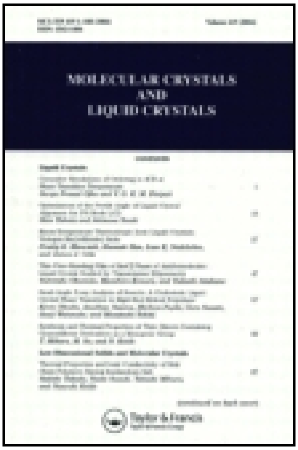

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Near-Field Fluorescence Microspectroscopy of Tetracene Microcrystals

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A near-field microspectroscopy system was developed for fluorescence analyses of tetracene microcrystals. Topographies, fluorescence images, and spectra of microcrystals with size of sub μm ~ a few μm were measured with ~100 nm spatial resolution. The relative intensities of two emission bands of the fluorescence spectra were shown to be different between individual microcrystals. The dependence of fluorescence spectra upon crystal thickness was found by correlating topographies with fluorescence images, and discussed in view of the distribution of defect-sites at the surfaces and interfaces.

Keywords near-field scanning optical microscope; fluorescence spectroscopy; tetracene; microcrystal

INTRODUCTION

Micrometer-sized organic crystals and aggregates have received much attention as attractive samples to be analyzed with near-field scanning optical microscopy (NSOM).[1-2] Microdomains, exciton-trapping defect-sites, inhomogeneous aggregation, and other mesoscopic irregularities are closely related to characteristic properties of microcrystals different from those of bulk materials.[3-4] Unfortunately, the spatial resolution of conventional confocal microscopes is not high enough to observe these nanometer inhomogeneities. Only spatially averaged information on the heterogeneously proceeding reactions are provided by the far-field microspectroscopy. For direct measurements of photophysical and photochemical phenomena occurring at each nanometer spot within the microcrystals and microaggregates, NSOM combined with high-performance spectroscopy techniques is indispensable.

In this paper, we focus our attention to microcrystals of tetracene. Bulk crystals of tetracene have been well investigated by conventional spectroscopy,[5-6] which established that three distinct peaks appeared in the emission spectrum, and these were ascribed to a free exciton band, emission from excitons trapped in defects, and a self-trapped-exciton band. However, spectroscopic works conducted from viewpoints of inhomogeneities in the microcrystal and/or size dependencies of the properties are limited. Arnold et al. dealt tetracene crystals doped with guest molecules, which demonstrated that triplet-exciton fusion producing singlet excitons can be enhanced with reducing sizes of crystalline domains in which triplet excitons move freely.[7] However, their experiments were based on spatially-unresolved spectroscopy, so that the ensemble average of exciton dynamic processes occurring in individual domains was discussed. Thus, we have examined fluorescence NSOM images and spectra of tetracene microcrystals, as well as their topographies, to elucidate inhomogeneous structures of emissive species within the microcrystals.

EXPERIMENTAL

The details of our near-field microspectroscopy system will be reported separately.[8] For preparing a probe tip, an optical-fiber was tapered by a fiber puller (Sutter Model P2000) and aluminum-coated by an evaporator with a fiber-rotating mechanism in a high-vacuum chamber. The aperture size of the probe was ~100 nm. A NSOM (Seiko SPI-300) was used, where the tip-sample distance regulation was modified from tapping to shear-force feedback modes. The separation distance was controlled to be ~10 nm by monitoring the differential signal of a 805-nm diode laser. The 488-nm line from an argon ion laser (Coherent INNOVA 300, <1 mW) was used as an excitation light source, that was coupled to the cleaved end of the optical fiber. Emission from a sample was collected by an objective lens (40×, 0.65 N.A., Olympus ACH40X) and introduced to a 520-nm long-pass filter for preventing the excitation light. For fluorescence imaging the emission passing through the filter was detected by a microchannel-plate photomultiplier (Hamamatsu Photonics R2809U-11) with a 40-nm band-pass filter centered at 550 nm. On the other hand, a fluorescence spectrum at each position was observed with a polychromator (Jasco CT-10) and a liquid-nitrogen-cooled CCD detector (Photometrics, SDS 9000).

