Ultrafast photo-induced metal – insulator transition in 1/4 filled organic crystal (EDO-TTF)$_2$PF$_6$

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Abstract. We report that the 1/4 filled $A_B$ salt (EDO-TTF)$_2$PF$_6$ developed as a candidate for organic superconductor unexpectedly shows highly sensitive and ultra-fast photo-induced phase transition (PIPT) from insulator (I) to metal (M). We show the results of time resolved experiments performed on this crystal. A large reflectivity change in the near infrared region (1.2-2 eV), which occurs within 2 ps for weak excitation intensity, has been observed. We also observed coherent vibrations in the dynamical process of this transition.

1. Introduction
Organic charge transfer (CT) type $A_B$ salts composed of donor (TMTSF, TMTTF, ET, DCNQI, Pd(dmit), etc.) and acceptor (I$_3^-$, PF$_6^-$, ClO$_4^-$, Cu(NCS)$_2^-$, etc.) in the ratio of 2:1 are becoming important target for materials science [1,2], because $A_B$ salts are classified as typical 1/4 filled system and they show various exotic natures such as superconductivity [1,2] and metal (M)-insulator (I) transition [1-3]. The appearance of charge ordering or Mott transition in 1/4 filled network of $A$ molecules with 1- or 2-dimensional structure are playing a key role as a base for these exotic natures [1,2]. Recent theoretical works [4-6], especially the one by Seo and Fukuyama[4] have revealed that the critical balance between some physical parameters in 1/4 filled system such as bandwidth, on-site Coulomb interaction and nearest neighbor Coulomb interaction is an origin of such exotic ground state. These previous studies stimulate us to search for the photo-induced phase transition (PIPT) in $A_B$ salts, because even weak photo-excitation may change the critical balance of physical parameters by switching the cooperative interaction channel leading to the macroscopic phase change [8, 9]. In such
organic salts (EDO-TTF)$_2$PF$_6$ shows a M-I phase transition ($T_c = 278$ K), which is also accompanied with Peierls transition, charge ordering, molecular deformations and anion ordering. The reflectivity spectra show large change around $T_c$. The reflectivity band at 1.4 eV has been assigned to the charge transfer excitation between the charge-ordered molecules of EDO-TTF [11]. Thus, this structure is a good probe for charge ordered phase. Because of the strong electron - lattice coupling, this crystal is a good candidate for the study of photo-induced phase transition. In addition we expect this transition to occur around room temperature because photo-response is usually enhanced near $T_c$.

2. Experiment
We performed time resolved experiments using pump probe technique. We used a Ti:sapphire laser (1.55 eV, 0.12 ps, repetition rate: 1 kHz). The crystal of (EDO-TTF)$_2$PF$_6$ with a surface of 0.1 mm by 0.2 mm was excited by the femto-second pulsed laser. The excitation energy (1.55 eV) is near the energy of the charge transfer band ($A^+A^- \rightarrow A^{2+}A^0$). The reflectivity change was probed using white light generated by non-linear optical method from a part of the femto-second pulse.

3. Results and discussion
Figure 1 shows the reflectivity change that occurs in this crystal. Dashed lines represent the spectral change accompanied by thermally induced phase transition between 290 and 180 K, and the plain lines show the photo-induced reflectivity change at -10 ps and 3 ps after photo-excitation. We observed a similarity between reflectivity change with photo-induced and thermal-induced transition. The reflectivity band at 1.4 eV decreases until a weaker band characteristic of the photo-induced metallic phase. Compared with the thermal-induced transition, the efficiency of the photo-induced transition reached almost 50% for an excitation intensity of $6 \times 10^{14}$ photon/cm$^2$, corresponding to the conversion of 500 molecules of EDO-TTF by only one photon. This high efficiency is the result of the important cooperative effect expected from the strong electron-lattice coupling.

![Figure 1](image_url)

**Figure 1.** Evolution of the reflectivity spectra between the I and M phase. Dashed lines show the thermally induced phase transition. Plain lines are the photo-induced phase transition at 180 K.

