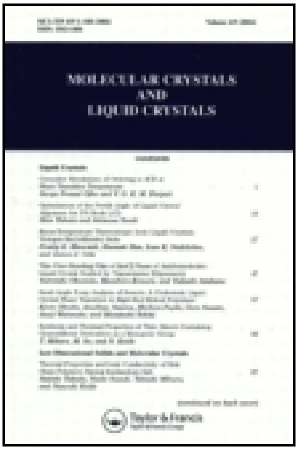

Molecular Crystals and Liquid Crystals

Tuning of critical temperature in an et organic superconductor

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TUNING OF CRITICAL TEMPERATURE IN AN ET ORGANIC SUPERCONDUCTOR

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A variety of superconductors having T_c from 3 to 10 K were produced by the replacement of small portion of $Cu(CN)_2$ in the anion layer of a Mott insulator, κ-$(ET)_2Cu_2(CN)_3$ by $N(CN)_2$. By the incorporation of $N(CN)_2$, some Cu^{+1} ions were changed to Cu^{+} ions. The complex is formulated as κ-$(ET)_2(Cu^{+1})_{2-x-y}(Cu^{+2})_x(CN)_{3\text{-}2y}[N(CN)_2]_y$, with mainly $y = 0$, 0.05, 0.3–0.4, 0.8 and 1.0 and $x = 0$–1200 ppm. The T_c depends on both x and y. The batches at $y = 0.3$–0.4 have different T_c's (3.1, 6.5, 7.5, 8.8, 10.2 K) suggesting the important role of the amount of Cu^{2+}.

Keywords: ET; organic superconductor; critical temperature; tuning; band filling; mixed anion; κ-type; Mott insulator

INTRODUCTION

The two-dimensional (2D) electronic nature of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF or ET) compounds has provided a variety of metallic and superconducting charge transfer (CT) complexes [1]. The T_c of the ET superconductors reached up to 13.1 K under pressure and 12.3 K at ambient pressure for κ-(ET-d_8)$_2$Cu[N(CN)$_2$]Cl [2] and κ-(ET-d_8)$_2$ Cu(CN)[N(CN)$_2$] [3], respectively, where ET-d_8 is the deuterated ET molecule. Due to the dimerization of ET molecules of the κ-, β- or β'-type packing, the calculated HOMO band is split into upper- and lower-ones. The upper-HOMO band is half filled provided that the magnitude of electron correlation, on-site Coulomb repulsion U, of the crystal composed of dimerized molecules is negligible compared to the bandwidth of the upper-HOMO band (W_U). The on-site Coulomb repulsion of a dimer, U_{dimer}, has been known to be approximated by Eq. 1, where ΔE is the energy splitting between upper- and lower-HOMOs of a dimer (dimerization energy).

$$U_{\mathrm{dimer}} = \Delta E + [U - (U^2 + 4\Delta E^2)^{1/2}]/2 \tag{1}$$

Since U of an ET molecule is much larger than ΔE values of ET molecules, U_{dimer} can be approximated by ΔE. Figure 1 summarizes the relation between the ΔE and W_U values within the extended Hückel method of the ET compounds including good metals with low T_c ($T_c \leq 8$ K), 10 K class superconductors and Mott insulators [3b]. The following aspects are pointed out: 1) A nearly linear relation exists between $W_U/\Delta E$ and W_U values among the ET compounds with a dimerized donor pair. 2) Typical Mott insulators (**1–4**) reside at the lower-left side, and good metals (**10,12–15**) are located at the upper right side. 3) The 10 K superconductors (**7–9, 11**) reside between the Mott insulators and good metals with $W_U/\Delta E$ around 1.1–1.2.

