Molecular Conductor Based on Reduced π-System Donor: Insulating State of $(MeDH\text{-}TTP)_2AsF_6$

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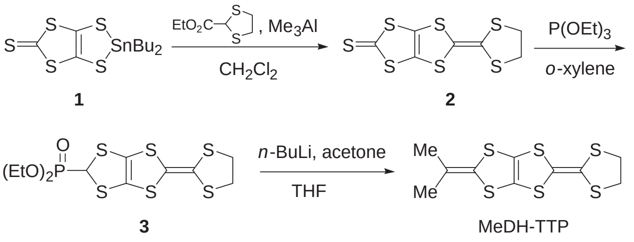
The transport properties of $(MeDH\text{-}TTP)_2AsF_6$, which crystallized in the κ-type structure, were investigated and found to be semiconductive with a small activation energy. ESR measurements suggested that the insulating state below 40 K should be antiferromagnetic, similarly to the Mott transition system represented by quasi-two-dimensional κ-ET [ET = bis(ethylenedithio)tetrathiafulvalene] salts.

Controlling the physical parameters of organic conductors such as on-site Coulomb energy (U) and intermolecular transfer integral (t) by the chemical modification of organic donors is crucial to realizing various electronic states: superconductivity, antiferromagnetism, charge ordering (CO), and so on.[1] In order to control these parameters, we have designed and synthesized an organic donor with a new π-electronic system, DODHT [(1,4-dioxane-2,3-diyldithio)dihydrotetrathiafulvalene], and developed pressure-induced superconductors composed of this donor.[2] The DODHT molecule fulfills both the molecular design requirements of U and t; the reduction of the π system of the TTF (tetrathiafulvalene) skeleton and the introduction of a bulky dioxane ring lead to the enhancement of U and the decrease of t, respectively. The insulating state of β''-$(DODHT)_2PF_6$ at ambient pressure corresponds to a CO state.[3] On the other hand, we have also investigated donor molecules, DH-TTP (dihydrotetrathiapentalene) systems, that meet only the requirement for the enhancement of U because of no bulky substituent.

The crystal structure and the electrical conducting properties of the radical cation salts of the methyl derivative of DH-TTP, $(MeDH\text{-}TTP)_2X$ [MeDH-TTP = 2-isopropylidene-5-(1,3-dithiolane-2-ylidene)-1,3,4,6-tetrathiapentalene, X = AsF_6, $Au(CN)_2$, or I_3], have already been reported.[4] The crystal structure of the AsF_6 salt showed κ-type donor arrangement. The temperature dependence of the resistivity of $(MeDH\text{-}TTP)_2AsF_6$ was very weak down to ca. 50 K and below this temperature, a hump was observed around 30 K. The electrical resistivity at low temperature was ambiguous because of its non-Ohmic response.

In this study, we re-examined the transport properties of $(MeDH\text{-}TTP)_2AsF_6$ and performed magnetic measurements in order to determine the nature of the insulating state. An improvement of the synthetic method of MeDH-TTP is also presented.



Scheme 1.

The synthesis of MeDH-TTP was improved as shown in Scheme 1. In the previous method,[4] the last step gave a very low yield and purification was very difficult owing to impurities that were hardly removed from the target molecules depending on the alkyl substituents. Tin dithiolate **1**, which was prepared from $(^nBu_4N)_2[Zn(dmit)_2]$ (dmit = 4,5-dimercapto-1,3-dithiole-2-thione), reacted with ester in the presence of Me_3Al to give thione **2** in 71% yield. The reaction of **2** with triethylphosphite (285 equiv.) in o-xylene under dilute condition (3.5 mM) was allowed to proceed at 90 °C until the solution turned green, and then refluxed overnight, giving phosphonate **3** in 55% yield.[5] Treatment of **3** and acetone with ^nBuLi in THF at −78 °C gave MeDH-TTP in 75% yield. This improved method offers the following advantages: decrease in the total number of reaction steps, high total yield, and easy purification of MeDH-TTP in the last step. Cation radical salts were prepared electrochemically in chlorobenzene at 5 °C.

Figure 1a shows the resistivity of $(MeDH\text{-}TTP)_2AsF_6$ as a function of temperature measured in the conducting layer. The electrical conductivity at room temperature is 1.4 S cm^{-1}, which is the same as the value reported previously.[4] Although the temperature dependence of resistivity from room temperature to ca. 100 K is very weak, similarly to the previous report,[4] no hump was observed in the low-temperature region, but a small anomaly was observed around 50 K. This anomaly was clearly seen in the plot of the resistivity as a function of inverse temper-

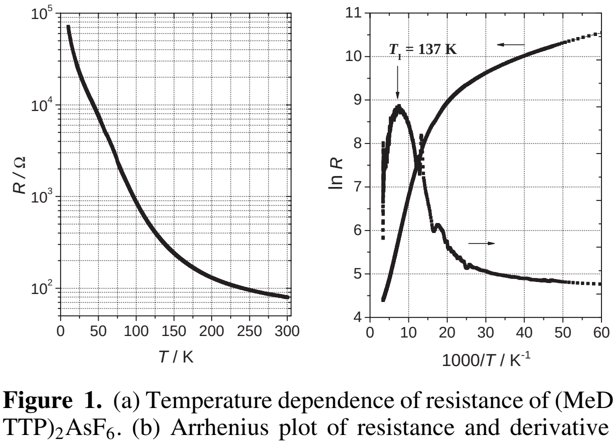


Figure 1. (a) Temperature dependence of resistance of $(MeDH\text{-}TTP)_2AsF_6$. (b) Arrhenius plot of resistance and derivative of resistance.

