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This report summarizes the novel features of the title complex so far investigated. $(EDO\text{-}TTF)_2PF_6$ showed the first-order metal-insulator (MI) transition at 280 K, of which mechanism was assigned to the cooperated one of Peierls, charge-ordering, and order-disorder transitions. The origin of the mixing of the transition mechanisms is regarded to be the distinct molecular deformation during the phase transition. In the examination of the effect of a pulsed laser light, the insulating phase showed the ultra-fast and highly efficient photo-induced phase transition, which needed ca. 1.5 ps and one photon per ca. 500 donor molecules to produce the highly conductive metastable state. The preliminary results of the thermally induced MI transition observed in the newly obtained isostructural complexes are also mentioned.

Keywords: electron-phonon coupling; metal-insulator transition; molecular deformation; organic metals; photo-induced phase transition; pump-probe method

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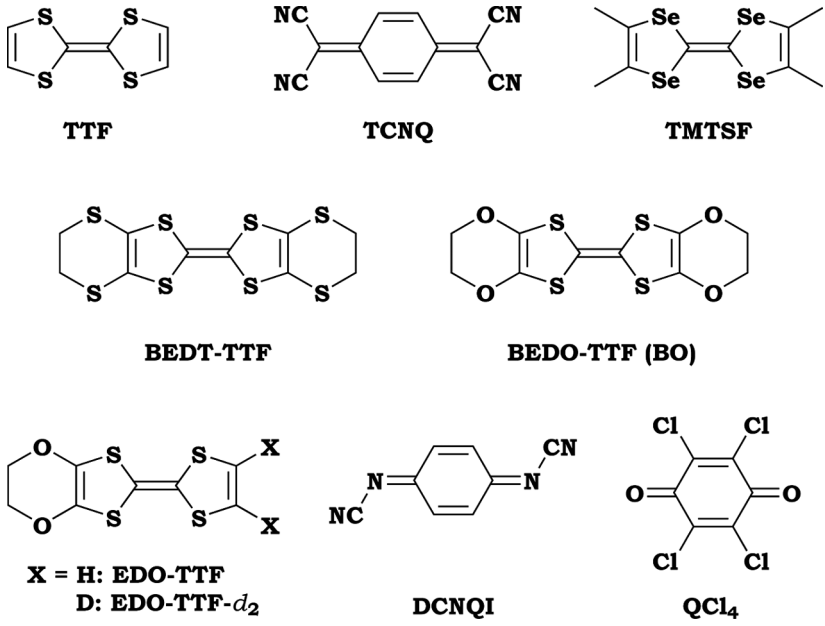
INTRODUCTION

Since the discovery of the perylene-bromine complex [1], the studies on charge-transfer (CT) complexes have brought about numerous numbers of semiconducting and metallic molecular solids. The history to realize the superconductivity for molecular crystals can be regarded as the succeeding trials to suppress the metal-insulator (MI) transition. The first organic metal of (TTF)(TCNQ) showed the Peierls instability due to the almost pure one-dimensional (1D) electronic structure (For the chemical structures corresponding to the abbreviations, see Scheme 1) [2].

The introduction of heavier atoms to the TTF skeleton effected to increase the dimensionality of the electronic structures of CT complexes. The cation radical salts of selenium containing donor molecule provided the first organic superconductors of $(TMTSF)_2X$ where X = monovalent inorganic anions such as ClO_4, PF_6, and so on [3]. Although the salt of X = ClO_4 showed the superconducting transition at ca. 1 K under ambient pressure, most of the salts in this series showed MI transitions due to the formation of spin-density wave (SDW) states below 20 K based on the quasi-1D nature of the Fermi



SCHEME 1 The chemical structures of the compounds appear in the text.

surfaces. In some cases, however, the order-disorder (OD) transition of the counter anion caused the MI transition.

In stead of the enlargement of the size of chalcogen atoms, the increased number of the sulfur atoms in BEDT-TTF reinforced the intermolecular interactions along the lateral directions of the molecule to afford the two-dimensional (2D) electronic structures of the complexes [4]. The 2D organic metals based on this donor molecule contained superconductors with the transition temperatures of 0.3–12.3 K at ambient pressure, while some of the complexes showed MI transitions. Since the 2D Ferimi surface resists to the nesting, charge-ordering (CO) is one of the mechanisms of these MI transitions. Also, some Mott insulators based on this donor molecule showed metallic and superconducting behaviors under pressure.

