

(BEDT-TTF)(F₁TCNQ) and (BEDT-TTF)(F₂TCNQ)_x(TCNQ)_{1-x} (*x ca. 0.5*): all-organic metals down to 2 K

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Crystal structures and solid-state properties are reported for all-organic metals, (ET)(F₁) and (ET)(F₂)_x(TCNQ)_{1-x} (*x ca. 0.5*), which are isostructural with each other and preserve metallic states down to 2 K.

Cation-radical salts derived from the organic donor, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET), have attracted considerable interest because of the rich variations of the crystal structures and the two-dimensionality of their electronic structures, affording various solid-state properties such as superconductivity,¹ fermiology,² etc. In contrast to most ET salts, represented as (ET)₂X (X = inorganic counter anion), investigated so far, the advantage of the title materials, which are ET-based donor-acceptor (DA) type charge-transfer (CT) complexes, is that the organic acceptor molecules can be designed by chemical modification to have variable electron affinity or molecular polarizability, which may enable control of the crystal structures and electronic properties.

TCNQ and its fluorinated derivatives, 2-fluorotetracyanoquinodimethane (F₁TCNQ, abbreviated F1) and 2,5-difluorotetracyanoquinodimethane (F₂TCNQ, F2), are chosen for this purpose. Among these CT complexes, the structure and properties of (ET)(TCNQ) have been investigated, and the strong electron-electron correlations are found to be responsible for its metal-insulator transition at *ca. T* = 330 K.^{3,4} To investigate the fluorine-substitution effect on (ET)(TCNQ), the following two types of single crystals for the DA complexes have been synthesized; the CT compounds (ET)(F_{*n*}TCNQ) (*n* = 0, 1, 2) and the ternary CT compounds (ET)(F_{*n*}TCNQ)_{*x*}(TCNQ)_{1-x} (0 < *x* < 1). It is noted that the electron affinity of F_{*n*}TCNQ can be controlled by the number (*n*), without changing the molecular volume significantly.⁵

F₁TCNQ and F₂TCNQ were synthesized using a new route reported by Uno *et al.*⁶ Single crystals of (ET)(F_{*n*}TCNQ) (*n* = 0, 1, 2) were obtained by slow cooling of concentrated solutions of the salts in chlorobenzene or 1,1,2-trichloroethane. Among (ET)(F_{*n*}TCNQ) (*n* = 0, 1, 2), a low electrical resistivity was observed in (ET)(F₁), of the order of 10⁻² Ω cm at room temp. Conversely, the resistivity of a single crystal of (ET)(F₂) is extremely high, *ca.* 10⁵ Ω cm. Such dependence of the resistivity on *n* is not directly associated with change of the electron affinity of F_{*n*}TCNQ,⁷ but is attributed to the drastic variation of their crystal structures.

Fig. 1 shows the crystal structure of (ET)(F₁)[†] from which it is seen that the donors and acceptors form sheets independently along the 010 plane. The ET molecules are stacked face-to-face along the *c*-axis, and arranged side-by-side along the [100] and the [101] directions [Fig. 1(b)]. The intermolecular S...S distance is found to be 3.48 Å between ETs aligned along [101] and 3.71 Å along [100], indicating the two-dimensional nature of the conducting sheet. Molecular packing of ETs is uniform in the sheets, which is in contrast to most other ET-based conductors. In (ET)(TCNQ), for example, ET molecules are dimerized in their two-dimensional donor sheets.³

The effect of fluorine substitution becomes more apparent in (ET)(F₂)_{*x*}(TCNQ)_{1-x} (0 < *x* < 1). The electrical resistivity of

the compaction sample becomes lowest (*ca.* 10⁻² Ω cm) at *x ca. 0.5* being 50 times smaller than that of (ET)(TCNQ), and *ca.* 10⁵ times smaller than that of (ET)(F₂), as seen in the inset of Fig. 3.

X-Ray powder diffraction patterns were measured to investigate the crystal structures of (ET)(F₂)_{*x*}(TCNQ)_{1-x}. The samples used for the measurements were obtained by evaporating the solvent from the whole concentration solution, ensuring that the nominal ratio of the ingredients in solution is identical to the chemical composition of the sample.[‡] The results are presented in Fig. 2 for (ET)(F₂)_{*x*}(TCNQ)_{1-x} 2' at *x ca. 0.5*, together with those of (ET)(F₂) 1, (ET)(F₁) 2 and (ET)(TCNQ) 3. The structures of 1, 2 and 3 are clearly different from each other. In the ternary system, on the other hand, the highest conductive compound, (ET)(F₂)_{*x*}(TCNQ)_{1-x} 2' (*x ca. 0.5*), is considered to be isostructural with 2.[§] This means that the introduction of a fluorine into each TCNQ, on the average, commonly gives isostructural compounds. The diffractograms for the samples at *x ca. 0.25* and *0.75* clearly show that they are composed of two phases, *e.g.* 1 + 2'.

