Photoinduced Phase Transition in an Organic Radical Crystal with Room-Temperature Optical and Magnetic Bistability

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A phase control by photoirradiation is successfully achieved in a spin-Peierls system of the organic radical crystal, 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA), which exhibits optical and magnetic bistability around room temperature with a large hysteresis loop. A nanosecond laser pulse is found to induce a transition from a diamagnetic low-temperature phase to a paramagnetic high-temperature phase both inside (296 K) and outside (11 K) the hysteresis loop. Comparison of the excitation energy dependence between transition efficiency and photoconductivity suggests that the photoinduced transition is driven by suppression of the spin-Peierls instability by the accumulation of photocarriers.

Control of the macroscopic properties of solids by photoirradiation has recently attracted considerable attention [1–5]. In particular, photocontrol of magnetic properties is an important subject not only in terms of fundamental science, but also with regard to potential applications in novel magneto-optical devices. Photoinduced (PI) changes in magnetization have been reported for several kinds of materials, including molecule-based magnets [1], magnetic semiconductor heterostructures [2], and manganese oxides [3].

A key strategy toward realizing the photoswitching of magnetism is exploration of materials near magnetic transition boundaries. The optical control of magnetic transitions requires the magnetic instability of the material to be enhanced or suppressed by light. Since light fields do not couple directly with spin states, it is necessary to find an effective mechanism that combines electronic excitation induced by photoirradiation with magnetic instability.

A promising candidate for the optical control of magnetic transitions is the family of spin-Peierls (SP) systems, in which one-dimensional (1D) paramagnetic spin ($S = 1/2$) states are converted to dimerized diamagnetic states at low temperature. Chemical doping of carriers or nonmagnetic impurities can cause SP states to become unstable, as observed in (DMe-DCNQI)$_2$Li (DMe-DCNQI = 2,5-dimethyl-N,N'-dicyanoquinonediimine) [6] and CuGeO$_3$ [7]. Therefore, it can be expected that photocarrier doping and the resultant modified spin states in SP systems would lead to a macroscopic change in magnetic properties, as discussed in 1D $S = 1/2$ spin system of K-TCNQ (TCNQ = tetracyanoquinodimethane) [4,8]. The target material in this Letter is the organic radical ($S = 1/2$) crystal, 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA), which has the molecular structure shown in Fig. 1(a). This material exhibits an SP-like magnetic transition at around room temperature.

Figure 1(c) shows the temperature dependence of the paramagnetic susceptibility χ_p for TTTA [10]. In the cooling run, χ_p begins to decrease at around 230 K and approaches zero at 170 K. The gradual increase in χ_p below 100 K is due to Curie impurities. When heated from the lowest temperature, χ_p remains at almost zero over the range 80–300 K, increasing abruptly at 305 K. Thus, TTTA exhibits a first-order magnetic
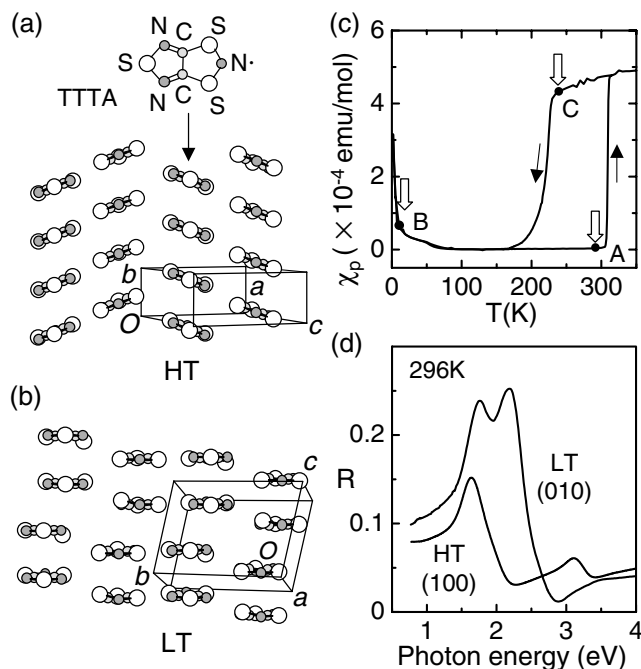