Among the TTF derivatives, BEDO-TTF (BO), which is a partially oxygen substituted analogue of BEDT-TTF, exhibits the self-assembling nature to afford stable 2D electronic structures of the complexes [5]. The origin of this property is regarded as the molecular shape and the intramolecular atomic arrangement; the flatness of the molecular width allows the effective side-by-side intermolecular atomic contacts including the inner sulfur atoms, and the terminal ethylenedioxy groups enable to form the weak hydrogen-bond network along the molecular stacking direction. However, BO complexes are poor to show phase transitions including superconducting one.

To suppress the self-assembling nature partially, we examined the removal of one of the ethylenedioxy groups in BO. As a result, EDO-TTF showed the complete vanishing of the self-assembling nature [6], while an unexpected type of MI transition was found out. This report summarizes the peculiar features of the thermally induced and photo-induced transitions observed in the title complex.

CRYSTAL AND ELECTRONIC STRUCTURES AND THE THERMALLY INDUCED MI TRANSITION OF (EDO-TTF)$_2$PF$_6$

As was reported previously, (EDO-TTF)$_2$PF$_6$ prepared by the electrocrystallization method consisted of the alternating donor and anion layers, in the latter of which the octahedral anion showed rotational disorder on the center of inversion [7]. The columnar stacks of EDO-TTF formed the donor layer. The head-to-tail type stacking provided barely dimerized feature of the intermolecular interactions as shown in Figure 1a. The calculated intermolecular overlap integrals (s) within the column were 27.3 and 27.4×10^{-3} for the room temperature (RT) crystal structure, while the magnitudes of those between the columns were less than 30% of these values. As a result, the calculated

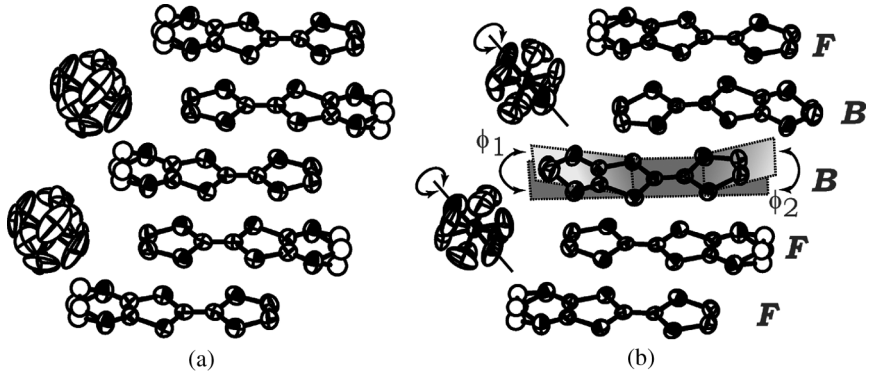


FIGURE 1 Crystal structures of $(EDO\text{-}TTF)_2PF_6$ at room temperature (a) and at 260 K (b). The thermal ellipsoids correspond to the 60% possibility. The terminal ethylene groups in (a) and of ***F*** molecules in (b) show positional disorder. In (b), the definition of the dihedral angles ϕ_1 and ϕ_2 is indicated. The lines and round arrows at the anions show the direction of the uniaxial rotation.

Fermi surface showed a quasi-1D feature, which was very similar to those of $(TMTSF)_2X$ and hence the formation of a kind of density wave states was expected. In fact, $(EDO\text{-}TTF)_2PF_6$ exhibited a first-order MI transition at ca. 280 K, just below RT.

To understand the mechanism of the high temperature MI transition, the crystal structures of the low temperature (LT) phase was studied based on the X-ray diffraction data at 260 K. The most distinct feature was the deformation of the half numbers of EDO-TTF to afford the bent shaped molecules (***B*** in Figure 1b), while the residual donor molecules showed more flattened shape than that in the RT phase (***F*** in Figure 1b). The dihedral angles of ϕ_1 and ϕ_2 were 6.0° and 0.3° for RT phase, 11.1° and 7.9° for ***B*** and 0.8° and 2.1° for ***F*** molecules at 260 K, respectively.

