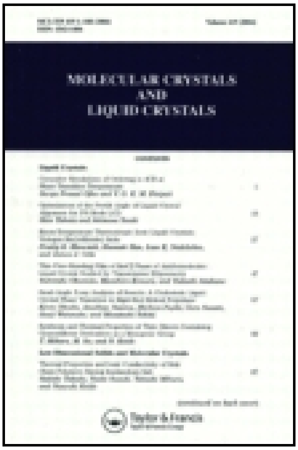

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Highly-Oxidized States of Organic Donor Bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF)

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HIGHLY–OXIDIZED STATES OF ORGANIC DONOR BIS(ETHYLENEDIOXY)TETRATHIAFULVALENE (BEDO–TTF)

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Abstract The monocation and dication salts of bis(ethylenedioxy)-tetrathiafulvalene (BEDO–TTF) were newly obtained by chemical oxidation by iodine. Their structural and physical properties are discussed.

INTRODUCTION

The molecular conductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF or ET) have attracted considerable interest because of rich variety in the physical and structural properties as well as the discovery of a number of superconductors.[1] The oxygen analog of ET, bis(ethylenedioxy)tetrathiafulvalene (BEDO–TTF) have revealed different peculiarity, namely, strong stabilization of self–assembled structure and of metallic state in the charge–transfer (CT) complexes.[2,3] However, the oxidation state of BEDO–TTF in the metals are partial CT ground state only between +1/3 and +2/3. In order to realize the control of conducting properties by tuning the band filling, we have started to explore various oxidation state of this donor. In the present study, chemical oxidation afforded three new phases of (BEDO–TTF)–I system, which include monocation and dication salts of BEDO–TTF. This paper describes their structural and physical properties.

PREPARATION OF BEDO–TTF SALTS

The chemical oxidation of BEDO–TTF by I_2 in acetonitrile solution produced three new salts; (BEDO–TTF)I_3 (2), (BEDO–TTF)$(I_3)_2$ (3), and (BEDO–TTF)I_{10-y} (y = 0.4–0.5) (4), whereas (BEDO–TTF)$_{2+x}I_3$ (1) (x = 0.2) precipitated by the oxidation in THF. Table I summarizes the conditions of preparation and appearances of these salts. The single crystals of 2 were grown by diffusion method and the mixture of single crystals of 3 and 4 were obtained by slow cooling. The stoichiometries were determined by the elemental analysis (±0.3 % for C, H, O, and I) for 1, 2, and 4, and by x-ray structural analysis for 2 and 3. The stoichiometry of 1 is close to that of known metallic $(BEDO\text{-}TTF)_{2.4}I_3$ salt.[4] The salt 4 was also found to be non-stoichiometric by the elemental analysis performed after eliminating crystals of 3 under the microscope. However, at present, it is not clear whether the non-stoichiometric character is due to remaining slight amount of contaminant 3.

TABLE I Preparation and appearances of (BEDO-TTF)-I salts.

Solvent	Mixing Ratio $(BEDO\text{-}TTF:I_2)$	Products	Mp (dec.) (°C)	Appearance
THF	3:4	$(BEDO\text{-}TTF)_{2+x}I_3$ (1) (x = 0.2)	151-155	greenish lustrous needles
CH_3CN	2:3	$(BEDO\text{-}TTF)I_3$ (2)	155-160	black plates
CH_3CN	1;11	$(BEDO\text{-}TTF)(I_3)_2$ (3) (minor)	157-162	black plates
		$(BEDO\text{-}TTF)I_{10-y}$ (4) (y = 0.4-0.5) (major)	152-155	black hexagonal rods

