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Photo-induced phase transition: From where it comes and to where it goes?

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Abstract. It is an attractive target for materials science to find a system which shows the phase transition triggered by external stimulation of light. The purpose of our study is to review experimental evidences indicating that the photo-injected local excitation can really trigger the cooperative phenomena in solids. In this sense, this unique photo-induced effect can be named as photo-induced phase transition (PIPT). Here, I will also make brief review on the experimental research on PIPT combining with a development of ultra-fast quantum electronics technology.

1. Introduction
It is well known fact that various phase transitions can be triggered in condensed matter by the changes in external conditions such as temperature, pressure, electric field and magnetic field. It is an attractive target for materials science to find a system which shows the phase transition triggered by external stimulation of light. Of course, in the research history of the fields of photochemistry and solid-state physics, we can easily find that extensive studies have been made on the structural changes by optical pumping for a long interval. However, those studies have been mainly concerned with microscopic reactions confined in small molecules or local structure changes in crystals. Photo-induced cis-trans isomerization of the stilbene molecule, optically induced defect state in amorphous materials (fatigued photo-luminescence center) [1] and self-trapped exciton in alkaline-halide [2] are typical examples of such a local structure change by photo-excitation. By contrast, the purpose of this work is to review experimental evidences indicating that the photo-injected local excitation can really trigger the macroscopic phase transition by virtue of cooperative interactions such as electric correlation, spin-lattice interaction and electron-lattice coupling.

This unique effect induced by photo-excitation which is analogous to domino effect (see figure1) has been named as photo-induced phase transition (from now on, abbreviated as PIPT). Over sixteen years, extensive studies on PIPT have been accumulated and realistic examples have been reported for various materials such as charge transfer (CT) crystals [3], π-conjugated polymers [4], transition metal-oxides [5], spin crossover complexes [6], prussian-blue analogs [7], quantum structure of diluted magnetic semiconductors [8], low-dimensional transition metal organo complexes [9] and A₂B molecular crystals [10]. In all examples, it is essential to utilize the intrinsic instability in electronic,
magnetic and structural properties due to cooperative interactions for enhancement of photo-response. Especially, in case of the \(\pi\)-conjugated polymers which was the first example of the reversible PIPT, the bistability in free energy plays an essential role for promoting the growth process from localized excitations into macroscopic phase change. In the following part, we review the works on the dynamical behavior of PIPT in \(\pi\)-conjugated polymer as a typical example [4]. We also review our recent work on ultra fast dynamics of PIPT in 1/4 filled molecular crystals relating with the importance of femto-second (fs) time-resolved structural study. [11]

2. **Strategy for achieving reversible and quasi permanent PIPT in Polydiacetylene crystals**

Polydiacetylenes (PDAs) are a family of representative \(\pi\)-conjugated polymers, and available in various forms such as cast films, vacuum deposited films and single crystals. One of unique properties in PDAs is a thermally induced chromic phase transition between two spectroscopically distinct A- and B-phases [12]. Figure 2 shows the changes in reflection and Raman spectra for one of a family of PDA (poly-4U3) single crystals accompanied with the A-B transition. As observed in this figure, reflectance changes at 1.95 and 2.35 eV on the A-B transition are so large that the A-B transition is easily traceable by monitoring the reflectivity around these two photon energies. As an example, temperature dependence of the reflectivity at 1.95 eV is plotted in figure 3. Temperature was changed in a sequence of the numbers in this figure (1->2->3->4->5). In the heating process (1->2->3), the system was kept in the A-phase below 400K, but showed an abrupt decrease of the reflectivity at 1.95 eV around 400 K in coincidence with the A-to-B transition. The A-B transition in poly-4U3 showed a hysteresis and the crystal was kept in the B-phase down to 360K in the cooling process (3->4->5) as shown in figure 3. The thermally induced A-B transition was reversible if the crystal was not heated up beyond the melting temperature.

