Pump-probe study of $\beta'$-(BEDT-TTF)(TCNQ) crystal near antiferromagnetic transition

Hirofumi Mino\textsuperscript{1}, Shiho Tokuda\textsuperscript{2} and Masatoshi Sakai\textsuperscript{3}

\textsuperscript{1}College of Liberal Arts and Sciences, Chiba University, 1-33 Yayoi-cho, Inage-ku, 263-8522, Chiba, Japan
\textsuperscript{2}Graduate School of Education, Chiba University, 1-33 Yayoi-cho, Inage-ku, 263-8522, Chiba, Japan
\textsuperscript{3}Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, 263-8522, Chiba, Japan

E-mail: mino@faculty.chiba-u.jp

Abstract. The photo-excited state properties of an organic Mott-insulator $\beta'$-(BEDT-TTF)(TCNQ) crystal were investigated by pump-probe measurements. Considerable change in the pump-probe reflection signal with a wide spectral range was observed near the antiferromagnetic (AF) transition temperature of the TCNQ layers. In the time response, approach to the AF temperature induced the appearance of a slow decay signal whose lifetime was estimated to be about 3 msec maximum. These results indicate that a sustained mechanism exists for photo-excited states near the AF transition, which is probably related to a critical slowing down phenomenon.

1. Introduction
The study of photo-excited states in organic Mott-insulators has attracted a lot of interest in recent years from the viewpoint of a photo-induced insulator-metal transition. The differences in the insulator-metal transition by photo induction and thermal induction have been intensively studied for many years \cite{1}. Femtosecond spectroscopy has revealed that the photo-induced insulator-metal transition occurs extremely quickly, typically in less than several picoseconds. It is expected that this feature will be used for high-speed devices such as optical switches and memories. Besides the insulator-metal transition, the Mott-insulator shows various phase transitions caused by changes in temperature and pressure: antiferromagnetic (AF), superconductive, charge order, relaxer phases, and so on. However, near those phase transitions, few reports have considered the change of optical transition or photo-excited states by visible region spectroscopy. Furthermore, pump-probe studies investigating slow responses for the photo-excited states in time regions over a microsecond are relatively few compared to the fast response, in the femtosecond or picosecond time region.

In this study, we report pump-probe experimental results indicating a large signal in the visible spectra region, with a long lifetime reaching several milliseconds in an organic Mott-insulator $\beta'$-(BEDT-TTF)(TCNQ) crystal near the AF transition. This crystal consists of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) as the donor and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as the acceptor. They form a charge-transfer complex. The crystal is a layered structure, stacking two-dimensional BEDT-TTF sheets and one-dimensional TCNQ chains sheets. The $\beta'$-(BEDT-TTF)(TCNQ)
crystal is Mott-insulator at room temperature, and the metal-insulator transition occurs at 330 K [2]. It is known that the AF transition occurs on each BEDT-TTF layer and TCNQ layer at 20 K and 3.5 K, respectively [3, 4]. Many studies have reported its electronic state about the phase transition. However, there are few studies of electronic state change induced by photo-excitation. Therefore, to examine the phenomena that reflect the state change by photo-excitation, we used the pump-probe reflectance spectrum measurement and the pump-probe time-resolved measurement. Our results showed a large pump-probe signal approaching the AF transition temperature (= $T_N$) of TCNQ.

2. Experiment
Using the pump-probe spectrum measurement, we first investigated the reflectivity change in the visible light region in the $\beta'$-(BEDT-TTF)(TCNQ) crystal. Semiconductor CW lasers with wavelengths of 405 nm and 532 nm were used as the pump beam. Their intensity on the sample surface was 500 mW/cm$^2$ and 111 mW/cm$^2$, respectively. A white LED was used as a probe light source. The sample was placed in a cryostat and the temperature was changed from 20 K to 1.6 K. The pump-beam spot was coincident with the probe-light spot on the sample surface. The pump beam was modulated by an optical chopper at a frequency of 130 Hz. The differential reflectivity spectra ($\Delta R/R$) were detected using a spectrometer with a photomultiplier tube and lock-in amplifier.

