Photoinduced Phase Transition in the Organic Conductor α-(BEDT-TTF)$_2$I$_3$ at Temperatures near the Metal–Insulator Phase Transition

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Photoirradiation effects on conductivity in the organic salt α-(BEDT-TTF)$_2$I$_3$ at temperatures close to the metal–insulator (M–I) phase boundary are investigated using time-resolved measurements of photocurrent. The transient photocurrent at 115 K shows a remarkable persistence at the metallic conductivity and a nonlinear dependence on the light intensity, probably originating from the photoinduced M–I phase conversion in the presence of electric fields.

The photoinduced dynamical transformation of material properties is a research field that has attracted trans-disciplinary interests. Strongly correlated systems including organic charge-transfer salts have been, in particular, intensively investigated so far.[1–4] Molecular conductors based on bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) donor molecule are a family of compounds that show rich low-dimensional physics such as M–I phase transition and superconductivity.[5] The organic conductor α-(BEDT-TTF)$_2$I$_3$ is a metal at room temperature and shows the M–I transition at $T_{M-I} = 135$ K.[6] Spectroscopic and theoretical investigations have shown that a charge-ordering state is realized in the insulator phase.[7,8] At a low temperature far below the T_{M-I} (4 K), the M–I phase transition induced by the laser irradiation at 440 nm has been reported by Tajima et al.[2] However, they have reported that the photocurrent due to the M–I transition disappeared above 50 K.[2] Usually, enhanced responses even to externally applied weak stimuli are expected when the materials are put at conditions close to phase-transition boundary.[4] Therefore, we have investigated the photoirradiation effects on the electrical conductivity of the crystal using time-resolved measurements of photocurrent at temperatures near the T_{M-I}.

As a light source for photoirradiation experiments, a second harmonic (532 nm) of output from a Nd:YAG laser (10-ns pulse width, repetition rate of 8.3 Hz, diameter $\approx$0.4 mm) was used. The sample was placed in a cryostat (a temperature-controlled He buffer gas) using two gold wires separated by ca. 0.4 mm. We used a pulsed voltage of 1 ms as a bias voltage, and a temporal profile of the current was monitored using a digital oscilloscope.

Figure 1a shows transient photocurrents observed at 115 K with different values of irradiation light intensity (I_L). The applied voltage was 3 V, which corresponds to the field strength of 70 V·cm^{-1}. The onset of the transient photocurrent was essentially identical with the shape of the laser pulse, indicating that the rise time of the photocurrent is of the order of the duration of the laser pulse (ca. 10 ns). At low I_L, the transient photocurrent shows a peak at $t = 0$. With high intensity of the photoexcitation, the peak in the photocurrent is delayed, and a long tail appears. The transient conductance, which was calculated from the photocurrent and the applied voltage, is plotted in Figure 1b as a function of I_L. Obviously, the conductances at $t = 0$, 600 ns, and 2 μs show a nonlinear dependence on I_L. The plot of the conductance at $t = 0$ ns as a function of I_L has a threshold at ca. 1.7×10^{-5} J·pulse^{-1} (corresponding to ca. 3×10^{16} photons·cm^{-2}), above which the conductance abruptly increases with an increase of I_L. The threshold value increases with an increase of t. These results were reproduced for different samples. When the field strength was varied in the range from 0 to 80 V·cm^{-1}, it was found that the transient photocurrent was proportional to the applied field strength.

Figure 2a shows transient photocurrents observed at 80 K. Although the field strength used in this measurement (1.4×10^2 V·cm^{-1}) was twice as strong as that used in Figure 1, the magnitude of the current is much smaller at any intensity of I_L. The decay profile of the current is composed of two decay components, i.e., fast and slowly decaying components. The time profile of the fast component is close to the shape of the laser pulse, and the lifetime is shorter than 20 ns. The slow component appears as a tail, and its time profile is similar to that observed at 115 K at weak intensities of I_L. The plots of the conductance at the peak position as a function of I_L are shown in Figure 2b. The transient conductance that arises from the fast