This photo-induced reflectivity change is large enough to be distinguishable by our eyes as real image. Figure 2 shows the evolution of the reflected light coming from the sample’s surface as a real
image using a CCD camera, at 0.5 ps before and at 0.25 ps after photo-excitation by 0.12 ps light pulse.

**Figure 2.** Demonstration of the photo-induced reflectivity change by fs laser excitation observed utilizing CCD camera with the resolution time of 0.2 ps. (a) The reflected monitor light from the surface of (EDO-TTF)$_2$PF$_6$ crystal before photo-excitation. Inset shows the time profile of the photo-induced reflectivity change observed at 1.38 eV (b) the reflected light at 0.2 ps after photo-excitation.

As mentioned before, this photo-induced transition is also expected to occur at around room temperature because the $T_c$ for (EDO-TTF)$_2$PF$_6$ is 278 K and photo-phase switching can be induced below $T_c$. We measured the time profile of the transition at 1.38 eV. Figure 3 shows the $\Delta R/R$ time profile at 260 K for different excitation intensities. We also observed coherent vibrations in the dynamical process of this transition. As shown in the figure 3 by the dashed lines, the period of those vibrations seems to be independent of the excitation, while as shown in figure 4 the period is in function of the temperature.

**Figure 3.** Time profiles of $\Delta R/R$ for various excitation intensities observed at 260 K. The period of the observed vibration seems independent of the excitation intensity.
As shown in the Figure 5. (a) several Raman modes were observed in the insulator phase [13]. The peak energy of optical phonon mode that observed at around 84 cm\(^{-1}\) at 180 K (closed grey circles) decreases as the temperature increases. We observed the same behavior in the temperature dependence of the vibration in the \(\Delta R/R\) time profile.

**Figure 4.** Temperature dependence of time profile \(\Delta R/R\) at 1.38 eV for an excitation density of \(9.1 \times 10^{14}\) photons/cm\(^2\).

**Figure 5.** (a) Raman spectrum in the low-energy region for the insulator phase at 180 K.

(b) Temperature dependence of the Raman modes (opened black and closed grey circles) and the period of vibrations observed in the time profile (black squares). The 84 cm\(^{-1}\) band (grey hatched in panel (a)) observed in the Raman spectra has the same behaviour as the temperature dependence of the vibration interval estimated from the \(\Delta R/R\) time profile.
From these data we inferred that the dynamic oscillations is attributed to coherent phonon vibrations. The vibrational mode calculation for a single EDO-TTF molecule shows the existence of several modes at around 100 cm\(^{-1}\), which can characterize the bending of the molecular plane. This result shows that the observed coherent vibration in the time profile is the cause of the strong coupling between charge ordering and molecular deformation.

As mentioned before this transition is highly efficient. The photo conversion efficiency shows a non linear dependence on the excitation intensity. Figure 6 shows the photo-reflectivity change probed at 1.38 eV, 3 ps and 0.25 ps after photo-excitation. The threshold intensity of the photo-induced change was estimated at \(2 \times 10^{14}\) cm\(^{-2}\). The lifetime of the photo induced metallic phase depends on the excitation intensity [10]. For an excitation intensity near the threshold intensity the photo excited state lasts for only 1.5 ps but in the case of stronger excitation intensity it last for a few hundreds of picoseconds.

![Figure 6. Excitation intensity dependence of \(\Delta R/R\) observed at 3 ps (black squares) and at 0.25 ps (grey circles) after photo-excitation at 180 K. The threshold photon density was estimated at \(2 \times 10^{14}\) photons/cm\(^2\).](image)

4. Conclusion
We have demonstrated that an ultra-fast photo-induced insulator to metal phase transition can be induced with very weak excitation density at near room temperature. The observed photo-induced spectroscopic change indicates that the PIPT process is governed by the strong electron – lattice coupling and mediated by an optical coherent phonon. PIPT can be really attractive for application in switching device at room temperature operation. Ultra-fast PIPT studied by time-resolved X-ray crystallography will be also an important target to completely understand the complex mechanism that occurs during this phase transition.

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