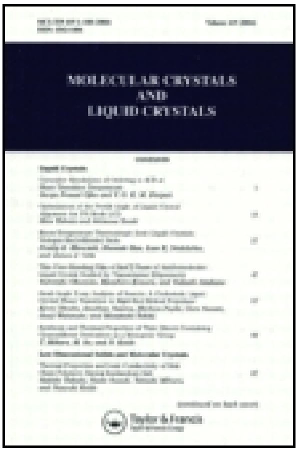

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Cation Radical Salts with Flexible Polycyano Anions having Tetracyanoallyl Skeleton

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Cation radical salts of BEDO-TTF (BO) with six kinds of polycyano counter anions of tetracyanoallyl derivatives (R-TCA; R: substituent) were investigated. Although the stoichiometries of the salts are different from salt to salt, the degree of charge transfer on BO molecules ranges from +0.4 to +0.5. 2-propoxy-TCA anion (PrO-TCA$^-$) provides a semiconducting salt, while the other anions afford metallic ones. The EtO-TCA$^-$ salt exibits successive metal-semiconductor and semiconductor-metal transitions near 150 K and 40 K, respectively. Magnetic susceptibility of this salt shows slight decrease near 100 K and it keeps non-zero value even at 1.9 K. The crystal structures of three kinds of the salts were solved. The salts of EtO-TCA$^-$ and cyanomethyl(CM)-TCA$^-$ have I_3-type packing motifs of the BO molecules. The salt of DHCP^{2-} (R = C(CN)C(CN)C(CN)$_2^-$) has a similar packing motif to I_3-type, however, the stacking direction of the BO molecules varies par five BO molecules.

Keywords Cyanocarbon; Organic anion; Charge transfer complex; Synthetic metal; BEDO-TTF (BO); Crystal structure

INTRODUCTION

Among various organic conductors, cation radical salts consisting of organic donors and inorganic counter anions have been most intensively investigated. However, the use of organic counter anions is expected to provide more variety of salts than inorganic ones. The large polarizabilities of the organic anions are also expected to stabilize the metallic states.[1] Furthermore, atomic contacts between heteroatoms of donor and anion molecules may increase the dimensionality of the salts. Considering these points, we have investigated radical cation salts with cyanocarbons, mainly tetracyanoallyl (TCA) derivatives, such as PCA$^-$, HCTMM^{2-}, RO-TCA$^-$ (R = Me, Et, n-Pr, n-Bu) and DHCP^{2-}.[2]

In this paper, BEDO-TTF (BO) salts with RO-TCA$^-$, CM-TCA$^-$ and DHCP^{2-} anions are described.

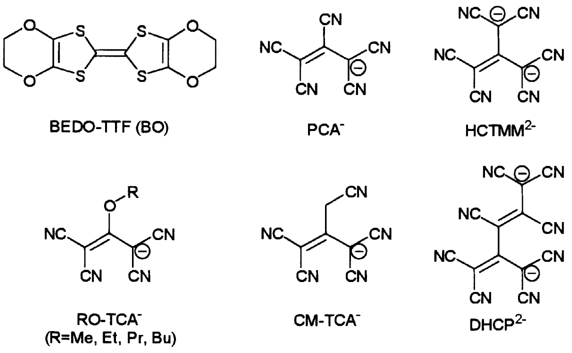

FIGURE 1 Structures of BEDO-TTF (BO) and polycyano anions.

RESULTS AND DISCUSSION

Preparation of BO Salts

RO-TCA$^-$, CM-TCA$^-$ and DHCP^{2-} were synthesized according to the literatures.[3] Cation radical salts were obtained by electrooxidation of BO in the presence of the tetraalkylammonium salt of the anion from tetrahydrofuran (THF) or acetonitrile (An). Stoichiometries, appearances and averaged formal charge of BO molecules (γ) of the salts are summarized in TABLE 1.

TABLE 1 Characteristics of BO salts

Anion	D:A	Appearance	γ^c	σ_{RT} ^{d}/ Scm^{-1}
MeO-TCA$^-$	9:4:5(H_2O)^a	Black plate	4/9	100
EtO-TCA$^-$	2:1^{a,b}	Black plate	0.5	10
PrO-TCA$^-$	2:1^a	Dark gray wool	0.5	16 ^{e}
BuO-TCA$^-$	5:2:0.5(THF)^a	Black wool	0.4	7 ^{e}
CM-TCA$^-$	5:2:2(An)^b	Black plate	0.4	50
DHCP^{2-}	5:1:2(THF)^b	Black plate	0.4	100

^{a} determined by elemental analysis; ^{b} determined by X-ray crystal structure analysis; ^{c} averaged formal charge on BO molecules; ^{d} conductivity at room temperature; ^{e} measured on compressed pellet.

