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Conducting charge-transfer and radical ion salts based on bitetrathiafulvalenes; an approach to organic metals using stoichiometry control

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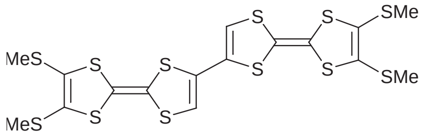
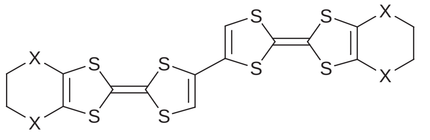
Charge-transfer and radical ion salts of 4,5,4‴,5‴-tetramethylthio-, 4,5,4‴,5‴-bis(ethylenedithio)-, and 4,5,4‴,5‴-bis(ethylenedioxy)-4′,4″-bitetrathiafulvalenes showed fairly high electric conductivities, reflecting the effect of stoichiometry control.

Since the discovery of the properties of TTF in 1970,[1] much effort has been devoted to designing new analogues of this π-donor in order to improve the electroconductive properties of the corresponding salts.[2] One of the most important concepts to realize the high electric conductivities is the enhancement of the dimensionality which can be attained by use of dichalcogen-capped TTF or by the extended π-conjugation of the TTF framework.[3] Recently, Bechgaard *et al.* proposed 'stoichiometry control in organic metals' by using a dimeric TTF as a donor component.[4] We now report here the first example of the highly conducting ion radical salts based on bitetrathiafulvalenes **1**–**3**, the simplest donors in the dimeric TTF group.



1 (TMT-biTTF)



2 (BEDT-biTTF): X = S
3 (BEDO-biTTF): X = O

Previously, we reported the synthesis of bitetrathiafulvalene (biTTF) using the palladium-catalyzed homo-coupling reaction of trialkylstannyl–TTF.[5,6] Since combination of dimeric donors and acceptors can be expected to lead to a 1:1 stoichiometry of charge-transfer and radical ion salts containing an interesting double Fermi surface,[4] we have investigated the CT-complexes and radical ion salts of biTTFs (**1**,[6a] **2** and **3**).† As estimated by oxidation potentials,† **3** formed CT-complex with TCNQ, whereas **1** and **2** formed those with DDQ. The radical ion salts were prepared by electrochemical oxidation of **1**–**3** in a suitable solvent containing the corresponding tetrabutylammonium salt (Table 1). The CT-complex derived from **3** with TCNQ showed a fairly high room-temperature conductivity (3.6 S cm^{-1}), whereas the **2**-DDQ complex is a semiconductor (0.84 S cm^{-1}). Although the ClO_4^- salt of **1** was a semiconductor, the I_3^-, AuI_2^- and BrI_2^- salts of **2** exhibited high conductivities (125, 778 and 80 S cm^{-1}) with metallic behavior down to 240, 285 and 240 K, respectively, being transformed at lower temperature to semiconductors with low activation energies. Furthermore, the ClO_4^- salt of **3** indicated semiconductive resistive temperature dependence (6.9 S cm^{-1}) with a small activation energy (35 meV), whereas the I_3^- salt of **3** was metallic (8.0 S cm^{-1}) down to 135 K. The ClO_4^- salt of **1** and **3** and the AuI_2^- and BrI_2^- salts of **2** consist of the 1:1 stoichiometry of the donor and its anion. If we assume each TTF moiety independent, the band may be 3/4 filled. In contrast, the **2**-DDQ complex and the I_3^- salt of **2** are made up of the 2:1 stoichiometry, the TCNQ complex and the I_3 salt of **3** being composed of the 3:1 stoichiometry. Thus, the formal charge-transfers in these compounds are 1/8 and 1/12, respectively, for one TTF unit, although the crystal structures of these compounds are unknown so far. It is worth noting that the stoichiometry control can be easily achieved by using biTTFs **1**–**3** to form a new type of organic metals with the desired 1:1, 1:2 and 1:3 donor-acceptor ratio.

In order to clarify the crystal packings of novel radical salts derived from **1**–**3**, the crystal structure of **3**·ClO_4 was determined by X-ray diffraction method.‡ As shown in Fig. 1 and 2, the radical ion salt of **3** shows a unique crystal packing, reflecting a dimeric TTF structure. The net charge on a donor molecule is expected to be +1 due to the 1:1 composition, the charge being half full in each TTF unit (the band is 3/4 filled). The biTTF framework in **3**·ClO_4 exhibits a planar structure, the maximum atomic deviation from the least-squares plane of the biTTF unit excepting the ethylenedioxy rings being 0.18 Å.

As shown in Fig. 1 and 2, the cation radical forms a conducting sheet in the *ac* plane to make a segregated column.

