Electron Transport

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Low-Field Negative-Resistance Effect in a Charge-Ordered State of Thiazyl-Radical Crystals**

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Nonlinear electrical transport in inorganic semiconductors has been utilized in various electric devices such as sensors, switches, diodes, and thyristors.[1] Recent developments in organic electric devices strongly indicate the importance of materials research for non-ohmic electrical behavior in organic compounds.[2] In fact, current–voltage characteristics of organic materials have been studied extensively, and nonlinear electrical transport phenomena, such as a switching effect with a so-called negative-(differential)-resistance effect, have been already discovered as a characteristic feature of organic semiconductors.[3–7] However, these effects were found to occur at low temperature in a high electric field, in an insulating state caused by charge ordering, neutral–ionic transition, and on-site Coulomb repulsion (Mott–Hubbard insulator). Thus, it is very important to develop organic materials that exhibit this nonlinear behavior under mild conditions.

Heterocyclic thiazyl radicals have unique chemical and physical properties.[8–15] Their molecular skeletons exhibit large electronic polarization, which leaves a positive charge on the sulfur atom and a negative charge on the nitrogen atom. Thiazyl-radical solids always involve a multidimensional network consisting of face-to-face π–π overlaps and side-by-side S···N contacts. Herein, we describe the crystal structure and the nonlinear electrical transport of the 3:1 salt of a thiazyl radical, naphtho[2,1-*d*:6,5-*d'*]bis([1,2,3]dithiazole), abbreviated as NT (Figure 1 a).

Single crystals of $[NT]_3[GaCl_4]$ were obtained by an electrochemical method. X-ray crystal analysis was carried out at 173 K.[16] The crystal structure includes two crystallographically independent 2D layers of NT molecules, layers **A** and **B** (Figure 1 b), though their structures are nearly the same. Each layer consists of a 2D square network of NT molecules with short intermolecular S···N contacts, in which the molecular planes of the NT molecules are parallel to the layer. The short S···N contacts reflect a large electric polarization of the NT molecular skeleton. Layer **A** includes the NT molecules **1** and **2**, and layer **B** includes the molecules **3** and **4**. Figure 1 c depicts a side view of the layered structure and shows the **BABBAB** stacking with large π–π overlaps. Four NT molecules of slightly different structure are included in the 3D network. The $GaCl_4^-$ counterion (not shown in Figure 1 b) is located in a cavity surrounded by four stacking columns of NT molecules.

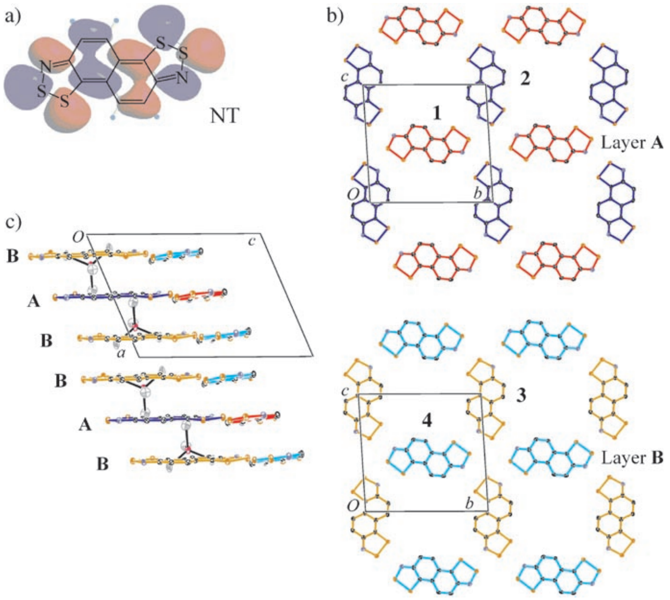

Figure 1. a) The HOMO of NT. b) Layers **A** and **B**, which consist of 2D square networks of NT molecules **1**–**4**, in the crystal structure of $[NT]_3[GaCl_4]$. c) Side view of the layered structure, showing the location of the $GaCl_4^-$ counterions. The colors of the NT molecules express their charges (see Figure 2 for color key).

