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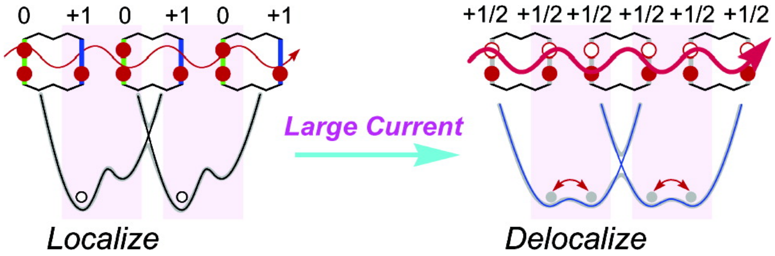

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Current-Induced Low-Resistance State and Its Crystal Structure of a TTF-Based Dimeric Donor Salt

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A mixed-valence state, which comes from the resonance between two ions with different oxidation states, is one of important concepts for understanding the electronic structure of assembled materials.[1] In the class I state, the oxidation states of each site are fixed discretely (e.g., D°, D^{+1}, D°, D^{+1}, ...), whereas they are equalized by charge delocalization (e.g., $D^{+1/2}$, $D^{+1/2}$, $D^{+1/2}$, ...) in the class III state. This concept is applied to molecular solids successfully. Recently, we found that the conductivity of an ion-radical salt of a donor molecule in the class I state increased drastically by application of a large current, and we explored the mechanism of this nonlinear response in the conductivity by analyzing the X-ray crystal structure of the salt during the current application.

In the ion-radical salt of a TTF-based cross-cyclophane-type donor (**1**)[2] (Figure 1a), **1**•Br•(TCE = 1,1,2-trichloroethane)$_2$, donor molecules are stacked with 4_1 screw symmetry along the *c*-axis (Figure 1c). Each donor unit of dimeric donor **1** straddles over two facing donor units of dimeric donors located above or below, respectively, shifting by a half of the donor unit (Figure 1d). Reflecting the 4_1 screw symmetry, one-dimensional side-by-side chains run along the *a*- and *b*-axes alternately, forming a log stack-like stacking structure along the *c*-axis. The bromide ion and two solvent molecules (TCE) are incorporated in a cavity formed by donor molecules, and the counterion is precisely located between two TTF units within the cross-cyclophane-type donor along the *c*-axis (Figure 1c). The dimeric donor **1** is an asymmetric unit in the crystal, and hence, two TTF units within each molecule are crystallographically nonequivalent. In reference to the bond lengths, two TTF units of sites, **P** and **Q** in Figure 1, disproportionate into cationic and neutral states, respectively (see Table 2).

The ion-radical salt **1**•Br•(TCE)$_2$ turned out to be a semiconductor, and the conductivity of the salt exhibited anisotropy—5.7 × 10^{-3} S•cm^{-1} (activation energy $\Delta E = 0.24$ eV) within the *ab* plane and 1.3 × 10^{-4} S•cm^{-1} ($\Delta E = 0.28$ eV) along the *c*-axis—which was consistent with the crystal structure.[3] The ion-radical salt showed paramagnetic behavior with a Curie constant of 0.375 emu•K•mol^{-1} for the composition of **1**•Br•(TCE)$_2$, which suggests that the moderate conductivity of this salt can be explained by a hopping mechanism.[4] According to the crystallographically nonequivalent structure of two TTF units and to the poor conductivity of the salt, the **1**•Br•(TCE)$_2$ salt can be classified as a class I complex.

