March, 1988] *Bull. Chem. Soc. Jpn., 61, 741—743 (1988)*

New Series of Organic Metal. Radical Salts of Unsymmetrical Donors Containing Pyrazino Group

Koichi KIKUCHI,* Hiroyuki KAMIO, Kazuya SAITO, Stelios Y. YIANNOPOULOS,†
George C. PAPAVASSILIOU,† Keiji KOBAYASHI,†† and Isao IKEMOTO
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Fukazawa, Setagaya-ku, Tokyo 158
†Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation,
48, Vass. Constantinou Ave., Athens 116/35, GREECE
††Department of Chemistry, College of Arts and Sciences, The University of Tokyo,
Komaba, Meguro-ku, Tokyo 153
(Received July 14, 1987)

The I$_3$, ClO$_4$, and PF$_6$ salts of unsymmetrical donors containing fused pyrazino groups (DMPDSDTF and DM(DMP)DSDTF) were prepared electrochemically and their electrical conductivities were measured. The I$_3$ salt of DM(DMP)DSDTF exhibited a metallic behavior down to about 120 K. The radical salts of unsymmetrical donors showed much larger conductivities than those of the corresponding symmetrical donors containing pyrazino groups.

In the past decade, much attention has been concentrated on the construction of organic superconductors. It has been recognized in such studies that higher dimensionality is preferred because low dimensional systems of electrons intrinsically possess the instability against to a lattice distortion with a period of $1/2k_F$. Indeed, at low temperature many organic conductors undergo a CDW (Peierls), SDW or spin-Peierls transition, below which they behave as insulators.

One way to increase dimensionality of the system is compression of a sample under high pressure. The first organic superconductor (TMTSF)$_2$PF$_6$[1] has been obtained through application of high pressure of 0.65 GPa. Besides physical compression, there exists another strategy to increase dimensionality, i.e. chemical decoration of a molecule. TMTSF[1] and BEDT-TTF,[2] of which radical salts have been discovered so far to undergo a superconducting transition, are in fact analogues of one of the most famous donor, TTF.

From the second point of view, the donors containing nitrogen atoms are interesting because the lone pair electrons will possibly enhance the dimensionality of electronic systems in crystals. However, only a few reports have been published so far about the salts of such donors.[3—7]

Very recently, the superconductivity in (DMET)$_2$Au(CN)$_2$[8] (DMET: dimethyl(ethylenedithio)diselenadithiafulvalene) and (DMET)$_2$AuBr$_2$[9] has been discovered, which indicates that a symmetrical donor is not necessary to organic superconductors. These situation prompted us to start the studies on the unsymmetrical donors containing a pyrazino group. The donors we have chosen are DMPDSDTF (dimethyl(pyrazino)diselenadithiafulvalene) and DM(DMP)DSDTF (dimethyl(dimethylpyrazino)diselenadithiafulvalene) (Fig. 1), which have a partial structure of TMTSF. If any properties of the partial structures of the donor contribute additively to the properties of crystals, enhanced dimensionality and high electrical conductivity will be realized. In order to clarify this point, some radical salts of the unsymmetrical donors were prepared and the electrical conductivities were compared with those of the corresponding symmetrical donors, BPTTF (bispyrazinotetrathiafulvalene) and BDMPTTF (bis(dimethylpyrazino)tetrathiafulvalene) (see Fig. 1).

