# Fluorescence Emission and Cycloaddition Reaction Induced by Ionizing Radiation in 2,5-Distyrylpyrazine Molecular Crystal: A Comparison to the Photo-Illuminated Systems

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(Received March 14, 1997)

Fluorescence emission and cycloaddition reaction induced in 2,5-distyrylpyrazine crystal by ionizing radiation were studied by means of pulse radiolysis and $^{60}$Co $\gamma$-ray radiolysis. Lifetimes of the fluorescence in the photo-illuminated crystal were also studied for comparison by using pico-second laser photolysis techniques. The fluorescence spectrum obtained by pulse radiolysis was similar to that obtained by laser-photolysis, which led us to conclude that excimers were formed by electron beam-irradiation as well. The occurrence of [2+2] cycloaddition reaction of DSP by $\gamma$-irradiation was monitored by observing the concentration change of the olefinic double bond. The high *G*-value, 4—5, for the decrease of the olefinic double bond suggested efficient activation of DSP in the irradiated crystal.

The cycloaddition reaction induced by a photon in 2,5-distyrylpyrazine (DSP) crystal is well known as a classical example of a topochemical reaction in which the reactions are restricted and controlled by the rigid lattice in the crystal.[1] With the light of longer wavelength than 400 nm, only 3—5 monomers can be added to each other to form oligomers, but further illumination with the light of shorter wavelength than 400 nm leads to the formation of crystalline polymers of high molecular weight.[2] Since the first report by Hasegawa and co-workers[1] the reaction system has drawn much attention and quite a few investigations have been made so far. Ebeid and Bridge made time-resolved fluorescence measurements and reported excimer formation both in powder-like microcrystals and single crystals.[3] Peachey and Eckhardt proposed, based on their experiments by using Raman spectroscopy and single crystal specular refraction spectroscopy, that $\pi^* \leftarrow$n exciton couples with the lattice photons to form a local dynamic distortion; the reactivity of DSP to form oligomers resulted from this distortion that served as a trap for the delocalized $\pi^* \leftarrow \pi$ exciton causing the reaction.[4]

The [2+2] cycloaddition reaction was initially reported to occur only on the surface of the crystal, but careful selection of the wavelength of the incident illumination made it possible to irradiate the crystal in a uniform manner and thus to obtain macroscopic single crystals of the oligomer.[5] Compared to UV or visible light, ionizing radiation such as X-ray and $\gamma$-ray is obviously advantageous in irradiating crystals throughout the bulk because of its high penetrability. However, according to the early report by Nakanishi et al, the reaction was not observed in the irradiated crystal by $^{60}$Co $\gamma$-rays.[6]

The purpose of this study is to clarify the optical emission and reaction in single crystals of DSP irradiated by ionizing radiation in the hope of applying $^{60}$Co $\gamma$-rays and electron-beams to the cycloaddition reaction of DSP. The fluorescence emission from samples illuminated by laser-pulse is also studied for comparison.

## Experimental

DSP was synthesized by refluxing the mixture of 2,5-dimethylpyrazine, benzaldehyde, and benzoic anhydride in the dark.[1] It was recrystallized in xylene solution after washing by ethanol and ether. It was purified further by passing through a silica gel 60 and by repeating recrystallizations. Monocrystalline samples were grown slowly in THF and subjected to the measurements. Time-resolved fluorescence measurements were carried out by a cryostat system combined with Hamamatsu Photonics Pico-Second Fluorescence Measurement System. Laser pulses of 338 nm from $N_2$ laser were used as excitation light source and the photon counting method was used for recording the spectra.[7] FWHM of the laser pulse was 0.4—1.0 ns. The cycloaddition reaction was monitored by observing the infrared absorption peak of the double bond which has carbon atoms connected to trans-positioned hydrogen atoms. The pulse radiolysis measurements were made by using a 45-MeV Electron Linear Accelerator in Hokkaido University. The experimental setup

was the same as described elsewhere[8] except that the xenon lamp for analyzing light source was turned off. Radiation does was measured by Fricke dosimetry for $^{60}$Co $\gamma$-ray and alanine/ESR dosimetry for electron beam.