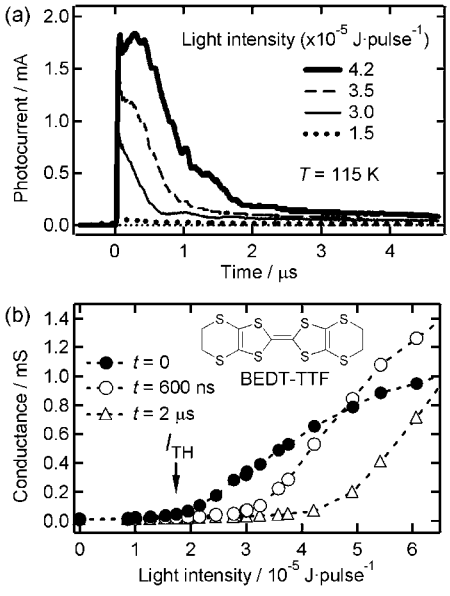

Figure 1. (a) Transient photocurrent at 115 K. (b) Conductance of the sample observed at $t = 0$, 600 ns, and 2 μs after the photoexcitation versus the light intensity. I_{TH} represents the threshold intensity for the photoinduced change in the conductivity.

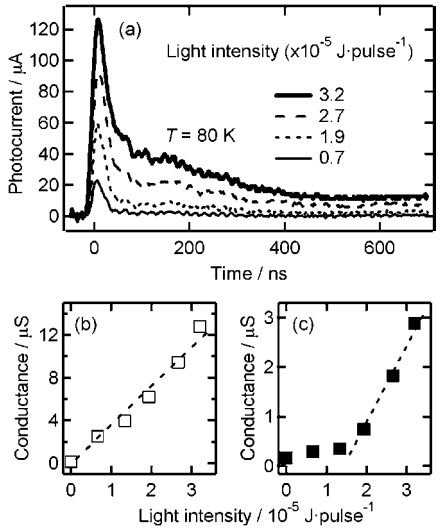

Figure 2. (a) Transient photocurrent at 80 K. (b) Peak conductance of the sample versus the light intensity. (c) Conductance of the sample at 300 ns after the photoexcitation. The broken line is a guide to the eye to show a threshold-like behavior in the light intensity dependence of the conductance.

component linearly increases with I_L. To examine the I_L dependence of the slow component, the conductance was also measured at $t = 300$ ns. The results are shown in Figure 2c. The slow component shows a nonlinear behavior, which is similar to that observed at 115 K. Further, the result indicates that the slow component relative to the fast one increases, as I_L increases.

We cannot straightforwardly ascribe both the transient photocurrent at 115 K and the slow component at 80 K to a conventional photoconductivity,[9] as mentioned follows: The slow component of photocurrent at 80 K and the photocurrent at 115 K showed a nonlinear dependence on I_L, and the current is proportional to I_L^m with $m > 1$; the slow component of photocurrent becomes relatively stronger as the I_L increases at 80 K (Figure 2), and at 115 K, the decay profile appears to be prolonged at high intensity of I_L (Figure 1a); we observed a significant temperature dependence, i.e., the photocurrent is much larger at 115 K than that at 80 K.

The transient conductance at $t = 0$ at 115 K appears to saturate at ca. 1 mS, as I_L increases above 4×10^{-5} J·pulse^{-1} (see Figure 1b). This conductance can be converted to a conductivity by considering the photoexcited area and the optical penetration depth of a crystal, i.e., approximately 1 μm.[10] The conductivity of ca. 1×10^1 S·cm^{-1} is obtained for the photoexcited volume. This value is in good agreement with the conductivity in the metallic phase.[2] On the other hand, the photocurrent showed a persistent profile from $t = 0$ to ca. 1 μs at higher intensities of I_L where the saturation of the conductivity was observed, as shown in Figure 1a. These results indicate that a fraction of a crystal is converted to a metastable metallic phase by the photoexcitation, and this metallic state persists to ca. 1 μs after the photoexcitation. A similar persistence of the photocurrent at a metallic conductivity has been reported for the organic salt $Cu(DCNQI)_2$, which shows a photoinduced phase transition.[3] Furthermore, the fact that the rise of the photocurrent is close to the shape of the laser pulse suggests that the photoconversion is nearly completed within the duration of the laser pulse (ca. 10 ns).