Figure 2a shows the *I*−*V* characteristics (*I* // c) of the ion-radical salt at 170 K.[5] The circuit included a sample and a load resistor, R_L (1 MΩ), in series to elucidate the resistance precisely in a wide dynamic range.[6] As the voltage was increased, the current increased abruptly from 1.1 × 10^{-5} to 2.9 × 10^{-4} A at 330−340 V, and then the plot approached to a linear *I*−*V* dependence region governed by the load resistor. The result suggests that the resistance of the sample became much smaller than the load resistor in this region.[7] Furthermore, the sample exhibited hysteretic behavior; the low-resistance state remained even when the voltage was decreased below 340 V, returning to the initial resistance value at around 180 V. When the *I*−*V* dependence was converted to the conductivity (σ) of the sample versus current density (*J*) by subtracting the contribution of the load resistor (R_L), σ increases monotonically over a range of 10^4 as *J* increases (Figure 2b).

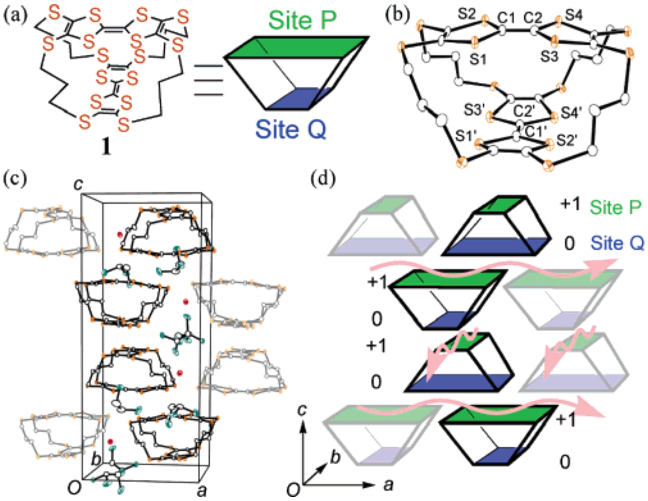

Figure 1. (a) The molecular structure of the cross-cyclophane-type donor **1**. (b) Molecular structure of **1** in **1**•Br•(TCE)$_2$ crystal. (c) The crystal structure of **1**•Br•(TCE)$_2$ at 133 K. Tetragonal, $P4_1$, $a = 12.3265(6)$ Å, $c = 29.663(2)$ Å, $V = 4507.0(4)$ Å^3, $Z = 4$, $R_{all}/R_{I>2\sigma} = 0.045/0.042$. (d) Stacking model of the dimeric donors in the crystal.

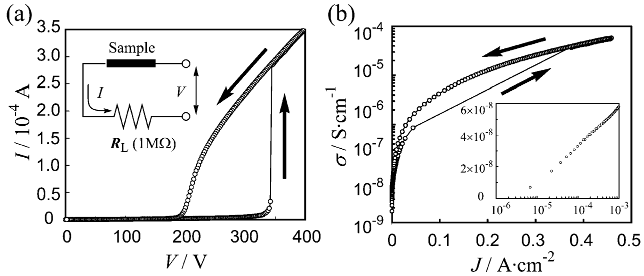

Figure 2. (a) *I*−*V* characteristics of **1**•Br•(TCE)$_2$ along the *c*-axis at 170 K. (b) The *I*−*V* characteristic of the entire circuit was transformed into the relation between the electric field *E* ($E = V/L$, L = length of the sample) and the current density *J* ($J = I \times S^{-1}$, S = cross section of the sample), by deducting the contribution of the load resistor, and then converted to σ-*J* dependence.

Appearance of the current-induced low-resistance states in several organic conductors, such as TTF−chloranil complex and K•TCNQ salt, has been reported by Tokura et al.[8−10] In the case of the K•TCNQ salt, the nonlinear conductivity was interpreted as the dimerized donor column became uniform, in accord with infrared spectroscopic evidence.[10] The nonlinear conductivity of **1**•Br•(TCE)$_2$, however, must be explained by some other mechanism