It is well known that the S–N bond length is a good indicator of the charge on the thiazyl and thiazole compounds; removal of an electron from the highest occupied molecular orbital (HOMO) results in a shortening of the bond length, because the HOMO has antibonding character of the S–N bond (Figure 1 a). Figure 2 depicts the relation between the average S–N bond length l_{SN} and the charge ρ on NT for the neutral NT molecule,[17] the NT^+ cation in [NT]Cl,[18] and the cation in [NT][TCNQ], which is in a mixed valence state (TCNQ is 7,7,8,8-tetracyanoquinodimethane).[18] For [NT][TCNQ], l_{SN} is 1.626 Å and ρ can be estimated to be 0.60 from the C–N stretching frequency (2199 cm^{-1}).[19] Figure 2 indicates an empirical linear relation between l_{SN} and ρ (gray line) that is similar to that of the thiazyl compound, 1,3,2-benzodithiazolyl (BDTA).[20] In the crystal structure of $[NT]_3[GaCl_4]$, the average S–N bond lengths of the NT molecules are as follows: **1** 1.617, **2** 1.645, **3** 1.626, **4** 1.643 Å. The standard deviations for these lengths are all less than 0.004 Å. By fitting the empirical relation to these interatomic distances, the values of ρ were roughly estimated to be: **1** 0.8, **2** 0, **3** 0.5, **4** 0.1. The colors of the NT molecules in Figure 1 were taken from the color bar in Figure 2.

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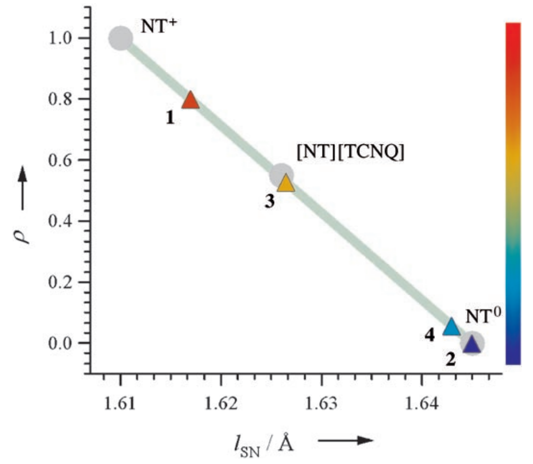

Figure 2. Correlation between the charge ρ and the S–N bond length l_{SN} in NT compounds; the gray line expresses the empirical linear relation between them; $l_{SN} = 1.645$ Å for NT^0[17] and 1.610 Å for NT$^+$.[18] The right side bar is a color key for the charge on NT.

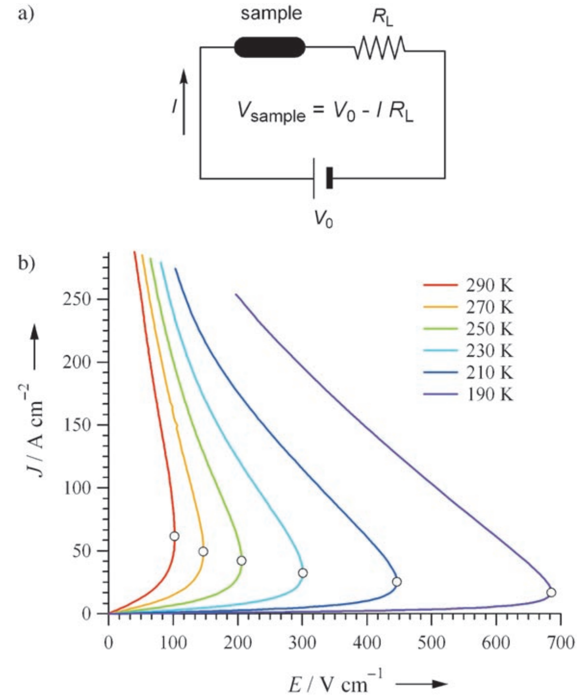

Figure 3. a) Electric circuit used to measure the current–voltage characteristics of samples. b) Plot of J versus E for a crystal of $[NT]_3[GaCl_4]$ at various temperatures, measured with a pulse field (25-ms width and 300-ms interval). The open circles show the turning points for the negative-resistance effect.

Since the unit cell includes one each of NT molecules **1** and **2**, and two each of **3** and **4**, the average charge on NT is calculated as: $[0.8+0+(2\times0.5)+(2\times0.1)]/6=0.33$. This value, which is estimated from the molecular structures, is in good agreement with the chemical formula $[NT]_3[GaCl_4]$ with $\rho=0.33$ and thus justifies the analysis presented in Figure 2. From this analysis, we conclude that the present crystal includes a significant charge disproportionation; molecules **1** and **3** are charge-rich (R), while **2** and **4** are charge-poor (P). Figure 1 depicts the alternation of charges in the 3D crystal structure; the charge-rich and charge-poor molecules alternate according to the pattern RRPRRP or PPRPPR along the a axis (π-stacking direction) and occupy the warp and weft positions in the 2D square network parallel to the bc plane such that the combination of P–P or R–R is ruled out. This 3D charge alternation is gaining much attention as a characteristic insulating state induced by intermolecular Coulomb repulsions in strongly correlated systems.[21,22]

