Ultrafast gigantic photo-response in (EDO-TTF)$_2$PF$_6$ initiated by 10-fs laser pulses

Jiro Itatani[1,2], Matteo Rini[1], Andrea Cavalleri[3], Ken Onda[2,4], Tadahiko Ishikawa[4], Shin-ya Koshihara[2,4,5], Xiangfeng Shao[2,4], Hideki Yamochi[6], Gunzi Saito[7], and Robert W. Shoenlein[1]

[1] Lawrence Berkeley National Laboratory, 1 Cyclotron Road, MS 2-300, Berkeley, CA 94720 USA
[2] Non-equilibrium Dynamics Project, ERATO, Japan Science and Technology Agency, c/o 1-1 Oho, Tsukua 305-0801, Japan
[3] Department of Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom
[4] Department of Materials Science, Tokyo Institute of Technology, 2-12-1-H61, Oh-okayama, Meguro-ku, Tokyo 152-8551, Japan
[5] High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukua 305-0801, Japan
[6] Research Center for Low Temperature and Materials Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan
[7] Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan
E-mail: JItatani@lbl.gov

Abstract. We photo-exited a charge-ordered organic salt (EDO-TTF)$_2$PF$_6$ with sub-10-fs optical pulses. The photo-induced metallic phase appeared within 80-fs after pumping, characterized by large changes in reflectivity ($\Delta R/R \sim 0.8$) followed by strong coherent phonon modulation

1. Introduction

The recent discovery of a gigantic photo-response ($\Delta R/R > 1$) in 1/4-filled-band organic salt (EDO-TTF)$_2$PF$_6$ at high temperature ($T < 270$ K) has uncovered a new class of charge-ordered (CO) materials whose physical properties can be drastically altered by applying external fields on the femtosecond time scales [1]. The underlying physics of this phenomenon are the critical balance between electron-electron and electron-lattice interactions in the low-dimensional charge-ordered ground state. Previous studies of the photo-induced phase transition (PIPT) in (EDO-TTF)$_2$PF$_6$ has been investigated in visible and infrared wavelengths on the 100-fs time scale, focusing on the energy transfer process from the electron system to the lattice [1]. It has been revealed that (i) the PIPT process is accompanied by strong phonons oscillating at 1 and 2 THz, (ii) the photo-induced metallic phase decays in 200 μs to the insulating ground state, and (iii) the reflectivity spectrum of the photo-induced metallic phase differs from that of thermally induced phase in infrared. The early dynamics of the PIPT and associated CO melting in (EDO-TTF)$_2$PF$_6$ are of fundamental interest, and are addressed for the fist time in these studies via pump-probe measurements with sub-10-fs near infrared pulses.

2. Experimental Methods

We produced sub-10-fs pulses by compressing the output from a Ti:sapphire chirped-pulse amplifier with a Krypton-filled hollow fiber and dispersion compensation mirrors. Figure 1 shows the compressed pulse spectrum that ranges from 1.3 to 2.2 eV. This spectrum covers (i) the highest charge transfer absorption band ($D^+D^0D^0D^+ \Rightarrow D^{2+}D^0D^0D^0$) peaked around 1.4 eV and (ii) the isosbestic point of the reflectivity curves at 1.6 eV, where the thermally-induced insulator-to-metal transition shows $\Delta R=0$. The pump and probe pulses are focused non-collinearly on the samples, that are kept at 180 K in a cryostat. All the measurements were done at a pump fluence of ~10^{16} photons/cm^2.

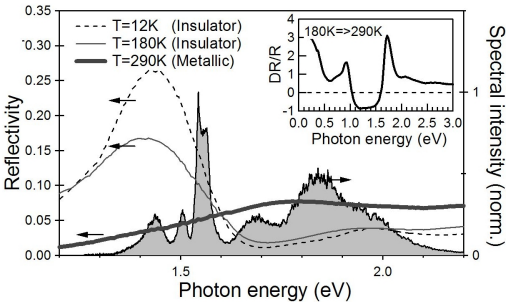

Fig. 1. Static reflectivity of (EDO-TTF)$_2$PF$_6$ at T=12, 180, and 290 K (left axis), and the spectrum of the sub-10-fs laser pulses used as pump and probe (shaded area, right axis). Inset: $\Delta R/R$ for thermally-induced phase transition for the temperature change from 180 K (insulator) to 290 K (metallic).

