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Nonlinear Absorption Microspectroscopy of Single Perylene Nanocrystals with a Multichannel Double Lock-In Amplifier

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Nonlinear confocal absorption microspectroscopy of single nanocrystals at low temperatures was introduced in the study of perylene nanocrystals. By the stationary pump–probe method, single nanocrystals were photoexcited into metastable excited states, and difference absorption spectra due to excited-state absorption and ground-state depletion were simultaneously recorded using a multichannel lock-in amplifier. It was revealed that the free Frenkel exciton band for single perylene nanocrystals is broader in width than that for the bulk crystal at low temperatures, suggesting that the exciton band is inhomogeneously broadened even for single perylene nanocrystals.

Keywords: perylene, single nanocrystal, single nanoparticle spectroscopy, molecular crystal, low temperature, confocal microspectroscopy, organic molecule, nonlinear absorption, Frenkel exciton, self-trapped exciton

1. Introduction

In recent years, optoelectronic devices based on organic molecular crystals, such as electroluminescence devices and solar cells, have been attracting much interest. Perylene, a typical polycyclic aromatic molecule, and its derivatives are readily crystallized to form crystals of high quality and to function as a semiconductor. Therefore, they are extensively studied meant for optoelectric devices.[1,2] In addition, fundamental research on nanoscale organic molecular crystals is also stimulated because simple methods to produce organic nanocrystals have been developed such as the reprecipitation method[3,4] and others.[5,6] Such crystals show optical features different from both bulk crystals and single molecules. For example, it is reported that perylene nanocrystals show blue-shifted exciton absorption and excimer luminescence compared with bulk crystals, despite their relatively large sizes (hundreds of nanometers).[7,8]

The physical mechanism underlying such unique characteristics, however, has yet to be clarified. One of the reasons resides in the difficulty in the optical measurement of a single nanocrystal. Although it is relatively easy to measure photoluminescence spectra of single nanocrystals by confocal microscopy and using highly sensitive photodetectors,[9] it is difficult to measure absorbance spectra of single nanocrystals. Therefore, absorption spectra are usually recorded as an ensemble average, which conceals unique optical properties of individual nanocrystals behind inhomogeneously broadened spectra. The measurement of the absorbance spectra of single nanocrystals especially at low temperatures has been highly demanded for the clarification of optical properties of nanocrystals. In this paper, nonlinear absorption microspectroscopy of single organic nanocrystals is reported for the first time.

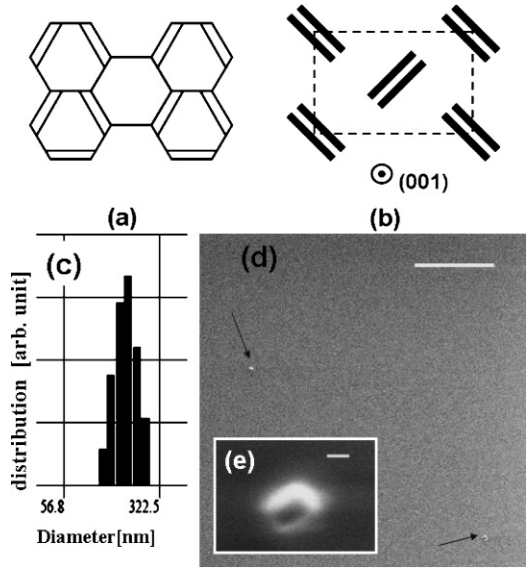

Fig. 1. (a) Perylene molecular structure. (b) Crystal structure of α-perylene observed from (001) surface. (c) Logarithmic size distribution of perylene nanocrystals prepared by the reprecipitation method measured by the DLS method. (d), (e) SEM image of perylene nanocrystals. (d) $\times$2000, (e) $\times$50000. The diameter is about 300 nm, and the number density of nanocrystals is about $1.27 \times 10^{-4}/\mu m^2$. The longer white bar corresponds to 10 μm, and the shorter white bar corresponds to 100 nm.

A perylene α-crystal has a dimer structure in a unit cell, as shown in Fig. 1. Perylene has been investigated widely from both sides of experiment and theory.[10–12] Thus perylene is an ideal molecule to examine the effect of organic molecular nanocrystals. Perylene nanocrystals are photoexcited into free Frenkel exciton states by a stationary pump light.