## Results

### A. Time-Resolved Fluorescence Measurements.

Figure 1 shows a transient fluorescence spectrum observed from MTHF solution at liquid nitrogen temperature (77 K) together with decay profiles observed at different wavelengths. The spectrum with a maximum at 435 nm and a shoulder at 456 nm is due to the $\pi^*\leftarrow\pi$ transition of isolated DSP monomers. The spectrum of single crystal is much wide and more complex, as shown in Fig. 2, with the maximum being shifted from 456 to 493 nm. The structure shown in the shorter wavelength side of the peak can be compared to each of the peak and shoulders of the solution spectrum. Therefore, the band from 440 to 480 nm is ascribed to the vibrational structure of DSP monomer.

The broad, complex band extending from the 500 up to 650 nm is obviously different from that of the monomer component. Decay profiles observed at the bandwidth 480±45 nm were non-exponential and showed long-lasting tails; the apparent decay rate depended on the wavelength and bandwidth monitored. In the previous study, the time-profiles in this wavelength region could not be analyzed in a quantitative manner,[3] but here the time-constants of each component were precisely determined by using tentative deconvolution methods.[9] As illustrated in Figs. 1 and 2, the complex band was deconvoluted to several different components by assuming a Gaussian shape for each of them. The bandwidths at which each of the time profiles was recorded were determined so that each of the decay curves followed a single exponential process. In the case of solution, all of the components fit to approximately a single exponential decay, as shown in the bottom of Fig. 1, which proves the structure to be due to different vibronic modes in the same electric state. But in the case of the crystal, each of the components had a different decay time-constant, as shown at the bottom of Fig. 2. The time-constants determined are summarized in Table 1.

The time-constant determined at 452 nm corresponds to

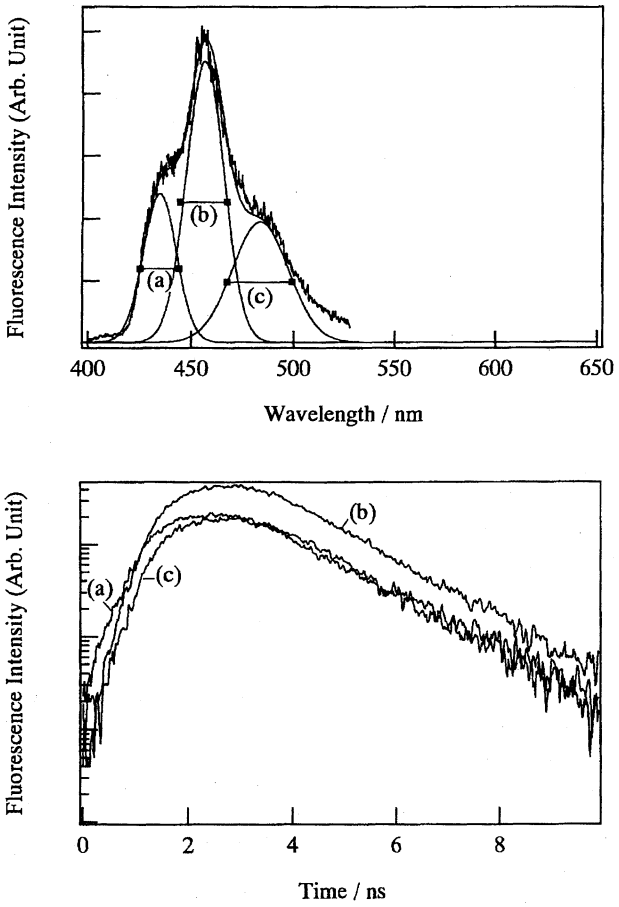


Fig. 1. Top: Transient fluorescence spectrum of DSP observed at 77 K from MTHF solution. The horizontal bars indicate bandwidths at which each of the decay profiles in the bottom were recorded; solid lines indicate the Gaussian functions used for tentative deconvolution analysis. Bottom: The decay profile observed at (a) (435±10) nm, (b) (456±12) nm, and (c) (484±16) nm.