Fig. 3 shows the temperature dependence of the electrical resistivity of single crystals of (ET)(F₁) and of the crystalline flake samples of (ET)(F₂)_{*x*}(TCNQ)_{1-x} (*x ca. 0.5*), obtained by slow cooling of concentrated solutions. Metallic properties are preserved down to 2 K. *R*(room temp.)/*R*(4.2 K) is *ca.* 70 and 30 for (ET)(F₁) and (ET)(F₂)_{*x*}(TCNQ)_{1-x} (*x ca. 0.5*), respectively, providing unambiguous evidence for good metallic character down to 4.2 K.

Finally we speculate as to why the introduction of a fluorine into TCNQ commonly stabilizes the structure of a highly conducting phase. Although the orientation of F₁TCNQ is

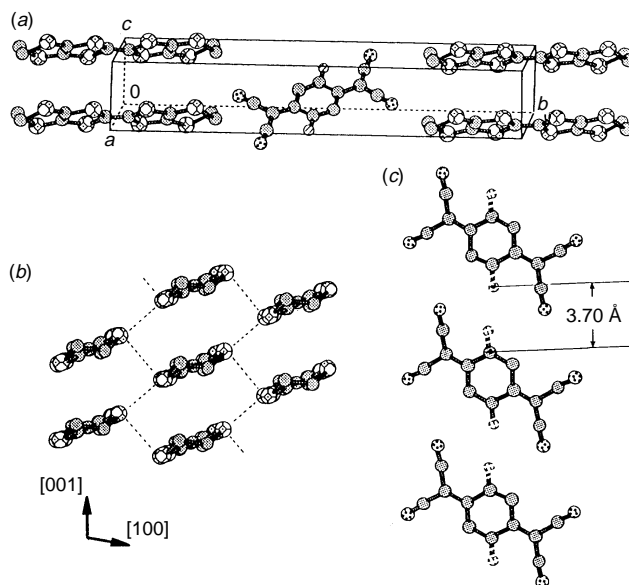


Fig. 1 (a) Crystal structure of (ET)(F₁); (b) view of molecular packing of ETs along the long molecular axis; (c) molecular arrangement of F₁

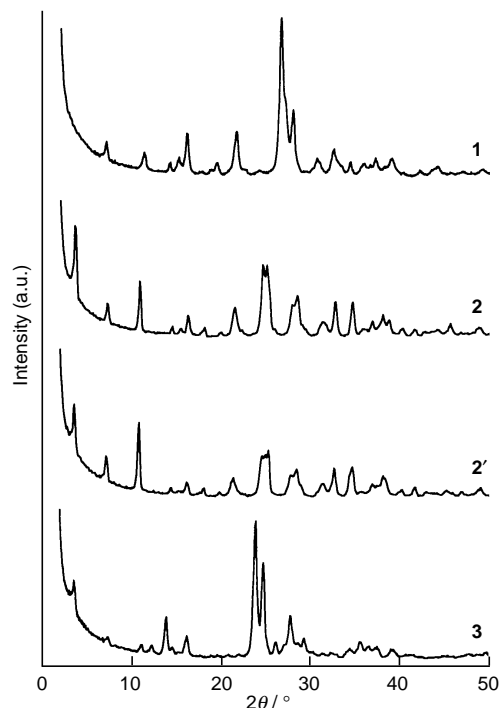


Fig. 2 X-Ray powder diffraction pattern of $(\text{ET})(\text{F}_2)_x(\text{TCNQ})_{1-x}$ **2'** (x ca. 0.5) in comparison with those of $(\text{ET})(\text{F}_n\text{TCNQ})$ ($n = 0, 1, 2$). $(\text{ET})(\text{F}_2)$ **1**, $(\text{ET})(\text{F}_1)$ **2** and $(\text{ET})(\text{TCNQ})$ **3**. The structure of $(\text{ET})(\text{F}_2)_x(\text{TCNQ})_{1-x}$ **2'** (x ca. 0.5) is similar to that of $(\text{ET})(\text{F}_1)$ **2**.