Tetracene microcrystals were prepared with the following procedures. Tetracene (Tokyo Kasei Kogyo Co., Ltd., GR grade) was sublimed twice. One drop of dichloromethane solution of tetracene (1×10^{-4} mol/dm^3) was placed on a microscope cover glass and spread by a spin-coater at 2000 rpm. The central portion of the glass plate was covered with size of sub µm ~ tens µm microcrystals, which was confirmed by microscope pictures in transmission mode. By use of a far-field fluorescence microscope (Olympus BX50-FLA), we could observe greenish yellow emission spots from microcrystals. The sample plate was mounted on a piezo actuator of the NSOM system. All the measurements were performed at room temperature in air.

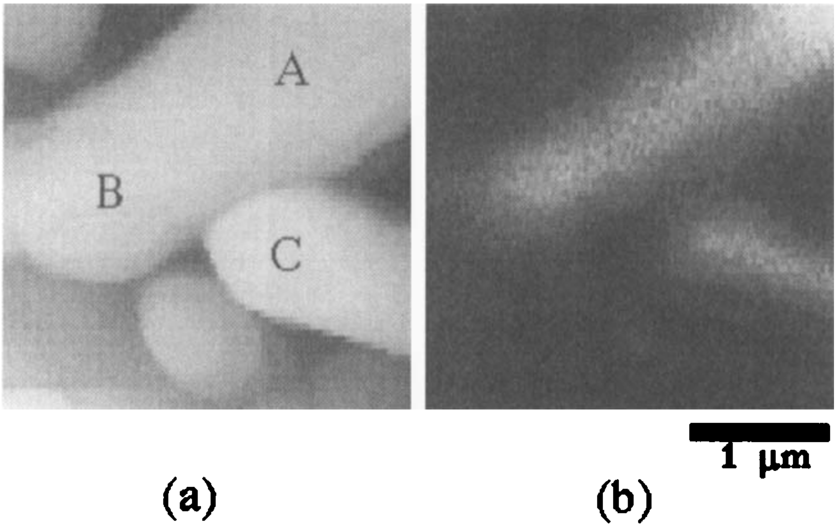

FIGURE 1 (a) Topography and (b) fluorescence images of tetracene microcrystals measured by the near-field microspectroscopy system.

RESULTS AND DISCUSSION

Most representative areas giving some aggregated microcrystals were chosen and NSOM was applied. Figure 1, one of such examples, shows topography and fluorescence images of tetracene microcrystals which were simultaneously measured by the near-field microspectroscopy system. The size of the image is 3 μm×3 μm (256 pixels, 64 lines), and the scan speed was 20 s/line. Some domain structures in the topography correspond to intensively fluorescent areas but less emissive parts are clearly observed. Even when emission is enough strong, the fluorescence spectral shape varies from position to position. Figure 2 shows fluorescence spectra measured at positions A, B, and C in Figure 1(a), where the emission intensity was normalized to the peak height at ~538 nm. A free exciton band (band 1) and an emission peak of excitons trapped in defect (band 2) appeared at ~538 and ~570 nm, respectively, which well agreed with those of bulk crystals.[5] Weak emission of a self-trapped exciton band was also observed in >590 nm region. The spectra show that the relative intensities of band 1 and band 2 are different depending on the positions. It was reported that a tetracene film deposited on a low-temperature substrate gave amorphous structures and it gave broad excimer emission band

