

# Ultrafast Gigantic Photo-Response in Charge-Ordered Organic Salt (EDO-TTF)<sub>2</sub>PF<sub>6</sub> on 10-fs time scales

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**Abstract.** The initial dynamics of photo-induced phase transition in charge-ordered organic salt (EDO-TTF)<sub>2</sub>PF<sub>6</sub> was investigated using 10-fs near-infrared laser pulses. We observed sub-20-fs gigantic photo-responses ( $|\Delta R/R| > 100\%$ ) due to intra-molecular vibration and a clear signature of a structural bottleneck ( $\sim 50$  fs) for the first time.

## Introduction

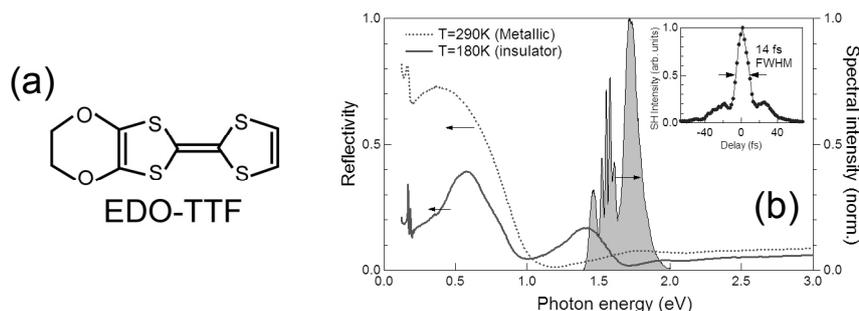
The recent discovery of the gigantic photo-responses in a 1/4-filled organic salt (EDO-TTF)<sub>2</sub>PF<sub>6</sub> has uncovered a new class of molecular systems whose physical properties can be drastically altered under optical excitation on femtosecond time scales [1]. Underlying physics of these gigantic photo-responses are considered to be the light-induced melting of its unusual [0110]-type charge order in an EDO-TTF tetramer at low temperature ( $T < 280$  K). The charge-order melting induces an imbalance in the electron-lattice coupling, which initiates the photo-induced phase transition (PIPT) process. Previous studies have investigated this insulator-to-metal PIPT on the 100-fs time scales, focusing on the sub-picosecond dynamics and the photo-induced quasi-stable state [2]. They have revealed that (i) PIPT is accompanied by strong coherent intermolecular vibrations, and (ii) the reflectivity spectrum of the photo-induced quasi-stable phase differs from the thermally-induced phase especially in the infrared. Recent theoretical studies also support these observations, and suggest that the photo-induced metallic-like state is indeed the [1010]-type charge ordered state [3]. While there has been a significant progress in understanding the photo-induced phase in (EDO-TTF)<sub>2</sub>PF<sub>6</sub>, little is known about the initial dynamics of the PIPT, which is of fundamental interest for understanding the

interplay between various molecular/lattice/electronic degrees of freedom in strongly correlated systems. It is also crucial to examine if the PIPT is driven purely by electronic processes or by the photo-induced change of molecular conformation in order to understand the nature of the phase transition [4].

We have investigated the ultrafast dynamics of the reflectivity changes in  $(\text{EDO-TTF})_2\text{PF}_6$  during the insulator-to-metal PIPT initiated with 10-fs laser pulses. We observed (i) a large reflectivity modulation ( $\Delta R/R \sim 100\%$ ) on 10-fs time scales, and (ii) a clear signature that the PIPT is driven by the change of molecular conformation.