We then used the pump-probe time-resolved measurement to investigate the relaxation process of photo-excited states. A 405-nm semiconductor CW laser and He-Ne laser (633 nm) were used as the pump and probe beam, respectively. They were changed into pulsed lasers using an acousto-optic (AO) modulator. The width of each pulse, pump and probe was 70 μsec, and the interval of each pulse was 10 msec. The time delay between pump pulses and probe pulses was controlled by a pulse generator. These beams were focused on the same position on the sample surface, and their intensity was 560 mW/cm$^2$ and 1.4 mW/cm$^2$, respectively. The intensity change of the probe pulse was detected using a photomultiplier tube and a lock-in amplifier. The temperature was changed from 15 K to 2.8 K.

3. Results and Discussion
Figure 1 shows the differential reflectivity spectra obtained by photo-excitation with the 405-nm (3.06 eV) laser. Positive values of $\Delta R/R$ indicate an increase of reflectivity under photo-excitation. At 20 K, the reflectivity change appears, and it increases as the temperature becomes lower. It is around 0.2% in the spectrum region from 1.9–2.9 eV at 9.0 K, and significantly increases at 4.2 K (around 0.5%). This result suggests that the optical transition change in the broadband region is induced by photo-excitation as the temperature approaches the $T_N$ of the TCNQ layers. The $\Delta R/R$ signal intensity systematically decreases with increasing temperature, and is difficult to observe above 20 K. In addition, there is no signal intensity peak at 20 K, which is the $T_N$ of the BEDT-TTF layers. These results suggest that the one-dimensional electric structure of the TCNQ layers may be strongly related to the $\Delta R/R$ signals.

To examine the temporal behavior of the reflectivity change, He-Ne laser pulses chopped by the AO modulator were used as a probe light source. Figure 2 shows time-resolved pump-probe signals with 405-nm laser pulse excitation at various temperatures from 15 K to 2.8 K. It is evident that the photo-

![Figure 1](image-url)
excited state relaxation processes are strongly dependent on temperature. All signals show decay profiles, and signal intensity increases as temperature decreases from 15 K to 4.2 K. This result is in agreement with Fig. 1. In contrast, the signal intensity decreases as temperature decreases from 4.2 K to 2.8 K. It is evident that the largest signal is obtained near the $T_N$. The $\Delta R/R$ signal may thus correlate strongly with the AF transition in the TCNQ layers. These data are well fitted by a double exponential curve $I_A \exp(-t/\tau_A) + I_B \exp(-t/\tau_B)$. Here the $I_A$ ($I_B$) and $\tau_A$ ($\tau_B$) together indicate the intensity and the relaxation time of the fast (slow) relaxation components. This means that photo-excited states are ruled by two different relaxation mechanisms. In Fig. 3(a), the $\tau_A$ and $\tau_B$ are plotted against the temperature. The $\tau_A$ without depending on temperature is about 0.15 msec. On the other hand, the $\tau_B$ becomes longer as the temperature approaches the $T_N$ of the TCNQ layers, and the longest relaxation time of 2.93 msec was obtained at 4.2 K. The relaxation behavior of $\tau_B$ shows that there is the mechanism lengthening the photo-excited state lifetime. It appears to be related to electron spin ordering for the AF transition. In Fig. 3(b), both $I_A$ and $I_B$ increase near the $T_N$, indicating that the slow relaxation component is more effective than the fast one. Here, we consider the relaxation time order of both the $\tau_A$ and $\tau_B$. Even the fast one ($\tau_A$) shows sub-msec response. This time order is substantially longer than the general recombination lifetime of photo-excited electrons and holes that are optically allowed. Therefore the photo-excited states resulting in the $\Delta R/R$ signals are considered to be optically inactive, even though the origin of the two different relaxations is not currently clear.

