

Time-resolved Crystal Structure Analysis of Photo-induced Metastable State of Multi-instability Material

The rapid development of ultra-fast laser techniques has allowed the study on transient states. The optical responses are well investigated with high temporal resolution down to the 10-femtosecond (fs) time domain. As a result, the **transient intermediate state (TIS)** which appears in the initial stage of **photo-induced phase transition (PIPT)** in $(\text{EDO-TTF})_2\text{PF}_6$ has been revealed to show the (1010)-type charge arrangement in the donor column. In the thermally induced metal-to-insulator transition of this multi-instability material, the unit cell doubling (Peierls instability), (0110)-type charge-ordering and anion-ordering are observed for the low temperature (LT) phase. The **structural studies for the fast PIPT** processes are, however, limited by the poor time resolution for x-ray diffraction at synchrotron sources (ca. 100 picoseconds). The development of an ultrabright fs-electron source for **fs-electron diffraction (FED)** experiments has circumvented this obstacle. Recently, the temporal modulations of the crystal structure of $(\text{EDO-TTF})_2\text{PF}_6$ was revealed with sub-picosecond **time resolution**.

Employing about 40 Bragg reflections and the known structures for the LT and room temperature (RT) phases, model refinement calculations were performed on the base of three independent structural parameters, ζ_F , ζ_B , and ζ_P . These valuables represent the atomic parameters of charge-rich and -poor donors and counter anion, respectively. The LT and RT structures of $(\text{EDO-TTF})_2\text{PF}_6$ correspond to $(\zeta_F, \zeta_B, \zeta_P) = (0, 0, 0)$ and $(1, 1, 1)$, respectively. The differences between these phases are well described as the motions of charge-rich donor and anion along with the unbending of charge-poor donor as shown in Fig. 1(a).

Model refinement simulations of the observed intensity modulations of Bragg peaks during the PIPT process revealed that the motions of charge-rich donor and anion precede the unbending of charge-poor donor as shown in Fig 1(b). At 5 ps after the photo-irradiation (in TIS), the charge-poor donor shows almost no changes despite anion and charge-rich donor exhibit significant motions ($\zeta_B \ll \zeta_P < \zeta_F$) as shown Fig. 1(c). This result demonstrated the **sequence of structural change in the PIPT**.

The international collaboration proved the efficiency of FED method for low-atomic-number materials and revealed the structural feature of the PIPT in a multi-instability molecular conductor.

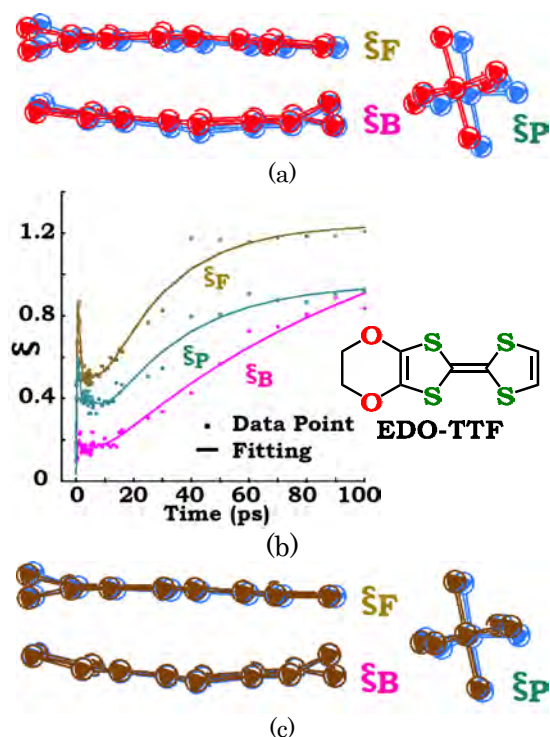


Fig. 1: Molecular motion and deformation in $(\text{EDO-TTF})_2\text{PF}_6$ (a) from the low (blue) to room (red) temperature phase and (c) from the former to the transient intermediate state at 5 ps after the photo excitation (brown). For each set, charge-rich and -poor donor molecules are drawn in upper and lower left side, respectively and the counter anion in right. (b) The temporal modulation of reaction coordinates ζ_F , ζ_B and ζ_P which correspond to the molecular motion and deformation indicated in (a) and (c). The inset shows the chemical structure of EDO-TTF.

For details, see an article, "Mapping molecular motions leading to charge delocalization with ultrabright electrons", *Nature*, **496**(7445), 343-346 (2013) by M. Gao, C. Lu, H. Jean-Ruel, L.C. Liu, A. Marx, K. Onda (A04), S. Koshihara, Y. Nakano (A05a), X.F. Shao (A05a), T. Hiramatsu (A05a), G. Saito, H. Yamochi (A05a), R.R. Cooney, G. Moriena, G. Sciaini, and R.J.D. Miller