The oxidation by iodine were found to be successful to yield a series of salts with various oxidation states of BEDO-TTF (+0.45, +1, and +2). According to the cyclic voltammetric measurements (in acetonitrile, 0.1 M $(TBA)BF_4$, 10 mV/s, Pt working electrode), the first reduction half-wave potential of I_2 ($E_{1/2}{}^1(I_2)$ = +0.66 V vs SCE) is 0.23 V higher than the first oxidation potential of BEDO-TTF ($E_{1/2}{}^1(D)$ = +0.43 V) and comparable to the second oxidation potential ($E_{1/2}{}^2(D)$) of this donor (+0.69 V). Therefore iodine can oxidize BEDO-TTF not only to +1 but also to +2 state. On the other hand for ET, $E_{1/2}{}^2(D)$ (+0.78 V) is 0.12 V higher than $E_{1/2}{}^1(I_2)$, indicating that iodine oxidation of ET is difficult to give +2 state compared with BEDO-TTF. In fact for ET-I system, although numerous crystal phases have been obtained by both chemical and electrochemical oxidation, no dication salts have been reported so far.

STRUCTURAL PROPERTIES

Table II shows the crystallographic data of 2, 3 and 4. The structural analysis of 4 is in progress.

TABLE II Crystallographic data.

	2	3	4
a (Å)	7.632(1)	7.989(2)	10.021(1)
b (Å)	7.654(3)	10.566(1)	11.165(1)
c (Å)	16.168(4)	7.2579(9)	7.325(1)
α (°)	76.51(2)	96.54(1)	94.17(1)
β (°)	82.73(1)	110.48(1)	110.79(1)
γ (°)	77.95(2)	92.08(1)	75.985(9)
V (Å^3)	895.2(4)	568.3(2)	743.3(2)
space group	$P\bar{1}$	$P\bar{1}$	(triclinic)
Z	2	1	
R	0.040	0.071	

(BEDO-TTF)I_3 (2)

Final positional parameters for 2 are given in Table III. The BEDO-TTF molecule is located on a general position, while each of two I_3^- anions occupies a center of inversion. The BEDO-TTF molecule is slightly bent into a tub-shape. Both I_3^- molecules are strictly linear and have I-I bond lengths of 2.92(2) Å.

The crystal packing contains mixed layers consisting of both BEDO-TTF and I_3^- anion molecules (Figure 1) as in the case of γ-$(ET)_3(I_3)_{2.5}$, δ-$(ET)I_3(TCE)_{0.333}$.[5] The dimerized BEDO-TTF molecules and I_3^- anions form alternating stack along the *a+b* direction in the mixed (BEDO-TTF)-I_3 layers, which are separated by layers of another crystallographically independent I_3^- anions. The BEDO-TTF molecules form a dimer with almost eclipsed face-to-face overlap in contrast with the other BEDO-TTF radical salts where the molecules overlap in slipped manner along the lateral direction of the molecule. Short intermolecular S··S distances are observed not only within a dimer (3.306-3.313 Å) but also between dimers (3.433-3.472 Å). On the other hand, the distances of atomic contacts between the I_3^- and BEDO-TTF molecules are longer than the van der Waals radii (vdW) sums,[6] indicating that the I_3^- molecules are loosely packed within the mixed layer. All the intermolecular I-I distances are longer than the vdW sums in this crystal.