Electric Conductivity and Magnetic Susceptibility

All of the salt except for that of PrO-TCA are metallic with conductivities at room temperature (σ_{RT}) listed in TABLE 1.

Among the metallic ones, EtO-TCA salt shows a metal-semiconductor transition near 150 K, then it changes again to metallic one below 40 K (FIGURE 2(a)). The activation energy (E_a) between 60

K and 100 K is about 6 meV. Magnetic susceptibility of this salt measured by SQUID magnetometer is about 4×10^{-3} emu mol^{-1} at room temperature (RT), and shows slight decrease near 100 K (FIGURE 2(b)). It remains about 80 % of the value of RT at lowest temperature after subtraction of Curie component coming from impurity, and has no anomaly near 40 K where the salt seems to recover the matallic behavior. The temperature dependence of magnetic susceptibility and the low E_a for conduction infer that though nearly one fifth of carriers are extinguished by the phase transition around 100 K, the low temperature phase keeps a metallic nature. The metal-metal transition is reported in $(BO)_2ReO_4 \bullet H_2O$,[4] though the temperature dependence of the conductivity is different from the EtO-TCA salt.

Compressed pellet sample of PrO-TCA salt is semiconducting even at RT with E_a of 100 meV (> 150 K) and 26 meV (< 100 K). Magnetic susceptibility is an activation type ($\chi = CT^{-1} \exp(-E_a / k_B T)$, k_B: Bolzmann constant) with E_a of 60 meV, which is consistent with the semiconducting behavior.

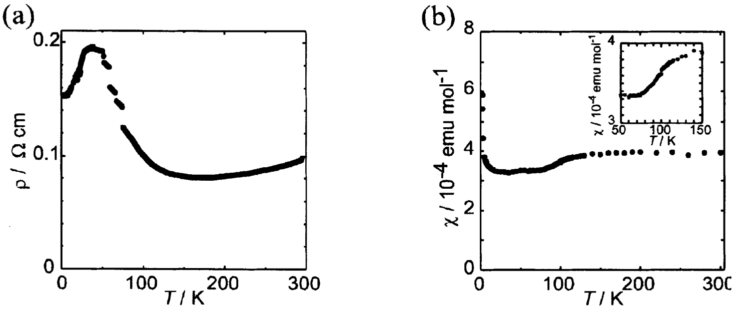

FIGURE 2 Temperature dependence of (a) resistivity and (b) magnetic susceptibility of $(BO)_2$(EtO-TCA). Inset of (b): expansion near 100 K.

Crystal Structures of EtO-TCA, CM-TCA and DHCP Salts

Among the six kinds of the salts, crystal structures of EtO-TCA, CM-TCA and DHCP salts were studied.[5]

In EtO-TCA and CM-TCA salt, BO molecules form I_3-type layered structures.[6] DHCP salt also has a similar layered structure. However, the stacking direction of BO molecules varies par five BO molecules as shown in FIGURE 3. This type of packing has not been reported yet.

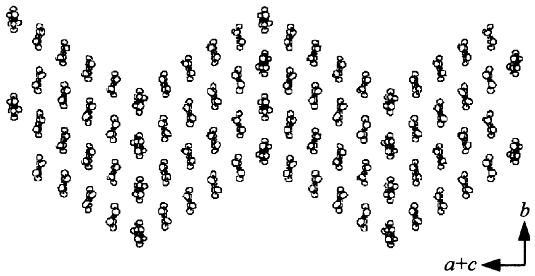

FIGURE 3 Donor layer of $(BO)_5(DHCP)(THF)_2$. Projected along the long axis of BO molecule.

CONCLUSION

Six kinds of TCA derivative anions afford solid BO salts that show not only metallic, semiconducting behavior but also the peculiar phase transition. $DHCP^{2-}$ salt has a novel packing motif of BO molecules. It is noticeable that the use of low symmetrical TCA anions provides relatively good quality of crystals, though it is known that most of the conducting BO salts has rather poor quality of the crystals.

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[5] Crystallographic data: For EtO-TCA salt; triclinic $P\bar{1}$, a = 8.093(1), b = 10.657(3), c = 20.401(4) Å, α = 103.85(1), β = 98.75(1), γ = 98.42(1)°, V = 1670.27(2) Å^3, Z = 2, R = 0.092. For CM-TCA salt; triclinic $P\bar{1}$, a = 7.2620(8), b = 14.972(4), c = 19.732(4) Å, α = 79.88(1), β = 82.84(1), γ = 87.38(1)°, V = 2094.9(7) Å^3, Z = 1, R = 0.082. For DHCP salt, monoclinic $P2_1$/n, a = 23.105(5), b = 12.0010(9), c = 30.707(5) Å, β = 102.128(7), V = 8324(2) Å^3, Z = 4, R = 0.142.

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