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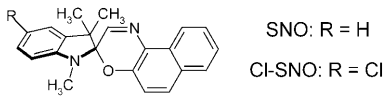
Cooperative Photochemical Reaction Mechanism of Femtosecond Laser-Induced Photocoloration in Spirooxazine Microcrystals**

Mototsugu Suzuki, Tsuyoshi Asahi,* and Hiroshi Masuhara*[a]

Microcrystalline powders of spirooxazine and spiropyran compounds do not show photocoloration under steady-state illumination, whereas they undergo photochromism on intense femtosecond laser-pulse excitation. We investigated the characteristic mechanism of the crystalline photochromism by studying the photocoloration of spironaphthooxazine (SNO) and its chloro-substituted derivative (Cl-SNO) with our femtosecond diffuse-reflectance spectroscopic system. In particular, femtosecond double-pulse excitation using 390+780-nm pulses and 390+390-nm pulses, with a variable time interval between the two pulses, was applied to reveal an intermediate species involved in the photocoloration. Although 780-nm excitation of an intermediate produced by 390-nm excitation did not lead to isomerization, the 390+390-nm excitation resulted in photocoloration. The yield for SNO decreased on increasing the interval from 40 ps to 5 ns, while that for Cl-SNO was constant. The photocoloration mechanism in the crystalline phase is considered from the viewpoint of the time-dependent density of short-lived transient species, and it is concluded that cooperative interactions of excited states and nonplanar open forms play an important role in femtosecond laser-induced photochromism in these crystals.

Introduction

Spiro compounds are well-known because of their interesting photochromic functionality that changes their color reversibly under UV/Vis irradiation, and their reactions have been widely reviewed as they have high potential for applications such as optical switching, optical memory storage, and optical lenses.[1–3] Spirooxazines (Scheme 1) consist of two perpendicularly connected moieties of indoline and oxazine rings. The photochromic reaction of spirooxazines involves the cleavage of the spiro carbon–oxygen (C_{spiro}–O) bond upon UV light irradiation and subsequent isomerization to the *trans*-planar open form, which is called photomerocyanine (PMC).[4] Indeed, the photochromic reaction of spirooxazines and spiropyrans involves a large change in molecular conformation. The PMC can be generated in solution, polymer films,[5,6] and amorphous molecular solids[7] which have a relatively large void around the molecules. On the other hand, no photocoloration is observed in the crystalline phase by conventional steady-state light irradiation due to the smaller void and the resultant restricted molecular motion.



Scheme 1. Spironaphthooxazine (SNO) and its chloro-substituted derivative (Cl-SNO)

Recently, we found that spirooxazines and spiropyrans show photocoloration in the crystalline phase by intense femtosecond laser excitation, and that the photocolored forms are similar to PMCs in solution.[8–10] The yield of PMC increa'ses nonlinearly with excitation-laser fluence, and the efficiency of photocoloration depends on the compounds. The mechanism of this unique photochromism has been investigated in detail by examining the effects of laser fluence and the number of laser pulses on the photocoloration, and by measuring the transient absorption spectra using femtosecond diffuse-reflectance spectroscopy.[9] It was revealed that the excited singlet-state lifetime of SNO is about 3 ps and that a nonplanar open form, whose molecular conformation closes to that of the spiro form, decays in 3 ns under weak excitation conditions. Cooperative interactions between the excited states and the short-lived nonplanar open form are induced by intense femtosecond laser pulses, which are responsible for generating the long-lived PMC. A double-pulse excitation experiment, in which two femtosecond excitation pulses irradiate the sample with a time interval of a picosecond to a nanosecond, will directly clarify the contribution of the nonplanar open form with a lifetime of a few hundred picoseconds. The dynamics is, of course, dependent on the chemical and crystal structures, and we have indeed reported that the ultrafast dynamics of the ring-opening and ring-closing reactions is quite different be-

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[**] *Examined by Femtosecond Double-Pulse Experiments.*

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tween SNO and Cl-SNO microcrystals.[11] Therefore, a comparison of the photocoloration of SNO and Cl-SNO by single- and double-pulse excitation is significant for understanding the photocoloration mechanism induced by intense femtosecond laser excitation.

Herein, we examine the photochromic reaction of SNO and Cl-SNO microcrystals by using femtosecond double-pulse excitation, and the results are compared with those of transient absorption experiments. We have proposed that the spiro form can change to PMC in SNO crystals where several excited molecules and nonplanar open forms are generated simultaneously in each other's neighborhood.[9] However, a quantitative discussion has not yet been carried out that covers, for example, the concentration of the excited molecules under the experimental conditions, the number of neighboring transient species for photocoloration, and so on. Here, a detailed experiment is conducted, a simulation based on our proposed model of cooperative photocoloration is carried out, and the simulated and experimental results are compared.