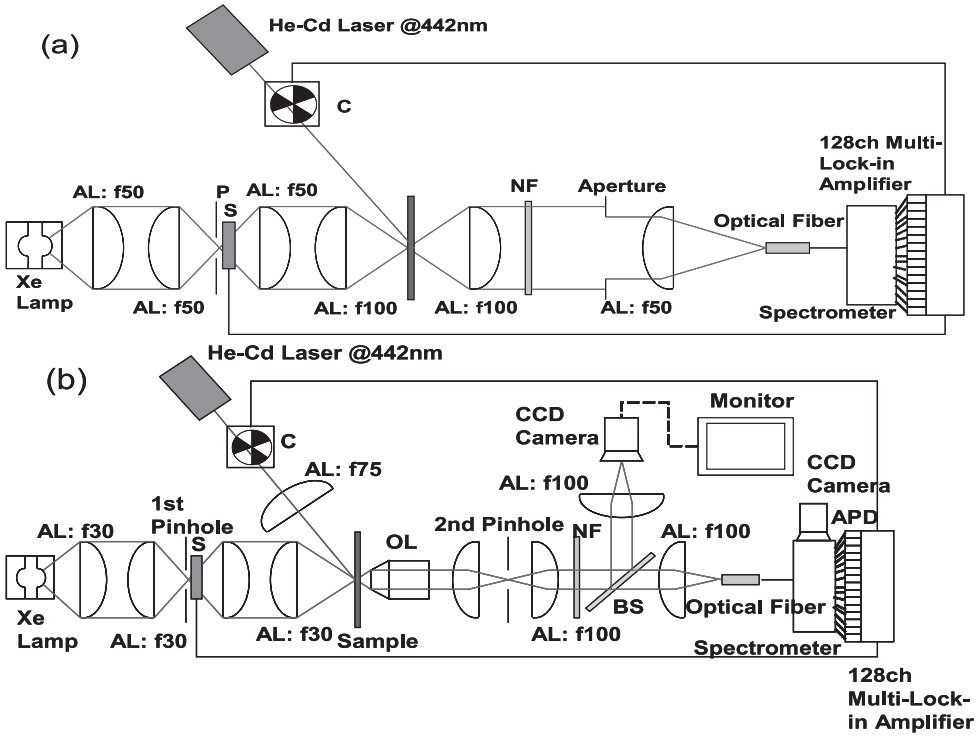

Fig. 2. Experimental setups for measurement of (a) ensemble average of perylene nanocrystals and (b) single perylene nanocrystals. A He–Cd laser and a Xe lamp were used as the pump and probe lights, respectively. The probe beam was focused through a 40 μm pinhole on the sample. AL, achromatic lens; S, shutter; P, pinhole; C, chopper; OL, objective lens; NF, notch filter; APD, avalanche photodiode; BS: beam splitter.

Electrons that are excited to free Frenkel exciton states relax into self-trapped exciton (STE) states rapidly as metastable excited states. Under this condition, we measured nonlinear absorbance spectra with a stationary probe light, as difference spectra with and without the pump, i.e., difference between the ground state and the metastable excited state. In the difference absorption spectra, excited-state absorption (ESA) as absorption increase and ground-state absorption (GSA) as absorption decrease due to ground state depletion were simultaneously recorded with a multichannel lock-in amplifier. Pump-induced luminescence spectra were separated by tandem (or double) lock-in detection.[13,14]

2. Experimental Methods

2.1 Preparation of samples

Perylene used was purified by sublimation, and α-perylene nanocrystals were formed by a reprecipitation method[3,4] as follows: 200 μl of perylene/acetone solution (1 mM) was poured into 5 ml of distilled water with and stirring was maintained for half a day. As a result, perylene nanocrystals of about 300 nm in average size and dispersion of size estimated as approximately ±10% were obtained. As shown in Fig. 1, the perylene nanocrystals were relatively large, and their number density on the sample surface was approximately 1.27×10^{-4} dots/μm^2. The average size of the nanocrystals was determined by the dynamic light scattering (DLS) method and scanning electron microscope (SEM). Water dispersed with nanocrystals was mixed with poly(vinyl alcohol) (PVA)/water solution (3.0 wt %) by 1 : 1 volume ratio, to obtain 1.5 wt % PVA solution dispersed with perylene nanocrystals. A PVA film dispersed with nanocrystals was prepared by the spin coating method on a cover glass with dispersed this solution.