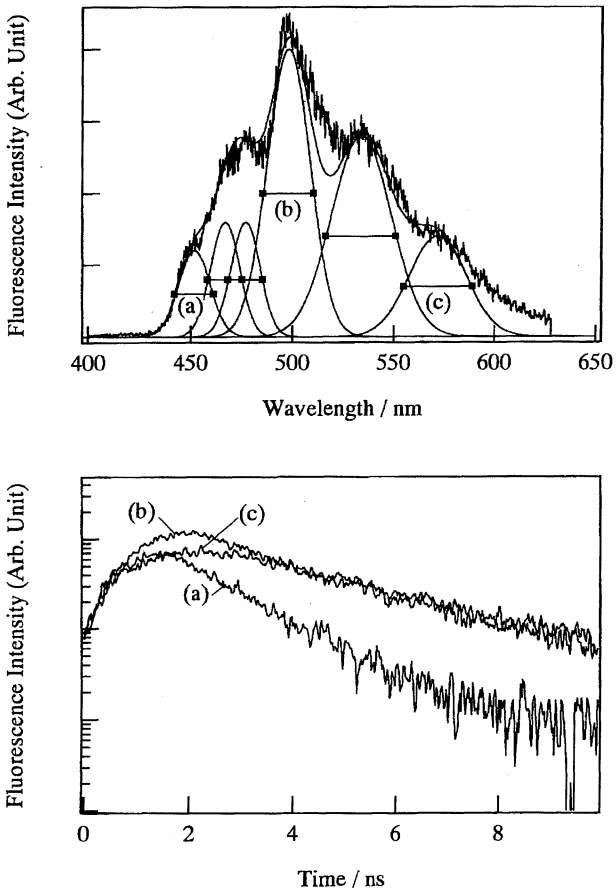


Fig. 2. Top: Transient fluorescence spectrum of DSP observed at 77 K from single crystal. The horizontal bars indicate bendwidths at which each of the decay profiles in the bottom were recorded; solid lines the Gaussian functions used for tentative deconvolution analysis. Bottom: The decay profiles observed at (a) (452±10) nm, (b) (493±8) nm, and (c) (572±17) nm.

Table 1. Fluorescence Lifetime of DSP at 77 K Determined by Photon-Counting Method[a)]

| Solution | | Single crystal | | $\gamma$-Irradiated crystal | |
|---|---|---|---|---|---|
| Peak/nm | Lifetime/ns | Peak/nm | Lifetime/ns | Peak/nm | Lifetime/ns |
| MTHF | | 452±10 | 1.50±0.38 | — | |
| 435±10 | 1.40±0.03 | 467±9 | 1.79±0.91 | — | |
| 456±12 | 1.39±0.09 | 477±9 | 1.87±0.64 | — | |
| 484±16 | 1.45±0.10 | 493±8 | 2.62±0.09 | 498±13 | 2.68±0.21 |
| | | 534±18 | 2.84±0.42 | 536±18 | 2.79±0.35 |
| | | 572±17 | 3.30±0.15 | 575±19 | 3.42±0.43 |

a) Experimental error indicates $3\sigma$ ($\sigma$: standard diviation).

that of the decay of monomer component. The lifetimes of the longer components determined at 493 and 534 nm were the same within the experimental error, but the one determined at 572 nm was longer than them. The broad, complex band in the longer wavelength side of the 500 nm peak has previously been ascribed to excimers produced in the crystal by photo-excitation.[3)]

Figure 3 shows a transient fluorescence spectrum and decay profiles obtained from DSP crystal after a prolonged irradiation by $^{60}$Co $\gamma$-ray. Details of the results will be discussed in the following sections.

The findings in the present fluorescence measurements of DSP crystal are summarized as follows.

(1) The emission band observed in the wavelength range 440—500 nm is ascribed to DSP monomer because of the similar vibrational structure.

(2) The 0–0 band of the $\pi^* \leftarrow \pi$ transition is supported to exist at about 440 nm from the leading edge of the monomer emission.

(3) The monomer band is observable at 77 K even in a fresh sample. In the previous study, the band appeared after photo-aging.[10)]

(4) In the wavelength range longer than 500 nm, excimer emission bands were observed with partially overlap with the monomer band. The excimer band can be divided into three components based on the peak positions and the lifetimes, which are tentatively ascribed to dimer, trimer, and so on.

(5) The relative intensity of monomer band to excimer band changed from crystal to crystal, suggesting its relevance to the way of crystallization.

