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We report that bi-directional neutral-ionic (N-I) phase transition in the single crystal of tetrathiafulvalene-chloranil (TTF-CA) can be triggered by pulsed laser excitation with 100 femto-second width. The excitation intensity dependence of the dynamics of N-I domain-wall indicates that cooperative electron-lattice and/or electron-electron interactions play a key role in the driving mechanism of N-I photoinduced phase transition.

Keywords: photoinduced phase transition; neutral-ionic transition; ultra-fast dynamics; domain-wall

INTRODUCTION

Charge-transfer (CT) complexes have been studied extensively due to their unique characteristics in the electronic, magnetic and optical properties. Among various CT crystals, tetrathiafulvalene-chloranil (TTF-CA) is a well known quasi-one-dimensional mixed-stack one which shows a neutral-

ionic (N-I) phase transition[1]. In TTF-CA the degree of charge transfer (ρ) between constituent donor (TTF: $D^{+\rho}$) and acceptor (CA: $A^{-\rho}$) molecules abruptly changes at 82K (T_c). In the high temperature phase, ρ is rather small (ca. 0.3) but it increases to about 0.6 when the crystal is cooled down to T_c. Therefore, the high and low temperature phases are called neutral (N) and ionic (I) phases, respectively. The N-I transition is also accompanied with a change in the crystal structure. 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.1(a) and (b)). From this point of view, the nature of the N-I transition in TTF-CA can be interpreted as due to the spin-Peierls transition.

The N-I transition in TTF-CA can be sensitively probed by the changes in the reflectance spectrum as shown in Fig.2(a) [2]. In this figure, the calculated differential spectra $(R_N-R_I)/R_I$ and $(R_I-R_N)/R_N$ are plotted. Here, the R_N and R_I are the typical reflectance spectra in the N- and I-phases, respectively. In the present study we demonstrate, by using the technique of the ultrafast time-resolved spectroscopy, that a pulsed laser excitation with 100 femto-second (fs) pulse width can trigger both I-to-N and N-to-I phase transitions (see schematics shown in Fig1(c)). In addition, we also observed the threshold-like nonlinear behavior in the excitation intensity dependence of the photoinduced N-I conversion efficiency. These results demonstrate that cooperative electron-lattice and/or electron-electron interactions play a key role in the driving mechanism of N-I photoinduced phase transition (N-I PIPT).

RESULTS AND DISCUSSION

Bi-directionally photoinduced N-I transition

The time-resolved photoreflectance spectra ($\Delta R/R$) induced by a 100 fs light pulse irradiation observed at 77K are plotted in Fig.2(b). The excitation

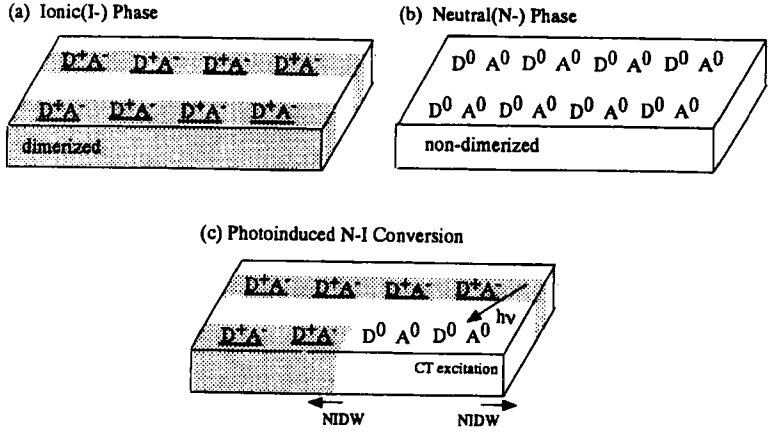

FIGURE 1 Schematic illustrations of the crystal structure of TTF-CA in (a) Ionic (I-) and (b) Neutral (N-) phase. (c) A model of the photoinduced N-I phase transition. NIDW denotes the domain wall between the N- and I-phases.

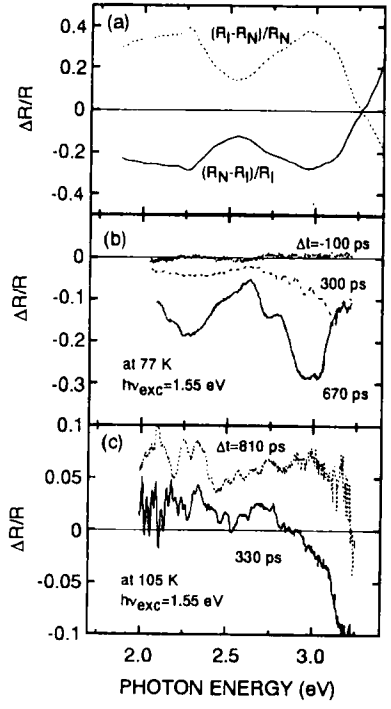

FIGURE 2 (a) The calculated differential spectra $(R_N-R_I)/R_I$ (solid line) and $(R_I-R_N)/R_N$ (dashed line). (b) Photoreflectance spectra ($\Delta R/R$) observed at 77 K. Δt denotes the delay time after the excitation by a 1.55 eV light pulse with 100 fs width. (c) $\Delta R/R$ spectra at 105 K observed 330 and 810 ps after the photoexcitation.

photon energy, the repetition rate, and the excitation photon density were 1.55 eV, 1 kHz, and $5x10^{18}$ photons/cm^3 (from now on abbreviated as cm^{-3}), respectively. The utilized value of the excitation photon density corresponds to the absorption of one photon by about 500 DA pairs. The excitation intensity dependence of the photo-conversion efficiency will be discussed in the next section.