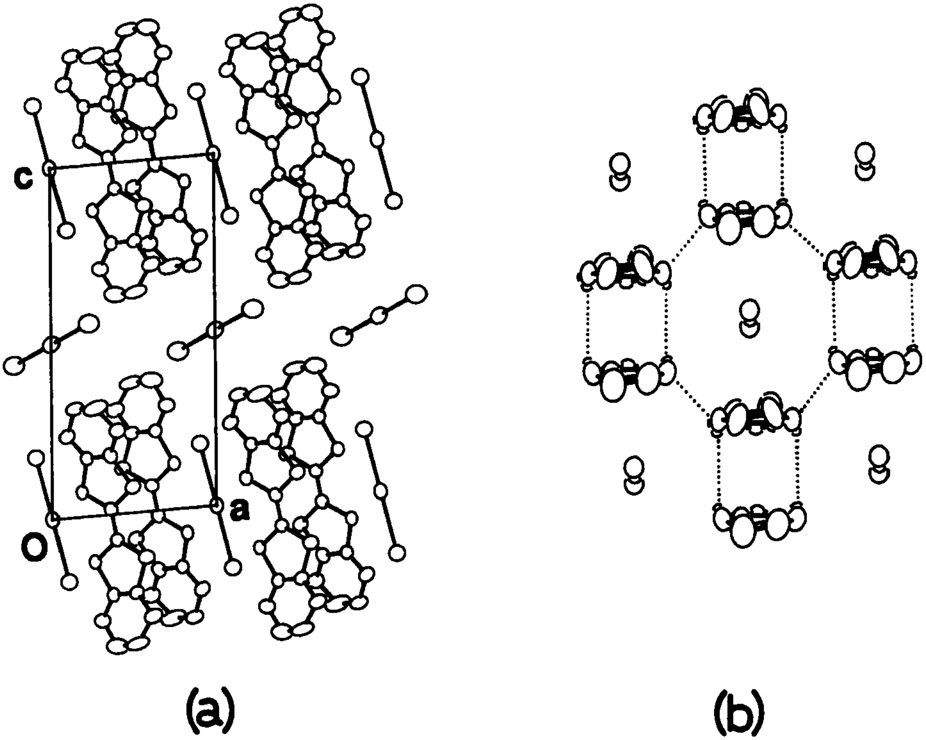


FIGURE 1 (BEDO-TTF)I_3 (2). (a) Crystal structure projected along the *b*-axis, and (b) molecular packing in the (BEDO-TTF)-I_3 mixed layer projected along the longitudinal axis of BEDO-TTF molecule. Intermolecular short S··S contacts are represented by dotted lines.

Figure 2 shows the energy dispersion and density of states based on the tight binding calculation within the framework of the extended Hückel method. Since the intradimer interaction is very large (overlap integral = 57.1×10^{-3}) compared with the interdimer interaction (25.2×10^{-3} and 23.8×10^{-3}), an energy gap opens between the two bands derived from HOMOs. With the oxidation state of BEDO-TTF$^+$, the lower band becomes completely filled, which qualitatively agrees with the insulating and diamagnetic nature of this salt (see below).

TABLE III Atomic coordinates and equivalent isotropic thermal parameters for (BEDO–TTF)I_3 (2).

Atom	x	y	z	B_{eq}
I1*	1.0000	1.0000	0.0000	3.28
I2*	1.0000	0.5000	0.5000	4.87
I3	0.9016(1)	0.8571(1)	0.17957(5)	4.38
I4	0.7710(2)	0.8570(1)	0.44930(6)	6.10
S1	0.5091(3)	0.8411(3)	-0.07400(15)	3.06
S2	0.8206(3)	0.5401(3)	-0.07034(15)	3.09
S3	0.4288(3)	0.7083(3)	0.12865(15)	3.21
S4	0.7416(3)	0.4104(4)	0.13003(15)	3.19
C1	0.6429(11)	0.6526(11)	-0.0151(6)	2.89
C2	0.6458(12)	0.8349(11)	-0.1677(6)	2.96
C3	0.7897(11)	0.6971(12)	-0.1650(5)	2.84
C4	0.734(3)	0.9580(19)	-0.3076(8)	5.98
C5	0.8617(18)	0.798(2)	-0.3100(7)	5.80
C6	0.6062(11)	0.5967(11)	0.0730(5)	2.75
C7	0.4877(12)	0.5747(13)	0.2264(6)	3.13
C8	0.6299(11)	0.4365(13)	0.2275(6)	3.03
C9	0.483(3)	0.530(3)	0.3709(8)	7.07
C10	0.608(3)	0.370(3)	0.3734(10)	7.42
O1	0.6025(9)	0.9666(10)	-0.2375(5)	3.88
O2	0.9099(10)	0.6723(11)	-0.2325(5)	3.90
O3	0.3886(11)	0.6169(12)	0.2971(5)	4.36
O4	0.6989(10)	0.3250(12)	0.2980(5)	4.23

* Site occupancy was 0.5.

$B_{eq} = (4/3)(B_{11}/a^{*2} + B_{22}/b^{*2} + B_{33}/c^{*2})$.