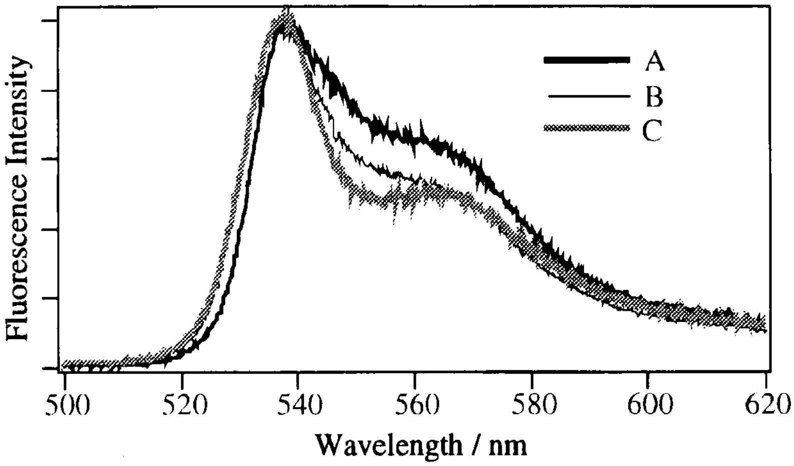

FIGURE 2 Fluorescence spectra of tetracene microcrystals measured at A, B and C in Figure 1.

near 610 nm.[9] The present results are quite different from those spectra, hence crystallinity of the microcrystals was good. While no systematic relation was obtained, we found a correlation between the ratio of two bands (band 2 / band 1) and the thickness of the microcrystals at individual positions, as shown in Figure 3. It is clearly demonstrated that the intensity of the second band relative to the first one increase as the microcrystal is thicker at the observed spot.

One possible origin of this thickness dependence is the reabsorption effect, namely, the emission of the band 1 will be attenuated by the tetracene microcrystal itself. To confirm this, we measured an absorption spectrum of the microcrystal with the known thickness by use of a conventional far-field transmission microscope with a small pinhole.[10] The absorption coefficient at 570 nm was negligibly small, while that at 538 nm was estimated to be 1200 cm^{-1}. This means that 93 % of 538-nm emission can be transmitted on a 500-nm path within the microcrystal. This value is too small to explain the result of Figure 3. Furthermore, the intensity of the shoulder (>590 nm) is almost constant for the normalized spectra of Figure 2, which also indicates that the reabsorption effect is not a dominant factor of the thickness dependence.

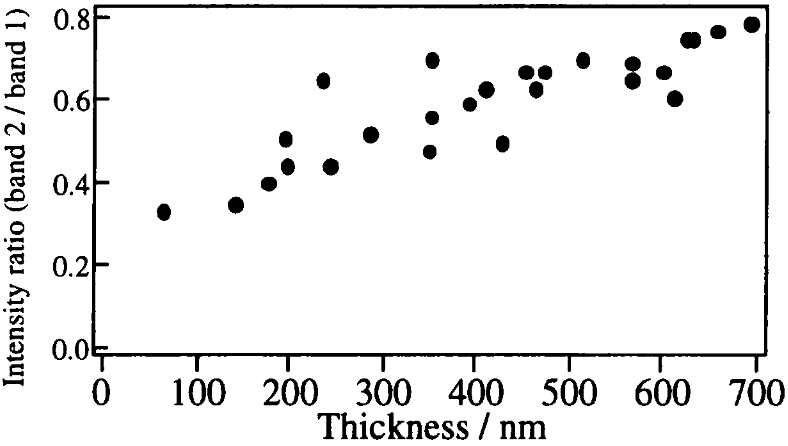

FIGURE 3 The dependence of the relative intensities of the band 2 to band 1 on crystal thickness.

Another explanation for the spectral change is inhomogeneity of the microcrystal. Surface and interface layers of microcrystals will have characteristic structures different from bulk crystals, and will provide different environments for emissive species. The contribution of the surface/interface layers will be increased for the thinner microcrystals. As emission of the band 2 is related to monomeric defects of tetracene crystals,[6] it is considered that the defect concentration is lower in the surface/interface layers and/or the efficiency of exciton-trap by defects is reduced in the surface/interface environments. In other words, pure crystal structure is possibly formed in the surface/interface.

CONCLUSION

Tetracene microcrystals have been analyzed by the near-field microspectroscopy system. The thickness dependence of the spectral shape was demonstrated and discussed on the basis of reabsorption and surface/interface effects. Simultaneous measurement of topographies, fluorescence images, and spectra was indispensable for the present analyses.

Acknowledgments

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