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Dynamics of Photd-Induced Phase-Transition in Low Dimensional Organic Crystals and the Role of Phomcarriers

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DYNAMICS OF PHOTO-INDUCED PHASE-TRANSITION IN LOW DIMENSIONAL ORGANIC CRYSTALS AND THE ROLE OF PHOTOCARRIERS

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Abstract We report the dynamics of a unique photo-induced phenomenon in quasi-one-dimensional organic crystals; i.e. phase transitions triggered by photo-excitation in conjugated polymers and charge-transfer crystals. Nano-second and pico-second time-resolved studies indicate that photo-generated charge-carriers (bi-polarons) play an important role in the driving process of the photo-induced phase transition (PIPT).

Keywords: phase-transitions, photocarriers, charge-transfer-crystals, conjugated polymers, spin-Peierls transition, time-resolved reflectance spectroscopy

INTRODUCTION

Various kinds of structural phase transitions are observed in quasi-one-dimensional organic crystals due to the strong electron-lattice and/or electron-electron interactions characteristic of these crystals. For an example, a spin-Peierls-like transition occurs in some charge-transfer (CT) complex crystals with half spins on each of their constituent molecules. Another example is a chromic transition which occurs between two distinctive color phases in conjugated polymer crystals as observed in polydiacetylenes (PDAs) ($\{CR\text{-}C\equiv C\text{-}R'C\}_n$ R,R';side-groups)[1]. Recently, we have confirmed that photo-excitation can trigger both spin-Peierls-like and chromic phase-transitions[2-4]. In this study, we apply the time-resolved pump-and-probe technique to investigate the early (nano-second and pico-second) dynamics of this unconventional phenomenon, which are referred below as the photo-induced phase transition (PIPT). First, we report the nano-second dynamics of the PIPT in alkyl-urethane-substituted PDA-4U3 crystals. The results of time-resolved reflectance spectroscopy

indicate that the initial PIPT process occurs within a period much faster than 50 ns if observed at a temperature around the phase-transition temperature of this crystal. Furthermore, a time-resolved photo-current measurement demonstrates clearly that the photo-generated carriers play an important role in the initial process of the PIPT.

Next, we report the picosecond time-resolved reflectance study of tetrathiafulvalene-p-chloranil (TTF-CA), a typical mixed-stack type CT crystal showing so-called neutral-ionic transition. On the basis of the experimental results, we can conclude that the photo-injected excited species evolve from a local phase into a macroscopically converted phase within a time of about 1 ns.

TIME-RESOLVED STUDY ON THE PHOTO-INDUCED EFFECTS IN PDA-4U3 CRYSTALS

1:NANO-SECOND DYNAMICS OF THE PHOTO-INDUCED PHASE TRANSITION (PIPT) PROBED BY SPECTROSCOPIC METHOD

PDA-4U3 is one of the alkyl-urethane substituted families of PDAs which can be obtained from diacetylene monomers R-C≡C-C≡C-R' (R=R'= $(CH_2)_4OCONH(CH_2)_2CH_3$) by solid-state polymerization[1]. In this crystal, the thermally-induced first-order phase transition occurs at about 400K which can be sensitively probed by the change in the electronic spectrum[1]. In the low-temperature (A-) phase, the PDA-4U3 crystal shows a strong optical transition due to the ^1B_u exciton at 1.95 eV (peak A in Fig.1(a)) with a phonon side-band (peak A'). This exciton band shifts abruptly at 408K to ca. 2.4 eV upon the transition to the high-temperature (B-) phase (Fig. 1(b)). A crystal in the B-phase returns to the A-phase showing a reversible shift of the exciton band back to 1.95 eV when it is cooled down to 300K. The A-B transition in PDA-4U3 is accompanied by a thermal hysteresis (with a width of ca.50K). For an example, in the left-hand side of Fig. 2 is shown the temperature dependence of the reflectivity observed at peak A (1.95 eV) during a thermal cycle 1->2->3->4->5.

