# Current-Induced Low-Resistive State in Organic Mott Insulator ET-TCNQ

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A molecular Mott-insulator ET-TCNQ [ET = BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, TCNQ = 7,7,8,8-tetracyanoquinodimethane] in which carriers are localized due to the electron correlation shows extremely nonlinear electric conduction or undergoes a dielectric breakdown upon application of a high electric-field. It was demonstrated that a current-driven low-resistive state of ET-TCNQ can be stabilized down to 2 K, suggesting that the conduction path generated by the current-injection is metallic in nature.

There have been reported many molecular metals, including more than 20 superconductors, with BEDT-TTF ( bis(ethylenedithio)tetrathiafulvalenme = ET ) as a constituent donor component.[1] A family of the ET-based molecular metals forms two-dimensional conduction paths in the crystal that are composed of donor (ET) sheets. Among them, $(ET)_2X$ salts ($X$ is inorganic monovalenet anion) as well as some ET-TCNQ derivatives have been attracting current interest since the electronic ground states in some compounds are known to be strongly electron-correlated.[2] Here, we report on the nonlinear electronic transport property of an ET-based Mott insulator ET-TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane).[3]

Two different crystal structures are known for ET-TCNQ, one of which is monoclinic[4] and the other is triclinic.[3] In the monoclinic phase, donors and acceptors are stacked alternately to form a columnar structure (mixed-stack). On the other hand, the triclinic phase crystal, investigated here, consists of the two-dimensional donor (ET) sheet and one-dimensional acceptor (TCNQ) columns. In scrutinizing the packing manner of donor and acceptor in the crystal, one finds that the both of donor and acceptor molecules are forming dimer. A previous study[3] revealed that the crystal of ET-TCNQ undergoes a metal-insulator (MI) transition at $T_{MI}$ = 330 K at ambient pressure, although the band calculation predicts a metallic ground state. The MI transition has been assigned to a Mott transition on the basis of the magnetic and transport properties.[5] In this paper, we demonstrate that application of a high voltage or resultant current injection can induce a sort of dielectric breakdown of the Mott-insulating state in the ET-TCNQ crystal, giving rise to a gigantic reduction of the sample resistance at various temperatures.

Single crystals of ET-TCNQ were obtained as black plates with a typical size of 2 × 2 × 0.2 $mm^3$ from a 1,1,2-trichloroethane solution by slow evapolation of the solvent. The lattice parameters estimated by a four-circle X-ray diffractometer are the same as those in literature (triclinic form).[3] The current ($I$) *vs.* voltage ($V$) curves were measured on ET-TCNQ single crystals with two-terminal electrodes of carbon paste by applying voltage pulses parallel to the *bc* plane (in the donor sheet direction) with a pulse duration of 100 ms – 500 ms. In the measurement circuit, a load resistor $R_L$ (100 kΩ ~ 1 MΩ) was connected in series to prevent a burst of current as shown in the inset to Figure 1. The measurements were made at various temperatures while keeping the sample in a continuous flow of cold helium gas.

The circuit including a crystal of ET-TCNQ as a resistive element in series shows extremely nonlinear $I$-$V$ characteristics at various temperatures ($T \ll T_{MI}$), as shown in the Figure 1(a), when the current flows along the donor sheet (*bc* plane). There was observed no clear anisotropy between the $I$-$V$ curves for $I$ // $b$ and that for $I$ // $c$. This indicates that the resistive transition induced by current arises from the two-dimensional π-electron dynamics, *i.e.* on the donor sheets. In the Figure 1(b), the observed $I$-$V$ curves are converted to the $J$(current density)-$E$(electric field) ones at respective temperatures. The values of $J$ and $E$ were derived via the relation that $J = I / S$ and $E = (V - IR_L)/d$, $S$ and $d$ being the cross-sectional area and the distance between the electrodes, respectively. For example, when the electric field exceeding 3 kV/cm is applied at 40 K, the $J$-$E$ curve shows a negative differential-resistance features, in accord with the feature previously observed for one-dimensional complex, K-TCNQ[6] or Rb-TCNQ.[7] Without a load-resistor $R_L$, the current burst would show up for a given electric field, and hence the crystal would explosively break up. In this region, the resistivity of the sample $\rho$, defined by $\rho = J / E$, abruptly decreases by more than three orders of magnitude. That is to say, the crystal shows a current-induced switching from a high-resistive (insulating) to a low-resistive (conducting) state. In the negative differential-resistance region, increase of current ($I$) seems to correspond to volume extension of the low-resistive region in the crystal. The threshold voltage becomes higher with decreasing temperature, and as a result the resistance gap between high-resistive state and low-resistive state becomes larger. The switching process is represented by a hysteresis loop shown as hatched area in Figure 1(a). At lower temperatures the hystseresis area also becomes wider. The

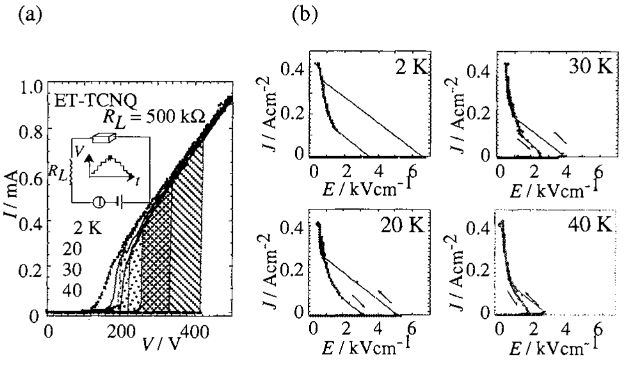

**Figure 1.** (a): Current *vs.* voltage ($I$-$V$) curves at 2, 20, 30, and 40 K for the circuit shown in the inset which is composed of an ET-TCNQ crystal and a load resister $R_L$. (b): Current density *vs.* electric field ($J$-$E$) curves in the crystal of ET-TCNQ at 2, 20, 30, and 40 K.

hystseresis effect arises from the current bistability in the circuit, which contains a negative-differential-resistance element, namely an ET-TCNQ crystal.[7] The seemingly different *I-V* curves at respective temperatures give the nearly temperature-independent *J-E* characteristics.