Experimental Section

Materials: 3-Dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphth-[2,1-*b*][1,4]oxazine] (SNO) and 5-chloro-1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′- [3*H*]naphth[2,1-*b*][1,4]oxazine] (Cl-SNO) (Aldrich) were recrystallized from hexane (spectral grade, Nacalai Tesque) in the dark. The microcrystals were dried under vacuum to remove the solvent, and then crushed to a powder with an average particle size of several tens of micrometers. The sample was contained in quartz cells with a 1-mm optical path length and degassed with a vacuum pump.

Steady-State Absorption Spectroscopy after Femtosecond-Pulse Excitation: The details of the femtosecond diffuse-reflectance spectroscopic system have been reported elsewhere.[12,13] Briefly, it consisted of an excitation light source comprising a continuous-wave self-mode-locked Ti:sapphire laser (Mira 900 Basic, Coherent), pumped by an Ar^+ laser (Innova 310, Coherent), and a Ti:sapphire regenerative amplifier system (TR70, Continuum) with a Q-switched Nd:YAG laser (Surelight I, Continuum). The fundamental output from the regenerative amplifier (780 nm, 3–4 mJ pulse^{-1}, 170 fs fwhm, 10 Hz) was frequency-doubled (390 nm) and used as a femtosecond excitation pulse. The excitation fluence dependence was examined by adjusting the pulse intensity using a polarizer and a $\lambda/2$ plate. The residual of the fundamental output was focused into a 1-cm quartz cell containing H_2O to generate a white-light continuum as the probe light. The diameters of the excitation and probe pulses at the sample were 2 and 1 mm, respectively.

UV excitation was carried out by 100 shots of femtosecond laser pulses (390 nm) with an interval of 10 Hz. After excitation, 100 shots of femtosecond white-light continuum pulses were used as the irradiating probe light and averaged. The absorption intensity of a photoproduct by femtosecond laser excitation was displayed as the percentage absorption, given by $\%\,\text{absorption} = 100(1 - R/R_0)$), where R_0 and R represent the intensity of the diffuse reflected light which was averaged for 100 shots of the probe pulses before and after excitation, respectively. The samples had no absorption in the visible region before UV excitation, therefore the spectral shapes represented by % absorption in the region corresponded to the absorption spectra of the samples after UV excitation. The excitation intensity was adjusted so that the maximum % absorption was less than about 25 in both the steady-state and time-resolved experiments. This guaranteed a linear relation between % absorption and the concentration of absorbing species under the present experimental conditions.[13]

The method of femtosecond double-pulse excitation was described in detail elsewhere.[9] One excitation pulse was split into two pulses with a half mirror, and the time interval was changed in the picosecond and nanosecond regions by an optical delay. Each fluence was adjusted by polarizers located at each optical path and by $\lambda/2$ plates. The polarization dependence could be neglected because the sample was a microcrystalline powder.

Femtosecond Transient Absorption Spectroscopy: The optical system was the same as that for steady-state absorption spectroscopy after femtosecond excitation, as described in the previous paragraphs. The transient absorption intensity was also displayed as % absorption, where R and R_0 represent the intensity of the diffuse reflected white-light continuum of a probe pulse with and without excitation, respectively. The spectral data at one delay time were measured several times by changing the position of the sample every 50 measurements, and the results were averaged.

Absorption Spectroscopy of the Ground State: The ground-state absorption spectra of powder samples were evaluated by the Kubelka–Munk function.[14] The diffuse reflectance was measured with a fluorometer (UV-3100PC, Hitachi). $BaSO_4$ powder, which has no absorption in the UV/Vis region, was used as a reference. The absorption was calculated using Equation (1):

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{1}$$

where K and S are the absorption and scattering coefficients, respectively, and R is the diffuse reflectance.

Results

Absorption Spectra of the Ground States

Figure 1 shows the absorption spectra of the SNO and Cl-SNO microcrystalline powders and their toluene solutions (10^{-4} M). The absorption around 350 nm is due to the oxazine moiety,[15] and the K/S value of this band is similar for both compounds. Although the backscattering coefficients depend on the com-

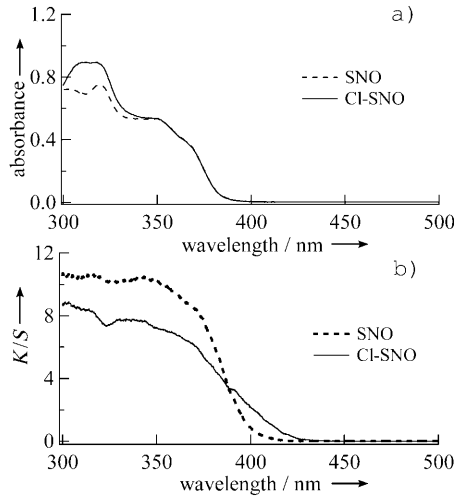

Figure 1. Absorption spectra of SNO and Cl-SNO as a) toluene solutions (10^{-4} M) in a 1-cm quartz cell and b) microcrystalline powders.

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pound and the particle diameter of the powders, the absorption of the oxazine part is in a similar wavelength region so that the backscattering coefficients of the powders can be consiedered comparable to each other. As shown in Figure 1 a, the absorption spectra of SNO and Cl-SNO in toluene are the same in a wavelength region of the oxazine part absorption. The absorbance and spectral shape around the oxazine absorption of each compound are the same within error limits.