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Table 1. Crystal Parameters of **1**·Br·(TCE)$_2$ in the Normal State (170 K), the Current-Induced Low-Resistance State (170 K), and the Simply Warmed Normal State (270 K)

	normal (170 K)	current-applied (170 K)	simply warmed (270 K)
crystal system	tetragonal	tetragonal	tetragonal
space group	$P4_1$	$P4_1$	$P4_1$
$a = b$/Å	12.3500(9)	12.395(1)	12.4007(3)
c/Å	29.748(3)	29.811(5)	29.833(1)
V/Å^3	4537.2(7)	4580.3(11)	4587.6(2)
Z	4	4	4
R_{all}	0.056	0.078	0.087
$R_{I>4\sigma}$	0.050	0.065	0.067

Table 2. Selected Bond Lengths (Å) of the Normal State (170 K), the Current-Induced Low-Resistance state, and the Simply Warmed Normal State (270 K)

		normal (170 K)	current-applied (170 K)	simply warmed (270 K)
P	C1═C2	1.387(6)	1.370(7)	1.374(9)
	C1−S1	1.717(5)	1.712(6)	1.722(7)
	C1−S2	1.713(5)	1.726(6)	1.720(7)
	C2−S3	1.721(5)	1.721(6)	1.723(7)
	C2−S4	1.726(5)	1.732(6)	1.726(7)
	C−S (av.)	1.719(5)	1.723(6)	1.723(7)
Q	C1′═C2′	1.336(7)	1.351(8)	1.319(10)
	C1′−S1′	1.742(5)	1.743(5)	1.768(7)
	C1′−S2′	1.759(5)	1.738(5)	1.729(7)
	C2′−S3′	1.755(5)	1.739(6)	1.749(7)
	C2′−S4′	1.735(5)	1.738(6)	1.756(6)
	C′−S′ (av.)	1.748(5)	1.740(6)	1.751(7)

because the dimerization is originated from the structure of the dimeric donor and cannot be diminished. Therefore, the current-induced low-resistance state of **1**·Br·(TCE)$_2$ was investigated by an X-ray crystallographic technique. The sample, which was connected with gold wires at both ends, was mounted on an X-ray diffractometer and was cooled to 170 K with a cold nitrogen-gas flow.[11] The current density of 0.57 A·cm^{-2}, which was high enough to cause the resistance transformation, was kept constant throughout the measurement by applying a constant high voltage (480 V) to the circuit composed of the sample and the load resistor (1 MΩ) in series.

The cell parameters of **1**·Br·(TCE)$_2$ in the normal state and its current-induced low-resistance state showed the same crystal system (tetragonal) and space group ($P4_1$), the lattice volume of the low resistance state being increased only by 1% compared with that of the normal state (Table 1). While the increased lattice volume corresponds to the volume at 270 K, the molecular structure of **1** in the crystal at 270 K did not differ significantly compared with the structure at 170 K. In contrast, the molecular structure of **1** in the current-induced low-resistance state can be distinguished from that in the normal disproportionated state. As shown in Table 2, the difference in the bond lengths of sites **P** and **Q** becomes smaller than 3σ. Therefore, they cannot be distinguished during the current application. In other words, the alternation (charge disproportionation) of the oxidation states along the stacking direction is almost eliminated upon the current application.

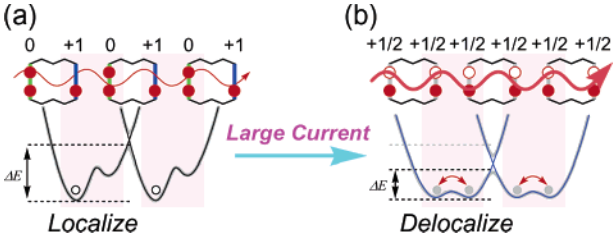

Figure 3. Schematic drawing of (a) the charge-disproportionated state and (b) the current-induced low-resistance state of the partially oxidized donor column in the crystal of **1**·Br·(TCE)$_2$.