A Mott insulator having $W_U/\Delta E$ close to unity (**5**) has been transformed into a superconductor with T_c of 3 K by applying pressure in 1991 [4]. While, we have obtained a metallic and superconducting ET salt

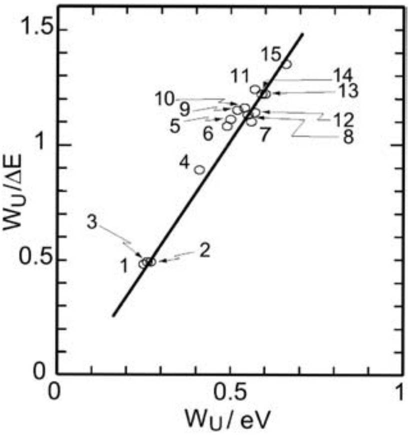

FIGURE 1 Plot of (band-width of upper-Hubbard band, W_U)/(dimerization energy ΔE) vs. W_U of several ET salts. **1–5:** Mott insulator, **7–9,11**: 10 K class superconductor, **10,12–15**: good metal with low T_c. **5**: κ-$(ET)_2Cu_2(CN)_3$, **6**: κ'-$(ET)_2Cu_2(CN)_3$.

having nearly the same crystal structure as that of κ-$(ET)_2Cu_2(CN)_3$ (**5**) in 1991 and named κ'-$(ET)_2Cu_2(CN)_3$ (**6**) to discriminate them [3,5]. EPR measurements indicated that the κ' salt contained small amount of Cu^{+2} while the κ one did not. Hence, we had formulated the κ' salt as κ-$(ET^{+0.5(1-\delta)})_2(Cu^{+1})_{2-\delta}(Cu^{+2})_\delta(CN)_3$ and rationalized its appearance of the metallic and superconducting nature to be a slight deviation of the band-filling from the exact half, which is most critical towards a Mott criterion. Since then we have continued the preparation of κ-$(ET^{+0.5(1-\delta)})_2$ $(Cu^{+1})_{2-\delta}(Cu^{+2})_\delta(CN)_3$ in order to elucidate the relation between T_c and δ values and hence the mechanism of superconductivity in this system.

Recently, we have found that the metallic and superconducting nature of the κ' salt is not only governed by the content of Cu^{+2} but also by the presence of $[NC\text{-}N\text{-}CN]^{-1}$, which replaces $[NC\text{-}Cu\text{-}CN]^{-1}$ in the layer of $Cu_2(CN)_3$, owing to the very close shape, size and charge between them [6]. We report here a series of $\kappa-(ET^{+0.5(1-x)})_2(Cu^{+1})_{2-x-y}(Cu^{+2})_x(CN)_{3-2y}$ $[N(CN)_2]_y$, the T_c's of which cover from 0 K (a Mott insulator, $x=y=0$) to 11.2 K ($x=0$, $y=1$) and are tuned from 3 K to 10 K by changing x and y between them. It should be emphasized that the crystal structures of them are nearly kept constant through such anion modification and this is the most significant feature in achieving the successful tuning of T_c in an organic superconductor.

PREPARATION

The single crystals have been prepared by electrocrystallization in the presence of the following supporting electrolytes with the preferential products in the parentheses (* indicates the major one): **1.** {CuCN+KCN+18-C-6} (κ); **2.** {$TBA\cdot Cu_3(CN)_4\cdot CH_3CN$} ($\kappa$); **3.** {$TBA_3[Fe(CN)_6]$+$Cu(CN)_2$} ($\kappa$) [7]; **4.** {$Cu[N(CN)_2]$+KCN+18-C-6} ($\kappa'$*,$\theta$); **5.** {CuCN+$Ph_4P[N(CN)_2]$} ($\kappa$,$\kappa'$,$\theta$*); **6.** {CuCN+$NaN(CN)_2$+18-C-6} ($\kappa$,$\kappa'$,$\theta$*). We have obtained 108 batches under constant condition (electrolyte **4**, PhCN+6% MeOH, 0.2 μA) at room temperature. Among them, the crystals in 99 batches are plates (κ,κ'), those in two batches are needles (θ), those in two batches are blocks (not identified) and others are powders. Among the first 99 batches, ca. 20 batches showed the superconductivity by SQUID measurements. Each single crystal has been examined by the combination of the following measurements to determine; 1) the content of Cu^{+2} (x) by EPR measurements, 2) the content of $[N(CN)_2]$ (y) by IR and Raman spectra, 3) T_c by the LFMA measurements and 4) the crystal structure or lattice parameters.

RESULTS AND DISCUSSION

Figure 2 shows the relation between the mixing ratio y and T_c in several batches of κ' salt so far measured and the followings are the noticeable features.