FIG. 1. Crystal structures of the (a) HT phase and (b) LT phase for TTTA, with its molecular structure. (c) Temperature dependence of χ_p upon cooling and heating. The PI effects were investigated at points A (296 K), B (11 K), and C (240 K). (d) Polarized reflectivity spectra for the light polarization $E_i \parallel$ stacking axis in the HT and LT phase at 296 K.

transition near room temperature with an anomalously large hysteresis loop ($T_{c\downarrow} = 230$ K and $T_{c\uparrow} = 305$ K).

The crystal structures of TTTA at room temperature are presented in Figs. 1(a) and 1(b) for the high-temperature (HT) and low-temperature (LT) phases, respectively [10]. In the HT phase, TTTA molecules stand face-to-face to form 1D regularly stacking columns along the b axis. Calculation of the intermolecular overlap integrals using the extended Hückel method reveals that the intercolumn overlap cannot be neglected, as compared with the intracolumn one. In fact, the temperature dependence of χ_p in the HT phase can be well reproduced by the modified Bonner-Fisher model with intercolumn interactions as the mean-field component. The evaluated intracolumn and intercolumn antiferromagnetic exchange energies in the HT phase are $J/k_B = -320$ K and $J'/k_B = -60$ K, respectively [10,11].

In the LT phase, the molecules are strongly dimerized along the c axis, giving a phase transition that is analogous to an SP one. The molecular packing in the LT phase differs considerably from that in the HT phase. The intracolumn molecular overlaps in the LT phase are considerably larger than those in the HT phase, while the intercolumn ones are almost identical. This results in an enhancement of one dimensionality in the LT phase. Thus, the transition is considered to include a degree of structural character as well as the SP mechanism. This is the reason why the transition observed for TTTA is not a second-order one expected in typical SP systems.

In the present study, it was found that the magnetic transition of TTTA could be driven with a nanosecond laser pulse at room temperature and 11 K by suppression of the SP instability through photocarrier doping. TTTA was prepared by a modification of the method described in Ref. [12]. Single crystals were grown by vacuum sublimation. Polarized reflectivity spectra were obtained using a specially designed spectrometer, equipped with a 25-cm grating monochromator, and an optical microscope. The obtained reflectivity spectrum was converted to an absorption coefficient (α) spectrum using the Kramers-Kronig transformation. Polarized Raman spectra were measured using a Raman spectrometer, equipped with a cw He-Ne laser (1.96 eV), and an optical microscope. A tunable optical parametric oscillator pumped with the third harmonics of a Q-switched Nd:YAG laser was employed to irradiate the sample with 6-ns pulses. In photoconductivity (PC) measurements, the applied dc electric field and the polarization of the exciting light modulated by an optical chopper were set parallel to the stacking axis. The photocurrent along the stacking axis was detected using a lock-in amplifier.

Figure 1(d) shows the polarized reflectivity spectra at 296 K. The strong bands observed below 2.5 eV are assigned to the charge-transfer (CT) transition between the neighboring molecules along the stacking axis in both phases. The two peaks around 1.8 and 2.1 eV observed in

the LT phase can be assigned to the intradimer and interdimer CT transitions, respectively [13]. The corresponding microscope images are shown in Figs. 2(a) and 2(b). Such clear chromism from yellow-green in the LT phase to red-purple in the HT phase makes it possible to observe the photoinduced phase transition (PIPT) visually. We have investigated the PI effect in the LT phase at 296 K (A) and 11 K (B) and in the HT phase at 240 K (C) [see Fig. 1(c)].

