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Hitoshi Kasai [a], Yuko Yoshikawa [a d], Toshihiro Seko [b], Shuji Okada [a], Hidetoshi Oikawa [a d], Hiro Mastuda [c], Akira Watanabe [a], Osamu Ito [a d], Hideki Toyotama [b d] & Hachiro Nakanishi [a d]

[a] Institute for Chemical Reaction Science, Tohoku University, Sendai, 980-77, Japan

[b] Tukuba Research Laboratory, Stanley Electric Co. Ltd., Tsukuba, 300-26, Japan

[c] National Institute of Materials and Chemical Research, Tsukuba, 305, Japan

[d] Research Center of Interdisciplinary Science, Tohoku University, Sendai, 980-77, Japan

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# OPTICAL PROPERTIES OF PERYLENE MICROCRYSTALS

HITOSHI KASAI[1], YUKO YOSHIKAWA[1,4], TOSHIHIRO SEKO[2], SHUJI OKADA[1], HIDETOSHI OIKAWA[1,4], HIRO MASTUDA[3], AKIRA WATANABE[1], OSAMU ITO[1,4], HIDEKI TOYOTAMA[2,4] AND HACHIRO NAKANISHI[1,4]

[1]Institute for Chemical Reaction Science, Tohoku University, Sendai 980-77, Japan
[2]Tsukuba Research Laboratory, Stanley Electric Co. Ltd., Tsukuba 300-26, Japan
[3]National Institute of Materials and Chemical Research, Tsukuba 305, Japan
[4]Research Center of Interdisciplinary Science, Tohoku University, Sendai 980-77, Japan

Abstract The optical properties of perylene microcrystals in wide range of crystal size from 50 nm to 1 μm were measured. The interesting behavior of exciton in microcrystals with less than 200nm was found. For example, with decreasing the crystal size, self-trapped exciton states in microcrystals shifted to the high energy side. Therefore, the strong luminescence from free-exciton was observed, and life time of self-trapped exciton became shorter .

## INTRODUCTION

Semiconductor microcrystals have been extensively investigated because of their enhanced third-order optical nonlinearity, which originates from a quantum confinement effect. Referring to these facts, studies on organic microcrystals seem to be interesting, too, though little have been reported so far.[1,2]

Recently, we found that a simple reprecipitation method could be applied to many kinds of π-conjugated organic compounds to obtain organic microcrystals dispersed in liquid.[3] In the case of perylene microcrystals, the size-dependent behavior was observed in their optical properties. In this report, perylene microcrystals in the range of size from about 50 nm to 1 μm were prepared by the reprecipitation method and a vapor-deposition method, and the changes of their absorption and emission spectra were investigated with crystal size. We will also discuss about the time-resolved fluorescence spectra of perylene microcrystals.

## EXPERIMENTAL

Perylene used in the reprecipitation method was purified by a zone-melt technique. For the vapor-deposition method, perylene was recrystallized in benzene, and then sublimed *in vacuo*.

The microcrystals with size less than 200 nm were prepared in water, using the reprecipitation method. By changing water temperature after the reprecipitation, perylene microcrystals with different size from about 50 to 200 nm were obtained.[4] In the case of vapor-deposition method, the microcrystals with size from 130 nm and 300 nm were obtained: The crystal sizes were controlled by changing the deposition time of perylene in this case.[5] On the other hand, the microcrystals with size from 600 nm and 1 μm were prepared, using the evaporation method in an inert atmosphere: The crystal sizes were controlled mainly by changing the inert gas pressure.[1] Those microcrystals made by any techniques could stably be dispersed in water for a long time.

The optical properties, including the time-resolved emission spectra,[6] of perylene microcrystals was measured in the state of water dispersion. The averaged size and the shape was determined by SEM and dynamic light scattering (DLS).[4] The crystal structure was evaluated by X-ray powder diffraction patterns.

## RESULTS AND DISCUSSION

The crystal structure of perylene microcrystals prepared by the reprecipitation method was confirmed to be α-type, the pattern of which was similar to that of bulk crystals, as shown in Figure 1. The crystal size was about 200 nm.

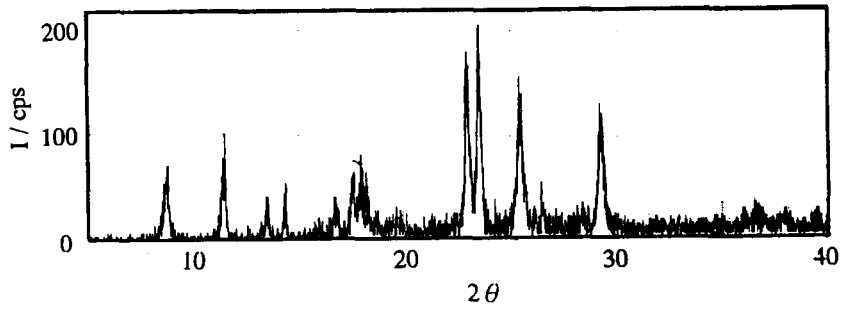


FIGURE 1 X-ray powder diffraction patterns of perylene microcrystals.

