The future of photo-induced phase transition (PIPT)  
-How fast and slow it can be changed? -

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Abstract. The study of photo-controlled nature of materials, including their optical, magnetic, and conducting properties, is a fascinating research field. The finding of photo-induced phase transition (PIPT) has triggered the search for inorganic and organic systems with highly efficient and ultrafast photo-responses. As a result of the recent progress in quantum-beam technologies, the time-resolved study of PIPT dynamics on the femto-second time scale, which is comparable with the single-cycle of phonon vibration, has become feasible. In contrast, ultra-slow dynamics on the time scales of a few seconds to several minutes play an important role in the cooperative phenomena in complex systems. Here, we review both the ultra-fast and ultra-slow dynamics of the photo-induced cooperative effects in a typical organic CT crystal (EDO-TTF)²PF₆ and a protein molecule, myoglobin (Mb). In the case of Mb, we discuss the results from the viewpoint of a unique photo-functionality, i.e., the photo-induced transportation of a small molecule in the “super-structure” of a protein molecule.

1. Introduction
It is an attractive target for photonic science today to find materials that show cooperative phenomena, such as phase transition triggered by external stimulation of light. It is well known that extensive studies have been conducted on photo-induced structural changes in the fields of photochemistry and solid-state physics. However, those studies have been primarily focused on microscopic reactions in small molecules or localized structural changes in crystals, such as cis-trans isomerization of organic molecules and self-trapped exciton in alkaline-halide. In contrast, the subject of our study is to find
experimental evidences indicating that photo-injected local excitation can trigger large structural and electronic changes in meso- and macroscopic systems by virtue of cooperative interactions, such as spin-lattice interaction and electron-lattice coupling. Such unique effect induced by photo-excitation has been named as photo-induced phase transition (PIPT) [1-3] since it is analogous to the domino effect as shown in Fig. 1.

As a result of extensive studies on PIPT in the past 20 years, real examples have been reported in various materials such as charge transfer (CT) crystals, π-conjugated polymers, transition metal-oxides, spin crossover complexes, Prussian-blue analogs, quantum structure of diluted magnetic semiconductors, low-dimensional transition metal-organo complexes, and A2B molecular crystals, as discussed at the PIPT meeting. These results clearly indicate that, for designing photoactive system with high sensitivity, the most effective strategy is to utilize the intrinsic instability in electronic, magnetic, and structural properties resulting from cooperative interactions. As shown in Figure 1, when the free energy shows bistability between two (A and B) phases, the photo-excitation may induce even persistent and bi-directional phase switching. Indeed, in the case of the manganite film, as discussed by N. Takubo et al. [4], as well as in π-conjugated polymer crystal, the bistability of the free energy plays an essential role for achieving persistent and bi-directional PIPT.

For understanding the dynamic process of PIPT, it is essential to determine how the excess energy (fuel) injected by photon can be distributed into the system to drive cooperative processes as shown in Figure 2 [3]. From this point of view, “ultra-fast” spectroscopy, especially in pico- and femtosecond (ps and fs) regions, is becoming an essential tool for PIPT studies, as predicted by C.V. Shank [5] and intensively discussed in this conference. Since the typical laser pulse duration is 100 fs that corresponds to the phonon vibration frequency of 10 THz (or 330 cm⁻¹), material properties can be tuned and probed with the fundamental time scales of the initial stage of structural changes. In Section 2, as a real example, we introduce ultrafast PIPT dynamics strongly coupling with molecular vibration in a charge-ordered organic CT complex utilizing a 10 fs time-resolved spectroscopic technique. In contrast, in Section 3, we report that the ultra-slow dynamics also plays an important role for cooperative phenomena in complex systems, such as proteins. This is because long- and large-scale structural changes are associated to the movement of molecules and/or molecular units that
are heavier than small molecules, will become heavy and thus decrease the speed of the dynamics, in contrast with the electronic change, which will be rather light. In particular, in the case of myoglobin (Mb), the structural change seems to be strongly correlated with the movement of the CO (carbon monoxide) molecule and seems to drive the transportation of CO from the inside to the outside of the protein molecule. We focus on this point in Section 3.

2. Ultra-fast dynamics of PIPT strongly coupled with molecular deformation

It is evident that the optical property of 1/4-filled organic salt (EDO-TTF)$_2$PF$_6$ can be drastically modified by optical excitation on the fs time scale [6]. The underlying physics of these gigantic photo-responses is 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), which changes it into a [1010]-type charge-ordered state [7]. While there has been significant progress in understanding the photo-induced phase in (EDO-TTF)$_2$PF$_6$, little is known about the initial dynamics of the PIPT, which is of fundamental interest for understanding the interplay among various molecular/lattice/electronic degrees of freedom in strongly correlated systems. It is also crucial to examine whether the PIPT is driven purely by the electronic processes or by the photo-induced change of the molecular conformation in order to understand the nature of the process. Recently, Itatani et al. investigated the ultra-fast dynamics of the reflectivity changes in (EDO-TTF)$_2$PF$_6$ during PIPT initiated with 10-fs laser pulses [8].