Dynamics of the Ring-Opening and Ring-Closing Reaction

The transient absorption spectra were examined under weak excitation conditions, and the dynamics of the excited states in SNO and Cl-SNO crystals was compared. Figure 2 shows the

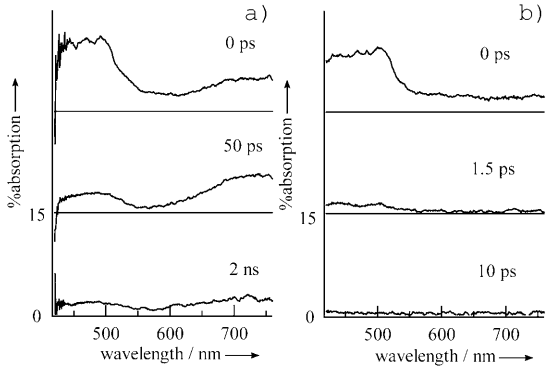

Figure 2. Transient absorption spectra of microcrystalline powders of a) SNO and b) Cl-SNO excited with a femtosecond laser pulse (390 nm, 0.5 mJ cm^{-2}). Delay times are given in the figure.

transient absorption spectra of SNO and Cl-SNO; the excitation fluence was about 0.5 mJ cm^{-2} and PMC was not detected after irradiation. In the case of SNO, the S_1 state of the spiro form with an absorption peak at 500 nm decays with a lifetime of 3 ps, and the subsequent nonplanar open form has two peaks around 460 and 740 nm. The nonplanar open form decays to the ground state of the spiro form in a nanosecond timescale. In the case of Cl-SNO, the transient absorption of the S_1 state of the spiro form was also observed just after excitation, and its lifetime was less than 1 ps. However, no transient absorption was observed after the decay of the S_1 state. These results show that the cleavage of the C_{spiro}–O bond occurs in a picosecond timescale for both SNO and Cl-SNO, whereas the reaction dynamics after bond cleavage is quite different. The nonplanar open form lives in a nanosecond timescale for SNO, but it may decay in 1 ps for Cl-SNO. This discrepancy will be a result of the crystalline and molecular structures.[11]

Photocoloration by Single-Pulse Excitation

The photocoloration of sample powders was examined by measuring the steady-state absorption spectra after excitation with 100 shots of intense femtosecond laser pulses (10 Hz repetition rate). Figure 3 shows the absorption spectra of SNO (a)

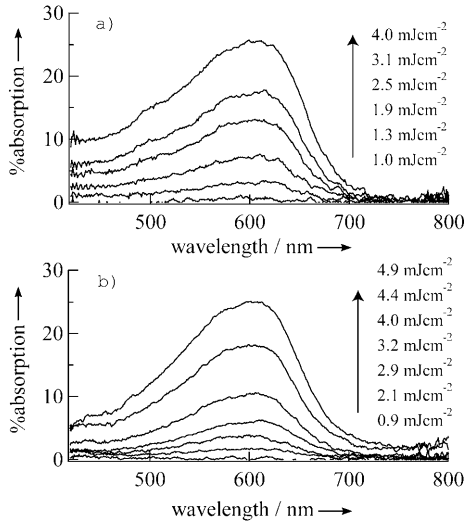

Figure 3. Absorption spectra after excitation with 100 shots of femtosecond laser pulses for a) SNO and b) Cl-SNO. The excitation intensity is given in the figure.

and Cl-SNO (b) after femtosecond laser excitation at various fluences. When the laser fluence was higher than 1 mJ cm^{-2}, absorption spectra with a peak around 600 nm were observed, and the spectral shape was independent of the fluence. The absorption spectra are in good agreement with that of PMC for each compound in solution, therefore we can conclude that PMC similar to that in solution is formed in the crystalline phase for both compounds.

As the absorption change induced by one-shot excitation is very small, even at a laser fluence of a few mJ cm^{-2}, multishot excitation is necessary for detecting sufficient absorption of PMC. Thus, excitation with 100 shots of femtosecond laser pulses induced the photocoloration shown in Figure 3. In this case a chemical species or crystalline defects produced by the former excitation pulses may absorb the next excitation pulse and thus may result in a new photoproduct. Such a multishot excitation effect can be checked by examining whether the absorption of PMC increases linearly with the number of excitation laser shots. The linearity was confirmed under the present conditions, which indicates that accumulation and incubation effects due to multishot excitation are not dominant in the photocoloration.