Figure 2(c) shows an image of the crystal after a single-shot irradiation at 2.64 eV at point A. The crystal exhibits a permanent color change from yellow-green to red-purple in the irradiated area. In addition to the color change, PIPT was measured based on Raman spectra, as shown in Fig. 3(a). The peaks at around 1350 cm^{-1} in both phases can be assigned to the C $=$ N stretching mode. After the thermal transition from the LT to the HT phase, the frequency of this mode increases slightly with a substantial reduction in intensity. The broken curve $1'$ shows the Raman spectrum after irradiation at 2.64 eV. The penetration depths of the pump laser (2.64 eV) and the probe laser (1.96 eV) are almost equal (~ 800 Å) from the values of the absorption coefficient (α). Thus, the probe laser is able to detect photoinduced changes in almost the entire volume irradiated by the pump laser pulse. The Raman signal for the irradiated region coincides well with that of the HT phase, showing clearly that a conversion from the LT phase (metastable state) to the HT phase (ground state) can be induced by photoirradiation, as illustrated in Fig. 3(c).

The LT-to-HT conversion with a similar color change was also observed at point B. The solid curve 3 and the broken curve $3'$ in Fig. 3(b) are the Raman spectra at 11 K before and after a 2.64-eV laser irradiation. Spectrum $3'$ resembles spectrum 2 in the HT phase, except for a broadening. When heated to about 200 K
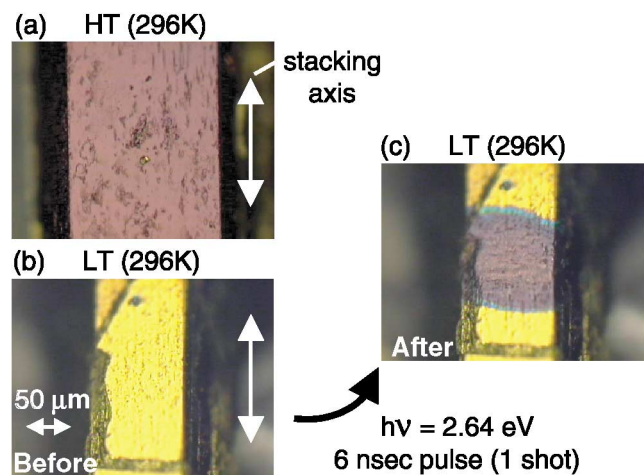

FIG. 2 (color). Microscope images ($E_i \parallel$ stacking axis) for (a) HT phase, (b) LT phase, and (c) after a single-shot irradiation at 2.64 eV ($E_{exc} \parallel$ stacking axis) at 296 K.
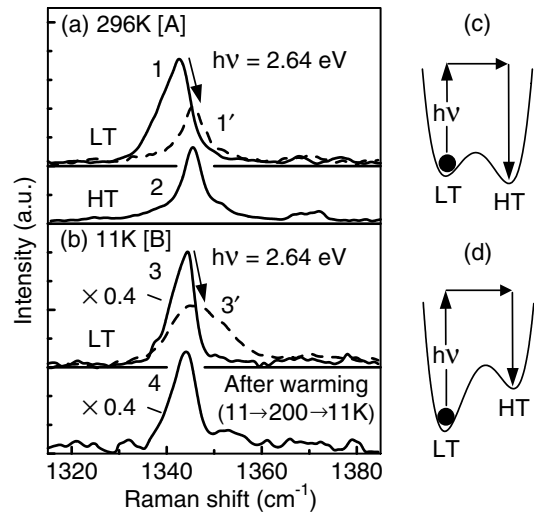
FIG. 3. (a) Raman spectra with polarization configuration of $z(xx)\bar{z}$ ($x \perp$ chain axis) at 296 K (point A). Solid curves 1 and 2 represent the spectra in the LT and HT phase, respectively. Broken curve 1′ represent the spectrum after the single-shot irradiation at 2.64 eV ($E_{exc} \parallel$ stacking axis) in the LT phase. (b) Raman spectra at 11 K (point B). Solid curve 3 and broken curve 3′ represent the spectra before and after the single-shot irradiation at 2.64 eV ($E_{exc} \parallel$ stacking axis). Solid curve 4 represents the spectrum after heating to about 200 K and then cooling to 11 K. (c) and (d) show the schematic energy potential curves at points A and B, respectively.