Table 1 Electrical conductivities of CT-complexes and radical ion salts derived from **1**–**3**

Donor	Acceptor	Solvent	D:A[a]	$\sigma_{rt}{}^b$/S cm^{-1}
1	ClO_4	THF	1:1[c]	9.4×10^{-2}
2	DDQ	C_6H_6	2:1	8.4×10^{-1}
2	I_3	THF	2:1	125 (metallic)
2	AuI_2	THF	1:1	778 (metallic)
2	BrI_2	PhCl	1:1	80 (metallic)
3	TCNQ	PhCl	3:1	3.6 ($E_a = 72$ meV)
3	ClO_4	THF	1:1[c]	6.9 ($E_a = 35$ meV)
3	I_3	PhCl	3:1	8.0 (metallic)

[a]Determined by elemental analysis. [b]Room-temperature conductivity measured on a single crystal by a four-probe technique. [c]Determined by X-ray analysis.

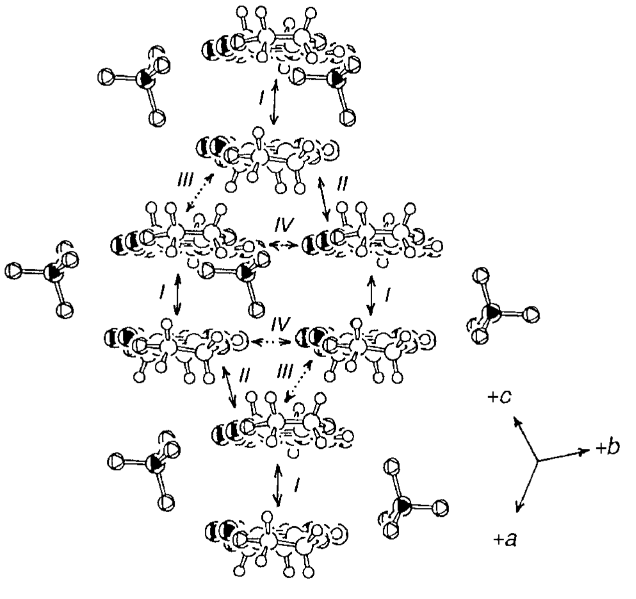


Fig. 1 Crystal structure of BEDO-biTTF **3**·ClO$_4$: the conducting path in the *ac* plane. The solid arrows indicate a full overlap of two biTTF units, the dashed arrows corresponding to a half overlap of two biTTF units. Overlap integrals ($\times 10^3$) of the conduction orbitals in **3**·ClO$_4$ are as follows (only the interactions $>1\times10^{-3}$ are indicated). [I: (A–A)=9.3, (A–B)=(B–A)=−22.7, (B–B)=−14.1; II: (A–A)=3.4, (A–B)=(B–A)=−11.1, (B–B)=−5.6; III: (A–A)=−4.0, (A–B)=(B–A)=−2.0; IV: (A–A)=1.7, (B–A)=−10.88, (B–B)=−4.1].

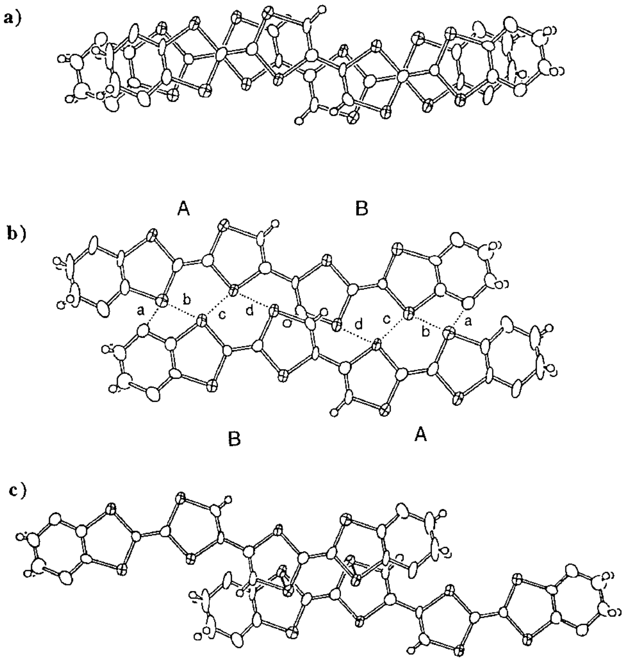


Fig. 2 The intra- and inter-stack overlaps of cation radicals in the structure of **3**·ClO$_4$: (a) the overlap I in Fig. 1; (b) the overlap II in Fig. 1 and inter-columnar S···S and S···O distances indicated by dotted lines (a=3.48, b=3.78, c=3.70, and d=3.83 Å); (c) the overlap III in Fig. 1 and intra-column short S···S contacts (3.69 Å) indicated by solid lines.

