Heterogeneous Photochemical Reaction on Optical Length Scale in Photomechanical Molecular Crystals

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Abstract

Photomechanical molecular crystals are promising materials as photon-powered artificial actuators. To design and control the photomechanical responses, the spatiotemporal distribution of photoproducts in crystal could be a key factor in addition to molecular structures, molecular packings, illumination conditions, crystal morphology, crystal size, and so on. In this study, we have found that single crystals of 2,5-distyrylpyrazine shows a smooth photomechanical expansion, and the photochemical reaction proceeds heterogeneously on the optical length scale by observation of the changes in color, fluorescence, and birefringence. Moreover, we have performed a numerical simulation to reproduce the experimental results and revealed that both the cooperativity effect and the surface effect in crystal are essential for the heterogeneous progress of the photochemical reaction. Our results would provide a framework for analyzing the heterogeneous reaction dynamics on optical length scale in photoresponsive molecular crystals and a benchmark for future studies of photomechanical molecular crystals.
Introduction

Artificial machines composed of a molecule or molecular assembly has inspired many scientists, and they have made large efforts to design and control the mechanical movement\textsuperscript{1,2}. The molecules that change their shape in response to external stimulus can work as mechanical materials in very small regions at the molecular level\textsuperscript{3,4}. On the other hand, to construct the materials working in the macroscopic region, in general, it is necessary to utilize polymer materials\textsuperscript{5,6}. However, in many cases, since the free volume around the molecule is large in polymer materials, it is difficult for the movement of each molecule to be directly linked to the macroscopic deformation of the material. The aggregates in which molecules are regularly arranged with a small free volume is preferable. From such a point of view, crystals are one of the promising materials as the aggregates. Under such a background, photomechanical molecular crystals have been attracting much attention for application to remote controllable microactuators that can directly convert light energy to mechanical energy without any physical contacts\textsuperscript{7,8}. As important factors to determine the mode of photomechanical responses, molecular structures\textsuperscript{9}, molecular packings\textsuperscript{10}, illumination conditions\textsuperscript{11}, crystal morphologies\textsuperscript{12}, and crystal sizes\textsuperscript{13} have been investigated so far because the actuation mode is determined by the strain tensor induced by photochemical reactions\textsuperscript{14}.

In addition to those factors described above, another important factor is the spatiotemporal distribution of photoproducts in photomechanical crystals. In the previous studies on the photomechanical crystals, the structural analysis by single crystal X-ray crystallography is often used to explain the direction and magnitude of distortion associated with photochemical reactions in crystal\textsuperscript{7,15,16}. However, it is a static method by averaging the molecular events in crystal and not enough to explain the dynamic photomechanical effects. The dynamic elucidation of the
relationship between the photomechanical effects and photochemical reaction dynamics is highly required. Despite its importance, there are only a few studies linking photochemical reactions to photomechanical effects.\textsuperscript{12,17} Even in those previous studies, the photochemical reactions in crystal are generally interpreted by first-order kinetics, and it has been considered that the photochemical reactions proceed homogeneously on the irradiated crystal surface. However, the photochemical reactions in crystal often cannot be explained by simple first-order kinetics but follow the model of heterogeneous nucleation and growth reaction on molecular scale like the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model\textsuperscript{18} and Finke–Watzky (FW) model\textsuperscript{19,20}. In these cases, the photoproducts accelerate the next photochemical reaction. This kind of reaction is called as a cooperative effect.\textsuperscript{21} From such a point of view, recently, we have reported the correlation between the photomechanical response and the photochemical reaction dynamics in 9-methylanthracene (9MA) crystals by simultaneous observation of absorbance and crystal shape changes.\textsuperscript{22} In this system, the absorbance changes corresponding to the photodimerization reaction of 9MA pairs followed a sigmoidal curve due to the cooperative effect on molecular scale. However, in contrast, the photoreaction process observed by fluorescence and birefringence change under microscope indicated that the photoreaction proceeded homogeneously on optical length scale (length scale visible by optical microscope) (Fig. 1a). In other words, the photochemical reaction took place simultaneously over the entire crystal. This is due to that the scale of the heterogeneous photochemical reaction is very small compared with that of the crystal size. Here, an open question is whether the heterogeneous photochemical reaction on optical length scale proceeds during the photomechanical response under uniform photoirradiation. In other words, it is whether the photochemical reaction starts from a specific position and spreads to the entire the crystal in the photomechanical molecular crystal as shown in Fig. 1b. If the heterogeneous photochemical
reaction on optical length scale can be realized and controlled, the photomechanical responses can be induced only in a specific region in the crystal even under uniform photoirradiation. This would lead to the generation of complex photomechanical motions without a focused laser light irradiation and the development of novel next-generation devices.

