Growth of β-Perylene Crystal

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Although perylene crystals have been known to show both dimeric (α) and monomeric (β) phases, to date only the stable α-crystals have been obtained under conventional conditions. Here, we propose a procedure for the selective growth of β-phase perylene crystals, in which a saturated toluene solution at 350 K was cooled to 298 K with a high cooling rate (-30 K/min). The sizes of β-phase crystals obtained were in the order of 100 µm.

Perylene crystals have been used as a model compound for organic electronic devices because of its high carrier mobility, availability of highly purified materials, and crystal sizes large enough to perform the various measurements.[1–3] Perylene has two crystal phases in ambient conditions: a dimeric structure (α-phase) and monomeric structure (β-phase).[4] It is known that the optical properties of perylene are sensitive to the crystals structure.[4–9] For example, an orange fluorescence is emitted by the α-phase and a green fluorescence by the β-phase. Crystals of perylene derivatives show various colors depending on the crystal phase and are used for practical pigments.[10] Therefore, perylene crystals can be used as a prototype to examine the phase dependence of the electronic and optical properties of the organic crystals. However, experimental studies have been made mainly on the stable α-phase perylene crystals. This is because the growth of the large β-phase crystal is not easy. The α-phase crystals can be grown using the conventional method such as the Bridgman method or sublimation method whereas a strategy for the preparation of the β-phase crystal has not yet been established. The β-phase crystal has been recognized as an unstable phase under ambient conditions and has been occasionally found as a minor product in the α-phase crystal formation. Although several attempts have been made to grow the β-phase crystal,[5–7,11] difficulties in the preparation of the β-phase crystal remain. In this contribution, we present a simple crystallization procedure for the selective preparation of β-phase perylene crystals from solution.

Perylene (Wako, GR-grade) was used without further purification, and toluene (Nakalai tesque, Spectral Grade) was used as a solvent. The crystallizations were performed by heating the sample solution to 350 K before cooling to room temperature (298 K) with various cooling rates. The concentration of saturated solutions was about 45 mM (350 K). After cooling down, the crystals were rinsed with toluene several times to remove small crystals.

The crystal phases were identified by their fluorescence colors and shape using a fluorescence microscope (Nikon, ECLIPSE TE2000U, excitation wavelength: 365 nm). Matsui and Iemura reported that the shape of the perylene crystals reflects the phase of the crystals with the crystal shape of α- and β-perylene being rectangular and rhomboidal shape, respectively.[11] The fluorescence spectra were measured with a homemade fluorescence spectrometer. As an excitation light source, a LED lump (365 nm, Hamamatsu, LC-L1) was used while fluorescence was detected with a photomultiplier (Hamamatsu, R374) after being dispersed by a monochromator (Acton, SP-2155).

Figure 1a shows fluorescence microscope images of the pelyrene crystals obtained with a rapid cooling (-30 K/min) of the saturated toluene solution. From a green fluorescence and a rhomboidal shape, the crystal phase can be assigned to the β-phase. The selectivity of the β-phase growth was estimated roughly to be above 90%. The sizes of crystals were typically on the order of 100 µm. The crystals were stable for at least several years in the sample tube. We also performed the crystallization of perylene with a gradual cooling (-1 K/min) of the sample solution. Figure 1b shows the fluorescence microscope image of orange rectangular pelyrene crystals obtained with the slower cooling rate. The phases of these crystals were easily assigned to the α-phase from their colors and shapes. Figure 2 shows the fluorescence spectra of the perylene crystals obtained by the gradual (orange line) and rapid cooling (green line) of the sample solution. The observed fluorescence spectra were in quantitative agreement with the reported fluorescence spectra for the α- and β-phase perylene crystals[6] at room temperature as expected. The small deviations from the reported fluorescence spectra can be explained by the effects of fluorescence reabsorption by the crystals[7] and by the small amount of the florescence from another phase of perylene crystals. The fluorescence images and spectra clearly indicated that the rapid crystallization is essential for the selective growth of the β-perylene crystals from solution. The use of the highly concentrated solution such as saturated toluene is necessary to achieve the high crystallization rate. Evidently a mixture of the α- and β-phase crystals was obtained by the rapid cooling of a diluted sample solution (20 mM).