There are four intra- and inter-stack interactions between the cation radicals. Interestingly, the two overlaps (I and II) are made up of the whole molecules, *i.e.*, Fig. 2(a) and (b), whereas the other two (III and IV) are constructed by the interaction between only one TTF moieties of the cation radical, *i.e.*, Fig. 2(c). The BEDO-biTTF molecules are stacked face-to-face to form a dimeric structure [Fig. 2(a)] and the dimers are arranged in the so-called β′-type structure to form a conducting sheet. Although this dimer structure resembles that of β′-(BEDT-TTF)$_2$·ICl$_2$,[7] the interdimer interactions are strong enough to lead to a two-dimensional conducting sheet. Since one molecule contains two TTF units, the next HOMO in the molecular orbital calculations has appeared very close to the HOMO level (ΔE=0.08 eV). The next HOMO and HOMO are mainly located on the left (A) and right (B) halves of the molecule, respectively [Fig. 2(b)], and have correct symmetry for the TTF HOMO. The A and B units within the same molecule have the interaction of the order of 0.5ΔE= 0.04 eV, *i.e.*, 4×10^{-3} as the orbital overlap, but this is no longer a intermolecular interaction as described below. Then, we have taken both the next HOMO and HOMO into account, so that each intermolecular interaction has four kinds of interactions (A–A, A–B, B–A, and B–B). This assumes intermolecular overlaps as if the A and B parts were independent molecules. The face-to-face distance in Fig. 2(a) is 3.40 Å, and the overlap integral of the conduction orbitals seems to be fairly large [I: (A–B)=(B–A)=-22.7×10^{-3}]. There are no short S···S contacts less than the sum of van der Waals radii (3.70 Å) in the side-by-side overlap in Fig. 2(b), but the six S···S contacts (3.70–3.83 Å) can contribute to make a conducting path [II: (A–B)=(B–A)=-11.1×10^{-3}]. The face-to-face interaction (III) and the side-by-side interaction (IV) seems to be strong through the S···S short contacts [III: 3.69 Å in Fig. 2(c); IV: 3.45, 3.46 and 3.59 Å]. Although the interactions III and IV are mediated by only one TTF part, these interactions are moderately large [III: (A–A)=-4.0×10^{-3}; IV: (B–A)=-10.9×10^{-3}]. Consequently, **3**·ClO$_4$ shows a fairly high conductivity with a small activation energy, reflecting a two-dimensional band structure in contrast to the one-dimensional β′-phase.

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Notes and references

†The starting materials **1**–**3** were prepared from the corresponding trimethylstannyl–TTF derivatives: E. Ogura, Y. Kuwatani and M. Iyoda, manuscript in preparation. The oxidation potentials of **1**–**3** measured by cyclic voltammetry are as follows. **1**: $E^1{}_{1/2}$=0.48 V, $E^2{}_{1/2}$=0.59 V, $E^3{}_{1/2}$=0.87 V; **2**: $E^1{}_{1/2}$=0.48 V, $E^2{}_{1/2}$=0.58 V, $E^3{}_{1/2}$=0.86 V; **3**: $E^1{}_{1/2}$=0.42 V, $E^2{}_{1/2}$=0.52 V, $E^3{}_{1/2}$=0.87 V.

‡X-ray intensity data were measured on a Rigaku AFC7R diffractometer with Mo-Kα radiations using a crystal with the dimension of $0.08\times0.15\times0.22$ mm. A total of 4167 reflections were collected up to 2θ=55.0°, of which 1371 had $I>3.00\sigma(I)$, and were used in the refinement. The crystal structure was solved by a direct method (SHELXS86), expanded using Fourier techniques (DIRDIF94), and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically, and the two hydrogen atoms attached to TTF nuclei were refined isotropically. Other eight hydrogens (methylene protons) were located at calculated positions.

Crystal data for **3**·ClO$_4$: C$_{16}$H$_{10}$O$_8$S$_8$Cl, M=622.18, triclinic, space group $P\bar{1}$ (no. 2), a=9.937(2), b=13.685(2), c= 8.431(3) Å, α=94.18(2), β=97.37(2), γ=100.32(1)°, V= 1113.2(5) Å^3, Z=2, D_c=1.856 g cm^{-3}, R=0.048 and R_w= 0.048 for 307 variables.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/129.

See http: //www.rsc.org/suppdata/jm/1998/335/ for crystallographic files in .cif format.

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