New α'-Type ET Salt $(ET)_2H_2F_3$ by Electrocrystallization Using Ionic Liquid

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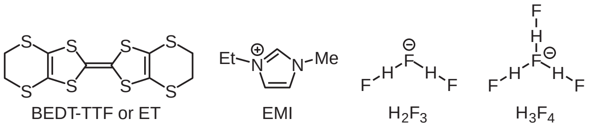
A new ET-based cation radical salt α'-$(ET)_2H_2F_3$ (ET: bis(ethylenedithio)tetrathiafulvalene) was obtained by an electrocrystallization method using a highly conductive ionic liquid $(EMI)[F(HF)_{2.3}]$ (EMI: 1-ethyl-3-methylimidazolium) as an electrolyte, and its structural, transport and magnetic properties were investigated. The salt shows the semiconducting behavior with an activation energy of 0.05–0.08 eV. Static susceptibility of 8.9×10^{-4} emu mol^{-1} at 300 K, in support of the transport behavior, is firm evidence of a Mott insulator.

Room-temperature (RT) ionic liquids, which are entirely composed of ions, have been an area of interest as potentially benign solvents both for electrochemical device[1] and organic/inorganic synthetic media.[2] Its special advantage over the traditional organic solvents is that their liquid behaviors such as miscibility, electrochemical and thermal stabilities, and ionic conductivity can be tailored by the selection of both cation and anion components.[3] In the area of condensed matter science, ionic liquids were first used by Osteryoung et al. for the crystal growth of tetrathiafulvalene (TTF) salts,[4] and we ourselves obtained a new organic superconductor $(TMTSF)_2NbF_6$ (TMTSF: tetramethyltetraselenafulvalene) by an electrooxidation of TMTSF using an ionic liquid $(EMI)NbF_6$[5] (EMI: 1-ethyl-3-methylimidazolium, Scheme 1) as an electrolyte in CH_2Cl_2.[6] Note that the electrocrystallization using $(TBA)NbF_6$ (TBA: tetra-*n*-butylammonium) gave poor-quality $(TMTSF)_2NbF_6$ crystals with no superconducting behavior.[7] More recently, a metallic $(EDO\text{-}TTF)_2SbF_6$ (EDO-TTF: ethylenedioxy-TTF) was obtained by the electrooxidation of EDO-TTF using an ionic liquid $(EMI)SbF_6$[8] in EtOH, whereas $(TBA)SbF_6$ give a semiconductive $(EDO\text{-}TTF)_4(Sb_2F_{11})_{0.85}(H_2O)_4$ with dimerized fluoroantimonate anions.[9] These findings stimulate our interest in investigation of the electrocrystallization of bis(ethylenedithio)-TTF (BEDT-TTF or ET, Scheme 1) salts using the EMI-based ionic liquids, as the ET molecule has afforded a very wide range of model electronic materials, ranging from metallic and superconducting behaviors through to nonmetallic magnetically ordered materials, with various packing patterns of ET molecules.[10] Importantly, such ionic liquids will offer a wider range of selection of organic solvent for the electrocrystallization, if the TTF analogues can dissolve in the ionic liquids. In the present paper, we report on a first ET-based cation radical salt prepared using an ionic liquid $(EMI)[F(HF)_{2.3}]$,[11] in which bent H_2F_3 and triangular H_3F_4 anions (Scheme 1) coexist at equilibrium and exchange very rapidly to each other through HF.[12] Several organic solvents were utilized, since the ET molecules are practically insoluble in $(EMI)[F(HF)_{2.3}]$. So far, the cation radical salt containing H_nF_{n+1} ($n > 2$) anion was limited to $(TMTSF)_2H_2F_3$, which was prepared by the electrocrystallization method using benzyltriphenylphosphonium–H_2F_3 in CH_2Cl_2.[13]



Scheme 1. Chemicals in text.

In a Pyrex glass H-type cell, solutions of ET (2–6 mM) and $(EMI)[F(HF)_{2.3}]$ (40–140 mM) were added to the cathodic and anodic compartments, respectively, which are separated by a glass frit, under helium gas in a glovebox (H_2O, $O_2 < 1$ ppm). Two Pt wire electrodes (cathode: 2 mmϕ, anode: 1 mmϕ) passing through Teflon holder were immersed into each solution, the interfaces between the Teflon holder and glass cell were tightly sealed with paraffin films, and then the cell was removed from the glovebox. A constant current of 0.5 µA was passed in the two electrodes over 2 weeks at RT. Whereas 1,2-dichloroethane, 1,1,2-trichloroethane, and benzonitrile solutions afforded polycrystals with poorer quality or no crystals, block-shaped black crystals with a typical dimension of $0.6 \times 0.3 \times 0.1$ mm^3 were grown on the cathodic Pt electrode in a tetrahydrofuran solution.

