Photocoloration of Spironaphthoxazine Microcrystalline Powder by Femtosecond Laser Pulse Excitation

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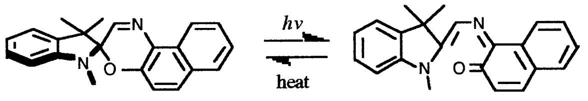
Photocoloration of microcrystalline powder of a spirooxazine compound by femtosecond laser pulse excitation, depending on its intensity, is reported with transient absorption spectral measurements of the powder. The mechanism is discussed in terms of light induced local heating and succeeding cooling of a small volume in the microcrystal.

Spironaphthoxazine (SpC, in Scheme 1) is one of the representative photochromic compounds which shows heavy tolerance to repeated cycles, as illustrated in the following scheme.[1,2] Upon ultraviolet irradiation, the bond between spiro carbon and oxygen undergoes fission within 1 ps, followed by a geometrical change to a stable planer merocyanine form with a characteristic absorption peaked around 600 nm up to several hundreds ps,[3-5]



SpC

Scheme 1.

The photochromic reaction was observed not only in solution but also in several polymer matrices,[1,6,7] while it is believed that it does not occur in crystalline phase because geometrical change to the stable planer merocyanine is restricted in the crystal. This is in contrast to other photochromic molecules such as diarylethene derivatives; it was recently reported that some of diarylethenes undergo ring-closure and opening cycles in crystalline phase. [8,9] In the present work, we have found novel photocoloration behavior of SpC microcrystalline powder by femtosecond laser pulse excitation, depending on its intensity. With transient absorption spectra measured by using a femtosecond diffuse reflectance spectroscopy, the mechanism will be discussed in terms of local heating by the excitation pulse and the succeeding cooling processes.

Transient absorption spectra of microcrystalline powder were measured with a femtosecond diffuse reflectance spectroscopic system.[10] Transient absorption is illustrated by % absorption = 100 x (1 - R / R_0), where R and R_0 are intensity of diffuse reflected light of a probe pulse (a femtosecond white-light continuum) with and without excitation, respectively. Excitation light is a second harmonic (390 nm) of an amplified femtosecond Ti: sapphire laser pulse (780 nm, 3 - 4 mJ / pulse, 170 fs, 10 Hz). The temporal resolution of transient absorption mesurements with this spectroscopic system is less than 1 ps for such a sample as organic microcrystalline powder having large absorption coefficient at the excitation wavelength.[11] SpC (Aldrich) was used without further purification, and its powder sample was contained in a quartz cell (2 mm optical length). All measurements were performed in air at 295 K.

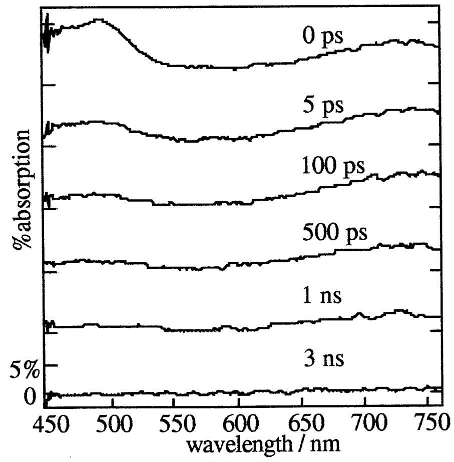


Figure 1. Transient absorption spectra of SpC microcrystalline powder excited with a femtosecond laser pulse (390 nm, 0.6 mJ cm^{-2}). Delay times are shown in the figure.

The transient absorption spectra of the microcrystalline powder are illustrated in Figure 1 (fluence ~ 0.6 mJ cm^{-2}). Their change is very similar to that in 1-buthanol solution (from -0.3 to 1.0 ps) before a planar merocyanine is formed.[4] Namely, following an absorption band with a peak at 490 nm assigned to the S_n-S_1 absorption of SpC, a broad absorption spectrum peaked around 760 nm remains. The latter spectrum was considered to be an absorption band of a primary transient, formed via the C–O bond cleavage, but with an orthogonal parent geometry of the oxazine and indoline chromophers.[4] The decay time of the S_n-S_1 absorption was estimated to be 3 ps from the time profile at 490 nm. The result suggests that the bond cleavage occurs also in crystalline phase with a rather slow time constant compared to that in solution. However, the transient absorption decayed completely up to 4 ns without further spectral changes, and any absorption due to merocyanine was not observed. Moreover, under the above excitation condition, no detectable coloration of the powder sample was observed after excitation with more than several hundred shots of the femtosecond laser pulses.