From the viewpoint of the crystal and electronic structures, the mechanism of this MI transition was assigned to the cooperative one of Peierls, CO, and OD transitions. In the LT phase, the periodicity of the intermolecular *s* was doubled to accommodate the arrangement of ***BBFF*** in a unit. The calculated *s* for the donor pairs of ***FB***, ***BB***, ***BF***, ***FF*** were $-23.0, 13.0, -23.0, 44.2 \times 10^{-3}$, respectively. The direction of the doubling corresponded to that expected from the shape of the Fermi surface to show the feature of Peierls transition. The comparison of the intramolecular bond lengths suggested that ***B*** molecule was less charged than ***F*** molecule. In fact, there expected the coexistence of

the donor molecules charged +0.1 and +0.9 from the Raman spectra observed at 4.2 K [8]. The CO pattern was experimentally confirmed by the accurate crystal structure analysis as [0, 0, +1, +1] type corresponding to the donor arrangement of ***BBFF***, which is unfavorable for the Coulombic repulsion [9]. Additionally, this MI transition also exhibited the OD transition feature. The rotational disorder of the anion observed in the RT phase was partially suppressed to show a uni-axial rotation at 260 K. The periodicity of the anion arrangement was doubled in the LT phase compared with that in the RT phase, the direction of which corresponded to that of the expected nesting vector. The cooperative feature of three mechanisms to bring about an MI transition was proved by the observation of the same type of phase transition in the isostructural complex of (EDO-TTF)$_2$AsF$_6$, of which transition temperature of 268 K was somewhat lower than that of the PF_6 complex.

As for the MI transition under uniaxial strains, a small strain of ca. 4 kbar along the interlayer direction raised the transition temperature by more than 60 K, while the in-layer strains affected inefficiently up to 6 kbar [10]. These results demonstrated the anisotropic sensitivity of (EDO-TTF)$_2$PF$_6$ to the mechanical strain, which may be related with the molecular deformation associated with this MI transition.

PHOTO-INDUCED PHASE TRANSITION OF (EDO-TTF)$_2$PF$_6$

The peculiar feature of the thermally induced MI transition of (EDO-TTF)$_2$PF$_6$ prompted the authors to examine the photo-induced phase transition (PIPT) [11]. Based on the reflection spectra observed at 6–290 K [8], the pump-probe method was applied to trace the time development of the reflectivity at 11.1 and $13.9 \times 10^3\,\mathrm{cm}^{-1}$ before and after the irradiation of 120 fs pulsed laser light of $12.5 \times 10^3\,\mathrm{cm}^{-1}$. In this region of the optical spectra, the CT band assigned to the transition of $D^+D^+ \rightarrow D^{2+}D^0$ appeared in the LT phase, while only the tail of the Drude-like broad peak in the low energy region was observed for the RT phase.

As is shown in Figure 2a, the reflectivity of the LT phase showed abrupt change after the pump light was irradiated to give the metastable state within ca. 1.5 ps [11]. This response time is ranked in the fastest class of PIPT so far investigated, e.g., the partially deuterated Cu(DCNQI)$_2$ showed insulator-to-metal PIPT, which needed around 20 ps to complete the changeover [12]. Based on the pump light intensity, absorption coefficient of the sample, and the magnitude of the reflectivity change, it was estimated that one photon caused the PIPT of ca. 500 EDO-TTF molecules. Also, the efficiency of the stimulating light was excellent. For comparison, 200 DCNQI molecules were

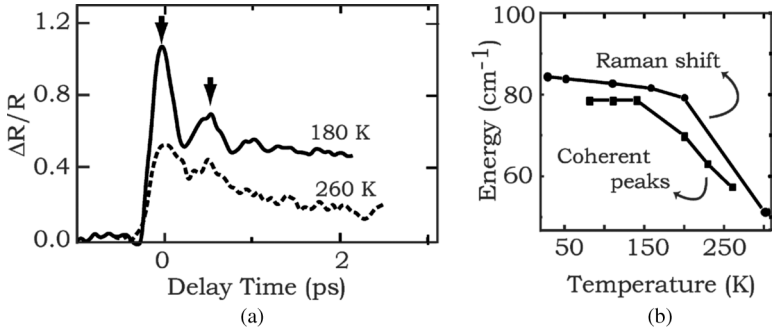


FIGURE 2 (a) Time development of the differential reflectively of (EDO-TTF)$_2$PF$_6$ during the photo-induced phase transition at 180 K (solid line) and 260 K (dashed line). The wave numbers of pump and probe lights were 12.5 and $13.9 \times 10^3\,\mathrm{cm}^{-1}$, respectively. Thick arrows point the coherent peaks. (b) Temperature dependences of the frequencies of coherent peaks and a Raman peak, the latter of which was observed at $85\,\mathrm{cm}^{-1}$ at 30 K.

