Compound	E_1	E_2	E_3	E_4	ΔE $(E_2 - E_1)$
1	0.46	0.75	0.91	0.98[b]	0.29
2	0.57	0.82	1.18		0.25
3	0.57	0.78	1.23		0.21
EDHT (**6**)	0.62	1.05			0.43

[a] In V *vs.* saturated calomel electrode (SCE), 0.1 M $NBu^n{}_4ClO_4$ in PhCN, Pt electrode, at room temperature, under nitrogen, scan rate 50 mV s^{-1}. [b] Two other peaks occur at more anodic potential.

Table 2 Electrical conductivities of radical-cation salts based on **1**–**4**

Donor	Acceptor	Solvent	D : A[a]	σ_{rt}/S cm^{-1}[b]
1	TCNQ	THF	1 : 1	45[c] (T_{MI}[d] = 110 K)
1	AuI_2	TCE[e]	5 : 4	450[f] (metallic down to 4.2 K)
1	ClO_4	TCE	—[g]	17[f] (T_{MI} = 32 K)
1	AsF_6	TCE	5 : 4	4.2[c] (T_{MI} = 150 K)
2	TCNQ	THF	1 : 1	0.08[c] (E_a = 24 meV)
2	I_3	THF	4 : 1	7.0[f] (E_a = 280 meV)
2	BF_4	TCE	5 : 2	33[f] (E_a = 41 meV)
2	ClO_4	TCE	—[g]	22[f] (E_a = 16 meV)
2	PF_6	TCE	5 : 2	130[f] (metallic down to 4.2 K)
2	AsF_6	TCE	5 : 2	170[f] (metallic down to 4.2 K)
3	TCNQ	THF	5 : 3	8.6[c] (E_a = 23 meV)
3	I_3	TCE	5 : 2	9.6[c] (T_{MI} = 160 K)
3	AuI_2	THF	2 : 1	14[f] (metallic down to 4.2 K)
3	BF_4	TCE	2 : 1	2.3[c] (E_a = 33 meV)
3	ClO_4	TCE	—[g]	18[c] (E_a = 40 meV)
3	PF_6	TCE	2 : 1	58[f] (metallic down to 4.2 K)
3	AsF_6	TCE	2 : 1	16[f] (metallic down to 4.2 K)
4	I_3	TCE	2 : 1	3.1[c] (E_a = 48 meV)
4	AuI_2	TCE	2 : 1	1.3[c] (E_a = 120 meV)

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

examined. In particular, the AuI_2^- salt of **1** as a single crystal exhibited high room-temperature conductivity (450 S cm^{-1}), and remained in the metallic state to 4.2 K. Among the MTDH–TTP based salts (**2**), those with octahedral anions (PF_6^-, AsF_6^-) showed metallic conducting behaviour down to 4.2 K. Similarly, the PF_6^- and AsF_6^- salts of EDDT–TTP **3** were also metallic down to 4.2 K. In addition, the compressed pellet of the EDDT–TTP salt with I_3^- was metallic down to 160 K, and the single crystal of (EDDT–TTP)$_2$AuI$_2$ exhibited a metallic temperature dependance of resistivity down to 4.2 K. On the other hand, the MDDT–TTP **4** salts with linear anions (I_3^-, AuI_2^-) indicated semiconductive resistive temperature dependence.

The crystal structure of (EDDT–TTP)$_2$AuI$_2$ was determined by X-ray diffraction.‖ The structure consists of κ-type sheets of EDDT–TTP donor molecules and sheets of AuI$_2$ anions, as illustrated in Fig. 1. It is significant that EDDT–TTP is the first TTF(s)-fused donor producing a κ-type 2 : 1 salt;[5] note that many organic superconductors are of this structure.[6] The interplanar distance between pairs of donor molecules is 3.41 Å and the dihedral angle of the molecular planes between pairs is 80.72°. These values are almost the same as those (3.38 Å, 88°) in κ-(ET)$_2$Cu(SCN)$_2$.[7] In (EDDT–TP)$_2$AuI$_2$, each donor molecule is also linked by several S···S contacts shorter than the sum of the van der Waals radii, in the sheet, as shown in Fig. 2, which is responsible for the metallic conductivity of this salt down to low temperature.