Recently we have confirmed that a large photo-induced reflectance change occurs in PDA-4U3 crystals at a certain temperature in the middle of the hysteresis region (at the points 2 and 4 in Fig.2): The right-hand side of Fig.2 shows the reflectance spectra at 375K

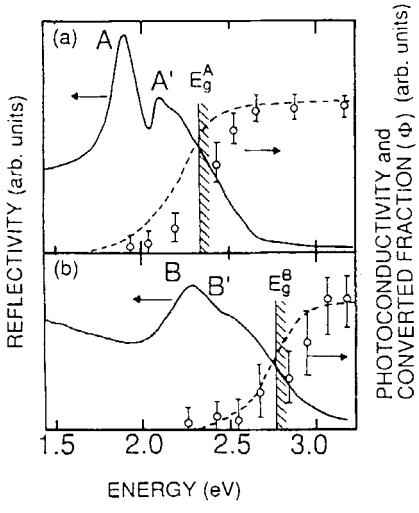

FIGURE 1: Reflectance spectra of the PDA-4U3 single crystals in (a) the A-phase and (b) B-phase (solid lines), together with the photo-conductivity action spectra (dashed lines). Open circles show the spectra of the photo-converted fraction (Φ) for (a) the A-to-B and (b) the B-to-A direction. Band-gap energies in both phases are denoted E_g with hatched lines. The structures A, B, A' and B' are reflection bands due to the ^1B_u exciton and their phonon side-bands in respective phases.

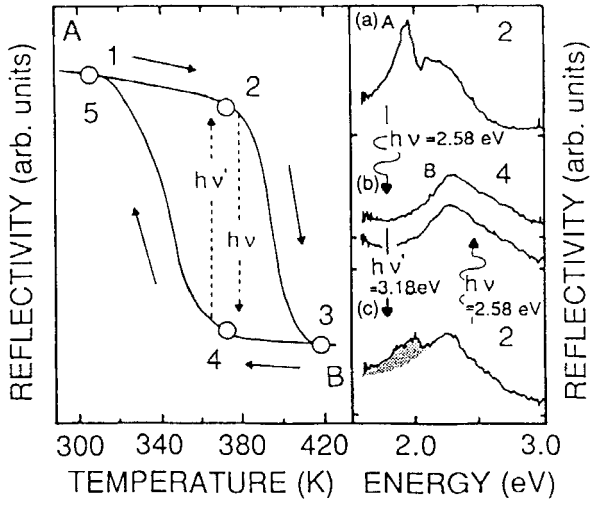

FIGURE 2: Temperature dependence of reflectivity in PDA-4U3 crystal at 1.95eV (left-hand side) and reflectance spectra before and after photo-excitation at 375K (right-hand side). The sample temperature 375K corresponds to points 2 and 4 in the middle of the hysteresis-loop. The crystal surface was irradiated with dichromatic light pulses at 2.58eV ($h\nu$) and 3.18eV ($h\nu'$) to observe the photo-induced effect.

before and after the photo-excitation. The spectrum before photo-excitation (Fig.2(a)) corresponds closely to that of the A-phase, indicating that the PDA-4U3 crystal was in the A-phase before the photo-excitation (see Fig.3(a)). By irradiation with a single shot of pulsed light (20 ns width) with the photon-energy of 2.58 eV (=hν), a dramatic change occurs in the reflectance spectrum. After the photo-excitation, the A-band around 1.95 eV disappears and a new band around 2.35 eV, characteristic of the B-phase, appears as shown in the upper part of Fig.2(b). After the first irradiation, the crystal was irradiated again with a single shot of 3.18 eV (=hν') light. It has been observed that the reflectivity decreases around the 2.35 eV region, and a new peak appears at around 1.95 eV (Fig.2(c)). The reflection band around 1.95 eV can be eliminated by a third photo-excitation pulse at 2.58 eV. After the third photo-excitation, the reflection spectrum returns to the original shape in the B-phase (lower part of Fig.2(b)). The observed spectral changes clearly demonstrate that bi-directional phase switching both in the directions of A-to-B (see Fig.3(b)) and of B-to-A (Fig.3(c)). In other words, a reversible PIPT occurs in the middle of the hysteresis, as denoted by the dashed arrows at the left-hand side of Fig.2.

The efficiencies (Φ) of the PIPT are plotted in Fig.1 by open circles for both directions. The Φ curves show quite nonlinear dependences on the excitation photon-energy. The Φ values are quite small in the exciton absorption region. To trigger the PIPT, it is necessary to use a light pulse with an energy larger than the band gap energy (E_g^A or E_g^B in Fig.1). For an example, in the energy region between 2.35 and 2.8 eV, a light pulse can trigger the A-to-B conversion with a high efficiency but it cannot trigger the B-to-A one. Therefore, if the energies of excitation photon is properly selected, one can control the direction of the PIPT in PDA-4U3 crystals. This is the reason why we have used dichromatic excitation lights at 2.58 and 3.18 eV for the reversible phase switching experiments shown in Fig.2. From these results, one can also conclude that the PIPT in this crystal is not caused by the laser heating effect, since the heating effect must be most significant in the exciton absorption region.