Figure 3 shows the time profile of $\Delta R/R$ at the early stage of PIPT, which reveals gigantic reflectivity modulation ($\Delta R/R \approx 100\%$) on 10-fs time scales. At around 1.65 eV, where the absorption is dominated by intra-molecular bands, we observed gigantic ($\Delta R/R \approx 100\%$) and extremely fast (T~20 fs) modulation. This vibration cannot be observed with 30-fs light pulses and is thus a typical example demonstrating that femtosecond technology is quite important in molecular semiconductor science. This modulation was rapidly dumped as the $\Delta R/R$ values reached a quasi-static value at 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, as shown in the right-hand side of Figure 3. The study on the role of ultra-fast molecular vibration that is strongly coupled to electronic channels in PIPT dynamics is an essential step for tuning the excess energy relaxation process, i.e., the control of the initial direction of the phase transition, utilizing the phase coherence of the excitation light.

3. Ultra-slow structural dynamics of protein coupled with the movement of a ligand molecule

Proteins have a number of cavities of relatively small volume. Although these packing defects are associated with the thermodynamic instability of the proteins, the cavities are also believed to play specific roles in controlling protein functions, e.g., ligand migration pathways and ligand binding sites...
in protein matrices [9]. This issue, which is the central theme of the structure-based drug design, has been extensively studied by using a well-known heme protein, myoglobin (Mb), a main logistic system of biologically active gas molecules in muscle [10]. As shown in Figure 4, Mb reversibly binds gas ligands at the heme site buried in the protein matrix and possesses several internal cavities in which ligand molecules can reside [11]. In spite of the many known details regarding gas molecules trapped in some of these internal cavities [12], there is no comprehensive picture of the overall ligand migration processes in Mb. X-ray structural analysis of Mb has revealed that these cavities are isolated, and no open channels from the solvent to the heme-binding site have ever been detected experimentally, which has been one of the unsolved puzzles of Mb.

![Figure 4. Structure of myoglobin (Mb) at 40 K. The ligand CO molecule is located at the heme site, as shown in this figure in the form of MbCO before photo-irradiation.](image)

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![Figure 5. Electron density map of MbCO around the heme site before (laser off) and after (laser on) photo-irradiation at 40 K. The initial stage of the photo-induced migration of the ligand CO molecule in MbCO is observed. The photo-dissociation of CO from the Fe(II) porphyrin (heme) center triggers this process accompanied with the small movement of the Fe(II) ion from the in-plane to the out-of-plane location, as indicated by arrows in the right-hand side. The surface of the white patterns corresponds to the electron density of 0.7 e/Å³](image)

Figure 5. Electron density map of MbCO around the heme site before (laser off) and after (laser on) photo-irradiation at 40 K. The initial stage of the photo-induced migration of the ligand CO molecule in MbCO is observed. The photo-dissociation of CO from the Fe(II) porphyrin (heme) center triggers this process accompanied with the small movement of the Fe(II) ion from the in-plane to the out-of-plane location, as indicated by arrows in the right-hand side. The surface of the white patterns corresponds to the electron density of 0.7 e/Å³.
Recently, a new method based on the continuous pulsed-laser excitation of MbCO at cryogenic temperatures has made it possible to study the slow migration dynamics of the CO molecule in the protein matrix even at 100-140 K. Obviously, at the initial stage of the migration of the ligand (CO) molecule, the photo-dissociation of CO from the Fe(II) porphyrin (heme) center triggers this process accompanied with the small movement of the Fe(II) ion from the in-plane to the out-of-plane location. This movement can be clearly observed at 40 K, as shown in Figure 5.

This method also enables visualizing the entire migration processes of CO in native Mb at atomic resolution and eventually unveils a new picture of the ligand migration in the protein matrix; the migration of the CO molecule in each cavity induces the structural deformation of the cavities, which promotes gating the ligand migration channel in a cooperative way. Figure 6 shows one example of the change of cavities induced by photo-irradiation by pulsed laser light. The observed changes are correlated with the change of the electron density due to the increase of the CO molecule density in the cavities. A detailed study is now in progress. Collaborative work with the researchers engaging in theoretical studies to clarify the relationship between ligand migration and the electronic potential, including the electronic state, will be essential to understand the cooperative phenomena in protein molecules. Although we cannot discuss the role of protons in this class of materials due to the limitations of probing method, a dynamic study of the proton network in proteins that focuses on the analysis of the relationship with ligand migration may be an attractive subject in the near future.

**Figure 6.** Electron density map of MbCO around cavities (indicated by cages) before (left-hand side) and 810 minutes after (right-hand side) photo-irradiation at 120 K. The cavities show concordant expansion correlating with the migration of the ligand CO molecule shown by white patterns inside the cages (cavities). The surface of the white patterns corresponds to the electron density of 0.3 e/Å³.

### 4. Summary

Here, we reviewed both the ultra-fast and ultra-slow dynamics of PIPT in a typical organic CT crystal, (EDO-TTF)₂PF₆, and a protein molecule, myoglobin. Experimental results demonstrate that, in both cases, the unique photo-functionality of these systems is strongly correlated with the cooperative and sequential deformations of the constituents. The time scale of the dynamics, of course, depends on what kind of photo-functionality is designed. For the future expansion of the PIPT field, it is
essential to develop the measurement techniques for ultra-slow time region combining with other probes, such as proton dynamics, as well as ultra-fast dynamics.

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