Photoinduced J-Aggregation of Photochromic Spironaphthooxazine in a Glass Forming Organic Mixture

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Low-temperature UV–vis spectra of spironaphtooxazine (SNO) in a glass forming organic mixture clearly evidenced the J-aggregate formation. J-Aggregate becomes unstable above 100 K and its quantum efficiency for the visible photoreaction was lower than that of monomeric open form B. In a dilute solution, the intensity of the J-band was maximized at 150 K while it decreases with temperature in a concentrated solution.

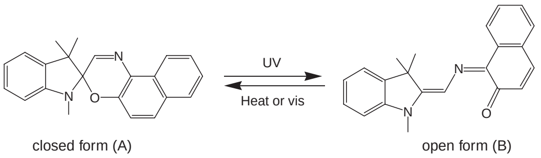
Spiropyrans (SP) and spirooxazines (SO), are families of best known photochromic and thermochromic compounds.[1,2] Upon UV irradiation, colorless closed forms (A) undergoes a reversible photochemical transformation into their colored open form (B) (Scheme 1).

Krongauz et al. found that B form of 6-nitrobenzospiropyran (NBSP) derivatives could interact with A to give dimer AB or charge-transfer complex $\mathrm{A}_n\mathrm{B}$ ($n = 2, 3, \ldots$) in nonpolar solvents.[3–5] Since Krongauz's work, many studies regarding on the aggregation of spirocompounds have been performed in solutions,[6–8] LB films[9] and polymer films[10] to elucidate its mechanism and application. Among many types of SP, most of these researches were concentrated on NBSP derivatives having long-chains. Contrary to SP, only limited number of papers regarding on the aggregation of SO are published. Examples are J-aggregation of spironaphthooxazine (1,3-dihydro-1,3,3-trimethylspiro-[2*H*-indol-2,3′-[3*H*]naphtho[2,1-b][1,4]oxazine], SNO) adsorbed on a zirconium diphosphonate fluoride[11] and H-aggregation of 9′-alkoxy-substituted SNO in heptane.[12]

Here, we report the J-aggregation of SNO in a mixed solution of methylcyclohexane and decalin. Its optical and photobleaching characteristics were also examined using low temperature UV–vis spectroscopy.

SNO solution was irradiated at the desired temperatures (25 or 200 K) with 337-nm pulses from a nitrogen laser. A He–Ne laser (632.8 nm) was utilized for the photobleaching experiment and a closed-cycle He cryostat controlled the temperature of the sample contained in a specially designed sample holder. Prior to UV irradiation and the spectrum measurement, the sample was kept at the desired temperature for at least 1 h.

Figure 1 shows the absorption spectra of 1.0×10^{-2} M SNO solution as a function of temperature. Although the solution forms glass during the temperature cycle, the absorption spectra reversibly changes within the experimental error. At 200 K, the absorption maximum is located at 610 nm and a shoulder at 578 nm. As the temperature decreases, the absorbance near at 625 nm drastically increases. Because the characteristics of the absorption band obtained at and below 150 K are very similar to that of the J-band of an amphiphilic spiropyran,[13] this sharp band can be attributed to the J-aggregate. However, the fact that this band is not as sharp as the typical J-band, the same as other SP, implies that the open forms in the J-aggregate are somewhat loosely packed. The evolution of J-aggregate at the expense of absorption loss in 460–570 nm range implies that the species absorbing at 460–570 nm range, probably the dimer and/or oligomers of SNO, participate in the formation of the J-aggregate.



Scheme 1. Photochromism of spironaphthooxazine.

The results of the photobleaching experiment performed at 25 K are shown in the Figure 2. After the colored modifications are produced by UV irradiation, the absorption spectra were measured as a function of visible irradiation time (burn wavelength, $\lambda_b = 632.8$ nm). The inset shows the difference spectra between the two adjacent spectra. Both the absorption spectra and the difference spectra dramatically changes with the irradiation time. The fact that the photoinduced reaction is still operative at 25 K implies that the potential energy barrier along the reaction path at the excited state is negligibly small.

The spectrum (a), which is quite different from those in the Figure 1, shows its maximum at 602 nm and two comparable shoulders at 568 and 622 nm. Because the sample is in the disordered glass state at 25 K, the relative amount of the colored modifications produced by the UV light can vary case by case. At the beginning of the photoreaction, two comparable dips (decreases in absorbance) at 598 and 565 nm are evolved according to the depletion of the corresponding absorbing species. We attribute the species absorbing at 598 and 565 nm to two different transoid isomers of B. However, the possibility that the dimers might be

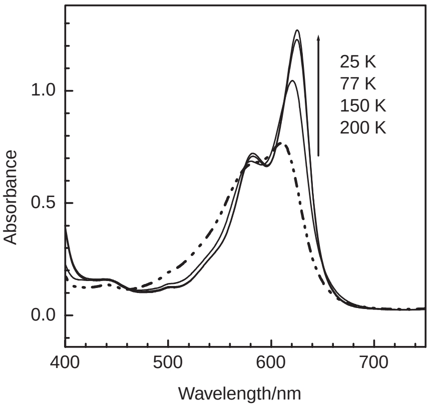


Figure 1. Temperature dependence of the absorption spectra of 1.0×10^{-2} M SNO solution. UV light was irradiated at 200 K and the spectra were taken at the specified temperatures during the cyclic temperature variation.

