# Donor-Acceptor Type Superconductor, $(BETS)_2(Cl_2TCNQ)$

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It was found that $(BETS)_2(Cl_2TCNQ)$ is an all-organic superconductor, where BETS is bis(ethylenedithio)tetraselenafulvalene and $Cl_2TCNQ$ is 2,5-dichlorotetracyanoquinodimethane. The superconducting critical temperature was 1.3 K±0.3 K under pressure.

More than 60 organic superconductors have been reported since the discovery of superconductivity in $(TMTSF)_2PF_6$.[1] Most of these charge-transfer (CT) compounds are known as a hybrid system composed of TTF-skeleton-based "organic" donors (or acceptors) with combination of "inorganic" counter-anions (or cations). One of the next target to be explored is the "donor-acceptor type" superconductor. In this type of material, one is able to control the band-filling and the electrical properties with use of the mixed-valent nature of organic $\pi$-electron-based molecules, as is observed in the conductivity of (TTF)(TCNQ) system at high pressure.[2] For this purpose, (BEDT-TTF)(TCNQ) analogues are promising since (1) TCNQ derivatives which have many kinds of electron affinities have been already synthesized,[3] (2) the combination with two dimensional (2D) donor layer suppresses the Peierls instability of one dimensional (1D) TCNQ column. In fact, recent investigations have revealed that one of this type of materials, (BEDT-TTF)(FTCNQ), maintains metallic properties down to low temperature.[4] Here we report synthesis, structure and electrical properties of $(BETS)_2(Cl_2TCNQ)$, which was found to be the donor-acceptor type superconductor.

The donors and the acceptors were synthesized according to the literature.[5,6] The crystals are obtained by slow cooling of the concentrated solution in chlorobenzene. The typical crystal size is 1.0x 0.5x 0.2 $mm^3$. Figure 1 shows the crystal structure of $(BETS)_2(Cl_2TCNQ)$,[7] (a) viewed along the stacking axis (c-axis), and (b) viewed along the molecular long axis of BETS. As seen in these figures, donors form 2D conducting layers, while acceptor columns are strongly isolated with each other. The structure of the donor layer is characterized by uniform "face-to-face" stack along the c-axis and double periodicity in the "side-by-side" direction along the a-axis. It is noted that the uniform stack is in sharp contrast to the quadratic periodicity of the $\lambda$-type BETS-based superconductors.[8]

The band structure of the conducting donor layer is calculated to be quasi-one-dimensional, both due to the large "face-to-face" overlap integral ($63.8x10^{-3}$) between donors along the stacks, and due to the small "side-by-side" overlap integral ($3\sim7.5x10^{-3}$) between donor columns in the unit cell.[9] From the observation of C≡N stretching mode at 2180 $cm^{-1}$ for $Cl_2TCNQ$, the valence of $Cl_2TCNQ$ is found at almost $-1$.[10] It indicates that there is almost one hole per two BETS molecules.

The electrical resistivity of $(BETS)_2(Cl_2TCNQ)$ was measured by four probe method along the stacking axis. Figure 2 shows the temperature dependence of the resistivity at 3.5 kbar,

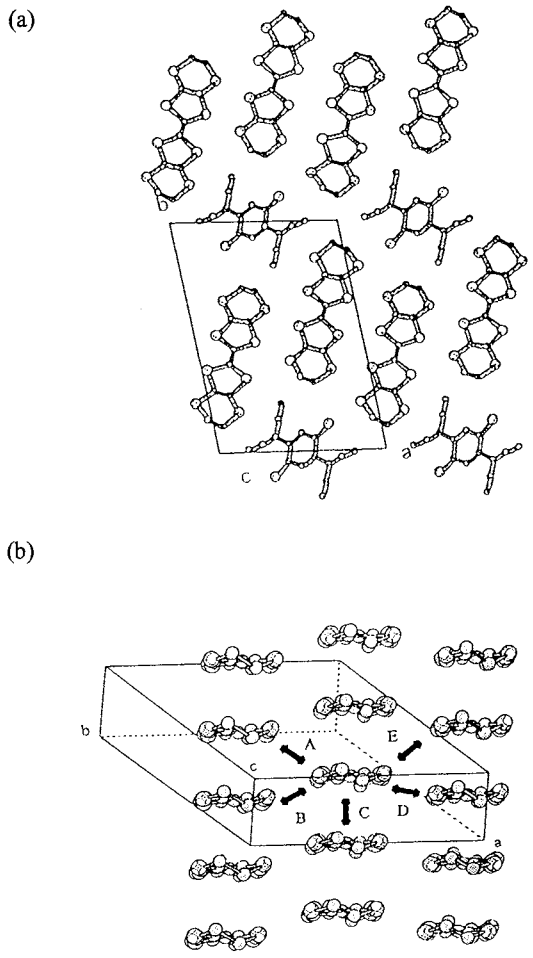


**Figure 1.** Crystal structure of $(BETS)_2(Cl_2TCNQ)$ (a) viewed along the stacking axis (c-axis). (b) BETS Molecular arrangement viewed along the molecular long axis.

6 kbar and 8.5 kbar.[11] As shown in Figure 2, the electrical resistivity keeps metallic behavior down to low temperatures at 3.5 kbar, Figure 3 shows the resistivity behavior at low temperature range. The resistivity dropped below 1.6 K and fell to almost zero below 0.6 K. Under magnetic fields above 0.5 T, the resistivity drop disappears. We also measured the AC magnetic susceptibility at 3.5 kbar, exhibiting a diamagnetic behavior below 1K. These observations provide an unambiguous evidence for the superconductivity in $(BETS)_2(Cl_2TCNQ)$ under pressure.