2.2 Apparatus

Absorption change spectra were measured using the pump–probe setup shown in Fig. 2. We investigated nonlinear absorption spectra in an ensemble average of nanocrystals and a single perylene nanocrystal. The intensities of the probe light from a Xe lamp were 32.5 and 30 W/cm^2 at the sample. A He–Cd laser (442 nm) was used as a pump whose intensities were 9.9 and 95.5 W/cm^2 at the sample position. The sample was set in a cryostat for microspectroscopy (Oxford MicrostatHe) for cooling from 150 to 20 K with liquid helium. A sample image, magnified by the objective lens (×20, NA = 0.45, Nikon), was focused onto the 10 μm pinhole placed outside of the side port of the microscope. This enabled us to detect the light transmitted through the sample within a selected area of 500 nm in diameter. By this method we measured the nonlinear absorbance of a single nanocrystal.

The difference transmittance (ΔT) was measured using a system combining a 30 cm monochromator (Roper SP-308) and a multichannel double lock-in amplifier. A detailed description of the multichannel lock-in amplifier is described in refs. 15 and 16. Since it has 128 detection channels connected to 128 avalanche photodiodes (APDs), all wavelengths in the region of interest extending from 400 to

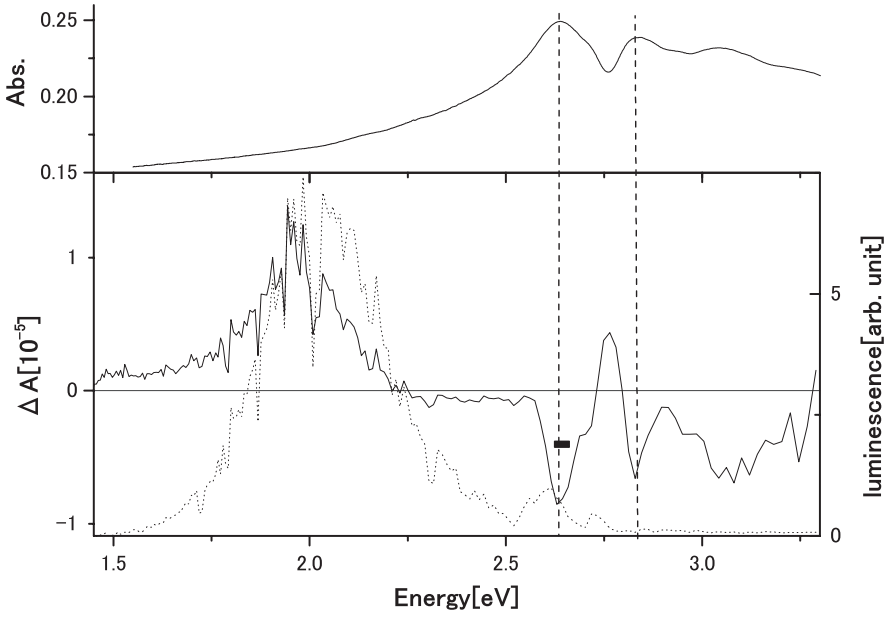

Fig. 3. GSA (top), nonlinear absorption (solid line), and photoluminecence (dashed line) spectra for the ensamble average of nanocrystals at 70 K. The solid bar shows resolution (FWHM) at approximately 2.86 eV.

550 nm were simultaneously measured. Furthermore, we employed a tandem (double)-lock-in detection scheme.[13,14] The pump and probe beams were modulated at 225 Hz by a chopper as the first reference signal and at 0.05 Hz by a shutter as the second reference signal, respectively. The time constants were 3 s for the first lock-in and 300 s for the second lock-in so that the measurement times were 9 s and 15 min for the first and second lock-ins, respectively. Four measurements were averaged.

3. Results and Discussion

Figure 3 shows the nonlinear absorption spectra for the ensamble average of nanocrystals at 70 K. GSA (absorption decrease) shows the lowest free-exciton band with a width of 100 meV owing to inhomogeneous broadening. ESA (absorption increase) shows a much broader band in the lower energy region.