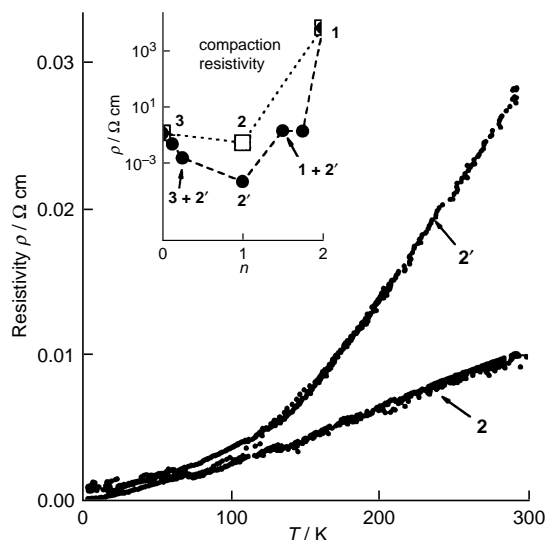


Fig. 3 Temperature dependence of electrical resistivity for an $(\text{ET})(\text{F}_1)$ single crystal and $(\text{ET})(\text{F}_2)_x(\text{TCNQ})_{1-x}$ (x ca. 0.5) crystalline flake sample. Inset shows compaction electrical resistivity vs. average number (n) of F atoms per TCNQ. Open squares are for $(\text{ET})(\text{F}_n\text{TCNQ})$ ($n = 0, 1, 2$) and filled squares for $(\text{ET})(\text{F}_2)_x(\text{TCNQ})_{1-x}$.

disordered in $(\text{ET})(\text{F}_1)$, the intermolecular $\text{F}\cdots\text{C}$ distance of 3.70 Å [Fig. 1(c)], which is shorter than the sum of the van der Waals radii of the $\text{F}\cdots\text{H}-\text{C}$ arrangement,⁸ strongly suggests the presence of a local structure represented as $\cdots(\text{TCNQ})\text{F}\cdots(\text{TCNQ})\text{F}\cdots(\text{TCNQ})\text{F}\cdots$, based on the hydrogen-bond-like interaction between CH and F. A similar local structure is also expected in $(\text{ET})(\text{F}_2)_x(\text{TCNQ})_{1-x}$ to form a $\cdots\text{F}(\text{TCNQ})\text{F}\cdots(\text{TCNQ})\cdots\text{F}(\text{TCNQ})\text{F}\cdots(\text{TCNQ})\cdots$ arrangement, which accounts for the exclusive formation of the $(\text{ET})(\text{F}_1)$ structure when one fluorine is introduced per TCNQ (at x ca. 0.5).

In summary, we obtained two kinds of ET-based all-organic metals, $(\text{ET})(\text{F}_1)$ and $(\text{ET})(\text{F}_2)_x(\text{TCNQ})_{1-x}$ (x ca. 0.5), preserving metallic states down to 2 K. Between them, $(\text{ET})(\text{F}_2)_x(\text{TCNQ})_{1-x}$ (x ca. 0.5) is an all-organic ternary metal and is isostructural with $(\text{ET})(\text{F}_1)$, in both of which the specific hydrogen-bond-like interaction is suggested to stabilize the structures affording highly conductive compounds.

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Footnotes

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† Crystal data for $(\text{ET})(\text{F}_1)$: triclinic, space group $P\bar{1}$, $a = 5.893(2)$, $b = 24.866(8)$, $c = 4.237(2)$ Å, $\alpha = 90.53(2)$, $\beta = 98.35(2)$, $\gamma = 97.14(1)$, $Z = 1$, $U = 609.53$ Å³, $T = 300$ K. The structure was solved by direct methods (SHELXS86; G. M. Sheldrick, in *Crystallographic Computing 3*) and refined using 1531 reflections. The final R value was 0.08. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/485.

‡ The results of elemental analysis (mass ratio) at the nominal ratio of $x = 0.5$ is C, 43.24; H, 1.94; N, 9.20; S, 42.42; F, 3.31% which corresponds to the nominal composition C, 43.54; H, 1.827; N, 9.23; S, 42.27; F, 3.13%. The observed difference may be due to some impurities such as decomposed material as well as small amounts of $(\text{ET})(\text{F}_2)$ crystals.

§ All the peaks are indexed in terms of a single phase with triclinic cell parameters obtained from powder diffraction, assuming the space group $P\bar{1}$, (300 K): $a = 5.884$, $b = 24.841$, $c = 4.246$ Å, $\alpha = 92.94$, $\beta = 97.87$, $\gamma = 96.96^\circ$, $U = 603.63$ Å³.

References

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