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New organic metals based on a BEDT-TTF derivative with steric hindrance

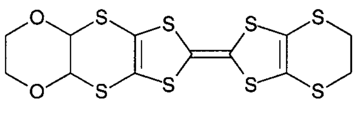
Jun-ichi Yamada,*[a]† Satoru Tanaka,[a] Hiroyuki Anzai,[a] Tatsuo Sato,[b] Hiroyuki Nishikawa,[b] Isao Ikemoto[b] and Koichi Kikuchi*[b]‡

[a]*Department of Material Science, Faculty of Science, Himeji Institute of Technology, 1479-1 Kanaji, Kamigori-cho, Ako-gun, Hyogo 678-12, Japan*

[b]*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan*

The conducting behaviour of radical cation salts based on the dioxane-fused BEDT-TTF derivative is reported, two of which show metallic conducting properties.

For the electrical conductivity of one-dimensional organic metals composed of π-electron donor and acceptor molecules, it is well known that intermolecular donor–donor interactions (face-to-face interactions) in the segregating donor stack provide the pathway for electron conduction.[1] Therefore, one important aspect of the hitherto known molecular designs for π-electron donors is an attempt to reduce the steric hindrance, which would prevent face-to-face interactions, on a donor molecule.[2] On the other hand, we have already reported the synthesis of a BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] derivative condensed with a 1,4-dioxane ring by *cis* fusion [(1,4-dioxanediyl-2,3-dithio)ethylenedithiotetrathiafulvalene, DOET].[3] If such a BEDT-TTF derivative with steric hindrance could give metallic radical cation salts, further extension of the molecular designs for the development of π-electron donors leading to new organic metals would be possible.[4] In this paper, we disclose the conducting behaviour of DOET-based radical cation salts and the crystal structure of $(DOET)_2BF_4$.



DOET

As reported previously,[3] the room temperature conductivity of the TCNQ complex of DOET was $<10^{-6}$ S cm^{-1} for a compressed pellet. So, in order to explore the metallic radical cation salts derived from DOET, the preparation of the DOET salts with suitable anions was examined by electrochemical oxidation with a controlled current[5] in 1,1,2-trichloroethane (TCE), THF, 5% EtOH–TCE, or 5% EtOH–PhCl containing the corresponding tetra-*n*-butylammonium salt. The conducting behaviour of the resulting DOET salts is summarized in Table 1. In a series of the DOET salts with linear anions, $(DOET)_2Au(CN)_2$ showed high room temperature conductivity (13 S cm^{-1}) for a single crystal, and the temperature dependence of its resistivity revealed that this salt was metallic down to about 30 K. In addition, the salt with BF_4^- exhibited metallic conductivity with a metal to semiconductor transition.

Table 1 Conducting behaviour of the DOET salts

anion	solvent	D:A[a]	σ_{rt}/S cm^{-1}[b]
Cl_2Br^-	TCE[c]	3:1	2.9[d] ($E_a = 89$ meV)
Br_2Cl^-	TCE	4:1	2.4[d] ($E_a = 83$ meV)
Br_3^-	TCE	3:1	$<10^{-6}$[d]
Br_2I^-	TCE	5:3	$<10^{-6}$[d]
I_2Br^-	TCE	5:3	1.2[d] ($E_a = 30$ meV)
I_3^-	THF	1:1	2.2[e] ($E_a = 37$ meV)
$Au(CN)_2^-$	5% EtOH–TCE	2:1	13[e] (T_{MI}[f] $= 30$ K)
$AuCl_2^-$	TCE	1:1	12[d] ($E_a = 76$ meV)
AuI_2^-	TCE	1:1	0.033[d] ($E_a = 220$ meV)
BF_4^-	TCE	2:1	27[e] ($T_{MI} = 100$ K)
ClO_4^-	TCE	—[g]	1.0[d] ($E_a = 79$ meV)
ReO_4^-	TCE	3:1	0.43[d] ($E_a = 110$ meV)
PF_6^-	TCE	2:1	0.95[d] ($E_a = 110$ meV)
AsF_6^-	TCE	2:1	0.35[d] ($E_a = 120$ meV)
SbF_6^-	5% EtOH–PhCl	2:1	0.63[e] ($E_a = 23$ meV)

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

The X-ray analysis of $(DOET)_2BF_4$† shows that the mode of the molecular overlap is very similar to that in a famous organic superconductor β-$(BEDT\text{-}TTF)_2I_3$ (Fig. 1). The DOET molecules are stacked face-to-face to form a column along the [110] direction. In the β-structure, molecular dimerization is usually observed in a stack. In the case of $(DOET)_2BF_4$, the dimerization is rather smaller than that in β-$(BEDT\text{-}TTF)_2I_3$ [the overlap ratios of p_1 to p_2 are 1.6 and 2.1 in $(DOET)_2BF_4$ and β-$(BEDT\text{-}TTF)_2I_3$, respectively], and interestingly, the bulky dioxane ring exists within a hollow