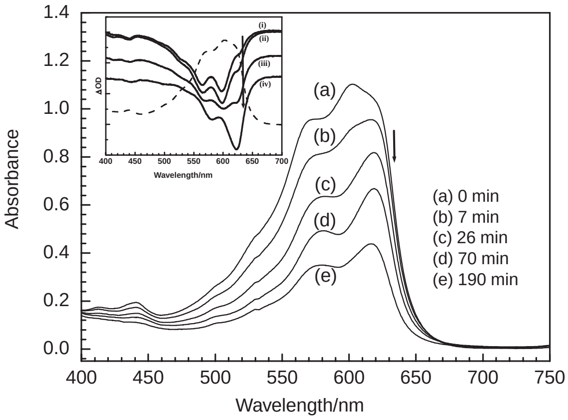


Figure 2. Absorption spectra as a function of irradiation time. The UV–visible irradiations, and the spectrum measurement were performed at 25 K and the arrow indicates the burn wavelength, 632.8 nm. The inset shows the difference spectra between the two adjacent absorption spectra: (i) (b)–(a), (ii) (c)–(b), (iii) (d)–(c), and (iv) (e)–(d).

responsible for the absorption at 565 nm cannot be completely excluded.[14]

Although the shoulder at 622 nm, previously assigned to J-aggregate, is closer to λ_b, the difference spectra (i) shows only a trace at that position. Similar results were obtained regardless of λ_b in the range from 532 to 632.8 nm. This implies that the photoreaction quantum yield of J-aggregate is smaller than that of B. It predicts that the photobleaching of J-aggregate does not mainly start until B is mostly bleached and the Figure 2 evidences the prediction. As the irradiation gets longer, the absorption spectrum ((c)–(e)) becomes similar to the J-band and, therefore, the photobleaching of J-aggregate becomes significant. The dip at 580 nm owes its origin in part to the vibronic transition of J-aggregate and in part to B.

Figure 3 represents the spectral changes of 1.0×10^{-5} M SNO solution. It looks resemble with the Figure 1 at a glance. However, two corresponding spectra measured at 25 K are quite different from each other in both figures. Instead, the spectrum at 25 K in the Figure 3 was similar to that of B obtained at 25 °C by the thermochromic reaction.[14] Although the absorbance of B were similar both in the dilute and in the concentrated solutions by adjusting the UV irradiation time, the intensity of the J-band measured at 25 K does depend on the total SNO concentration. In general, because the formation reaction of the J-aggregates is exothermic, its concentration should decrease with temperature. However, only the concentrated solution shows its characteristic temperature dependence. In a dilute solution, on the contrary, more aggregates are formed at 200 K than at 25 K and its concentration was maximized at 150 K. In order to obtain the better understanding of the differences in the temperature dependence of the J-aggregate formation between in the dilute solution and in the concentrated solution, further studies are in progress. Both Figures 1 and 3 show that the J-aggregate becomes unstable above 100 K and this explains why only the limited number of studies regarding on the formation of the J-aggregates of spirooxazines are reported so far.

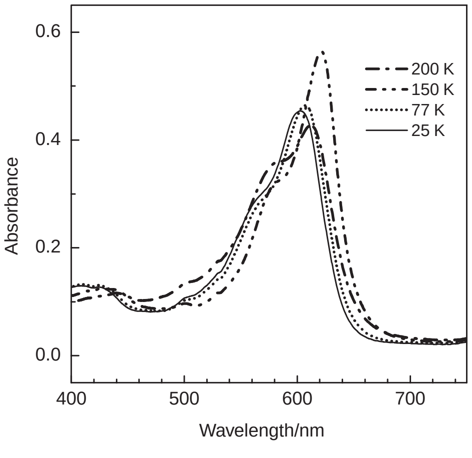


Figure 3. Temperature dependence of the absorption spectra of 1.0×10^{-5} M SNO solution. UV light was irradiated at 200 K and the spectra were taken at the specified temperatures.

In summary, we observed the J-aggregate of SNO in a glass forming organic mixture. J-Aggregate becomes unstable at above 100 K and its photoreaction quantum yield was small compared with monomer B. In a dilute solution, more J-aggregates are formed at 200 K than at 25 K and its intensity was maximized at 150 K while it decreases with temperature in a concentrated solution.

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