X-ray diffraction data of the crystal were collected at RT on an imaging plate type diffractometer (Mac Science DIP-2020K) with monochromated Mo Kα radiation.[14] The crystallographic study reveals that the composition of the salt is $(ET)_2H_2F_3$, indicating the formally $+1/2$ charge on each ET molecule. Triangular H_3F_4 anion included in the electrolyte was not detected. In the crystal, there are one crystallographically independent ET molecules, which are twisted with respect to neighboring molecules along the stacking *a* axis (Figure 1, α'-type packing pattern[15]). The charge on each ET molecule is estimated to +0.55(9) on the basis of intramolecular bond lengths,[16] which is in good agreement with that expected from the chemical formula. The short heteroatomic contacts (van der Waals radii: 3.6 Å[17]) were observed for $S_{in}\cdots S_{out}$ (3.429–3.468 Å) and $S_{out}\cdots S_{out}$ (3.456–3.496 Å) but not for $S_{in}\cdots S_{in}$ along the side-

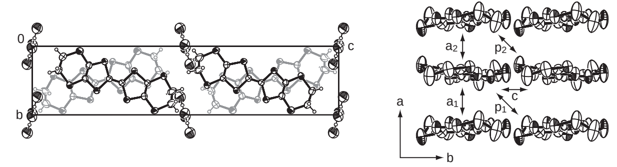


Figure 1. (a) Crystal structure of α'-$(ET)_2H_2F_3$ viewed along the *a* axis. (b) Packing pattern of ET molecules. Overlap integrals ($\times 10^{-3}$) are: $a_1 = 9.37$, $a_2 = 2.95$, $c = 1.84$, $p_1 = 0.44$, and $p_2 = 0.67$.

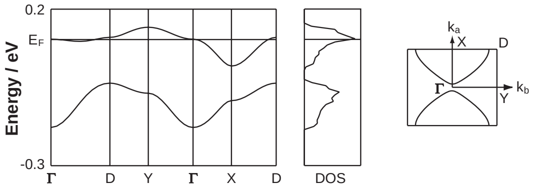


Figure 2. Calculated band structure, density of states (DOS), and Fermi surface for α'-$(ET)_2H_2F_3$.

by-side direction, where S_{in} and S_{out} are the sulfur atoms in the TTF skeleton and ethylenedithio group, respectively. The H_2F_3 anion is located on an inversion center and is disordered over two orientations. The anion is slightly bent with an F···F···F angle of 161.59°, which is significantly large in comparison with those in KH_2F_3 (130, 139°),[18] CsH_2F_3 (141.2(6), 148.4(6)°),[19] and $(Me_4N)H_2F_3$ (125.93(2)°).[19] Each H_2F_3 anion is connected with the ET molecules through C–H···F hydrogen bonding type interactions (>3.112 Å). Floatation method in a mixed solution of bromoform and tetrachloromethane affords the density of $1.77\,g\,cm^{-3}$, which is consistent with $1.789\,g\,cm^{-3}$ estimated from the crystallographic data, within experimental error ($\pm 0.03\,g\,cm^{-3}$).

The electronic band structure was calculated by a tight-binding model based on the extended Hückel method with single-ξ parameters excluding d orbitals of sulfur atoms. As seen in Figure 2, the energy dispersion along Γ–X (stacking direction) is comparable to that along Γ–Y (side-by-side direction), indicating the quasi two-dimensional (2D) electronic structure. The HOMO bands substantially split owing to the two unequal and alternating overlap integrals (9.37×10^{-3}, 2.95×10^{-3}) within the stack, and it is thus apparent that the +1/2 charged ET molecules form a dimer with $S = 1/2$ spin.

DC electrical conductivity measurement was performed along the stacking direction (Figure 3), using a standard four-probe technique by attaching gold wires (15 µmϕ) on a single crystal with gold paint. The electrical conductivity is determined as $1.0\,S\,cm^{-1}$ at RT and shows the semiconducting behavior with activation energies of 0.081 eV (>150 K) and 0.049 eV (<130 K), which are significantly low in comparison with those of most α'-$(ET)_2X$ salts,[15] for instance, 0.24 eV for $X = AuBr_2$, 0.30 eV for $X = Ag(CN)_2$, and 0.20 eV for $X = CuCl_2$.[20] Static susceptibility data of the polycrystalline sample was collected by a SQUID magnetometer (Quantum Design MPMS-XL) under an applied magnetic field of 10 kOe. The value is estimated to be $8.9 \times 10^{-4}\,emu\,mol^{-1}$ at 300 K and exhibits a round maximum at around 70 K. Such magnetic behavior indicative of the spin-1/2 quadratic layer antiferromagnet (QLAF)[21] with $|J|/k_B = 37\,K$, in support of the conductivity data allows us to assert that the salt is allocated within the regime of a Mott insulator.