On the other hand, the % absorption at the peak wavelength increases nonlinearly with the laser fluence (see Figure 4). The photocoloration of Cl-SNO is less than that of SNO in the crystalline phase at the same laser fluence, and the slope in the % absorption versus fluence relationship is different for the two compounds. These results mean that the efficiency of PMC formation for Cl-SNO is less than that for SNO, because the absorption coefficient of the PMC is the same for each compound.[16]

Photocoloration by Double-Pulse Excitation

The nonlinear fluence dependence suggests that mutual interactions between excited states and nonplanar open forms are

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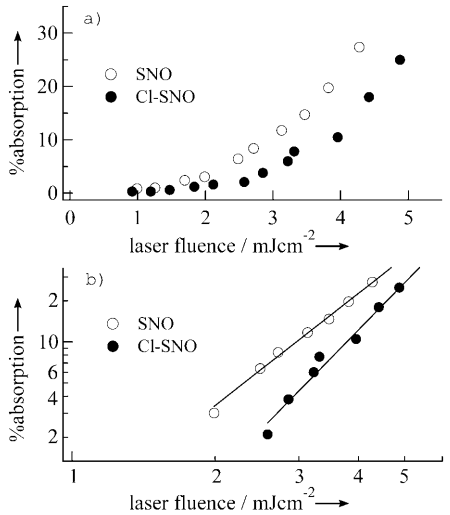

Figure 4. Excitation fluence dependence of the %absorption at 580 nm after irradiation with 100 shots of femtosecond laser pulses (390 nm) for a microcrystalline powder at room temperature. Plots of the %absorption as a function of the laser fluence for SNO (○) and Cl-SNO (●); a) conventional plots and b) log–log plots. The slopes of the log–log plots are 2.7 and 3.6 for SNO and Cl-SNO, respectively.

significant. We examined the kinds of transient species responsible for the nonlinear photocoloration by using a double-pulse excitation experiment. Temporal information on the species was obtained by changing the time interval between the first and second excitations. Figures 5a and 5b show the photocoloration of SNO and Cl-SNO, respectively, as a function of the time interval from 40 ps to 5 ns for first and second pulses of the same intensity. In both plots, the absorption at 0 ps is

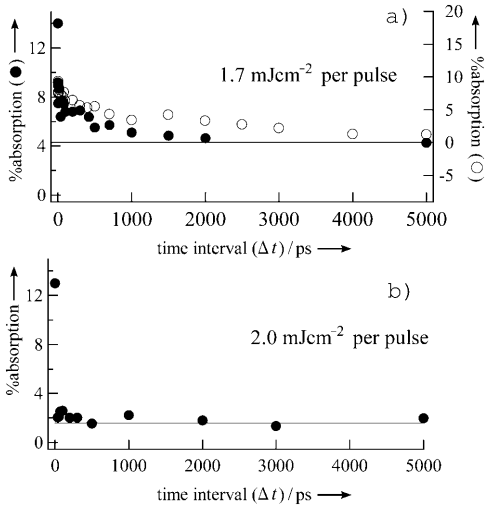

Figure 5. Plots of the %absorption at the peak wavelength by double-pulse excitation as a function of time interval between first and second pulses for a) SNO and b) Cl-SNO (●, left axis). The absorptions by single-pulse excitation at 3.4 and 4.0 mJ cm^{-2} (time interval 0 ps) are also shown in (a) and (b), respectively. The solid line represents the sum of the %absorption values by independent single-shot excitation with the first and second pulses. The decay profile of the nonplanar open form for SNO under weak excitation conditions is also shown (○, right axis). The laser fluence of the first and second pulses is given in the figure.

the result obtained by single-pulse excitation at the total fluence of the first and second excitations. The absorption by single-pulse excitation is much larger than that by double-pulse excitation, even though the total excitation fluence is the same. The solid line represents the sum of the absorption by two independent single-pulse excitations. In the case of SNO, the absorption decreased with an increase in the time interval, which has two components of a few picoseconds and a few hundred picoseconds, respectively. The correlation of PMC absorption with the time interval in double-pulse excitation almost disappeared in 3 ns, and the components can be related to the lifetime of the transient species involved. On the other hand, for Cl-SNO only a fast decrease was observed and the absorption was constant in the time interval over 40 ps.

We also examined the double-pulse photocoloration at high laser fluence. Figure 6 shows the absorption of the PMC for

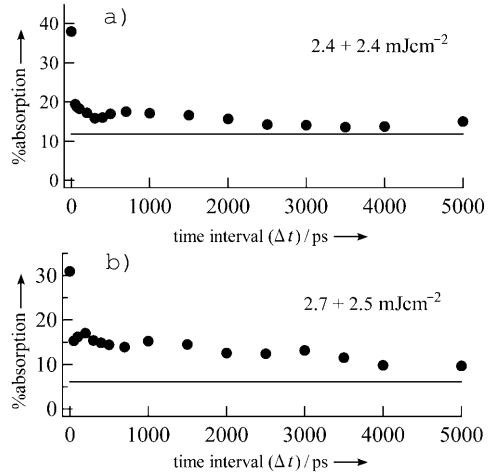

Figure 6. Plots of the %absorption at the peak wavelength by double-pulse excitation as a function of time interval between first and second pulses for a) SNO and b) Cl-SNO. Excitation fluences of the first and second pulses are 2.4 and 2.4 mJ cm^{-2} in (a), and 2.7 and 2.5 mJ cm^{-2} in (b), respectively. The absorptions at the time interval of 0 ps were obtained by single-pulse excitation at fluences of 4.8 and 5.2 mJ cm^{-2}, respectively. The solid line represents the sum of the %absorption values by independent single-shot excitation with the first and second pulses.