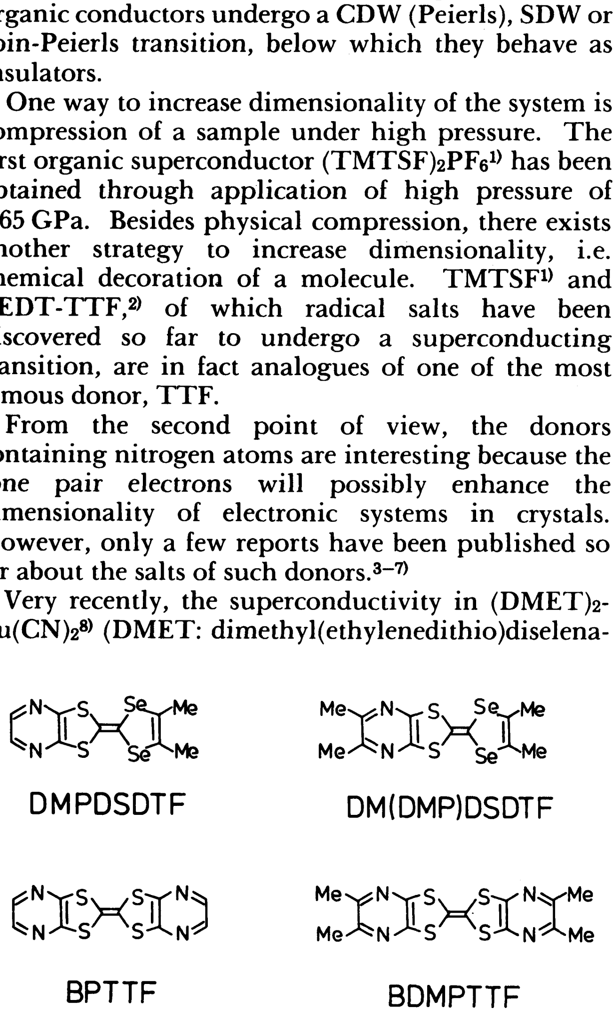

Fig. 1. Molecular structures of the donors.

Experimental

The unsymmetrical and symmetrical donors were synthesized according to the methods described previously.[10] The radical salts of the donors were grown at room temperature by the electrochemical method with constant current of 2 μA in dichloromethane. The supporting electrolytes used were (n-Bu)$_4$N·I$_3$, (n-Bu)$_4$N·ClO$_4$, and (n-Bu)$_4$N·PF$_6$, which cover a variety of counter anions of linear, tetrahedral, and octahedral structures. The single crystals of ClO$_4$ salts of the unsymmetrical donors and of the PF$_6$ salt of BDMPTTF were needle-like, and others were plate-like.

The electrical conductivities were measured along the growth axis of the crystal by standard four probe AC (20 Hz) and DC methods at constant current (1—10 μA) between liquid nitrogen and room temperatures. As both methods of conductivity measurements gave consistent results, we will not mention about the methods in the following. The size of the samples used for conductivity measurements was typically 2×0.3×0.03 mm^3.

Results and Discussion

The room temperature conductivities of radical salts are tabulated in Table 1. While all of the radical salts of DMPDSDTF, BPTTF and BDMPTTF

Table 1. Electrical Properties of Radical Salts. Room Temperature Conductivities in S cm^{-1} and Band Gap Energies in eV (in Parenthesis)

	PF$_6$	ClO$_4$	I$_3$
Unsymmetrical			
DMPDSDTF	Semiconductor 4.0(0.12)	Semiconductor 1.5(0.56)	Semiconductor 1.6(0.10)
DM(DMP)DSDTF	Semiconductor 3.2(0.25)	Metal[a] 44	Metal[b] 92
Symmetrical			
BPTTF	Semiconductor 0.68(0.38)	—[c]	—[c]
BDMPTTF	Semiconductor 0.060(0.20)	—[c]	—[c]

a) Below about 250 K, semiconductor with the band gap energy 0.09 eV. b) Below about 120 K, semiconductor with the band gap energy 0.04 eV. c) Single crystals could not be prepared.

exhibited semiconducting behaviors at room temperature, two radical salts of DM(DMP)DSDTF behaved as metallic. The band gap energies were deduced from Arrhenius plots of conductivities in semiconducting region and are also given in Table 1.

It is interesting to compare the properties of the single crystals of radical salts of symmetrical and unsymmetrical donors. Only a series of PF$_6$ salts is available for this purpose, as radical salts of other anions with symmetrical donors could not be prepared. The room temperature conductivity of the DMPDSDTF salt is larger than that of the BPTTF salt by an order of magnitude. Similarly, that of the DM(DMP)DSDTF salt is larger than that of the BDMPTTF salt by a factor 50. Moreover, ClO$_4$ and I$_3$ salts of DM(DMP)DSDTF showed metallic properties. Thus, introduction of a partial structure of TMTSF increases an electrical conductivity. It is noteworthy that in the case of I$_3$ salt of DM(DMP)DSDTF the conductivity perpendicular to the crystal growth axis was smaller than that along the axis by only a factor 5, which suggests that the salts have high dimensionality. Similar effects were observed also in salts of the unsymmetrical donor,[7] PEDTTTF, which has a partial structure of BEDT-TTF. Hence, we conclude that partial structures of a donor contribute additively to the electrical property of radical salts.