In Fig.4, the time-resolved reflectance spectra and the time-dependent photo-induced reflectance change ($\Delta R/R$) at 1.9 and 2.4 eV (see inset)

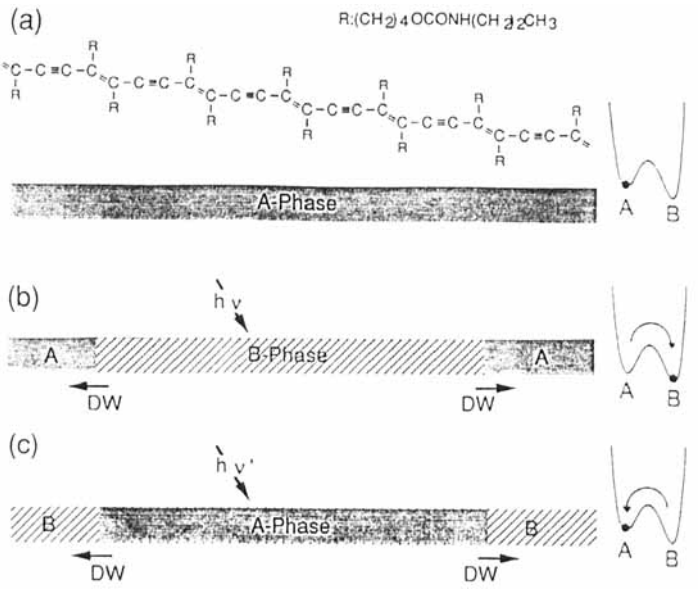

FIGURE 3:Schematic illustration of the bi-directional PIPT in PDA-4U3 crystals, (a) before photo-excitation, (b) A-to-B conversion by the first excitation pulse (2.58 eV) and (c) following B-to-A conversion by the second (3.18 eV) light pulse. Free energy diagrams are shown in the right-hand side.

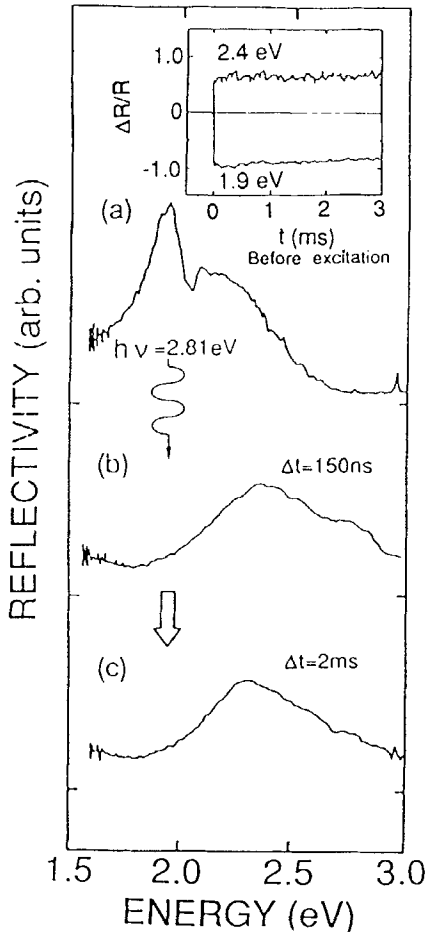

FIGURE 4:Time-resolved reflectance spectra observed (a) before, (b) 100 ns after and (c) 10 ms after photo-excitation with a 2.81 eV light pulse. The inset shows the time-dependent reflectance change ($\Delta R/R$) at 1.9 and 2.4 eV.

are plotted for the case of the A-to-B phase change. These results indicate that the primary process of PIPT in PDA-4U3 crystals occurs within the resolution time of experimental system (50 ns).

In the spectroscopic measurements of the PIPT and its nano-second dynamics reported above, the excitation photon density was maintained at a level of 6.5×10^{18} photons/cm^3 (hereafter abbreviated as cm^{-3}). This corresponds to the absorption of one photon by about 140 repeated units [$\{$CR-C$\equiv$C-RC$\}$] units. The excitation intensity dependence of the photo-conversion efficiency (Φ) will be discussed in the next section.