SNO and Cl-SNO at total fluences of 4.8 and 5.2 mJ cm^{-2}, respectively. A remarkable difference compared to the result in Figure 5 is that the absorption, even at an interval of 5 ns, is larger than the sum of the absorption by two independent single-pulse photocolorations, although the %absorption decreases gradually in a nanosecond time region. The results indicate that some other effect in addition to mutual interactions between transient species should be taken into account under the higher-fluence excitation. The details will be discussed later.

Two-Color Double-Pulse Excitation

In the double-pulse excitation experiment, the second pulse may excite the short-lived species generated by the first pulse when irradiated during the intermediate lifetime. It is possible

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that the excitation of the nonplanar open form by the second pulse may lead to planar PMC. To examine this reaction channel, we conducted a two-color double-pulse excitation experiment, where the first pulse was at 390 nm and the second was at 780 nm. The second pulse selectively excites the nonplanar open form because it absorbs around 780 nm (see Figure 2).

Figure 7 shows a transient absorption spectrum of two-color double-pulse excitation and its scheme. A probe pulse was irradiated 100 ps after the second-pulse excitation, the second pulse was irradiated 40 ps after the first-pulse excitation of 390 nm, and the transient absorption was calculated as the difference spectra with and without a second-pulse excitation of 780 nm. A negative absorption signal was observed, and the shape is similar to the upside-down spectrum of the nonplanar open form in Figure 2. It is considered that the ground state of the nonplanar open form reverts to the original spiro form from the excited state obtained by the second-pulse excitation.

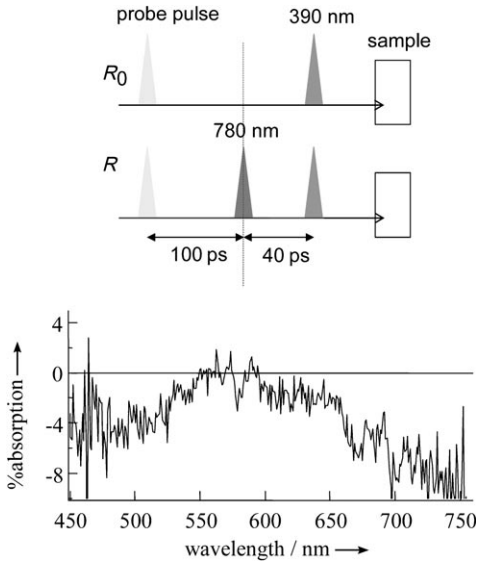

Figure 7. Schematic representation of a transient absorption measurement in two-color double-pulse excitation and a transient absorption spectrum under the conditions shown in the scheme. The wavelength and fluence of the first and second pulses are 390 and 780 nm and 4.0 and 6.1 mJ cm^{-2}, respectively.

The photocoloration induced by the two-color double-pulse excitation is shown in Figure 8, with the absorption spectrum obtained at a time interval of 40 ps. The PMC was generated by 380-nm pulses, but not by 780-nm pulses. It is interesting to see that the absorption by double-pulse excitation is less than that only by the first-pulse excitation, which is consistent with the result in Figure 7. The similar behaviors were obtained at different excitation fluences. Therefore, it is concluded that PMC formation is inhibited by the excitation of the nonplanar open form, and that the 390-nm double-pulse excitation phenomena shown in Figure 5 can be ascribed to the concentrations of the excited states of the spiro form and nonplanar open forms changing with time.

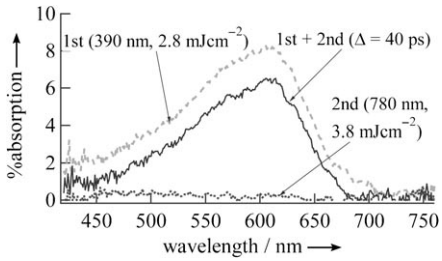

Figure 8. Steady-state absorption spectra in a two-color double-pulse excitation experiment on SNO microcrystalline powder, in which the wavelength and fluence of the first and second pulses are 390 and 780 nm and 2.8 and 3.8 mJ cm^{-2}, respectively. The solid line represents the spectrum after 100 shots of 10-Hz-repetition femtosecond double pulses with a 40-ps interval between the two pulses. The dotted and broken lines represent the steady-state absorption spectra after 100 shots of 10-Hz-repetition femtosecond single pulses of the first and second excitations, respectively.

