Crystal Size Dependence of Emission from Perylene Microcrystals

Hitoshi Kasai,[†] Hirokazu Kamatani,[†] Yuko Yoshikawa,[†,††] Shuji Okada,[†]
Hidetoshi Oikawa,[†,††] Akira Watanabe,[†] Osamu Itoh,[†,††] and Hachiro Nakanishi*[†,††]
[†]*Institute for Chemical Reaction Science, Tohoku University, Sendai 980-77*
[††]*Research Center of Interdisciplinary Science, Tohoku University, Sendai 980-77*

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In this study, we found that, in perylene microcrystals, luminescence peak position from free-exciton state was gradually shifted to high energy side with reducing the crystal size, even if the microcrystals were fabricated by different kinds of preparation techniques. The life time of luminescence from self-trapped exciton state became shorter when the crystal size reduced. The main reason was estimated to be based on the change of lattice state.

Microcrystals have been much interested in their optical and electronic properties. Studies on semiconductor and metal microcrystals have been widely reported so far, including theoretical researches.[1-5] However, there were only a few papers with regards to organic microcrystals, which were fabricated by a vapor method.[6,7] On the other hand, we have proposed that some kinds of organic microcrystals with the crystal size range from few tens nanometer to submicrometer could be prepared conveniently by the reprecipitation method, and have discussed their optical properties.[8] For example, in the case of perylene microcrystals, the excitonic absorption peaks were clearly dependent on crystal size.[9,10] However, since the range of crystal size was 50 nm to 200 nm, the observed phenomenon were not thought to be so-called a quantum confinement effect, which were often observed in semiconductor microcrystallites with crystal size below 10 nm. Matsui *et al.* reported that, the width of excitonic band of pyrene and anthracene microcrystals, which were deposited and crystallized in a polymer thin film, was narrowed, due to a quantum confinement effect.[11] Therefore, there seems to be two kinds of size effects for organic microcrystals: *i.e.*, conventional quantum confinement effect and the novel size effect which we found in one order larger size range not only for perylene microcrystals but also for polydiacetylenes, merocyanines and so on. To have deep understanding about these size effects, the optical properties of the microcrystals with more wide range of crystal sizes should be investigated in detail. In this study, different kinds of preparation techniques, *i.e.*, reprecipitation technique and vapor method, were employed to expand the crystal size range of perylene microcrystals, and the crystal size dependence of luminescence spectra have been investigated.

Perylene used in the reprecipitation method and in vapor deposition method were, respectively, purified by a zone-melt technique, and by recrystallization in benzene followed by sublimation in *vacuo*. The typical reprecipitation process was described elsewhere.[8,12] On the other hand, two kinds of vapor deposition methods were attempted to fabricate perylene microcrystals. One was in an inert gas. The perylene microcrystals with 130 nm, 300 nm, 600 nm and 1 μm in size were formed from evaporated perylene molecules at low pressure in He atmosphere. These data were used in Figure 3. The crystal size was controlled by changing the pressure of He. The other was the stratification deposition method, *i.e.*, alternating physical vapor deposition of water and sample in high-*vacuo* on a substrate at 77 K, and was used for preparing the microcrystals with less than about 300 nm in size. These data were used in Figure 1. The crystal size was controlled by changing the deposition amount.

Both dynamic light scattering (Otsuka Electronics, DLS-7000) and scanning electron microscope (Hitachi, S-900) were used to determine crystal size and shape. The UV-VIS absorption and emission spectra of perylene microcrystals dispersed in water were recorded on Shimadzu UV-240 and Hitachi F-4010 spectrometers, respectively. The time-resolved emission spectra were measured using Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S) pumped by an argon ion laser (Spectra-Physics, BeamLok 2060-10-SA) with a pulse selector (Spectra-Physics, Model 3980), a harmonic generator (GWU-23PS), and a streak camera (HAMAMATSU, C4334-01, sweep repetition rate 2 MHz). All the perylene microcrystals prepared was confirmed to be α-type by the measurement with powder X-ray diffraction.[10]

Figure 1 shows the emission spectra of perylene microcrystals with different size, which were prepared by the stratification deposition method. The excitation wavelength was 350 nm. The emission peak at 560 nm was due to the luminescence from self-trapped exciton (S-exciton). All the spectra are normalized by the peak of S-exciton. The peak around 440 nm was not shifted, and is considered to be based on monomeric luminescence. In the case of bulk crystals, Free-exciton (F-exciton) peak around 480 nm could not be observed at all at room temperature. On the other hand, in microcrystals with

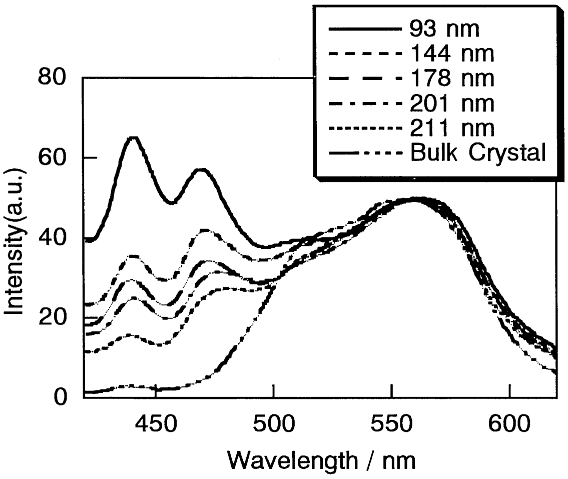

Figure 1. Emission spectra of perylene microcrystals with different size.