In this work, we have investigated the photomechanical behavior during the photochemical reaction in 2,5-distyrylpyrazine (DSP) single crystals. DSP (Fig. 2a) is the representative molecule that undergoes the photopolymerization reaction in the crystalline phase\textsuperscript{23}. However, the photomechanical responses of DSP in single crystals have never been reported. We prepared thin DSP crystals by sublimation and observed the changes in crystal shape, absorption, fluorescence, and birefringence for the DSP crystals upon ultraviolet (UV) light irradiation. Surprisingly, in the course of study, we found that the photopolymerization reaction in single crystals clearly proceeds heterogeneously on optical length scale in contrast to conventional photomechanical molecular crystals. We performed numerical simulations to qualitatively interpret the heterogeneous photochemical reaction.

**Results and Discussion**

**Characterization and photomechanical response of DSP single crystals**

Fig. 2b–e shows an optical microphotograph of DSP single crystals prepared by sublimation, along with the crystal shape, and the molecular packing viewed from the flat face. The hexagonal top surface of the crystal was identified as the (001) and (001) faces with a space group of Pbca\textsuperscript{24}. The single crystals have the parallel edges along \textit{b}-axis and DSP molecules are aligned along the \textit{b}-axis. From the molecular packing, we can find that DSP molecules undergo the photopolymerization reaction along \textit{b}-axis.
To investigate the photomechanical behavior, the DSP single crystal was exposed to UV light. Movie S1 and Fig. 2f show the crystal shape changes of the DSP crystal upon irradiation with 365 nm light. The crystal clearly exhibited a smooth width expansion along $a$-axis. This photomechanical behavior is good accordance with the changes in the unit cell dimensions shown in Table S1. The change in the crystal width relative to the irradiation time was plotted as shown in Fig. 2g. As can be seen, it showed a sigmoidal curve, suggesting that the photopolymerization reaction proceeds heterogeneously on molecular scale. This is very similar to the case of 9MA crystals, indicating that the presence of the photoproduct accelerated the next photoreactions of neighboring molecules$^{22}$.

**Change in color and fluorescence during photochemical reaction in single crystal**

Next, to elucidate the photopolymerization reaction dynamics on optical length scale, the crystal color change under 365 nm light irradiation was observed as shown in Movie S2 and Fig. 3a. The color of DSP crystals changes from yellow to colorless upon 365 nm light irradiation since the conjugation of both the monomer and the oligomer was broken accompanying to the photopolymerization reaction$^{25}$. The crystal color was homogeneously yellow before UV irradiation and kept until after 2 min irradiation. Then, interestingly, the crystal color gradually bleached from the edge and completely turned into colorless. These results qualitatively indicate that the photopolymerization reaction of DSP single crystals has an induction period and then proceeds heterogeneously from the edges. This kind of heterogeneous photochemical reaction on optical length scale has never observed in the case of any other photomechanical crystals.

To get the spatial information about the heterogeneous reaction in more detail, the observation of the fluorescence change in the single crystal was performed. Movie S3 shows the
change in the fluorescence image of a thin DSP single crystal under irradiation at 365 nm. A fluorescence image just after irradiation with UV light is shown in Fig. 3b. The edges of the crystal parallel to the \( b \)-axis are brighter than other places due to the anisotropic waveguide effect\(^5\). When the UV light irradiation was continued, the fluorescence intensity was anisotropically attenuated from the edge of the crystal as observed by the color change of the crystal. To quantitatively investigate the fluorescence attenuation, the time change of the intensity of the yellow line segment shown in Fig. 3b was analyzed (Fig. 3c). It was possible to quantitatively confirm that the fluorescence intensity decreased from the edge of the crystal. For example, at the stage of 40 seconds after starting UV light irradiation, the fluorescence intensity in the central portion (± 5 \( \mu \)m) hardly changed, while the fluorescence intensity was clearly attenuated on the outside.