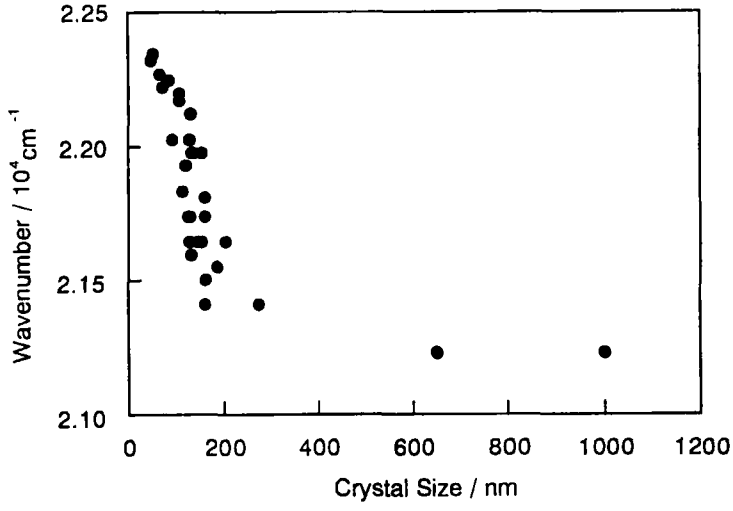


FIGURE 2 Relationship between size of microcrystals and excitonic absorption peak position.

The relationship between crystal size and absorption peak position of free exciton is shown in Figure 2. The excitonic absorption peak shifted to high energy side with decreasing crystal size. The positions at more than 200 nm in size were roughly the same as those of bulk crystals. The size effect was also confirmed in luminescence spectra. Interestingly, strong fluorescence from the free-exciton energy level, in the case of microcrystals with size less than 200 nm, which has not been detected in the bulk crystals, could be observed even at room temperature.

Luminescence with two different life times were observed at around 485 nm, as shown in Figure 3. The excitation wavelength was 250 nm. One is a luminescence from free-exciton energy level, and the life time is about 10 ps.[7] The other is from self-trapped exciton state. Figure 4 shows the change of life time of the self-trapped exciton ($\tau_{st}$), depending on crystal size. The $\tau_{st}$ became short with decreasing crystal size. The $\tau_{st}$ value for bulk crystals, which was purified by the zone-melt method, is quite long and about 40 ns.[8] These results imply that the self-trapped exciton state in microcrystals must be raised to the high energy level. Therefore, the relative difference in energy between the free exciton and the self-trapped exciton states becomes small, compared with bulk crystals. The softening of crystal lattice and the influences of surface properties are considered to be major causes of these phenomena.

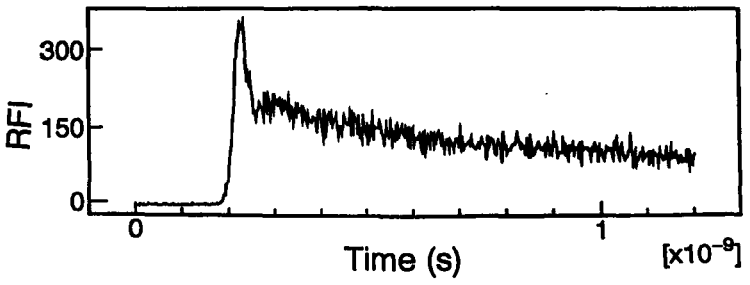


FIGURE 3 Life time profile of fluorescence of perylene microcrystals. The excitation wavelength was 250 nm.

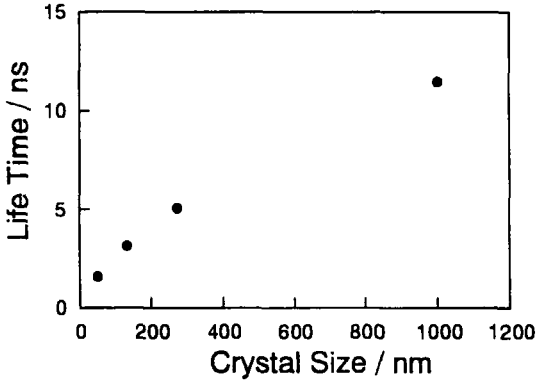


FIGURE 4 Size dependence of life time of luminescence from self-trapped exciton in perylene microcrystals.

In conclusion, the optical properties of perylene microcrystals in the wide range of crystal size 50 nm to 1 μm were measured, and the interesting behaviors of exciton could be clearly observed in microcrystals at less than 200nm in size. The preparations of microcrystals smaller than 50 nm is now in progress.

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