and then returned to 11 K, spectrum 3′ in the irradiated region changes to spectrum 4, which is in agreement with spectrum 3 before photoirradiation. Such a recovery of the initial LT phase excludes the possibility of sample damage as the origin for the broadening of spectrum 3′. Spectrum 3′ cannot be fully reproduced by superposition of the HT spectrum 2 and LT spectrum 3, even if the ratio of the two spectra is varied. It suggests that the PI phase is different from the HT one and that the coexistence of the LT phase and the PI one is responsible for the observed spectral broadening. Judging from the clear color change to red-purple in the irradiated area, however, the PI phase is essentially the same as the HT one. Therefore, the difference between the PI phase and the HT one will be small. Such a difference between the PI phase and the thermally induced HT one has been reported in the PIPT of a spin-crossover complex, [Fe(2-pic)$_3$]Cl$_2$EtOH [14]. The PI phase of TTTA persists at least for several hours at 11 K, suggesting that the system preserves the double minima in the free energy as illustrated in Fig. 3(d).

The conversion efficiency (ϕ) of PIPT is shown in Figs. 4(a)-(i) and 4(a)-(ii) for points A, B, and C as a function of the absorbed photon density per unit volume (I). The energy of the pump laser is 2.64 eV. Here, I was evaluated by considering the value of α and the reflection loss of the excitation light, and ϕ was estimated from the photoinduced change in the C $=$ N Raman stretching bands. At point A, ϕ increases nonlinearly with I, with
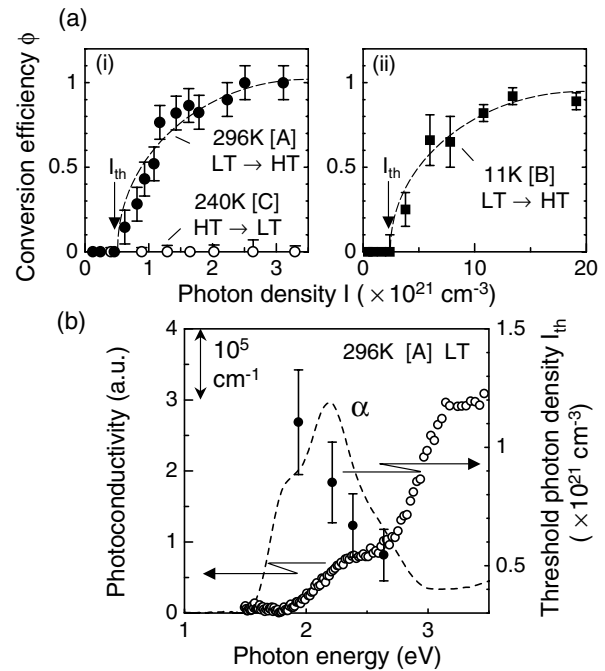

FIG. 4. (a) Excitation density dependence of LT-to-HT and HT-to-LT conversion efficiency at (i) points A (296 K), B (240 K), and (ii) C (11 K). Excitation energy was 2.64 eV ($E_{exc} \parallel$ stacking axis). (b) Excitation energy dependence of I_{th} for LT-to-HT conversion at 296 K (right ordinate). Open circles show the excitation profile of PC along the stacking axis, and the broken curve shows α for $E_i \parallel$ stacking axis in the LT phase at 296 K (left ordinate).

a clear threshold at $I_{th}(A) \sim 5.5 \times 10^{20}$ cm^{-3}. At point B, ϕ also exhibits a threshold at $I_{th}(B) \sim 2.4 \times 10^{21}$ cm^{-3}. $I_{th}(B)$ is about 4 times as large as $I_{th}(A)$, reflecting that the LT phase is much more stable than the HT one at point B, as schematically shown in Fig. 3(d). The observed threshold behavior at points A and B suggests that a cooperative effect between photoexcited species plays an important role in the growth of the macroscopic phase change, as discussed in the PIPT of the CT complex, tetrathiafulvalene-p-chloranil (TTF-CA) [5]. In contrast, at point C, where the material is in the metastable HT phase, the HT-to-LT transition could not be driven by irradiation at 2.64 eV, even at the excitation densities of up to 5×10^{21} cm^{-3} [see Fig. 4(a)-(i)].