In Figure 2 is shown temporal response of the switching at 20 K measured with a storage oscilloscope. While the applied voltage is lower than 100 V, current flowing in the circuit is small and reaches a constant value within 20 msec. Once the applied voltage exceeds 100 V, the current in the circuit jumps up to about 10% of the final value instantaneously within a resolution limit of the voltage source ( = 1 msec). Then the current grows up gradually and reaches a constant value after 100 - 200 msec. When the applied voltage is higher than 180 V, the current reaches a constant value within the resolution time. The slow process, which is observed at the applied voltage being between 100 and 180 V, may be explained in terms of the growth of the conducting-path volume.[5]

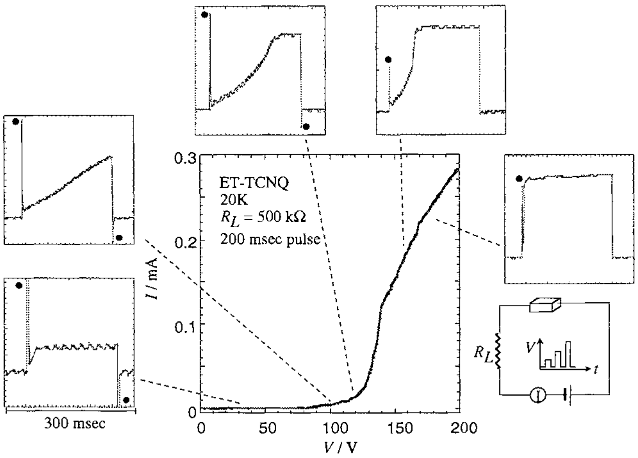

**Figure 2.** Temporal response of the switching at 20 K for the circuit shown in the inset. Solid circles (•) in the respective panels indicate electrical noise from a voltage source.

Figure 3 shows temperature dependence of the resistance of the crystal with constant $R_L$ (= 100 kΩ) in the circuit upon application of constant-voltage (5, 100, 150 V) pulses. A $\rho$-$T$ curve measured under the constant-current condition (by the four-probe method; $I = 1$ μA) is also shown. The resistivity ($\rho$) at a low voltage (5V) diverges with decreasing temperature in the same manner as in the constant-current measurement. Once the voltage of 100 V is applied, the resistance is decreased by an order of magnitude at 50 K, but abruptly jumps up to the original high-resistivity at 15 K. From the time response (Figure 2), the process of switching in the resistive state was completed within 10 msec when an ample voltage was applied to the sample at 20 K. During this period, the inflow of heat ($Q = V^2/R \times t$) at $V = 100$ V is estimated to be $1.3 \times 10^{-8}$ J (Here, $R$ was estimated to be 8 GΩ from the conventional 4-probe method measurement with an activation energy $E_a = 0.03$ eV in Figure 3). The heat capacity of the sample is calculated to be $C = 7.4$ μJ/K, since the $T^3$-coefficient of the specific heat is 20 mJ $K^2$/mol, that is typical value of ET-based complex. With use of these values, the rise of temperature ($\Delta T = Q/C$) that was caused by the applied voltage should be 2 mK. The resistance of the sample at 20 K under the $V = 100$ V is as small as that measured with constant current at 70 K. If the switching process ware driven by Joule-heating, we would expect the increase of temperature by more than 50K. Therefore, the low-resistance measured with high voltage cannot be explained by simply heating alone.

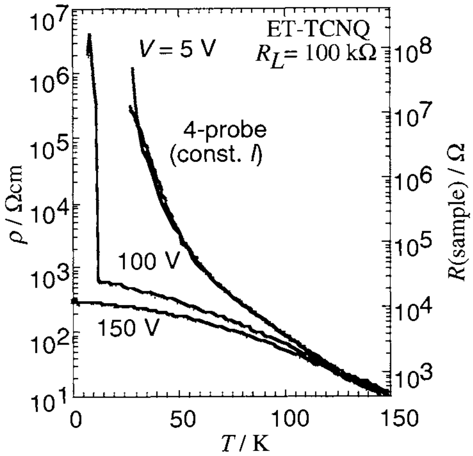

**Figure 3.** Temperature dependence of resistance ($R$) or the resistivity ($\rho$) of an ET-TCNQ crystal measured with various voltage pulses (5, 100, 150 V; 200 ms-duration). The low-field resistivity of the same crystal measured by the conventional four-probe method with a constant low current (1 μA) is also shown.

When the applied voltage is higher than 150 V, however, the resistance does not diverge with decreasing temperature even down to 2 K. This suggests that the low-resistive state or the conduction path generated by the current is metallic in nature. The nominal resistivity $\rho$ at $V = 150$ V is still considerably large ($\approx 3 \times 10^2$ Ωcm) as the metallic one. Note, however, that the value of $\rho$ was estimated with dimension of bulk crystal, not that of conduction path (which may be much smaller than whole crystal volume). Therefore, the calculated $\rho$-value does not give a resistivity of the conduction path. Namely, the local conduction paths may have a metallic conductivity. In other words, in the crystal of ET-TCNQ insulating and metallic states may coexist under the high voltage or current flow. The metallic patches may be viewed as realized by the dielectric breakdown of the Mott insulating state.[8]

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## References and Notes

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