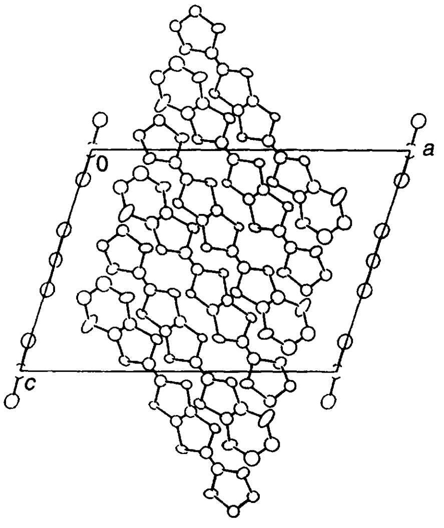


Fig. 1 Crystal structure of (EDDH–TTP)$_2$AuI$_2$ viewed down the *b* axis

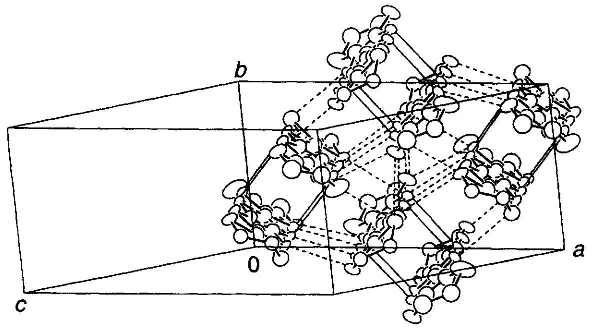


Fig. 2 Structure of the donor sheet in (EDDH–TTP)$_2$AuI$_2$; intrapair short S···S contacts (< 3.70 Å) are indicated by lines, and interpair short S···S contacts are indicated by dotted lines

Further investigations on preparation and X-ray characterisation of radical-cation salts based on TTF(s)–DHTTF fused donorare in progress.

Footnotes

† MDHT = methylenedithiodihydrotetrathiafulvalene, see ref. 1.

‡ *Physical and spectroscopic data* for **1**: mp 210 °C (decomp.); ^{1}H NMR (400MHz, CDCl$_3$–CS$_2$) δ 3.50 (s, 4 H), 6.35 (s, 2 H); MS *m/z* (% relative intensity) 382 (100, M$^+$); HRMS *m/z* 381.8229. Calc. for C$_7$H$_6$S$_6$ *m/z* 381.8235.

§ EDHT = ethylenedithiodihydrotetrathiafulvalene, see ref. 2.

¶ *Abbreviations*: DTDH–TTP, 2-(1′,3′-dithiol-2′-ylidene)-5-(1″,3″-dithiolane-2″-ylidene)-1,3,4,6-tetrathiapentalene; MTDH–TTP, 2-[4′,5′-bis-(methylthio)-1′,3′-dithiol-2′-ylidene]-5-(1″,3″-dithiolane-2″-ylidene)-1,3,4,6-tetrathiapentalene; EDDH–TTP, 2-[4′,5′-(ethylenedithio)-1′,3′-dithiol-2′-ylidene]-5-(1″,3″-dithiolane-2″-ylidene)-1,3,4,6-tetrathiapentalene; MDDH–TTP, 2-[4′,5′-(methylenedithio)-1′,3′-dithiol-2′-ylidene]-5-(1″,3″-dithiolane-2″-ylidene)-1,3,4,6-tetrathiapentalene.

‖ *Crystal data* for (EDDT–TTP)$_2$AuI$_2$: (C$_{12}$H$_8$S$_{10}$)$_2$AuI$_2$, *M* = 1396.49, monoclinic, space group $P2_1/c$, a = 18.599(5), b = 8.028(2), c = 13.712(4) Å, β = 107.61(2)°, U = 1951.5(9) Å^3, Z = 2, D_c = 3.199 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, μ = 63.82 cm^{-1}, F(000) = 1314. The data were collected on a Mac Science MXC18 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 Au, I and S atoms and anisotropic for C atoms) to R = 0.061 and R_w = 0.068 for 1194 observed [$I \geqslant 5\sigma(I)$] reflections from 3970 independent reflections. All calculations were performed using CRYSTAN (MacScience, Japan). 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 182/263.

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