At the temperature point 2 in figure 3, the system is kept in the A-phase perhaps due to the large potential barrier although the B-phase is expected to be more stable. Then it can be expected that the highly efficient A-to-B phase conversion at this temperature (point 2) is induced by irradiation of even a single shot of light pulse. Indeed, at 390K, as shown in figure 2 by dashed lines, large spectroscopic changes which can be attributed to the A-to-B phase conversion was induced by irradiation of a single shot of 2.81 eV (=\(h\nu\)) light pulse (20 ns width) with excitation intensity of 7x10^{18} photons/cm^2 [4]. (From now on, excitation intensity, i.e. a density of absorbed photons on the
The crystal surface is simply denoted in unit of cm\(^3\). The A-to-B phase conversion efficiency (\(\phi\)) estimated from the change in the integrated intensity of absorption and Raman bands reached almost 100% in the present excitation condition. The photo-induced spectroscopic change was permanent even if the sample temperature was not cooled down below the hysteresis region. At the temperature point 4 (370 K), large photo-induced changes in the reflectance and Raman spectra were similarly observed as shown in figure 2. From the obtained results, the 50% of the B-phase was considered to be converted to the A-phase by a single shot irradiation with 3.18 eV (=h\(\nu\)) light pulse (20 ns width) at the excitation intensity of 7 \times 10^{18} \text{cm}^{-3}[4]. The spectroscopic changes was also permanent even if the sample temperature was not heated up beyond the hysteresis region. These results demonstrates that the gigantic photo-response which leads to reversible PIPT (both A-to-B and B-to-A directions) can be really achieved by utilizing the bistability in the free energy (see right hand side of figure 3) as a result of cooperative electron-lattice interaction. Based on the similar strategy, various PIPT has been achieved tuning the free energy by addition of external fields such as pressure and magnetic field [13]. In addition, it was also reported that the tuning of the energy potential curve not only in the ground state but also in the photo-excited state makes possible to control the PIPT dynamics. Indeed, in the case of the spin crossover complexes, rather week magnetic field makes a large effect on the dynamical process of PIPT [14].

**Figure 2.** Spectra of the imaginary part of the dielectric constant (\(\varepsilon_2\)) for the exciton absorption (left part) and Raman spectra (right part) at various temperatures. The temperature points labeled 1-5 are indicated on the hysteresis loop shown in figure 3. Dashed lines in the spectra at temperature points 2 and 4 show those observed after photoexcitation by a single shot of pulsed laser [4].

**Figure 3.** Temperature dependence of reflectivity in a poly-4U3 crystal at 1.95 eV (left side), and schematic diagram of free energy with the minima corresponding to the A and B phases (right side). At temperature points 2 and 4, the crystal surface was irradiated with a single shot of a pulsed laser as denoted by dashed lines [4].
3. Characteristics of PIPT in PDAs

Figure 4 shows the excitation intensity dependence of the photo-induced phase conversion efficiencies ($\phi$) for the A-to-B (observed at 390 K) and B-to-A (at 370 K) directions [4]. The excitation photon energies were set at 2.81 and 3.18 eV for the A-to-B and B-to-A conversions, respectively. A nonlinear (threshold like) dependence of $\phi$ on the excitation intensity was clearly observed: The photo-excitation with an intensity weaker than $2 \times 10^{18}$ cm$^{-3}$ induces no permanent change in Raman nor absorption spectra. $\phi$ abruptly increases for each A-to-B or B-to-A case when the excitation intensity exceeds $2 \times 10^{18}$ cm$^{-3}$. The threshold intensity ($I_{th}$) is shown by an arrow in figure 4. The value of $2 \times 10^{18}$ cm$^{-3}$ ($=I_{th}$) corresponds to the absorption of one photon in the fraction of about 480 repeated units of the polymer. $\phi$ reaches the maximum (ca. 1.0 for A-to-B and 0.5 for B-to-A) with the excitation intensity of ca. $6 \times 10^{18}$ cm$^{-3}$ for the respective transitions and keep these optimum values as far as the excitation intensity does not exceed the damage threshold value ($8 \times 10^{18}$ cm$^{-3}$). The observed high conversion efficiency clearly indicates the important role of the cooperative mechanisms in the driving process of PIPT in PDAs as expected.