2: TIME-RESOLVED PHOTO-CURRENT MEASUREMENT

The spectra of photo-conversion efficiencies (Φ's) in both directions are quite similar to the photo-current action spectra under a weak monochromatic steady light irradiation (see Fig.1). This suggests that there is a close relation between the photo-carriers and PIPT. Photocurrents in one-dimensional conjugated polymers with a degenerate ground state are considered to be carried by bi-polarons[5]. The free energies of the A- and B-phases are nearly equal in the PDA crystals at a temperature around the hysteresis-loop-region, so that the system may be regarded as a nearly degenerate polymer. We can speculate therefore that the photo-generated domain-wall (DW) pairs in PDAs have a nature similar to bi-polarons.

In order to substantiate the suggested relationship between the photo-carriers (bi-polarons) and DWs, we have measured the photo-carrier dynamics by changing the excitation photon-energy and intensity. The time-resolution was 80 μs. Figure 5 shows the results of time-resolved photo-current measurement at three excitation intensities; (a)1×10^{18}, (b)2×10^{18} and (c) 6×10^{18} cm^{-3}). The sample temperature was kept at 360K and the crystal was originally in the A-phase before the photo-excitation. The excitation photon-energy was set at 3.18 eV in order to trigger the A-to-B transition. (At 2.01 eV, no photo-current was observed even though the excitation photon density was increased to ca. 1×10^{19} cm^{-3}.) The results indicate that the photo-current decay is consisted with two components, the first (F) and slow (S) ones (see Fig.5(c)). The lifetime of F is shorter than 80 μs. This component can be observed only when the excitation intensity is

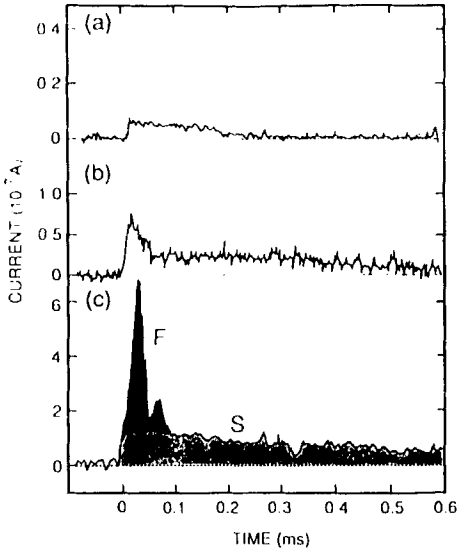

FIGURE 5:Time-dependences of the photo-current at 360K with various excitation intensities; (A) $1x10^{18}$ and (b) $2x10^{18}$ and (c) $6x10^{18}$ cm^{-3}.

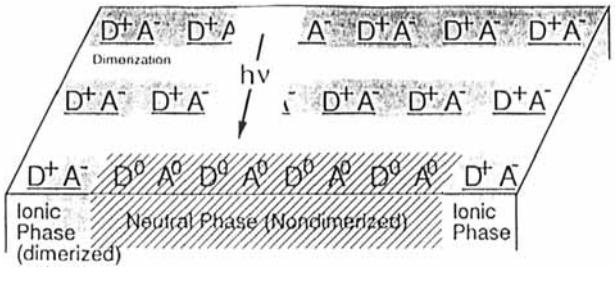

FIGURE 6:Schematic illustration of the crystal structure of TTF-CA and a model of the photo-induced I-to-N phase transition.

stronger than $2x10^{18}$ cm^{-3}. In a previous study, it has been shown that there is a threshold excitation intensity of about $2x10^{18}$ cm^{-3} for the PIPT, below which no PIPT is observed even though the excitation is made above the band-gap energy[4]. These results suggest that the fast component F is attributable to the movement of the DWs (see Fig.3). This is consistent with the finding that the movement of photo-generated DWs occurs within a short time (<50 ns) after photo-excitation.

PICOSECOND DYNAMICS OF THE NEUTRAL-IONIC (N-I) PIPT IN TTF-CA CRYSTAL

TTF-CA crystal is a quasi-one-dimensional mixed-stack charge-transfer (CT) crystal. As is well known, a phase transition occurs at 82K[3] accompanied by a change in the degree of the CT (ρ) between constituent molecules. In the high temperature phase, ρ is rather small (ca. 0.3) but it abruptly increases to about 0.6 when the crystal is cooled down to transition temperature (82 K). Therefore, the high and low temperature phases are called neutral (N) and ionic (I) phases, respectively. The crystal structure also changes at the transition temperature. The lattice is distorted in the I-phase by the dimerization of molecules along the stack axis, whereas the molecules are equidistantly stacked in the N-phase (see Fig.6). The characteristic nature of the N-I transition in TTF-CA is interpreted as due to the spin-Peierls transition.