As shown in Figures 1b and 2c, the photoinduced conductivity suddenly increases at a certain value of I_L as I_L increases. The presence of such a threshold of I_L in photoinduced conversion of material property has been observed for a variety of materials.[1,11] As reported in those systems, the origin of the presence of the threshold of I_L can be ascribed to cooperative interaction, which can mediate the growth from locally generated species with a concentration higher than a certain critical value to a macroscopic phase.

Given the full conversion to the heating, the absorption of light with the energy of 3×10^{-5} J gives rise to the temperature rise of ca. 1 K at most for the samples used in the measurements. This value is too small to explain the observed change in the conductance. A thermal quenching rate is proportional to $\kappa \times C_p^{-1}$, where κ is a thermal conductivity and C_p is a specific heat of the sample. For α-(BEDT-TTF)$_2$I$_3$ in the temperature range from 80 to 300 K, C_p is 0.35–0.95 J·g^{-1}·K^{-1} and κ is $6–7 \times 10^{-3}$ W·cm^{-1}·K^{-1}.[12,13] Then, it is unlikely that such small changes in κ and C_p can cause the change in the thermal quenching rate as large as the change in the decay profiles observed in the present study. Thus, the thermal effect by the light absorption is insignificant for the observed photocurrent. The present results show that the photoinduced M–I transition can take place even at temperatures near the T_{M-I} in contrast with the result in Ref. 2. Thus, the photoconversion process observed in our study may be different from that at 4 K.[2]

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References

1 M. Chollet, L. Guerin, N. Uchida, S. Fukaya, H. Shimoda, T. Ishikawa, K. Matsuda, T. Hasegawa, A. Ota, H. Yamochi, G. Saito, R. Tazaki, S. Adachi, S. Koshihara, *Science* **2005**, *307*, 86.
2 N. Tajima, J. Fujisawa, N. Naka, T. Ishihara, R. Kato, Y. Nishio, K. Kajita, *J. Phys. Soc. Jpn.* **2005**, *74*, 511.
3 F. O. Karutz, J. U. von Schutz, H. Wachtel, H. C. Wolf, *Phys. Rev. Lett.* **1998**, *81*, 140.
4 S. Koshihara, Y. Takahashi, H. Sakai, Y. Tokura, T. Luty, *J. Phys. Chem. B* **1999**, *103*, 2592.
5 R. P. Shibaeva, E. B. Yagubskii, *Chem. Rev.* **2004**, *104*, 5347.
6 K. Bender, I. Hennig, D. Schweitzer, K. Dietz, H. Endres, H. J. Keller, *Mol. Cryst. Liq. Cryst.* **1984**, *108*, 359.
7 a) T. Takahashi, Y. Nogami, K. Yakushi, *J. Phys. Soc. Jpn.* **2006**, *75*, 051008. b) R. Wojciechowski, K. Yamamoto, K. Yakushi, M. Inokuchi, A. Kawamoto, *Phys. Rev. B* **2003**, *67*, 224105.
8 H. Seo, C. Hotta, H. Fukuyama, *Chem. Rev.* **2004**, *104*, 5005.
9 R. H. Bube, *Photoconductivity of Solids*, John Wiley & Sons, New York, **1960**.
10 H. W. Helberg, *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 899.
11 a) S. Koshihara, Y. Tokura, K. Takeda, T. Koda, *Phys. Rev. Lett.* **1992**, *68*, 1148. b) N. Hosaka, H. Tachibana, N. Shiga, M. Matsumoto, Y. Tokura, *Phys. Rev. Lett.* **1999**, *82*, 1672. c) H. Matsuzaki, W. Fujita, K. Awaga, H. Okamoto, *Phys. Rev. Lett.* **2003**, *91*, 017403. d) Y. Ogawa, S. Koshihara, K. Koshino, T. Ogawa, C. Urano, H. Takagi, *Phys. Rev. Lett.* **2000**, *84*, 3181. e) H. W. Liu, K. Matsuda, Z. Z. Gu, K. Takahashi, A. L. Cui, R. Nakajima, A. Fujishima, O. Sato, *Phys. Rev. Lett.* **2003**, *90*, 167403.
12 N. A. Fortune, K. Murata, M. Ishibashi, M. Tokumoto, N. Kinoshita, H. Anzai, *Solid State Commun.* **1991**, *79*, 265.
13 D. Schweitzer, E. Gogu, I. Hennig, T. Klutz, H. J. Keller, *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 890.

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