(6) A previously reported excimer band with a lifetime longer than 10 ns was not observed.[3)]

**B. Irradiation by Ionizing Radiation.** Thin single-crystals of DSP monomer were irradiated at ambient temperature by electron pulses from the electron linear accelerator. The emitted light from the crystal was monitored by a monochromator at several different wavelengths. Figure 4 shows a transient fluorescence spectrum observed immediately after electron pulse. There is a broad maximum at 500—550 nm and a shoulder at 550—600 nm; both of them are a little shifted to the longer wavelength side in comparison with the spectrum obtained by photo-illumination at 77 K. The spectrum is analyzed as being composed of a weak monomer band and relatively strong excimer band. The spectrum suggests that the excimers are formed, like

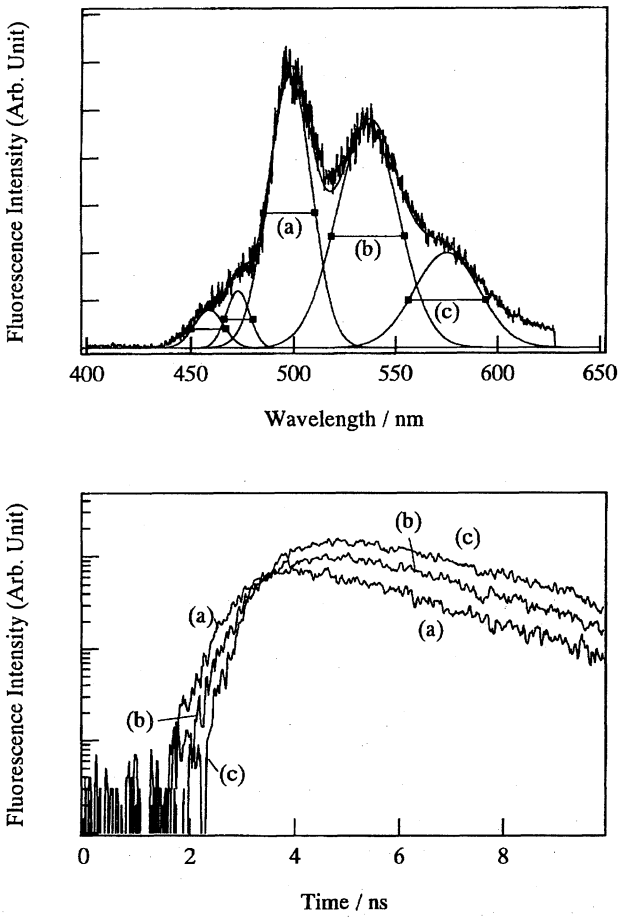


Fig. 3. Top: Transient fluorescence spectrum obtained by photon counting method from DSP crystal after a prolonged irradiation by $^{60}$Co $\gamma$-ray at 77 K. The horizontal bars indicate bandwidths at which each of the decay profiles in the bottom were recorded; solid lines indicate the Gaussian functions used for tentative deconvolution analysis. Bottom: The decay profiles in the bottom observed at (a) (498±13) nm, (b) (536±18) nm, and (c) (575±19) nm.

the photo-illuminated system, at the very end of the energy degradation processes of the ionizing radiation.

The time-profile of the emission after 10 ns electron pulse monitored at 520 nm was fairly different from the case of photo-illumination. Although the duration time of the electron pulse is much longer than the excitation laser pulse and so direct comparison of the time-profile is not possible, it is apparent from Fig. 5 that the electron-pulse induces fluores-

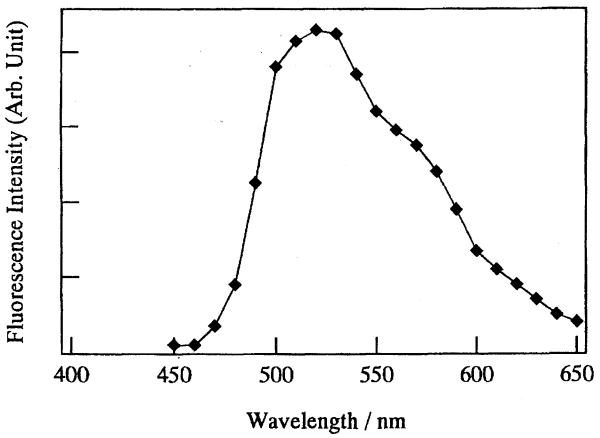


Fig. 4. Transient fluorescence spectrum of DSP microcrystals observed immediately after electron-pulse.

