Fluorescence color changes of a mechanofluorochromic molecules during the crystallization process

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In solution crystallization, the formation of crystal nuclei is a fundamental issue in determining crystal structure, size and polymorph. However the crystal nuclei has not directly observed yet. The model of the crystal nuclei formation is roughly divided two theories; classical nucleation theory and the two-step nucleation theory. In classical nucleation theory, molecules add on one by one to extend the crystal lattice and form an embryonic nucleus in a one-step process. The classical model for crystallization visualizes the formation of a metastable crystalline nucleus that reaches a critical size through density fluctuations and grows into a stable crystal. Some experimental and computational results, however, cannot be considered based only on classical nucleation theory. Recently, the two-step nucleation model involving an intermediate such as a liquid-like cluster prior to nucleation has been developed to explain polymorphism appearance for non-photochemical laser-induced crystallization, and has been shown to be of more general validity.[1] It is postulated that liquid-like clusters originate from disordered liquid or amorphous metastable clusters.

We have focused on the fluorescence detection for the molecular aggregation or crystal formation process. In principle, fluorescence spectroscopy can be used to probe the progress of molecular assembly on the scale of just a few molecules or that of a bulk process. The fluorescence spectra are sensitive to molecular environment and aggregation state. We previously investigated the fluorescence spectral changes of a cyanostilbene derivative displaying aggregation-induced emission during evaporation or re-precipitated liquid.[2, 3] It provides information about molecular assembly and the nucleation and growth of crystals of fluorescent organic molecules from the viewpoint of the sequence of molecular species appearing the aggregations. In this paper, we reports the direct visualization of the two-step nucleation model for crystallization of a dibenzoylmethane boron complex which has mechanofluorochromic properties during the solvent evaporation probed by fluorescence changes.[4]

We measured the fluorescence changes of 4,4′-di-*tert*-butyldibenzoylmethanatoboron difluoride (BF_2DBMb) during evaporative crystallization from solution to detect the molecular assembly process. Figure 1 shows fluorescence images obtained during solvent evaporation from a droplet of 3.1×10^{-2} mol·dm^{-3} BF_2DBMb in 1,2-dichloroethane. Just after dropping, the fluorescence of the droplet was purple. The emission color changed to orange from the edge of the droplet. The emission of the whole droplet was orange. Solvent evaporation caused the orange emission to form a doughnut-like shape. After that, the region of purple emission shrunk from both in- and outside the droplet. Finally, most of the droplet exhibited blue emission with small remaining regions with orange emission. The evaporation of solvent from the inner region of the droplet probably originated from an analogous

mechanism to gas bubbles, which has been observed for a molecular assembly during evaporation of solvent with low vapor pressure. Orange emission is not observed even at high concentration; it was exhibited only from a supersaturated solution. This strongly suggests that the molecular state or assembly with orange emission can only exist in solution in a non-equilibrium state. The fluorescence spectra of BF_2DBMb in 1,2-dichloroethane were also measured during solvent evaporation as a function of time. The series of fluorescence spectral changes corresponds to the changes of fluorescence images.

We detected transitional emission from the amorphous state prior to crystallization, with emission color changing from purple to blue via orange during crystallization. This is the first demonstration of the directly observation of the two-step nucleation model based on fluorescence color changes (Figure 1). In this model, the intermediate state such as a liquid-like cluster has an important role in polymorphic expression, so is key to understanding the origin of crystallization. This methodology can be used to understand growth kinetics from monomer to crystal via crystal nuclei. In addition, it can also allow direct visualization of Ostwald's rule of stages during the phase change of organic solids.

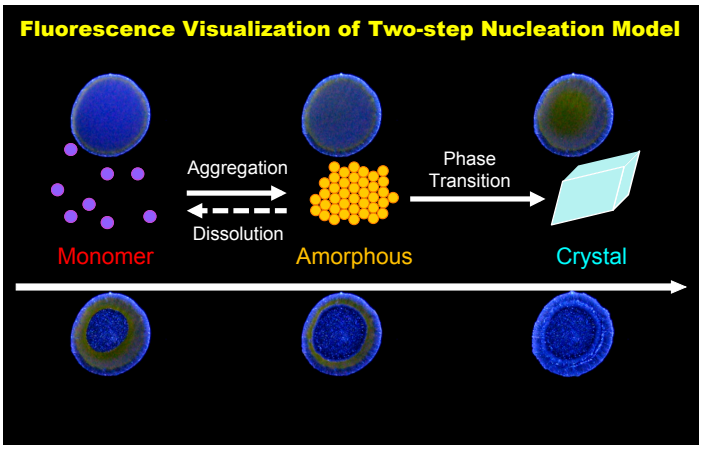

Figure 1. Fluorescence color changes of dibenzoylmethane boron complex during the solvent evaporation process and schematic representation of molecular assembling process.

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