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† *Crystal data* for $(DOET)_2BF_4$: $(C_{12}H_{10}O_2S_8)_2BF_4$, $M = 968.19$, triclinic, space group $P1$, $a = 6.630(4)$ A, $b = 8.995(3)$ A, $c = 16.638(6)$ A, $\alpha = 91.96(3)°$, $\beta = 96.14(4)°$, $\gamma = 111.17(3)°$, $V = 917.2(7)$ A^3, $Z = 1$, $D_c = 1.782$ g cm^{-3}, $\mu = 9.589$ cm^{-1}, $F(000) = 493$. The data were collected on a Mac Science MXC18 diffractometer equipped with graphite monochromated Mo-Kα ($\lambda = 0.71073$ A) radiation using the ω–2θ scan technique to a maximum 2θ of 60°. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares analysis (anisotropic for C, O and S atoms and isotropic for B and F atoms) to $R = 0.058$ and $R_w = 0.062$ with GOF $= 1.46$ for 2763 observed $[I \geqslant 2\sigma(I)]$ reflections from 4203 independent reflections ($R_{int} = 0.063$). After the refinement of the DOET molecule, three large peaks remained near the position (0.5, 0.5, 0) in the difference Fourier map, so BF_4 anions were considered to be orientationally disordered and these peaks were assigned to F atoms with 2/3 occupancy. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.58 and -0.51 e A^{-3}. 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 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/39.

† E-mail: yamada@sci.himeji-tech.ac.jp
‡ E-mail: kikuchi-koichi@c.metro-u.ac.jp

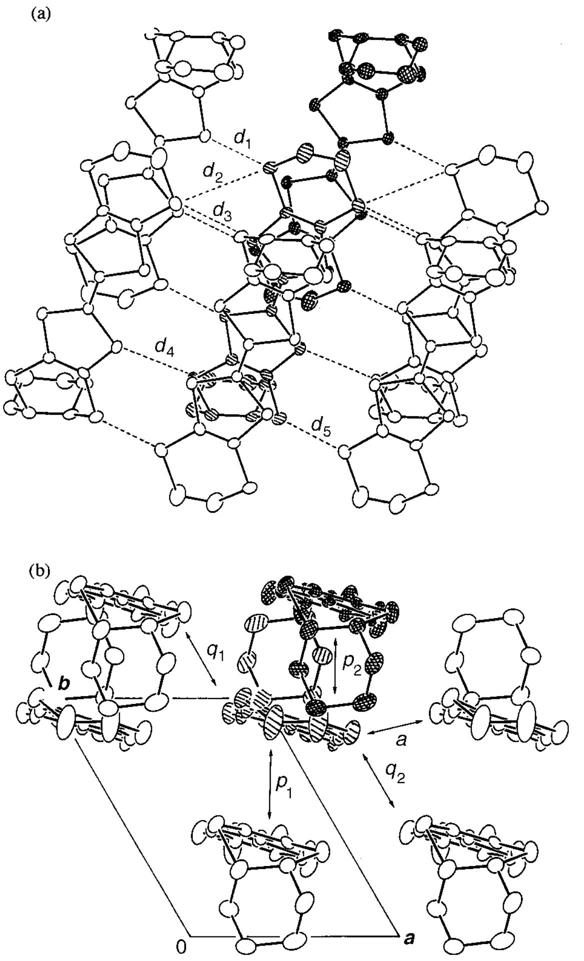

Fig. 1 Donor arrangement of $(DOET)_2BF_4$. (a) Intermolecular S···S contacts (<3.70 A) are indicated by dotted lines: $d_1=3.543(3)$ A, $d_2=3.695(3)$ A, $d_3=3.486(3)$ A, $d_4=3.455(3)$ A, $d_5=3.654(3)$ A. (b) Intermolecular overlap integrals ($\times 10^{-3}$) a, p_1, p_2, q_1 and q_2 are −4.66, 23.81, 15.17, 7.05 and 5.34, respectively.

space of the donor stack. There are many S···S contacts between stacks shorter than the van der Waals distance (3.70 A) instead of no short S···S intermolecular contact within a stack. Therefore, the anisotropy of the interaction is small in the ***ab*** plane and the conduction band is 3/4 filled, leading to its 2D band structure with a nearly isotropic closed Fermi surface (see Fig. 2). This band structure suggests metallic behaviour down to low temperatures, but this salt becomes a semiconductor around 100 K. According to the X-ray analysis, the orientation of BF_4 anions is completely disordered, so this random potential of BF_4 anion layers might disturb the electron conduction and make this salt a semiconductor at low temperature.

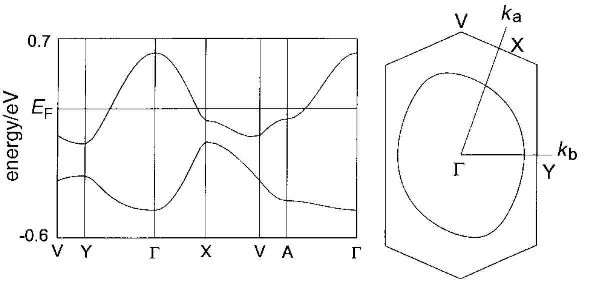

Fig. 2 The energy band structure and the Fermi surface of $(DOET)_2BF_4$

In conclusion, we found two kinds of new organic metals based on a π-electron donor with steric hindrance which is anomalous from the viewpoint of the ordinary molecular design. This finding may be not only useful for new molecular designs of π-electron donors, but also contributable to structural factors enhancing the dimensionality of the conduction in molecular-based organic metals. Investigations on X-ray analysis of the other DOET salts and preparation of radical cation salts using the DOET analogues as π-electron donors are in progress.

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References

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