1) Between a Mott insulator (point **a**) and a 11 K superconductor (point **e**), superconducting crystals appear with the preferential ratio y of 0.05 (point **b**), 0.3 (point **c**) and 0.8 (point **d**). It is worth mentioning that even 5% of $N(CN)_2$ induces superconductivity. The mixing of the two kinds of ligand in the anion layer was found to be uniform and homogeneous; namely both a simple mixing of 95% of a Mott insulator κ-$(ET)_2Cu_2(CN)_3$ and 5% of κ-$(ET)_2Cu(CN)[N(CN)_2]$, for $y = 0.05$ within a layer and layer-by-layer and also random orientation of NC−X−CN (X=Cu or N) in a single crystal were denied (Figure 3) [6]. Almost all the crystals in a batch have the same x and y values (the errors in x and y are ca. 10 and 5%, respectively).

2) In general higher T_c is realized with larger y with scatter, which is related to the scatter of the content of Cu^{+2} in a fixed y. The content of Cu^{+2} is non-zero (80–1200 ppm) except the two extreme cases of $y = 0$ and 1.

3) At $y = 0.3$ the T_c covers from 3 K to 10 K and the crystals having different T_c's have different x values. A tendency is observed of the higher T_c with larger content of Cu^{+2} up to 400 ppm and then T_c decreases, though the relation between T_c and the content of Cu^{+2} is not satisfactory determined yet due to the lack of sufficient data.

4) The similar size and shape and the same charge of CN-X-CN (X = N, Cu) enable the exchange of ligand between the anion layers of $Cu_2(CN)_3$,

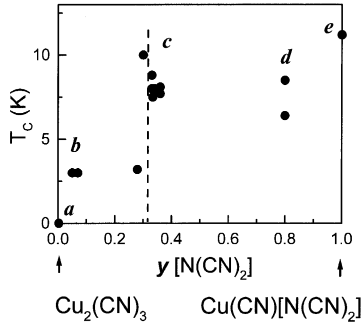

FIGURE 2 Relation between the content of $N(CN)_2$, y and T_c in several crystals of κ' salt: κ-$(ET)_2(Cu^{+1})_2(Cu^{+2})_{2-x-y}(CN)_{3-2y}[N(CN)_2]_y$. As for points **a–e**, see text. Dashed line indicates the samples of $y \approx 0.3$.

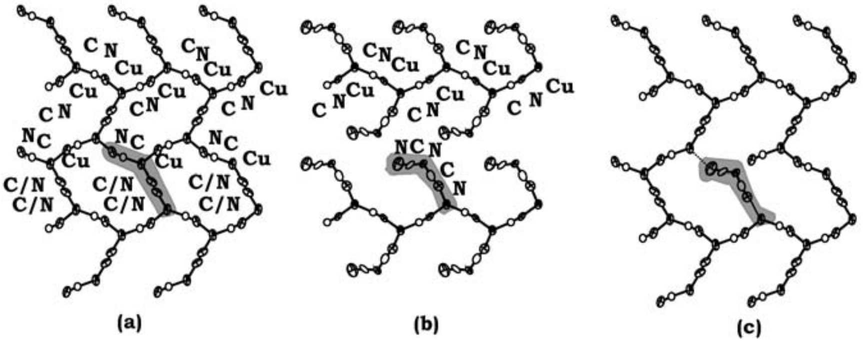

FIGURE 3 The anion structures of (a) κ-$(ET)_2Cu_2(CN)_3$, (b) κ-$(ET)_2Cu(CN)[N(CN)_2]$ and (c) schematic figure of κ'-$(ET)_2Cu_2(CN)_3$ with $y = 0.1$.

which is equal to $\{(CuCN)^0 + (NC\text{-}Cu\text{-}CN)^{-1}\}$, and $Cu(CN)[N(CN)_2]$, which is equal to $\{(CuCN)^0 + (NC\text{-}N\text{-}CN)^{-1}\}$, rather freely and result in very similar lattice parameters among κ-$(ET)_2Cu_2(CN)_3$, κ-$(ET)_2$-$Cu(CN)[N(CN)_2]$ and κ' salts (Figure 3) [3,5]. These facts suggest them to be excellent candidates for a system of band filling control and making superlattice structure composed of Mott insulator/superconductor heterojunctions.

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