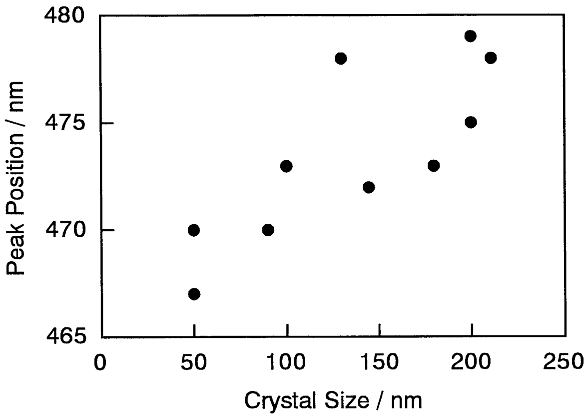

Figure 2. Relationship between the size of perylene microcrystals and the luminescence peak position of F-exciton.

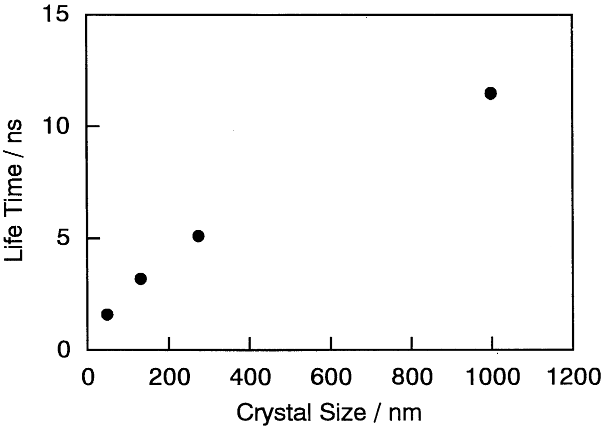

Figure 3. Relationship between crystal size and life time of emission from self-trapped exciton state

size of less than 200 nm, F-exciton peak was obviously detected. When the crystal size reduced, the F-exciton peak gradually became higher compared with S-exciton one. At the same time, the peak position of F-exciton was shifted to higher energy side. On the contrary, that of S-exciton was not changed with decreasing crystal size. In the case of samples made by reprecipitation method also showed the almost same tendency.

The relationship between the crystal size and the luminescence peak position of F-exciton is shown in Figure 2. The plot includes the data for perylene microcrystals not only by vapor method but also by reprecipitation method. In spite of different preparation, all of the data were put on one master line. Thus, we believe the dependence of these emission and/or absorption spectra published before[9] on crystal size may be common phenomena in organic microcrystals.

The relationship between the crystal size and life time of emission from S-exciton state around 500 nm was shown in Figure 3. The excitation wavelength was 350 nm. When the crystal size was small, the life time of S-exciton became short. In the case of bulk crystals, it was said that the purity and crystal perfection influence the life time of S-exciton. The longest life time of S-exciton in bulk crystal was reported to be about 70 ns. In this study the purification method was the same for all samples. Therefore, it is considered that the reduction of life time of S-exciton with reducing size is due to the change of lattice state.

It has already been reported[9] that the potential curve in perylene microcrystals was different from that in bulk crystals. In the case of microcrystals, the potential barrier from S-exciton to F-exciton states becomes lower, and the difference between potential bottoms for F-exciton and S-exciton states becomes smaller with decreasing crystal size. Therefore, population of F-exciton state becomes not negligible, leading to the emission from F-exciton state even at room temperature. This causes faster disappearance of S-exciton state, *i.e.* shorter S-exciton life time, in smaller size of microcrystals. This consideration also supported by the experimental result that the relative luminescence intensity of S-exciton to F-exciton became small with decreasing crystal size.

In our previous paper on the size-dependent excitonic absorption shift of perylene microcrystals, we estimated that the shift is not due to the surface part of crystallite lattice, but to the whole of lattice, because not two but single absorption peak appears and takes place size-dependent shift. It is very much likely that the S-exciton formation also depends on the lattice conditions. The difference in crystalline lattice, *e.g.* loosen lattice of smaller microcrystals, may be the reason for different life time of S-exciton found in the present study.

In conclusion, we have found the crystal size dependence on perylene microcrystals not only for absorption properties but also for emission. The present optical size effect may be useful for the controlling wavelength in electroluminescence or organic photoconductor.

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