The N-I transition in TTF-CA can be sensitively probed by the changes in reflectance spectrum as shown in Fig.7(a), similar to the case of the A-B transition in PDAs. Recently, we have made photo-reflectance measurements and have shown that the I-to-N phase conversion can be triggered by a 20 ns light pulse irradiation.

The results are plotted in Fig.7(b)[3], where the solid lines show the photo-reflectance spectra observed at 100μs after the irradiation of 2.05 eV light pulse (20ns width). In the I-phases (77K), a large photo-induced reflectance change ($\Delta R/R$) is observed whereas the change is very small in the N-phase (90K). The spectral shape of photo-reflectance change at 77K can be well explained by the calculated differential spectrum $(R_N-R_I)/R_I$ (the dashed line in Fig.7(b)). Here, R_N and R_I are the typical reflectance spectra in the N- and I-phases, respectively. These results indicate that the photo-induced I-to-N

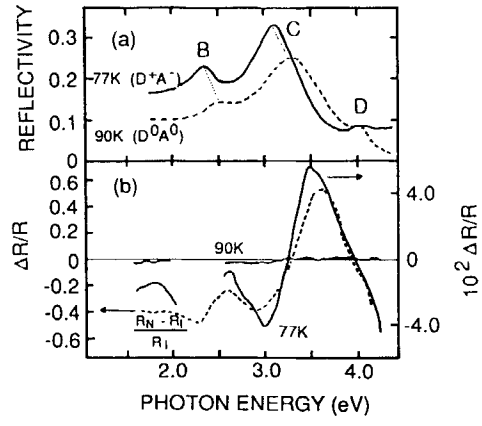

FIGURE 7:(a) Reflectance spectra of TTF-CA single crystal in the N-phase (90K: dashed line) and in the I-phase (77K: solid line). (b) Photo-induced reflectance (solid lines) spectra in the respective phases by 2.05 eV excitation light pulse (20 ns width). Dashed line in (b) shows the calculated differential spectrum using the observed I-phase (R_I) and N-phase (R_N) spectra shown in (a).

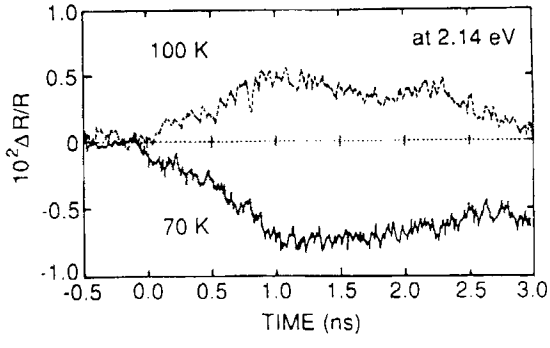

FIGURE 8:Time-resolved reflectance change ($\Delta R/R$) at 70 K (I-phase) (solid line) and at 100 K (N-phase) (dashed line) with pulsed excitation at 1.55 eV with a 150 ps time-resolution. The reflectance was monitored at 2.14 eV.

conversion (I-to-N PIPT) occurs in TTF-CA crystal at 77K as schematically shown in Fig.6. According to the results of nano-second time-resolved reflectance change measurement[3], the initial process of the I-to-N PIPT is much faster than 50 ns. In order to investigate the primary process of the evolution from the local photo-excited species into the macroscopic N-phase, we have attempted a pico-second time-resolved measurement. A typical result is shown in Fig.8 for the time-dependence of $\Delta R/R$ at 2.14 eV with 150 ps time-resolution, after a 60 ps pulse excitation at 1.55 eV. At 2.14 eV, it is expected that the reflectance will be decreased if the N-phase domain is injected into the I-phase crystal (see the dashed line in Fig.7(b)). The observed result at 70K (a solid line in Fig.8) indicates that the local excited species injected into the host crystal in the I-phase grow into the macroscopic N-phase domains within a period of 1 ns. This is consistent with the results of the nano-second measurements. When the sample temperature is set at 100 K where the crystal is kept in the N-phase, we have observed that the reflectance at 2.14 eV increases just after the photo-excitation, and then decays to the original value within a few nano-seconds (see a dashed-line in Fig.8). We suggest that the observed reflectance change is due to the photo-injected I-phase domain within the host of N-phase crystal. If so, the life-time of the I-domain will be very short, less than a few nano-seconds. Further detailed measurements of the pico-second time-resolved reflectance spectrum is now in progress, in order to elucidate the microscopic mechanisms of PIPT in conjugated polymers and CT crystals.

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