**Change in birefringence during photochemical reaction in single crystal**

Furthermore, we focused on the change in the birefringence associated with the photopolymerization reaction. The birefringence change is very sensitive to the photochemical reactions and the change is proportional to the conversion in the photochemical reactions\(^22,27,28\). Therefore, the observation of birefringence change during the photopolymerization reaction would provide precious information about the heterogeneous photochemical reaction dynamics. Then, we observed the change in interference color, which is originated from the birefringence change, of the DSP crystal during UV irradiation under crossed Nicols. As shown in Movie S4 and Fig. 4a, the interference color changed from yellow to dark from the edges to the center. Note that the final state of the crystal became dark but kept the crystallinity. In addition, this interference color change was maintained when the irradiation of the excitation light was stopped (Fig. S1). These
results indicate that the heterogeneous reaction on optical length scale is not caused by thermal effect. In other words, this phenomenon is not induced by thermal phase transition.

The change in birefringence was investigated in more detail. To prevent for the crystal to become dark like background under crossed Nicols, 546 nm light with a monochromatic filter over a white light source was used as the detection light under parallel Nicols. As shown in Movie S5 and Fig. S2, the crystal before UV irradiation was uniformly dark. When irradiated with UV light, it gradually became brighter, and became completely bright from the edges after about 210 seconds, as observed by crystal color and fluorescence. Next, the change in birefringence was investigated for the three locations shown in Fig. 4b by image analysis and was converted to the change in the conversion ratio in the crystal as shown in Fig. 4c (Supplementary Information). It was possible to confirm the induction period in which the reaction hardly progresses in the entire crystal until about 20 seconds after the irradiation with UV light. After that, the reaction proceeded uniformly in all locations until 100 seconds after the irradiation with UV light. Then, the progress of the reaction was confirmed in the order of 1, 2, and 3 (from the edge toward the center of the crystal), and the completion of the reaction was confirmed in the entire crystal after about 210 seconds. This quantitative evaluation of the reaction dynamics based on birefringence change is in good agreement with the color change of the crystal qualitatively observed in Fig. 3a.

**Numerical simulation for the heterogeneous photochemical reaction on optical length scale.**

An open question is why the photopolymerization reaction starts from the edge of the crystal even under uniform light irradiation. Previous studies suggested that the defects affect the reactivity of molecules undergoing photopolymerization reaction in crystals although the nature of the defects has not been clarified. Here, we focused on the special reactivity on the crystal
surface. It is generally known that the physical properties of the solid state differ between surface (about several nm) and bulk. The surface effect on the excitation process has also begun to be studied over the last decade, gradually revealing that surface has different properties than bulk. The results of such studies suggest that the reactivity may differ between the inside and the surface of crystals. To examine the surface effect, the reaction process of DSP crystals intentionally cut with a razor was followed by fluorescence. As shown in Movie S6 and Fig. S4, the fluorescent color changed from the original edge of the crystal and the edge artificially produced by cutting the crystal. This result suggests that the special reactivity on the crystal surface is the origin of the heterogeneous reaction on optical length scale in DSP crystals. However, the reaction propagation from the edge to the inward of the crystal cannot be explained by only the special reactivity of the crystal surface. Herein, we should remind that the photochemical reaction proceeds cooperatively in some photoreactive organic crystals. Therefore, we hypothesized that the heterogeneous photochemical reaction in DSP single crystals is caused by the cooperative effect in addition to the surface effect. To prove the hypothesis, we decided to theoretically reproduce the heterogeneous photochemical reaction. In general, a formula derived from a rate equation is used to analyze a photochemical reaction that progresses homogeneously. However, simple formulas are not enough to handle this heterogeneous photochemical reaction. Therefore, we decided to reproduce the experimental results using numerical simulation.