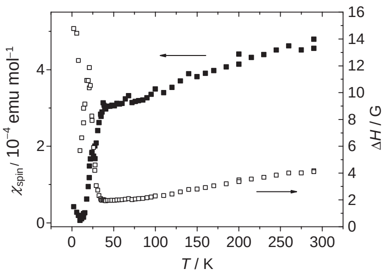


Figure 2. Temperature dependence of spin susceptibility (χ_{spin}) and peak-to-peak line width of (MeDH-TTP)$_2$AsF$_6$.

ature, $1/T$, shown in Figure 1b. The resistivity can be described by the activation-type conduction (Arrhenius plot), $\rho(T) = A\exp(\Delta E/k_BT)$, only above the temperature range of $80\,K < T < 300\,K$, where A is a temperature-independent constant, k_B, the Boltzmann constant, and ΔE, the activation energy. The activation energy in this temperature range was estimated to be 31.5 meV. Below 80 K, the deviation of the resistivity from the Arrhenius plot becomes large with decreasing temperature. In addition to the anomaly at 50 K, there exists an inflection point at 137 K in the derivative of the resistivity in the Arrhenius plot, suggesting that charge localization starts to occur at this temperature.

In order to investigate the insulating state, the magnetic properties were investigated by electron spin resonance (ESR) measurements of the powder sample in the temperature range between 290 and 2 K. From 290 to 27 K, Lorentzian line shapes were observed and the ESR signals were fitted by the Lorentzian function with the values of the resonance field, peak height (I_0), and peak-to-peak line width (ΔH_{pp}) as fitting parameters. Below 27 K, the ESR signals could be fitted by two Lorentzian curves, instead of a single Lorentzian curve, suggesting that two types of spin species exist below this temperature (see Supporting Information). Figure 2 shows the temperature dependence of spin susceptibility (χ_{spin}), which was the product of I_0 and the square of ΔH_{pp}, and that of ΔH_{pp}. The absolute value of χ_{spin} was determined with reference to the signal of $CuSO_4 \cdot 5H_2O$. With decreasing temperature down to 40 K, χ_{spin} decreases gradually, followed by a steep decrease below 40 K. Further below 27 K, the χ_{spin} value of one component also exhibits a sharp drop with decreasing temperature and connects smoothly to the χ_{spin} above 40 K. On the other hand, the χ_{spin} values and their temperature dependence of the other component are very small. Thus, we assigned the latter spin species to an impurity spin. As shown in Figure 2, ΔH_{pp} of the conduction electron is 4.1 G at 290 K and decreases gradually with decreasing temperature down to 40 K. Below this temperature, ΔH_{pp} corresponding to the conduction electron spin shows abrupt broadening and the ESR signals almost vanish. The broadening of ΔH_{pp} and the sudden decrease of χ_{spin}, which seem to correspond to the anomaly in the temperature dependence of the resistivity, indicate antiferromagnetic (AF) ordering accompanied by a transition to an insulating state such as the SDW (spin density wave) state or the Mott insulator.

Figure 3 shows the band structure and the Fermi surface calculated at the extended Hückel level on the basis of intermolecular overlap integrals[6] (see Supporting Information), which are similar to a series of κ-type ET salts,[7] some of which have a Mott insulating AF insulating state. The dimerization gap in the band structure of (MeDH-TTP)$_2$AsF$_6$, however, is fairly small, which makes the electronic structure of (MeDH-TTP)$_2$AsF$_6$ almost 3/4-filled. Recently, Hotta classified quasi-two-dimensional organic conductors into two groups by the degree of dimerization; under both the strong inter-site (V) and on-site (U) Coulomb interactions, the nondimerized or weakly dimerized 3/4-filled system provides the CO insulating state, whereas the strongly dimerized system becomes effectively half-filled and favors the Mott insulator instead of CO.[8] Although the κ-type salts represented by κ-ET salts are generally classified into the latter, the band structure of (MeDH-TTP)$_2$AsF$_6$ seems to be closer to the former case because of the relatively smaller anisotropy of the transfer integrals. Furthermore, since both MeDH-TTP and DODHT have the similar extent of the π-system, V values in (MeDH-TTP)$_2$AsF$_6$ are expected to be almost the same to those of DODHT salts, which has CO insulating state. As a whole, the MeDH-TTP salt cannot be simply identified as the Mott insulator but is possibly either the first κ-type salt with CO ground state or a new system that interpolates the CO and Mott insulator with the degree of dimerization as a parameter. Further experimental studies are underway including X-ray structural analysis at low temperatures in order to elucidate the insulating state of MeDH-TTP salt.

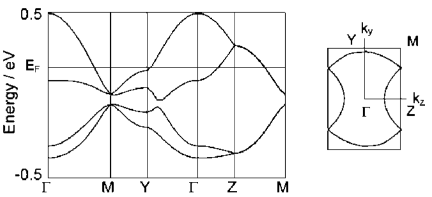


Figure 3. Band structure and Fermi surface of (MeDH-TTP)$_2$-AsF$_6$ (for intermolecular transfer integrals, see Supporting Information).

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References and Notes

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