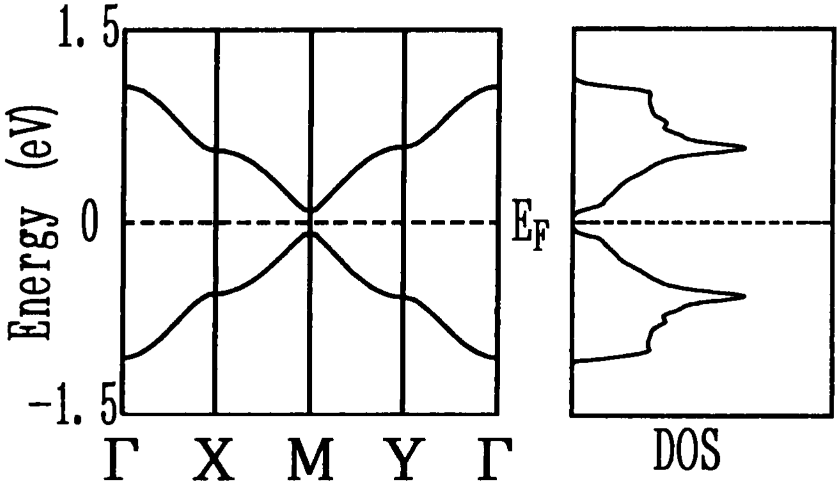


FIGURE 2 Calculated energy band and density of state (DOS) of (BEDO–TTF)I_3 (2). Γ = (0, 0), X = (a^*/2, 0), M = (a^*/2, b^*/2), Y = (0, b^*/2).

(BEDO-TTF)$(I_3)_2$ (3)

Final positional parameters for 3 are given in Table IV. The BEDO-TTF molecule and I_3^- anion are located on a center of inversion and on a general position, respectively. The I_3^- molecule is almost linear (I-I-I angle of 178.01°) and has I-I bond lengths of 2.887(2) and 2.959(2) Å. As shown in Figure 3, all molecules are oriented almost parallel to each other, and form DAA type stack along the *a-c* direction. The donor molecules are completely isolated from each other by the surrounding I_3^- anions, having a number of short S⋯I distances (3.60-3.78 Å). Short I-I distance (3.739(3) Å) is found between the I_3^- molecules neighboring along the long molecular axis with each other. It is interesting to compare the structures of the donor-anion mixed layer in 2 (Figure 1b) and of a layer of 4 (Figure 3b). Replacing the donor molecules and the I_3^- anions in the former salt with each other gives the packing pattern of the latter one.

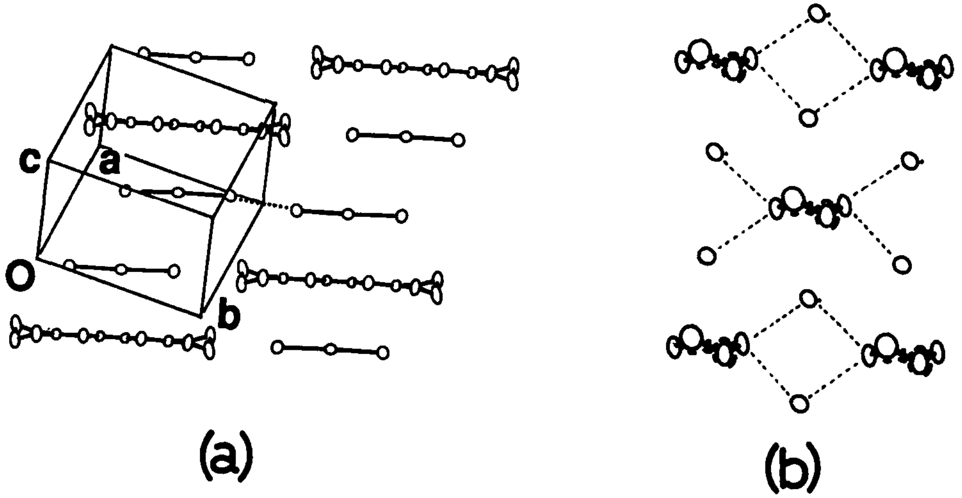


FIGURE 3 (BEDO-TTF)$(I_3)_2$ (3). Crystal structure projected along (a) the transverse and (b) longitudinal axes of BEDO-TTF molecule. Intermolecular short I⋯I and S⋯I contacts are shown by dotted lines.