$\phi$ also strongly depends on the excitation photon energy, as shown in figure 5 with filled circles, when the excitation intensity is kept constant at $6.5 \times 10^{18}$ cm$^{-3}$. There are two notable points in this
plot. At first, there is a close similarity between the excitation photon energy dependences of $\phi$ (filled circles) and those of the photoconductivity (open circles). This shows that the photo-excitation with the energy to generate itinerant carrier is necessary for triggering the photo-induced phase transition. In other words, the photo-carriers can really switch the photo-induced phase transition via cooperatively correlating channel. The second point to be noted is that the excitation spectra for the converted fraction show a threshold photon energy which is located at 0.3-0.5 eV higher than the exciton absorption peak. The efficiencies are very low near the exciton absorption peaks where the excitation light is strongly absorbed. This is in contradiction to the situation expected for the thermal phase changes induced by the laser-heating effect. An excitation light pulse with the photon energy between 2.3 and 2.9 eV can induce the A-to-B conversion with nearly 100% efficiency. However, the photo-conversion in the reverse direction (B-to-A) is not efficient in the above photon energy range and the optimum efficiency (ca. 50%) can be attained only when the photon energy is above 3.0 eV. These characteristics are important characteristics for the bi-directional photo-switching application controlling the conversion direction by properly tuning the excitation wavelength.

4. Transient PIPT observed at the temperature point outside hysteresis region

By the time-resolved reflectance spectroscopy at the temperature points outside the hysteresis region (points 1(5); 300 K and 3; 420 K), the occurrence of the transient domain injection of the unstable phase was observed [4]. For example, at 300 K (low-temperature side out of the hysteresis loop), only the A-phase is stable and the crystal was kept in this phase before excitation as shown in the figure 6(a). Within 50 ns after photo-excitation by 2.81 eV light pulse, the reflection band around 1.9 eV in the A-phase almost disappears and a new band around 2.5 eV whose spectral shape is characteristic of the B-phase appears (see figure 6(b) $\Delta t=100$ ns). At $\Delta t=100$ $\mu$s, the reflectance maximum shifts to 2.3 eV and the 1.9 eV band (A-band) begins to reappear. At $\Delta t=10$ ms, the spectrum comes back to the same one as before photo-excitation. The temporal shift of the photo-

![Figure 6. Photo-induced reflectance change at a temperature point (300 K) below the hysteresis region.](Image)

(a) shows the spectrum of the A-phase before photo-excitation. The time-resolved reflectance spectra (b), (c), and (d) were observed at 100 ns, 100 $\mu$s, and 10 ms after photo-excitation by 2.81 eV ($=hn$) pulse, respectively. Time-dependence of the reflectance change observed at 1.9 and 2.35 eV is plotted in the upper panel. Vertical dashed lines denote the photon energies at which the temporal behavior of the reflectance change is monitored [4].
injected B-phase band from 2.5 to 2.3 eV may reflect the slower relaxation process of the side-group configuration than the change in the polymer backbone structure. A similar transient domain injection into the B-phase ground state has been observed at 420K (high-temperature side out of the hysteresis) by the irradiation of the 3.18 eV light pulse. These results demonstrate that the transient phase switching can be achieved as expected from the energy potential surface in the out of hysteresis region.

5. Ultrafast PIPT combined with coherent phonon process

In the previous sections, the PIPT driven by cooperative electron-lattice interaction has been reported. However, it is a natural consideration that the speed of PIPT, i.e. the speed of the domino process for domain growth accompanied with structural changes, will be limited by phonon propagation process. For realizing molecular phase switching device controllable by light with THz response time, it is a key to develop the material which shows highly sensitive and ultra-fast PIPT phenomena. One way for realizing highly efficient and high speed PIPT is to utilize coupled changes in electronic and lattice structures mediated by coherent phonon process. If the electronic-lattice coupled change in mesoscopic region of crystal can be mediated by optical phonon mode with \( k = 0 \) via electron-lattice interaction channel, the phase change in mesoscopic domain may be induced at once just after ultra-short light pulse excitation. However, it has been to date under question that the electron-lattice (optical mode) strong coupling mechanism can really achieve high speed and efficient PIPT based on this idea though a possibility discussed in pioneer works of ultrafast photo-effect in VO\(_2\) and a neutral-ionic transition systems [3, 5, 15]. In the following part of this section, we show that 1/4 filled A\(_2\)B crystal seems to be supporting the idea that this mechanism so called as ‘photo-domino on phonon coherence’ is really useful for realizing this purpose even around room temperature [11].