Electrical transport measurements were carried out by using a conventional two-terminal method on samples with typical dimensions of length $l=1$ mm (along the a axis) and area $S=0.1$ mm^2 in cross section. Variable-temperature conductivity measurements revealed semiconductivity with a room-temperature conductivity of $\sigma_{RT}=0.5$ S cm^{-1} and a band gap of $\Delta E=0.18$ eV, despite the material being in a mixed-valence state and having a 3D network structure. This result could be ascribed to the charge ordering shown in Figure 1.

The current–voltage (I–V_0) characteristics were measured along the a axis by using an electric circuit in series with a load resistor R_L of 20 ko (Figure 3 a), which was connected in series to the sample to prevent a sudden burst of current. Since sample heating is generally a problem for these I–V_0 measurements, we used a pulse current/voltage source with a pulse width of 25 ms and a pulse interval of 300 ms. We confirmed that the data are independent of R_L, the pulse width, and the pulse interval. Figure 3 b depicts the current density J in the crystal as related to the applied electric field E, which were obtained from the equations $J=I/S$ and $E=(V_0-IR_L)/l$. At room temperature (290 K), the J–E curve exhibits a steep nonlinear rise and clearly indicates a negative-differential-resistance effect after passing through the turning point indicated by an open circle (Figure 3). This nonlinearity is caused by a partial melting of the charge ordering because, if there is no charge ordering, the material should have a five-sixths-filled band that brings about metallic conduction. The threshold values for the electric field E_T and the current density J_T are 100 V cm^{-1} and 60 A cm^{-2}, respectively. It is very rare that this type of negative-resistance effect is observed at room temperature in organic materials. In addition, the E_T value obtained for $[NT]_3[GaCl_4]$ is much lower than those of the other organic materials that show nonlinear conductivity.[3–7] Lowering the temperature from 290 K, the values of E_T and J_T exhibit a significant increase and decrease, respectively, making the negative-resistance effect more drastic.

We have revealed a negative-resistance effect in $[NT]_3[GaCl_4]$, which includes the charge ordering on the 3D network of the NT molecules. Surprisingly, this effect occurs under a very low electric field at room temperature. In a recent report, this type of nonlinear transport in a charge-ordered state had thyristor properties (conversion from direct current to alternating current), though this behavior was found only at liquid-helium temperatures.[23] Our results may be applicable to organic electric devices such as switching units, information storage media, and thyristors, in which room-temperature, low-field performance is extremely advantageous.

Experimental Section

The parent compound NT was prepared according to a previously reported method.[17] Single crystals of [NT]$_3$[GaCl$_4$] were obtained by electrochemical oxidation of NT (20 mg), with the electrolyte $[(n\text{-}C_4H_9)_4N][GaCl_4]$ (50 mg) in a 1:1 mixture of 1,2-dichloroethane and CS$_2$ at a constant current of 1 μA. Green needles were grown on the anodic electrode within 3–5 days.

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[16] X-ray diffraction data were collected with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) on a Rigaku Mercury CCD diffractometer. The absorption correction was applied by integration based on the crystal shape. The structures were solved by direct methods (SHELXS-97). A full-matrix least-squares method on F^2 with anisotropic thermal parameters was employed for the structural refinements (SHELXL-97). Hydrogen atoms were found by difference Fourier syntheses and were refined. Crystal data for [NT]$_3$[GaCl$_4$]: $C_{30}H_{12}Cl_4GaN_6S_{12}$ ($M_r = 1052.70$), green needle, $1.0 \times 0.3 \times 0.3$ mm^3, *triclinic*, $P\bar{1}$, $a = 10.870(3)$, $b = 13.591(4)$, $c = 13.823(4)$ Å, $\alpha = 88.382(13)$, $\beta = 67.244(7)$, $\gamma = 78.073(12)°$, $V = 1839.5(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.901$ g cm^{-1}, $T = 173$ K, $2\theta_{max} = 54.92°$, $F(000) = 1050$, reflections collected/unique 14980/8057 ($R_{int} = 0.0518$), parameters 478, final $R1 = 0.0551$ ($I > 2\sigma(I)$), $wR2 = 0.1311$ (all data), $S = 1.038$ (all data). CCDC-297988 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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