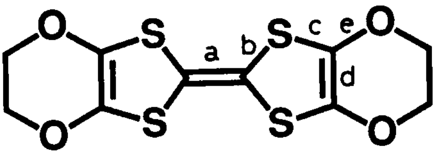
The averaged bond lengths of BEDO-TTF molecules with different oxidation states are summarized in Table III. Oxidation of BEDO-TTF results in an increase in C-S and C-O bond lengths (denoted by b, c, and e) and a decrease in C=C bond lengths (a and d). This qualitatively agrees with the MO calculation that the BEDO–TTF HOMO has nodes at C–S and C–O bonds.[3] Similar results are reported for the correlation between bond lengths and oxidation state (0–2) of ET molecule.[7]

TABLE IV Atomic coordinates and equivalent isotropic thermal parameters for (BEDO–TTF)$(I_3)_2$ (3).

Atom	*x*	*y*	*z*	B_{eq}
S1	0.7637(7)	0.3980(5)	0.2744(7)	2.57
S2	1.0291(7)	0.3222(5)	0.6239(7)	2.51
C3	0.957(2)	0.4369(15)	0.478(2)	2.05
C4	0.735(2)	0.2447(16)	0.316(2)	2.18
C5	0.869(2)	0.2058(17)	0.483(2)	2.28
C6	0.563(3)	0.055(2)	0.280(3)	3.68
C7	0.749(4)	-0.002(3)	0.377(4)	5.55
O8	0.597(2)	0.1673(14)	0.194(2)	3.14
O9	0.869(2)	0.0927(13)	0.535(2)	3.05
I1	0.0942(2)	0.1698(2)	0.0872(2)	3.62
I2	0.2702(2)	0.4245(1)	0.1743(2)	2.65
I3	0.4572(2)	0.6828(1)	0.2541(2)	3.22

$B_{eq} = (4/3)(B_{11}/a^{*2} + B_{22}/b^{*2} + B_{33}/c^{*2})$.

TABLE V Mean dimensions of BEDO–TTF (Å).



	BO	$BO_{2.4}I_3$*	2	3
Oxidation State	0	+0.42	+1	+2
a	1.357	1.347	1.398	1.427
b	1.762	1.741	1.723	1.702
c	1.754	1.733	1.727	1.702
d	1.333	1.312	1.350	1.420
e	1.368	1.365	1.352	1.309

BO = BEDO–TTF. * The bond lengths were cited from Ref.4.

PHYSICAL PROPERTIES

Optical Spectra

Figure 4a shows the IR spectra of the neutral BEDO–TTF and of the (BEDO–TTF)–I system recorded on the KBr disk. The most characteristic feature of the IR spectra is the large red shift of the ring C=C stretching band (indicated by arrows in the figure) upon the oxidation;

1646 (neutral BEDO–TTF), 1596 (1, +0.45 state), 1527 (2, +1), 1456 cm^{-1} (3, +2). The overall IR spectrum of 4 is very close to that of 3, indicating nearly +2 state of BEDO–TTF in 4. Figure 4b shows the UV–VIS spectra of salts 1–4 measured on the KBr disk and solution spectrum of neutral BEDO–TTF. The complex 1 shows the CT band at around $2x10^3$ cm^{-1}, indicating the partial CT state (band A). On the other hand for 2, 3, and 4 , the lowest absorption bands lie at much higher energy (band B and band C), which is consistent with their insulating nature. The radical (1, 2) and dication salts (3, 4) commonly show the band C, which is not observable in the neutral BEDO–TTF. This band is assigned to the transition from the second HOMO to HOMO.[3] Additional lower energy bands B ($7.4x10^3$, $9.1x10^3$ cm^{-1}) in 2 correspond to the CT among the BEDO–TTF radical cations.