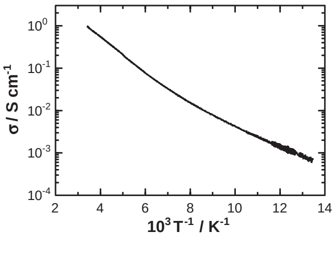


Figure 3. Temperature dependence of DC electrical conductivity of α'-$(ET)_2H_2F_3$ along the stacking direction.

In summary, we obtained the first ET-based cation radical salt formed with fluorohydrogenate anions, by the electrocrystallization method using an ionic liquid $(EMI)[F(HF)_{2.3}]$ as an electrolyte. The salt with α'-type donor packing pattern is a Mott insulator. To explore the electrooxidation of the other donor molecules with the fluorohydrogenate anions is in progress.

This work was in part supported by 21st Century COE program on Kyoto University Alliance for Chemistry and Grant-in-Aid for Scientific Research (No. 15205019) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. One of the authors (Y.Y.) also acknowledges the financial support of Grants-in-Aid for Scientific Research (No. 17750126) from Japan Society for the Promotion of Science (JSPS).

References and Notes

1 *Electrochemical Aspects of Ionic Liquids*, ed. by H. Ohno, John Wiley and Sons, New Jersey, **2005**, Chap. 14–17.
2 For selected reviews, see: a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071. b) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667.
3 For selected reviews, see: a) R. Hagiwara, Y. Ito, *J. Fluorine Chem.* **2000**, *105*, 221. b) P. Wasserscheid, W. Keim, *Angew Chem., Int. Ed.* **2000**, *39*, 3772.
4 a) M. T. Carter, R. A. Osteryoung, *J. Electrochem. Soc.* **1994**, *141*, 1713. b) J. Fuller, R. T. Carlin, R. A. Osteryoung, *J. Electrochem. Soc.* **1997**, *144*, 3881.
5 K. Matsumoto, R. Hagiwara, Y. Ito, *J. Fluorine Chem.* **2002**, *115*, 133.
6 M. Sakata, Y. Yoshida, M. Maesato, G. Saito, K. Matsumoto, R. Hagiwara, *Mol. Cryst. Liq. Cryst.* **2006**, *452*, 103.
7 K. Bechgaard, *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 1.
8 K. Matsumoto, R. Hagiwara, R. Yoshida, Y. Ito, Z. Mazej, P. Benkič, B. Žemva, O. Tamada, H. Yoshino, S. Matsubara, *Dalton Trans.* **2004**, 144.
9 H. Yamochi, G. Saito, et al., in preparation.
10 a) T. Ishiguro, K. Yamaji, G. Saito, *Organic Superconductors*, 2nd ed., Springer-Verlag, Berlin, **2005**. b) G. Saito, Y. Yoshida, *Bull. Chem. Soc. Jpn.*, in press.
11 a) R. Hagiwara, T. Hirashige, T. Tsuda, Y. Ito, *J. Fluorine Chem.* **1999**, *99*, 1. b) R. Hagiwara, T. Hirashige, T. Tsuda, Y. Ito, *J. Electrochem. Soc.* **2002**, *149*, D1.
12 Y. Saito, K. Hirai, K. Matsumoto, R. Hagiwara, Y. Minamizaki, *J. Phys. Chem. B* **2005**, *109*, 2942.
13 M. A. Beno, G. S. Blackman, J. M. Williams, K. Bechgaard, *Inorg. Chem.* **1982**, *21*, 3860.
14 Crystal data for α'-$(ET)_2H_2F_3$: $C_{20}H_{18}F_3S_{16}$, $M_r = 828.41$, monoclinic, space group $P2/n$, $a = 7.808(1)$, $b = 6.666(1)$, $c = 29.745(2)$ Å, $\beta = 96.556(5)°$, $V = 1538.0(3)$ Å^3, $Z = 2$, $\mu(\mathrm{Mo}\,K\alpha) = 0.579\,mm^{-1}$, $D_{calcd} = 1.789\,g\,cm^{-3}$, 1874 independent, 1718 reflections ($F > 4\sigma(F)$), 181 parameters, $R = 0.0611$, $R_w = 0.191$(all data), GOF = 1.103.
15 T. Mori, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2011.
16 P. Guionneau, C. J. Kepert, G. Bravic, D. Chasseau, M. R. Truter, M. Kurmoo, P. Day, *Synth. Met.* **1997**, *86*, 1973.
17 A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
18 J. D. Forrester, M. E. Senko, A. Zalkin, A. D. H. Templeton, *Acta Crystallogr.* **1963**, *16*, 58.
19 S. I. Troyanov, I. V. Morozov, E. Kemnitz, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1651.
20 I. D. Parker, R. H. Friend, M. Kurmoo, P. Day, *J. Phys.: Condens. Matter* **1989**, *1*, 5681.
21 M. E. Lines, *J. Phys. Chem. Solids* **1970**, *31*, 101.

Published on the web (Advance View) December 29, 2006; doi:10.1246/cl.2007.226