

Relationship between Cooperative Photodimerization Reaction Process and Size Change of 9-Methylantracene Single Crystal

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It is important to understand the mechanism of the photomechanical effect in photoreactive organic crystals based on photoreaction kinetics. In most cases, the photochemical reaction in the crystalline phase follows kinetics similar to a photochemical reaction in solution. However, the photoreaction of some molecules such as cinnamic acid and anthracene in the crystalline state follows the cooperative kinetics represented by the sigmoidal curve showing nucleation and growth.¹ In this study, we investigated the relationship between the cooperative photoreaction process and the photomechanical effect using a thin single crystal of 9-methylantracene (**9MA**).

9MA is a representative compound that undergoes [4+4] photodimerization in the crystalline phase. **9MA** thin crystals were prepared by the seeded-growth method.² The decay of absorption originated from monomer molecules by UV irradiation indicated the sigmoidal curve shown in Figure 1. During photodimerization, the size changes in **9MA** single crystal were observed as shown in Figure 2(a) and showed a clear sigmoidal curve having the induction period as shown in Figure 2(b). By the measurement of both the monomer absorbance decay and the crystal length change at the same time, it was revealed that the crystal shape change relative to the conversion ratio from the monomer pair to the dimer has a linear relationship. This result indicates that the sigmoidal change in the photoinduced crystal shape is induced by the additive accumulation of the internal strain due to the cooperative photodimerization reactions of **9MA** molecules.

- 1) F. Tong *et al.*, *Phys. Chem. Chem. Phys.* **2016**, 18, 31936–31945.
- 2) F. Tong *et al.*, *Angew. Chem. Int. Ed.* **2018**, 57, 7080–7084.

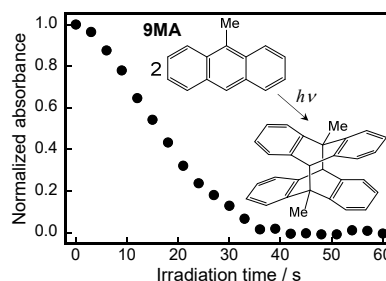


Fig. 1 Photoinduced absorbance change of monomer (irradiation wavelength: 365 nm and power: 2.4 mW cm⁻²)

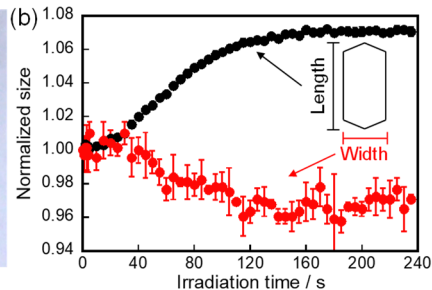
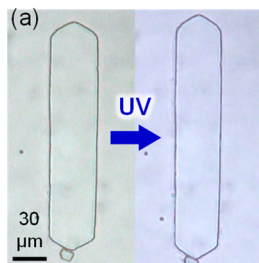


Fig. 2 (a) Photoinduced crystal shape change and (b) photoinduced crystal size change upon irradiation with 405 nm light. (irradiation power: 1.6 mW cm⁻²)