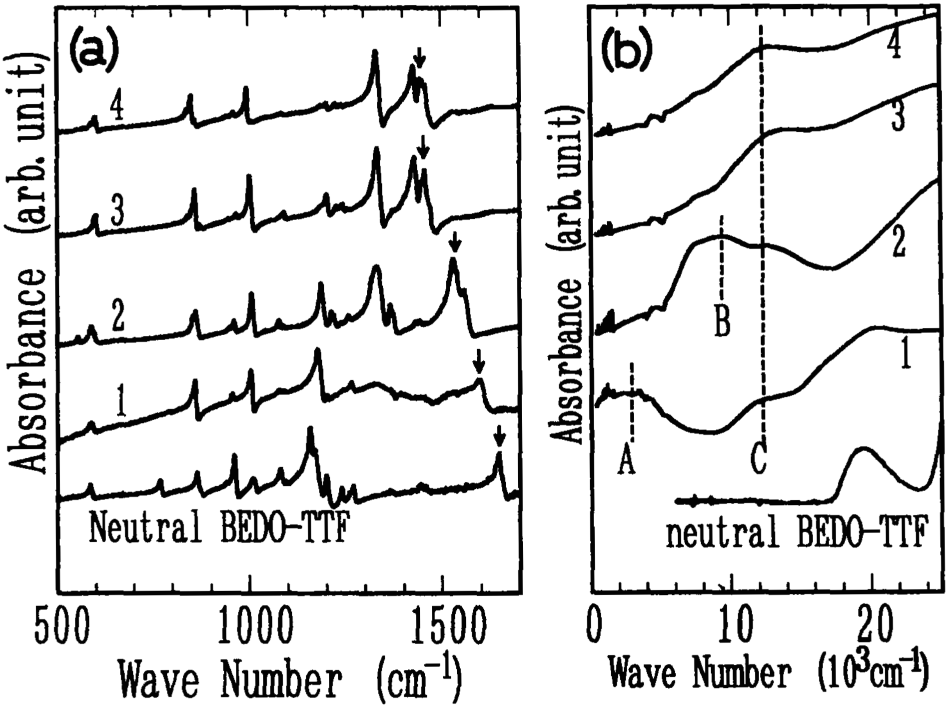


FIGURE 4 (a) IR and (b) UV–VIS spectra of neutral BEDO–TTF and (BEDO–TTF)–I salts (1–4). The spectra were measured on the KBr disk except the UV–VIS region of neutral BEDO–TTF (in acetonitrile solution). For arrows, see text.

Conducting and Magnetic Properties

The dc conductivities were measured on single crystals for 3 and 4, and on the compressed pellets for 1 and 2. Whereas 1 revealed high conductivity (σ_{rt} = 55 Scm^{-1}) and metallic behavior down to the low temperature (20 K), the other salts are insulating (2: $\sigma_{rt} = 1\text{x}10^{-6}$ Scm^{-1}, Ea = 0.43 eV; 3: $\sigma_{rt} < 10^{-9}$ Scm^{-1}; 4: $\sigma_{rt} = 8\text{x}10^{-7}$ Scm^{-1}).

The magnetic susceptibility measurements (SQUID) showed that 2 and 4 are diamagnetic for all the temperature region measured (2–350 K and 2–300 K, respectively). The insulating and diamagnetic nature of 3 and 4 can be ascribed to the completely oxidized +2 state of BEDO–TTF with closed-shell electronic structure. On the other hand for 2 with +1 state of BEDO–TTF, strong dimerization resulted in the band gap at Fermi level, which is responsible for the insulating and nonmagnetic ground state. In this case, singlet–triplet thermal excitation gives rise to the temperature dependent magnetic susceptibility as

$$\chi = \chi_0 + (2Ng^2\mu_B{}^2/k_BT)[3 + \exp(2J/k_BT)]^{-1},$$

where the first term is the Pascal diamagnetism. Taking the experimental error ($|\chi - \chi_0| < 2\text{x}10^{-4}$ emu·mol^{-1}) at 350 K into consideration, the energy gap between the singlet and triplet states ($-2J$) is deduced to be larger than 0.11 eV.

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