On the other hand, when increasing the excitation intensity to a few mJ cm^{-2}, coloring of the powder was detected by eyes. Figure 2 shows absorption spectra after excited with 300 shots of femtosecond pulses (10 Hz repetition rate). The absorption change increases nonlinearly with the laser fluence, and the spectral shape and the peak position are very similar to those of a planer merocyanine in solution.[12] The colored powder came to colorless one in several tens minutes. It is noted that the absorption change induced by one shot excitation is very small; about 0.3% when the fluence is 3.5 mJ cm^{-2}.

The photocoloration indicates that a photochromic reaction

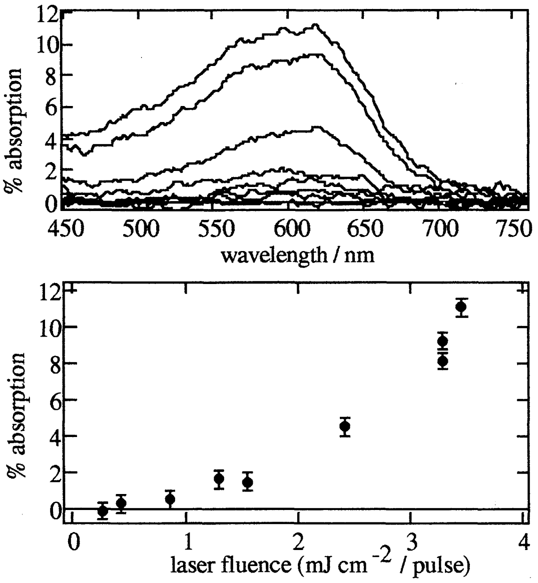


Figure 2. Excitation fluence dependence of an increase in the absorption of SpC microcrystalline powder after irradiation of 300 shots of femtosecond laser pulses. Absorption spectra (top) and a plot of the absorption at 620 nm against the laser fluence (bottom).

similar to that in solution can take place in the microcrystalline powder under intense pulse laser excitation, although the primary transient mainly relaxed to the ground state of SpC without a geometrical change to the merocyanine. The relaxation process finished within several nanoseconds after excitation, and any intense emission was not observed. Thus, the absorbed light energy should be converted efficiently to thermal energy in the time scale, resulting in rapid local heating of SpC microcrystals.

Indeed, significant heat generation is confirmed in general for laser pulse excitation of organic microcrystals and polymer films when they have a large absorption coefficient at an excitation wavelength. A remarkable high temperature, attained instantly when excited with an intense short-pulsed laser light, was proved by spectroscopic technique.[13-15] Hence, local heating due to the photo-thermal conversion should be responsible to a photochemical reaction of organic molecular crystals under pulsed laser excitation.

An increase in temperature of a SpC microcrystal (several micrometer size) is considered here, assuming that the laser light is perfectly absorbed by the microcrystal. The molar absorption coefficient of SpC in the near UV region is about 4 x 10^3 $mol^{-1}dm^3cm^{-1}$,[12] and with a molar density of 5 x 10^{-3} mol cm^{-3}, the penetration depth of the excitation pulse (390 nm) is about 5 x 10^{-5} cm. With a typical value of 200 J $K^{-1}mol^{-1}$ for the molar heat capacity of aromatic compounds, and in the assumption that there is no heat transport, the temperature rise of a small volume near the surface of the microcrystal at a few ns after excitation is estimated to be about 200 K for excitation of 3.5 mJ cm^{-2}.

At such a high temperature (200 K + room temperature), molecular vibrations and lattice motions are significantly active, so that a part of the primary transient can undergo a conformational change to a stable and planar merocyanine even in crystalline phase. The heat generated in a small volume of microcrystal will be transferred to the surroundings in a time scale of sum-microseconds. Then, a generated merocyanine should be frozen in the crystal, keeping its planar conformation. The following cooling process is very important, and it will be a key factor that distinguishes the present result from an experiment under a stationary high-temperature condition. In the latter case, a reverse reaction to SpC is so rapid that any coloration will not be observed.

In the present work, we have demonstrated photocoloration of SpC microcrystalline powder by intense femtosecond laser pulse excitation. The excitation intensity dependence was discussed in terms of a local heating process due to photo-thermal conversion and the following cooling one, although further detailed investigations should be needed to clarify the mechanism. We believe that the viewpoint of rapid heating and cooling will be very important for us to design and control of photochemical reaction of organic crystals, and this can be made possible only by using ultra-short pulsed laser.

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