Quite recently, quasi one-dimensional 1/4 filled A\(_2\)B salts (EDO-TTF)\(_2\)PF\(_6\) which shows the

![Figure 7. (a) Reflectivity spectra for the M (gray line) and I (black line) phases observed at 290 and 180 K, respectively. Inset: Reflectivity spectra in the wide photon energy region for the M (gray line) and I (black line) phases, respectively. (b) Reflectivity spectra observed at 10 ps before (\( \Delta t = -10 \) ps: solid lines) and 3 ps after (\( \Delta t = +3 \) ps: dashed lines) photoexcitation at the sample temperatures of 180 K (black lines) and 265 K (gray lines). The excitation density was 6x10\(^{18}\) cm\(^{-3}\). Inset: Time profiles for \( \Delta R/R \) at 1.72 eV (black line) observed at 180 K (black line) and 260 K (gray line). Triangles indicate the peak positions due to the vibratile structure observed at 180 K[11].](image-url)
transition between metallic (M) and insulator (I) phases at room temperature (T_c=275K) has been realized [16]. The origin of this transition has been attributed to the occurrence of charge ordering (CO) accompanied with large lattice and molecular structural changes (see figure 1) [17]. This I-M transition, i.e. melting of CO, in (EDO-TTF)$_2$PF$_6$ can be also sensitively probed by spectroscopic method as plotted in figure 7(a). Here, reflectivity change in the spectral region of 1.1-2.5 eV induced by 120 femto-second (fs) pulsed light was utilized for the confirmation of the occurrence of transition, and its dynamics. The crystal surface with the size of 0.1x0.2 mm$^2$ was excited by laser light and the excitation photon energy (1.55 eV) was resonant to the edge of the charge transfer excitation among constituent EDO (Donor: D) molecules (excitation from D$^+$D$^+$ to D$_2^+$D$_0^-$) [18]. Figure 7(b) shows the reflection spectra 10 ps before ($\Delta t$=-10 ps) and 3ps after ($\Delta t$=3 ps) photo-excitation observed at 180K and 260K, respectively. Similar large and fast reflectivity change triggered by photo-excitation was confirmed in the wide temperature range lower than T_c (T<265 K) and it disappeared above T_c. The obtained spectral changes indicate that optical band directly reflecting CO in I phase disappears and in contrast rather weak and broad one which seems to be characteristic for M-phase appears just after photo-excitation. These results clearly indicate that CO melting accompanied with I-to-M phase conversion occurs within 3ps just after excitation.

A time profile of the spectral changes observed at 1.72 eV with an excitation density of 6x10$^{18}$ cm$^{-3}$ is plotted in the inset of figure 7(b). For $\Delta t$ >1.5 ps, the $\Delta R/R$ value remained constant, and the spectral shape was consistent with the I-to-M transition as a result of CO melting; thus, it can safely be concluded that the phase conversion process was completed within 1.5 ps for a wide temperature region. Such an ultrafast photo-conversion process cannot be explained simply by the light-induced heating effect. In addition, a vibrational structure with a large magnitude was observed. The period of this vibration, estimated from the interval between the first and second peaks (about 0.5 ps (70 cm$^{-1}$) at 180 K) has little dependence on the probe photon energy. Thus we can conclude that the coherent phonon generation process via cooperative electron-lattice channel is really playing a key role for promoting such a ultrafast and highly efficient phase switching even at 260 K. In other words, the obtained results support the idea that ‘photo-domino on phonon coherence’ is an useful concept for realizing the material which shows ultrafast PIPT even around room temperature. Of course, this model is not definitive and further study utilizing fs time resolved crystallography is needed [15, 19].

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