Fig. 4 shows the reflectivity change spectra obtained by photo-excitation with a 532-nm (2.33 eV) laser. The average value of the reflectivity change was about 0.3%, from 1.9 eV to 2.9 eV at around the $T_N$ (4.2 K and 3.1 K). Under higher or lower temperatures than the $T_N$, the signal intensity was reduced. In addition, the pump-probe signals appeared in both higher and lower energy regions than the laser excitation energy, and the spectral shape of the signals was very similar to those in Fig. 1. These results indicate that similar photo-excited states were induced by both 405-nm and 532-nm laser excitation.

Here, we think about the energy of intramolecular transition in each BEDT-TTF and TCNQ molecule. A TCNQ crystal strongly absorbs around 2.8-eV light [5], and a BEDT-TTF crystal starts absorbing close to 2.1-eV light [6]. Assuming that the intramolecular transition in our sample is similar to those
of the TCNQ and BEDT-TTF crystals, it would seem that there is a difference in the pump-probe signals between 405-nm and 532-nm laser excitation. However, the result in Fig. 1 is similar to that in Fig. 4. This means that the pump-probe signal may not strongly depend on the intramolecular transition of the TCNQ molecule. Otherwise, there is a possibility that the above assumption is not appropriate.

It is also necessary to think about the intermolecular transition between the BEDT-TTF and TCNQ molecules. Taking into account that the lowest intermolecular transition of $\beta'$-(BEDT-TTF)(TCNQ) occurs at about 1.18 eV [7], the pump-beam energy fully satisfied the energy range of the intermolecular transition, and might have been able to induce the intermolecular transition.

Here, we consider that both the pump-probe signal intensity and relaxation time have maximum values near the $T_N$. In magnetic materials, it is well known that the electron-spin on each site has a long-range correlation near the critical point (second order phase transition), and that the relaxation time to equilibrium state becomes very long at the critical temperature [8]. This phenomenon is called the critical slowing down. According to Fig. 3, the relaxation time of the long relaxation component ($\tau_b$) drastically increases as the temperature approaches $T_N$. This result may be qualitatively explained by the critical slowing down. The photo-excitation may give rise to the long-range fluctuation in the AF spin ordering. It is also expected that the increase in the lifetime of photo-excited states would induce photocarrier accumulation or molecular distortion, resulting in the broadband region spectrum change. The reason why the above-mentioned critical phenomena are not observed at the $T_N$ of the BEDT-TTF layers (20 K) is not clear. The pump-probe investigation of other similar Mott-insulators near the AF transition would serve to clear up this and other questions regarding the origins of the critical phenomena.

4. Summary
Pump-probe measurements were performed in a $\beta'$-(BEDT-TTF) (TCNQ) crystal close to the AF transition temperature. Pump-probe signals reaching a broad spectrum range and showing large increases when approaching the $T_N$ of the TCNQ layers were obtained with both the 405-nm and 532-nm CW laser excitation. The dynamical behavior of the photo-excited state was investigated using time-resolved measurement, and the existence of slow relaxation component which may indicate critical slowing down at around the $T_N$ of the TCNQ layers was clarified.

References
[1] Nasu K ed 2004 Photoinduced Phase Transitions (Singapore: World Scientific)
[2] Mori T and Inokuchi H 1986 Solid State Commun. 59 355
[3] Iwasa Y, Mizuhashi K, Koda T, Tokura Y and Saito G 1994 Phys. Rev. B 49 3580
[4] Kawamoto A, Miyagawa K, Shimizu A and Kanoda K 1994 Synth. Met. 85 1601
[5] Girlanda R et al 1986 IL Nuovo Cimento D 7 469
[6] Kozlov M E, Tanaka Y, Tokumoto M and Tani T 1994 Chem. Phys. Lett. 223 318
[7] Torrance J B, Vazquez J E, Mayerle J J and Lee V Y 1981 Phys. Rev. Lett. 46 253
[8] Hohenberg P C and Halperin B I 1977 Rev. Mod. Phys. 49 435