Above 6 kbar, the resistivity turns to increase with

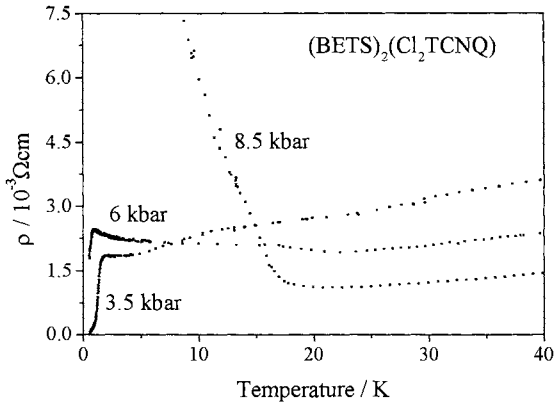


**Figure 2.** Temperature dependence of electrical resistivity of(BETS)$_2$(Cl$_2$TCNQ), at 3.5kbar, 6kbar, and 8.5kbar. The inset shows temperature dependence of electrical resistivity around Tc at 3.5kbar.

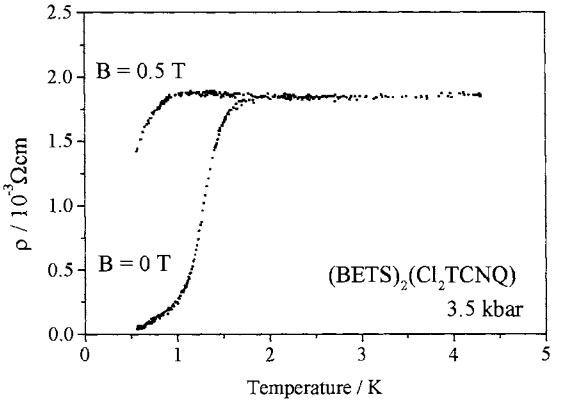


**Figure 3.** Superconducting transition of (BETS)$_2$(Cl$_2$TCNQ) at 3.5 kbar and recovery of resistance by magnetic field (0.5T)

decreasing of the temperature below 22 K, with a hump at 15 K, as shown in Figure 2. At this pressure, the superconducting transition was observed at around 0.8 K. At the higher pressure of 8.5 kbar, the superconducting phase is suppressed at least above 0.5 K.

The resistivity measurements were made on five samples synthesized in different batches. The superconductivity was found at 3.5 kbar for all the samples at the onset temperature of 1.3 K $\pm$ 0.3 K. However, the superconductivity at ambient pressure was sample-dependent; one sample shows the superconducting transition at 0.8 K, while another keeps metallic behavior down to 0.03 K.

In conclusion we have found a novel superconductor, (BETS)$_2$(Cl$_2$TCNQ), under pressure. The finding of the "donor-acceptor type" superconductor indicates that this kind of material should be more investigated since they provide additional freedoms which was absent in the organic-inorganic "hybrid" systems. For instance, it is open to question; whether the electrons on the acceptor columns are relevant to the superconductivity, or whether the behavior of the metal-insulator transition under high pressure is related with the variation of valence value of the acceptor molecules.

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**References and Notes**

1 T. Ishiguro, K. Yamaji, and G. Saito, "Organic Superconductors Second Edition," in "Springer Series in Solid-State Sciences 88," Springer-Verlag, Berlin Heidelberg (1998).

2 R.H.Friend, M.Miljak, and D.Jerome, *Phys. Rev. Lett.*, **40** 1048 (1978).

3 R.C.Wheland and J.L.Gilson, *J. Am. Chem. Soc.*, **98**, 3916 (1976)., R.C. Wheland, *J. Am. Chem. Soc.*, **98**, 3926 (1976).

4 T. Hasegawa, K. Inukai, S. Kagoshima, T. Sugawara, T. Mochida, S. Sugiura, and Y. Iwasa, *Chem. Commun.*, **1997**, 1377.

5 R.Kato, H.Kobayashi, and A.Kobayashi, *Synth. Met.*, **41-43**, 2093 (1991).

6 T.Mochida, T.Hasegawa, S.Kagoshima, S.Sugiura, and Y.Iwasa, *Synth. Met.*, **86**, 1791 (1996).

7 The crystallographic parameters (300 K): space group $P\bar{1}$, Z=1, a=13.176(5) Å, b=18.896(8) Å, c=4.193(5) Å, $\alpha$ =93.69(6)°, $\beta$ =92.71(5)°, $\gamma$ =101.98(3)°, V=1017.1 Å$^3$. The structure was solved by the direct method (SHELXS86; G. M. Sheldrick, in "Crystallographic Computing 3") and refined by using 2097 reflections. The final R value was 0.084.

8 H.Kobayashi, T.Udagawa, H.Tomita, K.Bun, T.Naito, and A.Kobayashi, *Chem. Lett.*, **1993** 1559; H.Kobayashi, H.Tomita, T.Naito, A.Kobayashi, F.Sakai, T.Watanabe, and P.Cassoux, *J. Am. Chem. Soc.*, **118**, 368 (1996).; H.Kobayashi, A.Sato, E.Arai, H.Akutsu, A.Kobayashi, and P.Cassoux, *J. Am. Chem. Soc.*, **119**, 12392 (1997).

9 The calculated overlap integrals are A=7.5, B=3.06, C=-63.8, D=-11.5, E=16.1$\times 10^{-3}$. The notations are shown in Figure 1 (b).

10 The C$\equiv$N streching mode for neutral Cl$_2$TCNQ crystal and K(Cl$_2$TCNQ) are observed at 2225 cm$^{-1}$ and 2200 cm$^{-1}$, respectively.

11 High pressure measurements were made by using a clamp-type cell. The value of the applied pressure was corrected by referring to the superconducting transition temperature of Sn.