After the excitation, photoreflectance signal was gradually enhanced as increasing the delay time (Δt) and reached the maximal value at Δt =670 ps (see Fig.2(b)). The spectral shape of $\Delta R/R$ observed sufficiently after the photoexcitation (Δt=670 ps) corresponds to the calculated differential spectrum $(R_N-R_I)/R_I$ (see solid lines in Fig.2(a) and (b)). From this result, we can conclude that photoinduced I-to-N conversion (I-to-N PIPT) occurs within 670 ps at 77 K. For further study on the dynamics of the N-I domain wall (NIDW), we have measured the time-dependence of the $\Delta R/R$ signal at 3.0±0.3 eV (see open circles in Fig.3). In the photon energy region between 2.7 and 3.3 eV, the $\Delta R/R$ signal is expected to be the negative sign when the N-phase domains are injected into the host I-phase crystal. The obtained result supports the idea of the occurrence of I-to-N PIPT in TTF-CA crystals at 77 K and it also shows that a localized photoexcited state has been converted into a macroscopic N-phase domain within about 700 ps.

The photoinduced spectral changes which can be attributed to the N-to-I conversion (N-to-I PIPT) was also observed at 105K with the excitation photon density of $1.5x10^{18}$ cm^{-3}. As shown in Fig.2(c), $\Delta R/R$ spectra observed sufficiently after photoexcitation can be basically explained by the calculated differential spectrum $(R_I - R_N)/ R_N$ (dotted line in Fig.2(a)). The $\Delta R/R$ signal observed at 2.8±0.2 eV gradually increased and reached a maximum at around Δt=800 ps as shown by the closed circles in Fig.3. Thus, it takes

about 800 ps to convert a photoinjected CT excited state into a macroscopic I-phase domain.

Excitation intensity dependence of the photoconversion efficiency

Lately, we have demonstrated that photoexcitation with the intensity stronger than some threshold value is necessary to trigger the A-B phase conversion in π-conjugated polymer polydiacetylene [3]. A threshold-like nonlinear behavior in the excitation intensity dependence of the converted fraction is an important characteristic of the photoinduced cooperative phenomena like PIPT. To make clearer the importance of the cooperative interaction in driving mechanism of the N-I PIPT, we have investigated the N-I conversion efficiency with changing the excitation intensity.

The result for I-to-N direction at 77K is shown in Fig.4. The integrated intensity of ΔR/R in the spectral region between 2.7 and 3.3 eV observed at Δt=700 ps was utilized to estimate the converted fraction. The threshold value was estimated to be about $5x10^{17}$ cm^{-3} which corresponds to the absorption of one excitation photon by 5000 DA pairs. When we excited an I-phase crystal with the intensity of $5x10^{18}$ cm^{-3}, one absorbed photon had neutralized about 500 DA pairs. The observed low threshold value and high conversion efficiency are considered to be related with the degeneracy in the energy levels of the two (I- and N-) phases.

Acknowledgments

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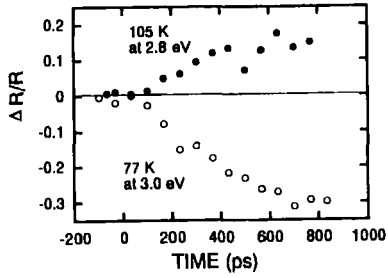

FIGURE 3 Time-resolved photoreflectance changes (ΔR/R) observed at 77 K (open circles) and 105 K (closed circles). The reflectance was monitored at 3.0 eV (open circles) and 2.8 eV (closed circles).

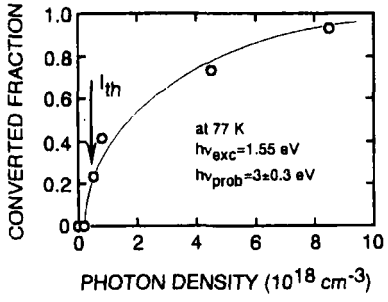

FIGURE 4 Excitation photon density dependence of the photoconverted fraction in the I-to-N direction observed at 77 K. The signal was observed at 700 ps after the excitation by a 1.55 eV light pulse. The monitor light integrated in the photon energy region between 2.7 and 3.3 eV was utilized as a probe of the converted fraction. The arrow denotes the threshold value to trigger the photoconversion.