Thus, the nonlinear conductivity of this crystal can be interpreted as the relaxation of the disproportionated structure. As the structure of two facing donor units becomes equal, the charge delocalizes over two facing donor units. This structural change makes the activation energy of electron transfer within dimeric donors much smaller than the original state. As a result, the resistance decreases substantially, as shown in Figure 3. Coupling between the structural equalization and the charge delocalization maintains the low-resistance state even after the applied current is decreased, causing the hysteretic behavior. The equalized structure and the charge distribution over two donor units in the current-induced low-resistance state can be regarded as a class III mixed-valence state.

Although the diffraction pattern study on the change of lattice constants of ferroelectric materials[12] and the diffuse X-ray reflection study in the sliding of the charge density wave in a one-dimensional conductors[13] have been reported, this is the first example in which the crystal structure analysis of the low-resistance state was carried out under the application of the current.

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Supporting Information Available: Experimental detail of transport measurements, X-ray crystallographic measurements, and crystal structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem*. **1967**, *10*, 247−422. (b) Kramer, J. A.; Herbstein, F. H.; Hendrickson D. N. *J. Am. Chem. Soc*. **1980**, *102*, 2293.
(2) (a) Tanabe, J.; Kudo, T.; Okamoto, M.; Ono, G.; Izuoka, A.; Sugawara, T. *Chem. Lett*. **1995**, 579−580. (b) Takimiya, K.; Shibata, Y.; Imamura, K.; Kashihara, A.; Aso, Y.; Otsubo, T.; Ogura, F. *Tetrahedron Lett*. **1995**, *36*, 5045−5048.
(3) Tanabe, J.; Ono, G.; Izuoka, A.; Sugawara, T.; Kudo, T.; Saito, T. *Mol. Cryst. Liq. Cryst*. **1997**, *296*, 61−76.
(4) Izuoka, A.; Tanabe, J.; Sugawara, T.; Kudo, T.; Saito, T. *Chem. Lett*. **2002**, 910−911.
(5) Because this crystal undergoes a structural phase transition at 160 K, which is different from the current-induced low-resistance state, the measurement was carried out above this temperature. See ref 3.
(6) Since the load resistor (R_L) decreases the voltage on the sample by *IR* drop, both voltage and current on the sample are regulated within a certain range even when the resistance changes severalfolds.
(7) The critical value of the voltage (340 V) corresponds to 54 kV·cm^{-1} or 4.1 mV per molecule, assuming that the depth of dimeric donor **1** is 7.5 Å. This value is substantially smaller than the activation energy of the hopping process (0.28 eV).
(8) Tokura, Y.; Okamoto, H.; Koda, T.; Mitani, T.; Saito, G. *Phys. Rev*. **1988**, *B38*, 2215−2218.
(9) Iwasa, Y.; Koda, T.; Tokura, Y.; Koshihara, S.; Iwasawa, N.; Saito, G. *Appl. Phys. Lett*. **1989**, *55*, 2111.
(10) Kumai, R.; Okimoto, Y.; Tokura, Y. *Science* **1999**, *284*, 1645.
(11) Crystal size was 0.15 × 0.15 × 3.0 mm^3, and the current was applied along the long axis of the crystal, which corresponds to the *c*-axis. Although a whole crystal must be thoroughly irradiated by an X-ray flux (0.3ϕ in this case) in a regular X-ray measurement, this measurement does not satisfy the condition. However, the intensity of the equivalent reflection spots obtained by the different irradiation angles can be calibrated with sufficient accuracy, and the crystal structure of the current-induced low-resistance state can be solved successfully.
(12) Ng, Y. S.; McDonald, A. D. *Ferroelectrics* **1985**, *62*, 167−168.
(13) (a) Tamegai, T.; Tsutsumi, K.; Kagoshima, S.; Kanai, Y.; Tani, M.; Tomozawa, H.; Sato, M.; Tsuji, K.; Harada, J. *Solid State Commun*. **1984**, *51*, 585−589. (b) Ravy, S. *Chem. Rev*. **2004**, *104*, 5609−5634.

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