Discussion

The double-pulse excitation experiments confirm the cooperative photochemical reaction model which is schematically illustrated in Figure 9. Under weak excitation conditions, SNO molecules cannot undergo photochromism in the crystalline phase, as *trans*-planar PMC is produced only after a large molecular structure change, which is prohibited in the crystal. On the other hand, high-intensity excitation above a certain laser fluence brings about photocoloration. Successive excitation of

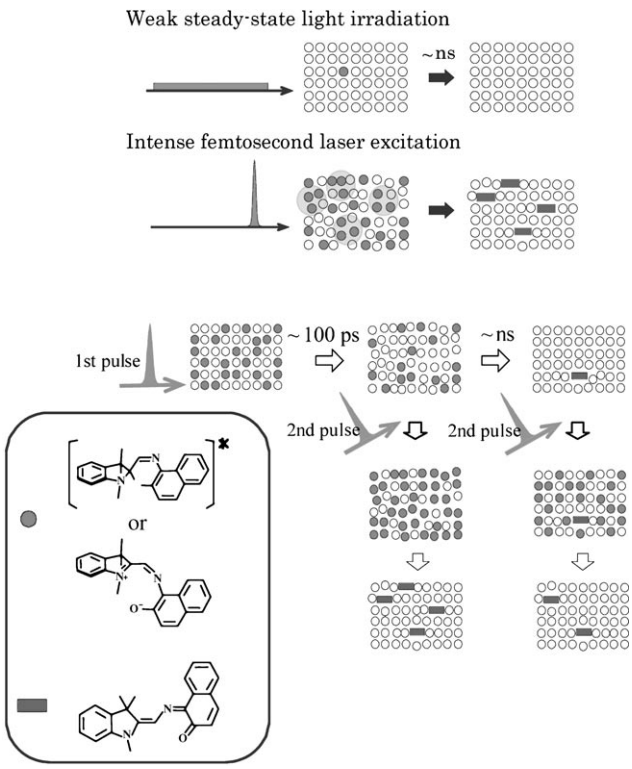

Figure 9. Schematic illustrations of the cooperative photochemical model and of the double-pulse excitation experiment.

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the transient nonplanar open form by another photon may induce PMC formation; however, this possibility was excluded by the two-color double-pulse excitation experiment. We consider that cooperative interactions between excited states and intermediates are critical, and we discuss the present results from the viewpiont of mutual interactions between transient species.

As shown in Figure 4, the dependence of the PMC yield on the excitation fluence in the single-pulse excitation differs between SNO and Cl-SNO. The result indicates that the colored forms of SNO are generated efficiently compared to those of Cl-SNO. It is in general quite difficult to examine the yield quantitatively in microcrystalline powder samples because of the multiple scattering of excitation-pulse light. However, we can safely attribute the difference in the PMC yield to the contribution of the nonplanar open form on the basis of the results from the transient absorption measurement and the double-pulse excitation experiment. The %absorption of SNO by double-pulse excitation with two 1.7 mJ cm^{-2} pulses (Figure 5) is 9% at a time interval of 40 ps, and about 4% at an interval of 5 ns. This means that the absorption of colored forms induced by the interactions between nonplanar open forms is about 5% under these conditions. On the other hand, in the single-pulse excitation at a fluence of 3.4 mJ cm^{-2} (Figure 4), the %absorption of the PMC for SNO microcrystalline powder is larger by 5% than that of Cl-SNO, for which the nonplanar open form decays in a few picoseconds after photoexcitation.

To verify the cooperative photochemical model, we carried out a simple Monte Carlo simulation on the number of clustering transient species. We considered a crystal system consisting of 50×50×50 molecules with a simple cubic lattice, where one molecule has six neighboring molecules. Some molecules were selected randomly in the crystal as excited molecules, and a group consisting of several excited molecules in each other's neighborhood was considered as a cluster of excited molecules. The number of clusters (N_j) consisting of j excited molecules was counted by changing the total number of excited molecules.

To compare the numerical simulation with the photocoloration experiment, it is necessary to know the density of the excited molecules under the experimental conditions. We estimated the absorption coefficient of the crystalline sample at the excitation wavelength by referring to the absorption of the solution. As shown in Figure 2, the diffuse reflectance spectrum (K/S) of SNO powder shows a similar shape to the absorption spectrum in a toluene solution in the wavelength region of 350 to 420 nm. Indeed, the shapes of the two spectra show a good overlap in the range of the absorption edge, when the absorption spectrum was shifted to a longer wavelength by about 15 nm. So we considered the molar absorption coefficient of the crystal at 390 nm to be the same as that of the solution at 375 nm ($\varepsilon = 1600\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). Using this absorption coefficient and the molecular density of the SNO crystal (3.72×10^{-3} mol cm^{-3}),[17] we can estimate the absorbance of the microcrystalline powder to be $\alpha = 1.4\times10^{4}\,\mathrm{cm}^{-1}$ and the penetration depth of the excitation pulse at 390 nm to be 0.8 μm. On the other hand, the excitation fluence of 1 mJ cm^{-2} at 390 nm corresponds to the photon density (2.0×10^{15} cm^{-2}). The density of excited molecules at a fluence of 1 mJ cm^{-2} is calculated to be about 1% by assuming that the sample absorbs homogeneously all irradiated photons in the penetration depth (the number of molecules in the penetration depth per area is about 2×10^{17} cm^{-3}). In the case of Cl-SNO, the absorption spectrum of the crystalline powder in Figure 2 shows a weak absorption tail around 400 nm, which may be ascribed to a weak charge-transfer interaction between the oxazine moiety and the Cl atom in the indoline ring, and is consistent with the X-ray crystalline structure.[11] Although the absorption spectra of Cl-SNO and SNO microcrystalline powders are not similar to each other, we assume here that the absorption coefficient of Cl-SNO crystals at 390 nm is equal to that of SNO. Consequently, we consider that the excitation fluence of 1 mJ cm^{-2} used in our experiment is equivalent to a density of 1% for excited molecules in both microcrystals.

