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PHOTO-INDUCED PHASE TRANSITIONS IN QUASI-ONE-DIMENSIONAL MOLECULAR SYSTEMS

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Abstract An overview is presented on photo-induced phase transitions in quasi-one-dimensional molecular systems. The phenomena are characterized by evolution of the local molecular domains induced by photo-excitations into the new macroscopic phase via collective interaction of domain wall excitations.

Organic crystals with quasi-one-dimensional electronic structures often show lattice-coupled electronic phase transitions. For example, most of ionic donor(D)-acceptor(A) compounds with half spins on each D and A molecules show the spin-Peierls like phase transition at some critical temperature, accompanying the dimerization of the DA stacks. In this context, the bond alternation structure in π-conjugated polymers can be viewed as a consequence of Peierls instability and some of the polymers can show distinct two (stable and metastable) bond structures. Here, let us consider the quasi-one-dimensional molecular systems with the Peierls-type lattice distortion, in which the two ground state phases are nearly degenerate and the corresponding minima of the free energy are separated by a potential barrier. What we have observed in a series of investigations is that the photo-injection of a mesoscopic size of long-lived

molecular domains with a metastable lattice (or bond) structure is almost always possible in such a organic solid as characterized by the above conditions. In some cases, the accumulated domains are observed to evolve into the permanent and macroscopic phase conversion, that is the photo-induced phase transition.

In Fig.1 and 2 we show prototypical examples for transient and permanent photo-induced phase conversions, respectively: Figure 1 shows the case for the photo-induced ionic(I)-to-neutral(N) phase conversion in single crystal of tetrathiafulvalene(TTF)-chloranil(CA) with DA mixed stacks.[1] It was estimated from a comparison between the observed (Fig.1(b)) and simulated (c) photo-reflectance spectra that one absorbed photon can convert as many as 160 DA pairs from the quasi-neutral (D^0A^0) to quasi-ionic (D^+A^-) state in the Peierls-distorted I-phase.

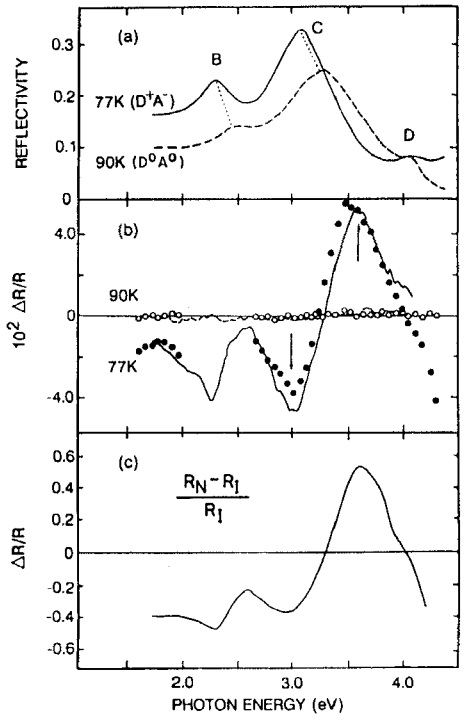

Fig.1: (a) Reflectance and (b)photo-reflectance spectra for molecular transitions at 77K (ionic phase) and at 90K (neutral phase) in TTF-CA crystal. Solid and broken lines in the photo-reflectance spectra (b) represent the results by pulse and cw laser excitations, respectively. The spectrum (c) is the calculated differential spectra using the respective ionic phase (R_I) and neutral phase (R_N) spectra shown in (a).

The photo-injected neutral domains eventually diminish and their total size changes temporarily according as the relation, $t^{-1/2}$, indicating the one-dimensional recombination process of the NI domain-walls[1].

Figure 2 shows the photo-induced phase transitions between the two (A- and B-)phases in single crystals of polydiacetylenes[2], which were probed by the exciton absorption (left) and vibrational Raman (right) spectra. Such a bi-directional switching between the two phases is possible when the crystal is held in the temperature region (320-420K) within the hysteresis loop for the first-order phase transition where the both A- and B-phases are stable. The threshold value for the absorbed photon density to cause the phase transition is as low as $3\times10^{18}cm^{-3}$. The excitation spectra for the photo-converted fraction clearly show that the precursory excitations for the phase conversion are not strongly photo-absorbing singlet excitons but polaronic charge-carriers.

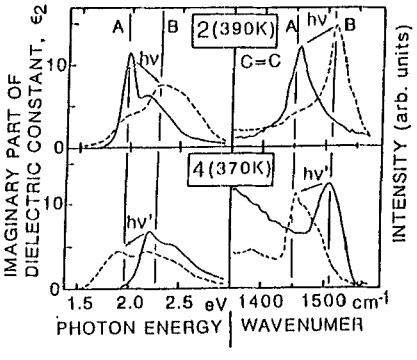

Fig.2: Spectra of imaginary part of the dielectric constant(absorption spectra) for the exciton transition (left part) and Raman spectra for the C=C stretching mode (right part). The temperature points, 2 and 4, position within in the hysteresis region where the both A- and B-phase are stable. Dashed lines in the spectra show those observed after a photo-excitation with a single shot of a pulsed dye-laser; 10ns duration, at photon energy of 2.81eV (left) and 3.18eV (right). The excitation photon density is $5\times10^{18}cm^{-3}$.

The photo-induced phase transition is argued as a new paradigm for photo-reactive phenomena in low-dimensional molecular systems.

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