The details of the simulation are described in Supplementary Information. Briefly, we developed a two-dimensional model focusing on a set of molecules shown in Fig. 5a and Fig. S5, and performed over 50 simulations considering the cooperative and the surface effects to reproduce the experimental result shown in Fig. 4c (Supplementary Information). Figs. 5b-e and Movie S7 show the cross-sectional view of the progress of the photochemical reaction in DSP crystal.
obtained by the best simulation (Simulation number 13 shown in Supplementary Information). The black and white areas indicate the unreacted and the reacted areas, respectively. Note that this shows the case where the photoirradiation is performed from the bottom of the cross section. As can be seen, the reaction starts from the bottom, where the light is irradiated, and the edges of the cross section, and it progresses toward the inside. This is good accordance with the experimental observations for the change in color, fluorescence, and birefringence. Fig. 5f shows the change in the conversion ratio at a certain region of the cross section in Fig. 5b. When focusing on the orange, yellow green, green, blue, and violet lines in Fig. 5f, the conversion ratio changed uniformly up to about 30%, and then it drastically increased from the edge to the inside. These simulations are very good accordance with the experimental results shown in Fig. 4c. Furthermore, the black line shows the change in the average conversion ratio of the entire crystal, and it is sigmoidal curve. This is consistent with the result observed for the photomechanical crystal shape change, indicating that the photomechanical response of DSP single crystal is caused by the accumulation of unit cell changes induced by the heterogeneous photochemical reactions. At this time, the total number of photons required to complete the reaction was $1.04 \times 10^{19}$ photons cm$^{-2}$, which is a slightly large but acceptable value as the simulated value when compared with the experimental result ($1.3 \times 10^{18}$ photons cm$^{-2}$) shown in Figs. 4b and c. Thus, we succeeded in reproducing the experimental results by a numerical simulation considering both the cooperative effect and the surface effect.

There are novel aspects found by the numerical simulations (Supplementary Information). First, the simulation results do not depend on the number of molecules in a set. Therefore, not only two-dimensional model focusing on a set of several molecules is sufficient to reproduce the experimental results, but also the obtained results can be extended and interpreted at the molecular level. Next remarkable finding is that the heterogeneous reaction could be reproduced only if we
assumed that the cooperative effect became prominent when the two surrounding molecules reacted. Thus, the numerical simulation developed in this work provide useful information about the reactivity at a local location in the crystal. Next, regarding the surface effect, the area affected by the surface effect is estimated to be within 10 nm. This is a reasonable value compared with the studies on the surface effect of the crystals reported previously.\textsuperscript{33,37} This result implies that the surface effect plays a key role for the heterogeneous photochemical reaction. The most interesting finding is that the heterogeneous photochemical reaction can be reproduced only when there is a huge difference (at least 5000 times) between the initial quantum yield and the quantum yield with the cooperative effect in addition to the special reactivity at the crystal surface. The large difference in the reactivity is more susceptible to the surface effect, resulting in the heterogeneous photochemical reaction from the edge of crystal. In the case of 9MA crystals, the initial quantum yield is on the order of $10^{-1}$, which is relatively large. Therefore, the heterogeneous reaction on optical length scale could not be observed for 9MA single crystals. At the present time, it is not clear what molecular crystals exhibit the heterogeneous photochemical reaction on optical length scale. However, there are several factors possibly affecting the reactivity such as type of photochemical reaction (intermolecular or intramolecular), electronic state of the molecules, molecular packings, and so on. Actually, even in the case of DSP crystal, the heterogeneous reaction from the edges along $b$-axis seems faster than the other crystal edges. Our future work includes the investigation of other photomechanical molecular crystals focusing on those factors.

**Conclusions**

The heterogeneous photochemical reaction on optical length scale during the photomechanical behavior was newly found for DSP single crystal, in contrast to the fact that the
homogeneous photochemical reaction is usually observed in molecular crystals. DSP crystals showed the smooth expansion by UV irradiation. The observation of the change in color, fluorescence, and birefringence demonstrated that the heterogeneous reaction proceeds from the edge of the crystal and spreads throughout the crystal. The numerical simulation based on the two-dimensional model focusing on a set of molecules, which was developed in this work, was performed to reproduce the experimental results. We found that the cooperative effect considering surrounding molecules and the surface effect play key roles for the heterogeneous photochemical reaction. Especially, it is found that the large difference in the quantum yield without/with the cooperative effect is necessary to undergo the heterogeneous photochemical reaction on optical length scale in molecular crystals. Our results would pave a way to analyze the heterogeneous reaction dynamics in photoresponsive molecular crystal and provide a benchmark for future studies of photomechanical molecular crystals.
Fig. 1 Schematic representation of the progress of photochemical reaction in photomechanical molecular crystals. a, Homogeneous photochemical reaction on optical length scale observed in conventional molecular crystals. b, heterogeneous photochemical reaction on optical length scale observed in this work.
Fig. 2 Characterization and photomechanical response of DSP single crystals. a, Molecular structures of 2,5-distyrylpyrazine (DSP). b, c, Optical microphotograph of DSP single crystals prepared by sublimation. d, Ideal crystal shape estimated by X-ray crystallographic data viewed from (001) face. e, Crystal packing change viewed from (001) face before and after UV irradiation. f, Dynamic shape change of a DSP single crystal upon UV irradiation. The wavelength and the power of the irradiated light are 365 nm and 3.1 mW cm$^{-2}$, respectively. g, Plots of the change in normalized width of a DSP crystal upon UV irradiation.
Fig. 3  Change in color and fluorescence during photochemical reaction in single crystal.  