To deduce the mechanism of the LT-to-HT transition observed at points A and B, ϕ was also measured as a function of I for various excitation energies (1.95–2.64 eV) at point A. The results reveal that ϕ is strongly dependent on the excitation energy. The most notable feature is that I_{th} increases gradually as the excitation energy decreases, as shown in Fig. 4(b). The observation of this phenomenon excludes the possibility that laser heating effects due to irradiation are responsible for the LT-to-HT transition.

It is reasonable to consider that the observed excitation energy dependence of I_{th} is associated with changes in the

nature of the initial photoexcited states. To obtain information regarding the initial photoexcited states, the excitation profile of PC was measured at point A, as plotted by open circles in Fig. 4(b). The PC is almost negligible around the intradimer CT band (~ 1.8 eV), suggesting excitonic character of the photoexcited states. The PC then gradually increases with excitation energy. As the PC around the interdimer CT band (~ 2.2 eV) is much smaller than the saturation value around 3 eV, the excitonic effects are considered to be still important in the interdimer CT excited state. I_{th} decreases as the PC increases, suggesting that photogenerated charge carriers can promote the PIPT more effectively than excitons.

Considering these findings, a possible scenario for the LT-to-HT transition is considered as follows. Dissociated charge carriers generated in the LT phase will be relaxed under the influence of electron (spin)-lattice interaction. Previous theoretical studies have expected that doped carriers may exist as charged (spinless) solitons (CSs) in SP systems [15]. Stabilization of CSs has in fact been observed in a CT complex, DAP-TCNQ (DAP = 1,6-pryrendiamine), which is known as a doping regime for an SP system [9]. Taking account of these studies, it is reasonable to consider that the charge carriers in TTTA will also exist as CSs. Since both the positive and negative CSs are spinless species, their presence will cause the dimerized states to become unstable. For a weak excitation density, the amount of spinless charge carriers is so small that the dimerizations will be suppressed only around them. In this case, the PIPT hardly occurs. When the excitation density is increased and spinless charge carriers concentrate above a critical value, the SP state becomes unstable, leading to the photoinduced LT-to-HT transition. Such a degradation of the SP state is analogous to the suppression of the SP state in $(DMe\text{-}DCNQI)_2Li_{1-x}Cu_x$ [6] by doping of charge carriers as well as in $Cu_{1-x}Zn_xGeO_3$ [7] by doping of nonmagnetic impurities.

The CT excitons are also spinless species and may contribute to the LT-to-HT transition. Important information related to the CT exciton has been obtained from the time-resolved luminescence measurements. In the LT phase at 296 K, the decay time of the exciton luminescence is evaluated to be 20 ps or less, which is much smaller than the radiative lifetime (ca. 60 ns) estimated from the oscillator strength of the CT band [16]. Namely, the CT exciton should decay nonradiatively. Because of the fast decay, the excitons hardly accumulate in the time domain of a laser pulse (~ 6 ns). Dissociated charge carriers will be rather stabilized as CSs or self-trapped carriers due to the strong electron (spin)-lattice interaction and have relatively longer lifetimes. This might be a reason why photocarriers induce the PIPT more effectively than CT excitons.

Optical excitation in the HT phase will also produce photocarriers as well as CT excitons. However, it is quite natural that such spinless excitations never enhance the SP instability in the HT phase. Hence, the HT-to-LT transition cannot be driven by photoirradiations, as observed in the experiments.

In conclusion, we have demonstrated a PIPT from a diamagnetic LT phase to a paramagnetic HT phase with a drastic color change for the organic radical crystal TTTA at both room temperature and 11 K using nanosecond laser pulses. Suppression of the SP instability by accumulation of photocarriers above a critical density was proposed as the mechanism driving this LT-to-HT transition. The photoswitching behavior in both optical and magnetic properties presented here will open new possibilities for future applications of organic radical crystals as optical switching units.

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