The simulation results of N_j for $j = 2$, 3, and 4 are shown in Figure 9 as a function of the density of excited molecules. In Figure 10 we compare the simulation result to the experimental fluence dependence of the photocoloration. N_j increases nonlinearly with the density of excited molecules, and the slope of the log–log plot in Figure 10b becomes large with increasing j. We cannot precisely compare the results because the quantum yield of PMC in the crystal is unknown. However, the slope of the photocoloration against the laser fluence is similar to the dependence shown by the simulation for N_4. The

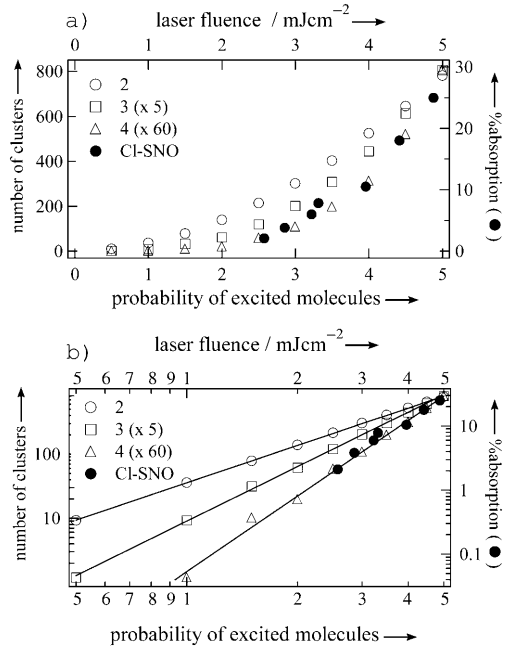

Figure 10. a) Linear and b) log–log plots of the cluster number (N_j) consisting of adjacent excited molecules versus the density of total excited molecules. The number of adjacent molecules (j) in a cluster is two (○), three (□, enlarged five times), and four (△, enlarged 60 times). The %absorption of the PMC against the excitation fluence for Cl-SNO is also shown (●, right axis).

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double-pulse excitation experiment, on the other hand, suggests that PMC formation in Cl-SNO crystals takes place only in clusters of the excited singlet state. Therefore, it is considered that PMC formation is induced by interactions between excited molecules in clusters consisting of four adjacent excited molecules.

In the case of SNO, the photocoloration yield was larger and the fluence dependence showed a gentle slope compared to the results for Cl-SNO (Figure 4). The slope of the experimental photocoloration is in good agreement with the simulation for N_3 in Figure 10. This result suggests that three neighboring excited molecules induce the formation of PMC. It should be mentioned, however, that photocoloration in the SNO crystal may be possible by interaction not only of the excited molecules but also of those in the nonplanar open forms. Furthermore, in the double-pulse photocoloration shown in Figure 5, we found two correlation times in the time interval between the first and second excitation pulses. These results imply that two kinds of clusters with different decay times are responsible for PMC formation. One is a cluster of four excited molecules generated immediately after excitation, which is similar to the case of Cl-SNO. The other consists of the nonplanar open forms that survive in the nanosecond time region. It is reasonable that two or three adjusting nonplanar open forms give *trans*-planar PMC, because the nonplanar form will induce larger deformation of the local lattice compared to the excited state of SNO. Here, we simulate the experimental photocoloration by tuning the number of adjusting molecules in the latter cluster and the yield from the excited state to the nonplanar open form. Figure 11 shows two examples of simulation results, where the total number of the clusters, N_4+N_2 and N_4+N_3, were calculated using the yields of 0.08 and 0.4 for N_2 and N_3, respectively. The simulation reproduces qualitatively the experimental photocoloration, although it is difficult to determine the optimized parameter because of unknown information such as the relationship between %absorption and the density of the PMC, the quantum yield from the excited state to the nonplanar open form, and so on.

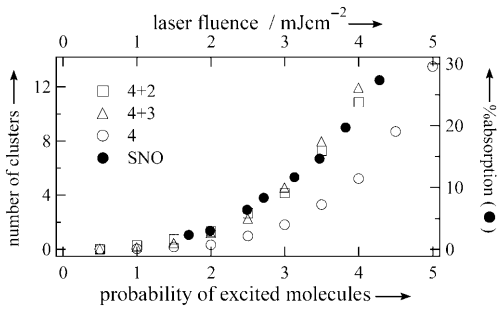

Figure 11. Plots of the cluster number, which is the sum of the four adjacent excited molecules and the two (□) or three (△) nonplanar open forms, against the density of the excited molecules. The %absorption of the PMC against the excitation fluence for SNO is also shown (●, right axis).