3. Results and Discussion

Figure 2 shows the reflectivity change at the probe photon energies of 1.44 eV and 1,63 eV, on either side of the isosbestic point, measured over 150-fs (left panel) and 1.2-ps windows (right panel), respectively. Following photoexcitation, a large transient decrease in reflectivity ($\Delta R/R$ up to -0.8) is observed on the low energy side (<1.5 eV), while a large transient increase ($\Delta R/R$ up to 0.8) is observed on the high energy side (>1.6 eV). As can be seen in Fig.2 (left panel), we observed a sharp increase (decrease) of $\Delta R/R$ within 80 fs on the higher (lower) energy side, respectively. These observations are consistent with the formation of the metallic state within ~80 fs.

The evolution of the spectral dependence of $\Delta R/R$ in 1.44-1.72 eV is shown in Fig.3. The lower energy sides (<1.65 eV) are all in good agreement to thermally induced phase transition, including the sign of the reflectivity changes, the amplitude of the reflectivity changes, and spectral location of the isosbestic point. This indicates that the insulator-to-metal phase transition is indeed being initiated by the 10-fs pump pulses. The discrepancy in the amplitude of $\Delta R/R$ at higher energy side (>1.7 eV) from the thermally-induced metallic state has been previously observed in PIPT induced by 120-fs pulses. Further investigation is needed to clarify the difference of thermally-induced ground-state metallic phase and the photo-induced transient metallic phase.

The early time dynamics provide new insight to the origin of this phase transition [2]. In particular, determining whether it is mediated by structural changes in the molecular crystal (structural bottleneck [2]), or by purely electronic correlation effects. The fact that the time scale of phase transition is much longer than the duration of the excitation pulse clearly shows the existence of the bottleneck whose time scale is 80 fs or less. This is consistent to the bending or in-plane phonon modes (120~500 cm^{-1}) observed by Raman scattering.

At a delay at >100 fs, phased oscillation with a period of ~ 0.5 ps becomes eminent at all the probe wavelengths. The observed modulation in reflectivity is nearly identical to the one as reported previously [1]. Although the role of these THz phonons to PIPT is not clear, the relaxation pathway of photo-induced metallic phase *selectively* couples to a few intermolecular phonon modes.

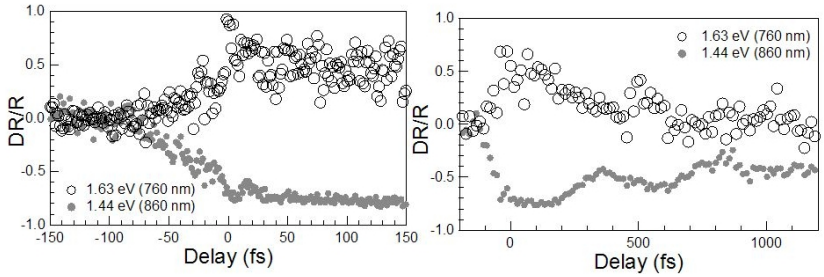

Fig. 2. Reflectivity changes (ΔR/R) at 760 and 860 nm in the 150-fs (left) and 1.2-ps (right) time windows.

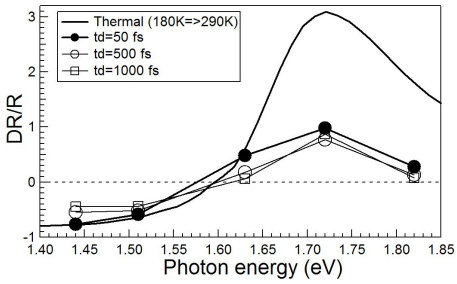

Fig. 3. Temporal evolution of ΔR/R at 1.44 eV (860 nm), 1.51 eV (820 nm), 1.63 eV (760 nm), and 1.72 eV (720 nm). Solid curve shows the ΔR/R spectrum for the case of thermally-induced phase transition.

4. Conclusions

We measured the ultrafast dynamics of the reflectivity changes associated with the insulator-metal transition in $(EDO\text{-}TTF)_2PF_6$ initiated with sub-10-fs laser pulses The melting of charge order occurred immediately, and a photo-induced metallic phase (|ΔR/R| up to 0.8) appeared within 80-fs after pumping. The existence of the structural bottleneck suggests the insulator-to-metallic phase transition is initiated by the efficient coupling of electronic excitation to high-frequency oscillating motion of EDO-TTF molecules.

Acknowledgements. This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 at the Lawrence Berkeley National Laboratory.

References

1 M. Chollet, L. Guerin, N. Uchida, S. Fukaya, H. Shimoda, T. Ishikawa, H. Yamochi, G. Saito, R. Tazaki, S. Adachi, and S. Koshihara, Science **307**, 86 (2005).

2 A. Cavalleri, Th. Dekorsy, H. H. W. Chong, J. C. Kieffer, and R. W. Schoenlein, Phys. Rev. B **70**, 161102(R) (2004).