At present the mechanism for β-perylene crystallization by rapid cooling of the saturated solution is unclear. From the present results, we tentatively propose that the first step to crystallization of perylene in toluene solution is a nucleation having the β-phase crystal structure. In the case of the gradual crystallization, the initial β-phase nucleus somehow changes into the α-phase crystal because of the preferential stability of α-phase crystals. If the initial nucleus structure is kept during the crystallization due to a more rapid cooling then the β-phase nucleuses do not have enough time for the phase transition to the α-phase. Nevertheless further studies are required to clarify the mechanism on the crystallization perylene from solution.

As can be seen in Figure 1, the perylene crystals obtained form larger aggregates. To investigate the optical and electronic properties of perylene crystals more accurately, studies on isolated crystals are required. Thus, we examined the rapid cooling

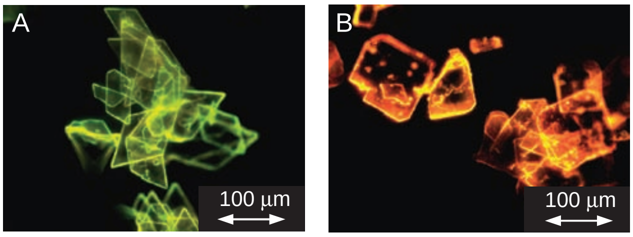

Figure 1. Fluorescence images of (a) β-phase perylene crystals obtained by rapid cooling (-30 K/min) of the sample solution and (b) α-phase perylene crystals obtained by gradual cooling (-1 K/min) of the same solution.

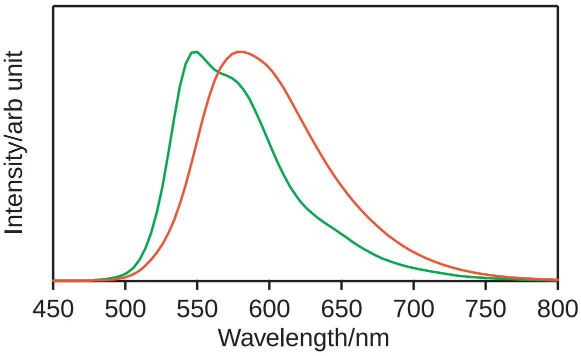

Figure 2. Fluorescence spectra of perylene crystals obtained by the gradual (orange) and the rapid (green) cooling of the sample solution, respectively.

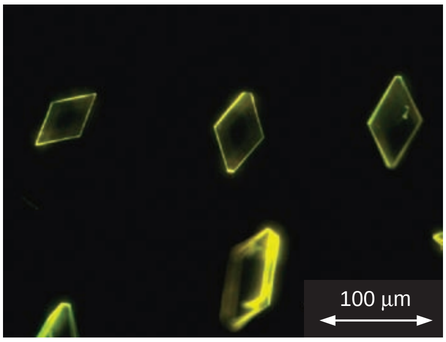

Figure 3. Fluorescence image of β-phase perylene crystals dispersed on a glass plate.

crystallization of the perylene on a glass plate. A drop of the sample solutions (350 K, 45 mM) was put on a room temperature glass plate by a pipette. The rapid cooling crystallizations were realized at the surface of the glass plate, and the crystal growth was proceeded by the evaporation of toluene. Figure 3 shows a fluorescence microscope image of the perylene crystals crystallized on a glass plate. Well-dispersed β-phase perylene crystals were obtained. Judging from the fluorescence spectra, the selectivity of the β-phase crystals was estimated to be 70%. On the other hand, the same crystallization procedure with the diluted sample solution (350 K, 20 mM) produced mainly the α-phase crystals owing to the slow crystallization rate.

In conclusion, we have shown that the β-phase perylene crystals can be grown by rapid cooling of the saturated toluene solution. With the crystals obtained by the present study, it is possible to measure the optical properties of the β-phase perylene crystals by microscope spectroscopy. Femtosecond transient absorption study on the photoexcited state of the β-phase perylene crystal with a microscope is now in progress.

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