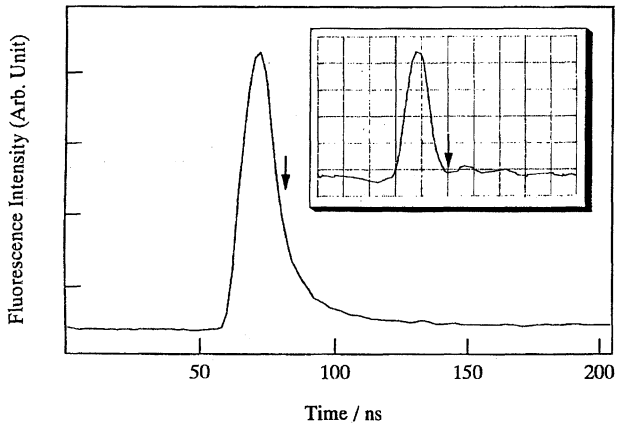


Fig. 5. Time-profile monitored at 520 nm of the emission after the irradiation of a 10 ns electron pulse. Insert shows the shape of the electron-pulse monitored by a Faraday cup. One division of the insert corresponds to 10 ns. The arrows show the end of the electron-pulse.

cence with a long-lasting tail extending over several hundred nanoseconds. Accurate analysis of the decay curve is not possible because of its highly nonexponential character, but the curve after the end of the pulse (indicated by the arrows in Fig. 5) could be divided formally into three components with the lifetimes of 13 ns, 60 ns, and $> 100$ ns. We thus confirmed the existence of the delayed fluorescence caused by the irradiation of ionizing radiation.

The occurrence of [2+2] cycloaddition reaction of DSP can be monitored by observing the concentration change of the double bond of olefin in DSP.[1] Figure 6 shows the IR absorption-intensity of the double bonds observed from the DSP crystal irradiated by $^{60}$Co $\gamma$-ray against the radiation does. The data, especially those obtained by electron-beam irradiation, were scattered, but more or less a linear decrease was observed. From this result, we can conclude that a similar cycloaddition reaction takes place in the crystal irradiated by ionizing radiation. Considering the experimental error, no difference in the effect of $\gamma$-ray and electron-beam was observed; the *G*-value for the decrease of the double bond was estimated to be 4—5 from the slope of the straight lines

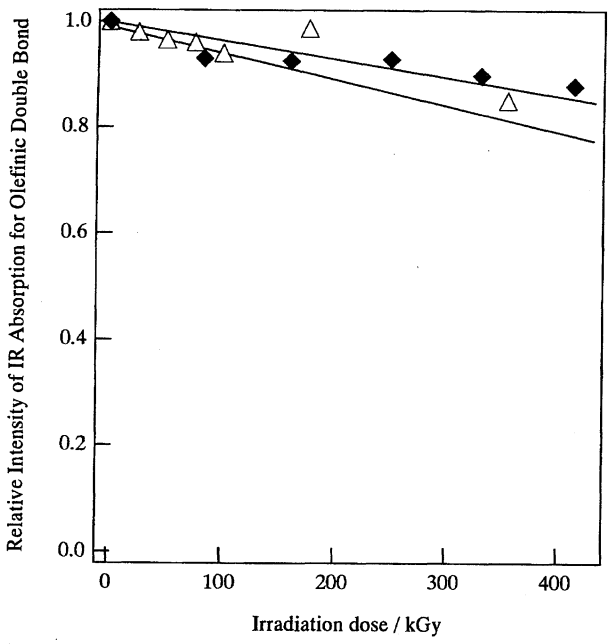


Fig. 6. Relative intensity of IR absorption for olefinic double bond in DSP crystals irradiated by (◆) $^{60}$Co $\gamma$-ray and (△) electron beams plotted against radiation does.

drawn in Fig. 6.

The fluorescence lifetimes obtained by the photon-counting method from the DPS crystal after $\gamma$-irradiation are summarized in the right-hand side column of Table 1. Although the lifetimes are similar to those obtained from the sample without $\gamma$-irradiation, the band in the range 440—480 nm is less pronounced; the band has a different origin from that of the band in the longer wavelength side.