Figure 4 shows the typical nonlinear absorption spectra (solid lines) and luminescence spectra (dashed lines) of single perylene nanocrystals at 77 K. They are characterized by a broad absorption increase due to an ESA at approximately 1.98 eV and a relatively sharp absorption decrease indicating the free exciton band in GSA at approximately 2.65 eV, spectral features of which varied from one nanocrystal to another. These spectra correspond to absorption from the STE state to the α^{**} state[17] and from the ground state to the free Frenkel exciton state, respectively. The α^{**} state is a high energy state of a single perylene excimer. In the upper panel, the free exciton band shows no or a slight blue shift compared with that for the perylene bulk crystal at 1.6[18] or 77 K,[19] and the lower panel shows the blue shifted absorbance by approximately 10 meV or less. The width of each free exciton band in GSA is approximately 30 meV, which is limited by wavelength resolution. Some nanocrystals show the peak in ESA immediately below the free exciton band (at 2.6 eV for the case of the lower spectrum in Fig. 4), but the others do not. This feature is observed for the first time, which was previously not detected by macrospectroscopy of the ensemble average, as shown in Fig. 3, because of inhomogeneous broadening.

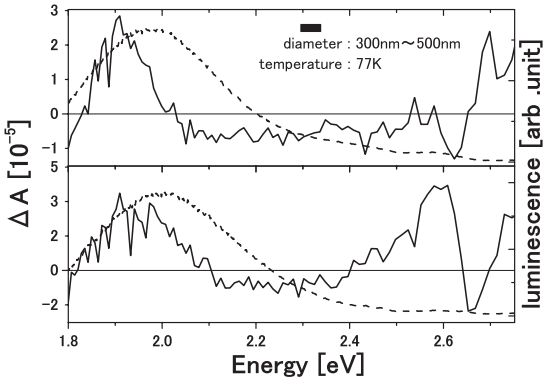

Fig. 4. Typical nonlinear absorption (solid lines) and luminescence (dashed lines) spectra of single perylene nanocrystals. The solid bar shows resolution (FWHM) at approximately 2.86 eV.

As shown in Fig. 5, we investigated the temperature dependence of absorbance from the ground state to the free Frenkel exciton state. The spectral peak is red-shifted and spectral width decreases with decreasing temperature. Although the perylene bulk crystal exhibits the same feature, the decrease in width tends to be saturated below 70 K for nanocrystals, and it is more than 20 meV even at 20 K. This is in sharp contrast to the case of single semiconductor quantum dots, which show band widths much smaller than 1 meV[20,21] at low temperatures. The width is broader than

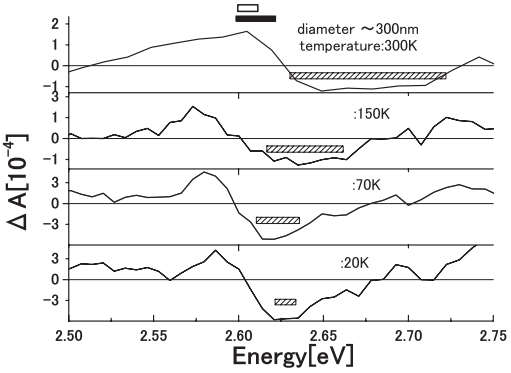

Fig. 5. Temperature dependence of nonlinear absorption for a single perylene nanocrystal. The solid bar (300 K) and the blank bar (150, 70, and 20 K) show resolution (FWHM) at approximately 2.81 eV. The striped bar shows the FWHM of the free exciton band in bulk crystal at each temperature.[19)]

that for a bulk crystal, which is around 10 meV.[19)] This suggests strongly that the free-exciton band of single perylene nanocrystals is inhomogeneously broadened substantially. In other words, free excitons are not fully delocalized coherently over the entire crystal but are localized within a limited coherence volume inside the crystal, i.e., the components of the inhomogeneous groups have different partial occupations. At present, however, this is only a hypothesis which needs further experimental support.

4. Conclusions

We obtained nonlinear absorption spectra of single perylene nanocrystals at low temperatures (from 20 to 300 K) to find characteristic spectra specific to individual nanocrystals. Moreover, we found that the spectral width of the free Frenkel exciton band is approximately two times larger than that for the bulk crystal at 20 K, suggesting that an inhomogeneous width as large as 20 meV exists even in single perylene nanocrystals.

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