a, Dynamic color change of a DSP single crystal upon UV irradiation. The wavelength and the power of the irradiated light are 365 nm and 3.1 mW cm$^{-2}$, respectively. Note that this observation was performed under parallel Nicols to emphasize the yellow color of DSP by taking advantage of the linear dichroism. The arrow indicates the direction of the polarizer and analyzer. b, Microphotograph of a DSP crystal observed under white light and dynamic fluorescent intensity changes of a DSP single crystal under excitation with 365 nm light (14 mW cm$^{-2}$). The images were observed by using a long-pass filter ($\lambda >$ 500 nm). c, Change in fluorescent intensity at the yellow line segment shown in (b) relative to the UV irradiation time.
Fig. 4 Change in birefringence during photochemical reaction in single crystal. a, Dynamic interference color change originated from the birefringence change of a DSP single crystal under crossed Nicols upon 365 nm light irradiation (6.0 mW cm⁻²). The dashed white line indicates the shape of the crystal. b, Optical microphotograph of a DSP single crystal observed under 546 nm light with a monochromatic filter over a white light source under parallel Nicols. The arrow shows the direction of the polarizer and analyzer. The different positions from the edge of the crystal to the center are marked as 1, 2, and 3. c, The conversion ratio relative to the irradiation time with 365 nm light (4.0 mW cm⁻²) at each position.
Fig. 5 Numerical simulation for the heterogeneous photochemical reaction on optical length scale. a, Extraction of a cross section from DSP single crystal for the simulation. b-e, Cross-sectional view of the progress of photochemical reaction in DSP crystal reproduced by the numerical simulation using the parameters of Simulation number 13. The values of $N_{\text{Loops}}$ are $15 \times 10^5$, $30 \times 10^5$, $45 \times 10^5$, and $60 \times 10^5$ for b-e, respectively. f, Change in the conversion ratio of DSP crystal relative to the value of $N_{\text{Loops}}$ reproduced by the numerical simulation using the parameters of Simulation number 13. The solid lines indicate the change in the average conversion ratio at a certain region in (b).
Graphical abstract

Photochemical reaction proceeds heterogeneously from the edges of crystal.
Method

Materials.

2,5-Distyrylpyrazine (DSP) was synthesized according to the procedures reported previously\textsuperscript{38}. Micrometer-size single crystals were prepared by sublimating the powder crystals to the glass slide at 160 °C for 3 hours.

Microscopic observation of crystals.

Optical microphotographs of DSP crystals were recorded using a Nikon ECLIPSE E600POL polarizing optical microscope equipped with a video camera system. UV light irradiation to the crystals was carried out using a super high-pressure mercury lamp (100 W; UV-1A filter (365 nm light excitation) attached to the polarizing optical microscope. The irradiation power of the incident light was measured by using a using a Neoark PM-335A power meter. The change in the fluorescence intensity was analyzed by using Image J software.

Numerical simulation.

For quantitative analysis of the heterogeneous photochemical reaction on optical length scale in DSP crystals, numerical simulation was performed with a home-built program written in Igor Pro ver. 8.0.4.2. The details are described in the Supplementary Information.

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Acknowledgements
This work was supported by JSPS KAKENHI Grant Numbers 20J20030 (K.M.), 21K14603 (D.K.), 21H01888, 21H05395 (H.S.), 21KK0092 (S.I.), 21H01889, 21K18934 (H.M.), 21H02016 (S.K.).

Author contributions
K.M., D.K. and S.K. conceived the research. K.M. synthesized the compound and carried out the experiments. K.M., D.K., and H.S. developed and performed the numerical simulation program. H.M. and S.I. provided the physicochemical insights on the research. The draft of manuscript was written by K.M. and D.K. All authors discussed the results and commented on the manuscript at all stages.

Competing interests
The authors declare no competing financial interest.
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