In addition to improvement of room temperature conductivity, there is another remarkable finding: Although all of three radical salts of DMPDSDTF were semiconducting, the radical salts of DM(DMP)-DSDTF showed a variety of temperature dependences of conductivity. The results of the conductivity measurements on a series of the salts of DM(DMP)-DSDTF are shown in Fig. 2. It is interesting that the higher is the symmetry of an anion, the lower is an electrical conductivity of the corresponding radical salt (Table 1). The PF$_6$ salt exhibits a semiconducting behavior in the temperature range studied. In contrast to the PF$_6$ salt, the I$_3$ salt behaves as metallic down to about 120 K, below which the salt is a semiconductor. It is emphasized that this is the second observation that an organic conductor consisting of an donor containing pyrazino group(s) shows a metallic behavior down to such a low temperature.[7] The ClO$_4$ salt is also metallic at room temperature though it is hardly recognized in Fig. 2. As the temperature dependence of the conductivity is very weak, it is hard to locate unambiguously the metal-insulator transition point on the basis of the present data.

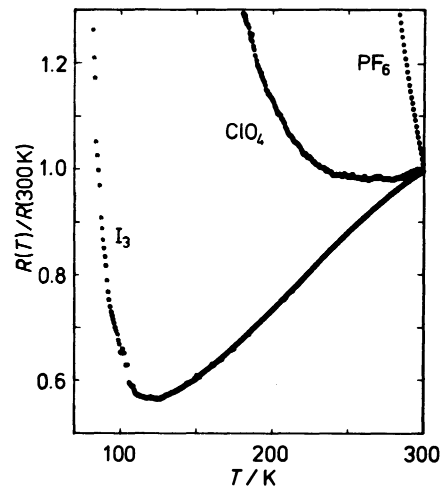

Fig. 2. Electrical resistivities of a series of radical salts of DM(DMP)DSDTF. Counter anions are indicated in the figure. For the values of R(300 K), see Table 1.

Structural and high pressure studies are interesting and in progress in this laboratory. These will be published shortly.

This study was supported by the Grant-in-Aid for Scientific Research No. 6143003 from the Ministry of Education, Science and Culture.

References

1) D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, *J. Phys. (Paris) Lett.*, **41**, L95 (1980).

2) S. S. P. Parkin, E. M. Englar, R. R. Schumaker, R. Ligaier, V. Y. Lee, J. Voiron, K. Carneiro, J. C. Scott, and R. L. Greene, *Phys. Rev. Lett.*, **50**, 270 (1982).

3) G. C. Papavassiliou, S. Y. Yiannopoulos, and J. S. Zambounis, *Mol. Cryst. Liq. Cryst.*, **120**, 333 (1986).

4) G. C. Papavassiliou, S. Y. Yiannopoulos, and J. S. Zambounis, *Physica*, **143B**, 310 (1986).

5) A. Terzis, A. Hountas, and G. C. Papavassiliou, *Acta Crystallogr., Sect. C*, **42**, 1584 (1986).

6) A. E. Underhill, B. Kaye, G. C. Papavassiliou, and S. Y. Yiannopoulos, *Mol. Cryst. Liq. Cryst.*, **134**, 59 (1986).

7) G. C. Papavassiliou, A. Terzis, A. E. Underhill, H. P. Geserich, B. Kaye, A. Hountas, and S. Y. Yiannopoulos, *Synth. Metals*, **19**, 703 (1987).

8) K. Kikuchi, M. Kikuchi, T. Namiki, K. Saito, I. Ikemoto, K. Murata, I. Ishiguro, and K. Kobayashi, *Chem. Lett.*, **1983**, 931.

9) K. Kikuchi, K. Murata, Y. Honda, T. Namiki, K. Saito, K. Kobayashi, I. Ishiguro, and I. Ikemoto, *J. Phys. Soc. Jpn.*, **56**, 2627 (1987).

10) G. C. Papavassiliou, S. Y. Yinnopoulos, J. S. Zambounis, K. Kobayashi, and K. Umemoto, *Chem. Lett.*, **1987**, 1279.