## Discussion

An important result in this study is that the cycloaddition reaction occurs even in the DSP crystal irradiated by ionizing radiation. The observed *G*-value of 4—5 for the decrease of the double bond is remarkable; it is comparable to the *G*-value of ionization in general. Thus it becomes possible to induce the topochemical reaction deep in the crystal efficiently by use of ionizing radiation such as electron beam and $\gamma$-ray. Since the energy of ionizing radiation absorbed in the crystal is much higher, the obtained result is not surprising. Many years ago, Hasegawa and co-workers reported that the reaction was not observed in the $\gamma$-irradiated crystal.[6] We can not know the reason for this discrepancy because of lack of important details of the experiments such as irradiation does and dose rate. Very probably, the total does in that experiment was not sufficient to detect the reaction.

In the previous studies, the oligomer formation by the light of longer wavelength than 400 nm was interpreted as meaning that biexcitonic $\pi^* \leftarrow \pi$ excitation was trapped and localized by the $\pi^* \leftarrow$n transition of DSP crystal, resulting in the restricted reaction region in the crystal.[4,11] This explanation inherently assumes the homogeneous nature of the crystal free from any kinds of defect. However, even in an as-grown single crystal, the alignment of the molecule can

not be perfect and there must be sites where two or more molecules are aggregated to each other. The results obtained in the present study, as well as those by Ebeid and Bridge,[3] are reasonably explained by assuming the existence of such defects: the photon energy absorbed in the crystal is first delocalized in the form of an exciton, then localized at one of these heterogeneous sites of the crystal, and ultimately lost by radiative transitions as well as non-radiative ones.

Excimer formation in crystalline pyrene is well known;[12] where dimeric excimer of self-trapped excition type may be easily formed by a slight rotation or displacement of the adjacent molecules in the lattice. However, the crystal structure of DSP is very different from that of pyrene. The molecular axis of the DSP molecule in the lattice is tilted by as much as 60° against *a*-axis of the crystal suggesting a small overlapping of the π-orbital.[4] Actually, as already pointed out by Ebeid and Bridge,[3] the wavelength of peak excimer emission did not depend on the temperature due to the thermal motion of the pair of molecules.[3] The DSP molecules are supposed to be more tightly constrained in the lattice. In view of these points, we prefer a model in which the excimer sites pre-exist before the photo-illumination.

The peculiar reaction of the DSP crystal depending on the incident light may simply be explained in terms of the extent of the π-conjugation of the DSP molecule. When the [2+2] cycloaddition takes place in one of the double-bond pairs in the crystal, the π-conjugation through the double bond is broken. The energy of the light $\lambda > 400$ nm is not enough to excite this isolated part of the molecule in terms of π-conjugation and further reactions may not occur. But, when the oligomerized crystal is illuminated by the light $\lambda < 400$ nm, the isolated styrylpyrazine part is excited to be committed to be the [2+2] cycloaddition reaction with the other isolated styrylpyrazine part of the oligomer.

Finally, it may be interesting to compare the energy flow of ionizing radiation absorbed in the DSP crystal to that of photon. In the case of the photon, only singlet excitons are produced in the crystal. But in the case of ionizing radiation, electrons ejected from DSP molecules first move in the conduction band and then recombine with positive hole leading to the formation of triplet excitons as well. The singlet excitons thus formed should follow exactly the same processes as those in the photo-illuminated system. The triplet excitons, on the other hand, live much longer and sometimes produce singlet excitons via triplet–triplet annihilation. This may be the reason for the delayed fluorescence observed on electron pulse irradiation. In any cases, the ionizing radiation is partially consumed in forming singlet excitions (and therefore singlet excimers) which may cause the cycloaddition reaction in the crystal.

The authors express sincere thanks to Professors Tsuneki Ichikawa, Nobuhiro Ota, and Hiroshi Yoshida, Hokkaido University, for their helpful discussions. This work is supported by a Grant-in-Aid for Scientific Research No. 06453013 from the Ministry of Education, Science, Sports and Culture. This work was partly carried out under the joint research program of Research Reactor Institute, Kyoto University.

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