We also simulated the photocoloration of SNO upon double-pulse excitation using the same model. The lifetime of the nonplanar open form was set to be 2 ns, and it decayed to the spiro form in the time interval. The excited molecules induced by the second pulse were counted under the experimental conditions. The total number of clusters, N_4+N_2 and N_4+N_3, were calculated, and the simulated and experimental results of the double-pulse excitation photocoloration are shown in Figure 11. The absorption at a time interval of 0 ps in the simulation is equivalent to the result calculated at an excitation density of 3.4%. Using the same parameters for the fluence dependence of the single-shot excitation experiment in Figure 12, we can reproduce well the time interval dependence of the double-pulse photocoloration. This result supports strongly the notion that PMC formation takes place due to interactions between excited molecules and between the nonplanar open forms; the former consist four adjacent molecules and the latter consist of two or three adjacent molecules in a cluster.

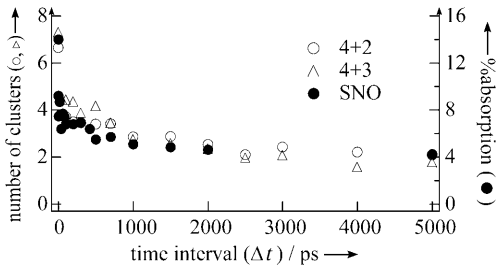

Figure 12. Plots of the cluster number against the time interval of the first and second excitation pulses at an excitation density and lifetime of the nonplanar open form of 1.7% and 2 ns, respectively. The number of adjacent nonplanar open forms in a cluster is two (○) or three (△). The %absorption of the PMC against the time interval for SNO is also shown (●, right axis).

This simple simulation has some problems, for example, the actual crystal system is not a simple cubic lattice, and the number of neighboring molecules is unclear, because it is not easy to estimate the effective range of the intermolecular interactions. In addition, the molecular packing is different for SNO and Cl-SNO crystals, so the simple comparison discussed above may not be perfect. However, the present numerical simulation can confirm the validity of our cooperative photochemical model. It will be necessary to investigate the details by molecular dynamics simulations.

The decrease of the PMC absorption with the time interval depends on the laser fluence of the first and second pulses (Figure 6). Especially, under the higher excitation conditions, the absorption at a time interval of 5 ns is more than the sum of the absorption by each single-pulse excitation. This means that some effects other than the interactions between the excited states and the nonplanar open forms contribute to PMC formation under the higher excitation conditions. One possible explanation is a photothermal effect, that is, a high temperature is attained in the solid immediately after intense short-pulse laser excitation. Ultrashort laser excitation of organic solids leads to significant heat generation, because various nonradiative decay channels of the electronically excited state are opened in addition to the occurrence of mutual interac-

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tions between transient species. Molecular vibrations and lattice motions facilitate a conformational change from the spiro form to the stable and planar PMC even in the crystalline phase. Once a crystal surface layer is excited by a laser pulse and heated rapidly, the high temperature would decay slowly through thermal diffusion. The exact cooling time is unknown, however, it can be estimated to be on the order of a microsecond,[9] which is much longer than the lifetime of the nonplanar open form. Thus, the second-pulse excitation in the time interval around a few nanoseconds may correspond to excitation of the hot crystal, which could result in large amplitude deformations. Therefore, photocoloration is brought about by the second-pulse excitation, although the excited states and the nonplanar open forms produced by the first pulse have already decayed.

Conclusions

We have investigated the mechanism of spironaphthooxazine photocoloration in the crystalline phase induced by intense femtosecond laser excitation from the viewpoint of dense formation of excited states and short-lived nonplanar open forms. The efficiency of photocoloration for SNO is higher than that for Cl-SNO. From the results of transient absorption measurements, the nonplanar open form with a lifetime of about 2 ns was observed for SNO, but not for Cl-SNO. The yield of the PMC by single-pulse excitation is larger than that by double-pulse excitation, with a time interval of a few tens of picoseconds at the same total excitation intensity for both compounds. Moreover, the yield of the PMC decreased with increasing time interval in the region of a few hundred picoseconds in the case of SNO. This behavior is similar to the decay profile of the nonplanar open form. Indeed, densely formed excited states and nonplanar open forms have a large influence on photocoloration in the crystalline phase. The experimental results and the simulation, namely, counting the numbers of clusters of excited molecules and the nonplanar open forms in a simple cubic lattice, show that cooperative interactions of the excited states and the nonplanar open forms result in local lattice deformations and collective motions of molecules, and lead to a change in molecular conformation to the *trans*-planar PMC.

Keywords: cooperative phenomena · photochromism · solid-state reactions · spiro compounds · UV/Vis spectroscopy

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