## Experimental Methods

We investigated the early dynamics of PIPT with 10 fs pump-probe spectroscopy. We produced near-infrared 10 fs pulses using a Ti:sapphire chirped-pulse amplifier with hollow-fiber pulse compression. We used a hollow-core fiber (core diameter: 150  $\mu\text{m}$ ) filled with Argon ( $\sim 2$  bar) and dispersion compensation mirrors to obtain nearly transform limited 10-fs pulses at the sample position in a cryostat. Figure 1 shows the spectrum of the compressed pulses and their autocorrelation trace (inset above) compared to the reflectivity of  $(\text{EDO-TTF})_2\text{PF}_6$  in the metallic ( $T=290$  K, dotted line) and insulator ( $T=180$  K, solid line) phases. The laser spectrum covers the highest charge transfer band ( $\text{D}^0\text{D}^+\text{D}^+\text{D}^0 \Rightarrow \text{D}^0\text{D}^{2+}\text{D}^0\text{D}^0$ ) peaked around 1.4 eV and the isosbestic point of the reflectivity curves at 1.6 eV where the thermally-induced insulator-to-metal transition results in  $\Delta R=0$ . The sample was kept at 180 K during the experiment to photo-excite the insulating ground state. The repetition rate of the laser was kept at 1 kHz since the relaxation from the photo-induced quasi-stable state to the insulating ground state occurs less than 1 ms.

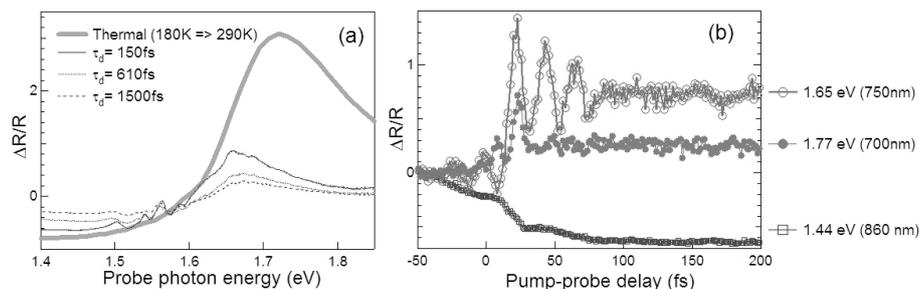


**Fig. 1.** (a) The structure of a single EDO-TTF molecule, (b, left axis) reflectivity at 290K and 180K, and (b, right axis and inset) spectrum of 10-fs pulses and their autocorrelation.

## Results and Discussion

Figure 2(a) shows the normalized reflectivity change ( $\Delta R/R$ ) in the spectral domain at the delay of 150, 610, and 1500 fs. They are similar to the thermally-induced reflectivity change (thick gray curve) on their signs and the location of the isosbestic point, except for the relative magnitudes. This result is consistent with the case of 150-fs pump pulses [1]. Figure 2(b) shows the time-resolved values of  $\Delta R/R$  at the early stage of PIPT. Around 1.65 eV where the absorption is dominated by intra-

molecular bands, we observed huge ( $\Delta R/R \sim 100\%$ ) and extremely fast ( $T \sim 20$  fs) modulation. This modulation was rapidly dumped as the  $\Delta R/R$  values reach the quasi-static value around  $\tau_d = 80$  fs. Based on this time scale, this modulation is likely due to the coherent vibrational motion of carbon double bonding in EDO-TTF molecules induced via the impulsive Raman process. At the photon energies below 1.6 eV where the absorption is dominated by inter-molecular charge transfer, the value of  $\Delta R/R$  goes negative. Since there is no periodic modulation on 10-fs time scales in this spectral region, we can clearly resolve the response of PIPT that is slower than the laser pulse duration. The existence of this delayed response, or the structural bottleneck time [4], suggests that PIPT is mediated by molecular conformational changes in contrast with prompt electronic transfer. The time scale of the structural bottleneck time was estimated to be  $\sim 50$  fs, defined by the delay where the  $\Delta R/R$  value reached 90% of the asymptotic value.



**Fig. 2.** (a) Reflectivity change in the spectral domain at different delays. (b) Reflectivity change in the time domain.

## Conclusions

We have investigated the initial dynamics of PIPT in charge-ordered organic salt  $(\text{EDO-TTF})_2\text{PF}_6$  using 10-fs laser pulses. We have observed gigantic photo-responses that are modulated by the impulsive Raman excitation of intra-molecular vibrational modes of carbon double-bondings. This oscillation is rapidly dumped as the reflectivity spectrum of the charge transfer band reaches to asymptotic values in 50 fs. The results suggest that the molecular conformation after charge-order melting initiates the PIPT.

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