affected by one photon in the above mentioned Cu(DCNQI)$_2$, and 310 donor-acceptor pairs per a photon were converted to the neutral phase from the thermally produced ionic phase in the neutral-ionic transition system of (TTF)(QCl$_4$), of which response time was reported to be a few tens to 1000 ps [13].

The thermal effects of the pump light should be concerned especially when the transition from a LT to high temperature phase is examined. Based on the observed heat capacity, along with the optical absorption coefficient, the temperature increment of (EDO-TTF)$_2$PF$_6$ during the PIPT examinations was estimated to be 0.1 K at most [14]. The observed variation in the reflectivity was, hence, really due to the PIPT.

To generate the metastable state by the PIPT, there existed the threshold intensity for the pump light. When the LT phase of (EDO-TTF)$_2$PF$_6$ absorbed more than 2×10^{18} photon/cm^3, the metastable state was persisted 3 ps after the pumping. It is noteworthy that the metastable state generated by the stronger pumping light, e.g., 6×10^{18} photon/cm^3, needed 300–400 μs to relax back to the LT phase. The long life-time of the metastable state allowed to record the time development of the electrical conductivity to show the excellent correspondence to that of the reflectivity. It was proved that the metastable state was a really conductive state.

Another interesting and important feature of the PIPT in (EDO-TTF)$_2$PF$_6$ is the vibration in the time development of the reflectivity.

As shown in Figure 2a, the frequency of this vibration was ca. 0.5 ps at 180 K, which corresponded to the wave number of 70 cm^{-1} of a wave having the velocity of the light. In the Raman spectra, there observed a peak at 85 cm^{-1} at 30 K, of which frequency was close to that of the above mentioned vibronic feature. The striking feature was that both of the frequencies of the vibration in reflectivity spectra and the Raman peak were softened according to the temperature as shown in Figure 2b. These results indicated that the time development of the reflectivity included the coherent peaks, which strongly suggested the strong coupling between the electronic state and the lattice and/or intramolecular vibrations.

SCOPES AT PRESENT AND IN FUTURE AS CONCLUDING REMARKS

As was demonstrated above, (EDO-TTF)$_2$$PF_6$ is a peculiar MI transition system having the 1/4 filled band (or 3/4 filled in terms of electrons). Along with the potential to construct the optic communication devices due to the ultra-fast and highly efficient PIPT at around RT, there remain problems to be solved from the viewpoint of basic science.

To understand the detailed mechanism of the PIPT, the ultra-fast time resolved X-ray structure analysis is needed. The technical difficulty will be rid of. In fact, it was reported that the X-ray diffraction data were recorded every 0.3 ps during the PIPT of an inorganic crystal having the simple crystal structure [15]. Also, the detailed analysis of the coherent peaks are desired to understand the detailed features of electron-phonon and/or electron-molecular vibration coupling; the investigation of the wavelength dependences of PIPT are underway by changing those of pump and probe lights.

From the standpoint of material preparation, the analogous complexes are needed to understand the peculiarities of (EDO-TTF)$_2$$PF_6$. Although the supporting electrolyte of (Bu_4N)X afforded the isostructural complexes when X = PF_6 and AsF_6, a different stoichiometry of the complex was provided in case of X = SbF_6. Recently, the isostructural (EDO-TTF)$_2$$SbF_6$ was obtained by using an ionic liquid to show the lower transition temperature of 240 K, the details of which will be reported elsewhere. Also, the preliminary examination of the partially deuterated complex of (EDO-TTF-d_2)$_2$$PF_6$ showed ca. 2.5 K higher MI transition temperature than that of non-deuterated complex.

The most difficult and challenging problem is the development of new systems which show the phase transitions based on the cooperation of the mechanisms and/or ultra-fast and highly efficient PIPT's. The authors are trying to carry out the investigations

according to the working hypothesis that a conducting component molecule having small sized flexible conjugated π-electron system will provide the desired complexes due to the molecular deformation during the phase transitions.

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