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Persistent hole-burning of perylene microcrystallites dispersed in PVA

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ABSTRACT

A persistent hole-burning is observed in β-perylene microcrystallites, which were embedded in poly-vinyl alcohol. By laser light excitation at 22,535 cm^{-1} and at 10 K, the hole is found at the excitation photon energy. The mechanism of the persistent hole-burning is interpreted in terms of the resolution of microcrystallites into smaller microcrystallites. This is a novel observation of the persistent hole-burning in aromatic microcrystallites. When the specimen, which includes a hole, is annealed at high temperatures, the resolved microcrystallites restore back to the old position as had been. The β-perylene microcrystallite specimen that we have grown was as small as 1.5 nm in average diameter. They are one order smaller in number of molecules included, compared to those that have been reported on aromatic microcrystallites, anthracene for example. Due to this, we were able to observe the 0–0 transition energy, which varied according as the number of molecules involved in the microcrystallites. We also observed the 0–0 absorption (excitation) spectrum, which depends on the molecular arrays in the microcrystallites. The 0–0 transition of a single molecule in poly-vinyl alcohol matrix is anticipated to be located at 22,885 cm^{-1}.

1. Introduction

Persistent hole-burning in organic materials was first studied in 1974 by Gorokhovskii et al. [1] and Kharamov et al. [2]. They worked on organic dyes. In 1992, Basché and his colleagues [3] worked persistent hole-burning on perylene molecules in poly-ethylene, and in 2003, Kanya and Ohshima [4] investigated anthracene–ammonia system. In our study we have worked on microcrystallites (MCs hereafter) of β-perylene.

It has been known that there are two types of crystal structure α (dimer form) and β (monomer form) in bulk perylene. The α form crystal gives a broad optical absorption and broad luminescence spectra, while β form crystal gives a sharp absorption and a sharp luminescence spectra. In order to study persistent hole-burning effect, β form MC specimens are advantageous. In our microcrystallite (MC) specimen, there exists only β form. Due to this bias property, we were able to observe a persistent hole-burning successfully in perylene MCs.

Analyzing persistent hole-burning spectrum, we will discuss the mechanism of the persistent hole-burning. In addition, we will discuss the 0–0 energy, which depends on the number of molecules included in β-perylene MCs. The 0–0 energy increases about 39 cm^{-1} for one molecule reduction. We will report subsidiary structures (absorption), which depend on molecular arrays in the MC.

2. Experimental

A method to obtain perylene MCs was developed by Kasai and his colleagues [5]. They ejected perylene dissolved in ethanol into water using an injector. We have modified their method. We have dissolved purified perylene in ethanol as they did and then the solution was ejected into aqua solution of poly-vinyl alcohol (PVA hereafter). In order to obtain a thin film specimen, a drop of the perylene–ethanol–PVA–water mixture on quartz plate was dried under reduced pressure. We thus obtained thin film of crystallite β-perylene in PVA matrix. In order to learn that if MCs include exclusively β-form, we examined luminescence spectrum. The thin film specimen we fabricated for this work always included β perylene MCs over the entire specimen and did not find even a trace of α form perylene.

We were able to change the average size of MCs, which depended on the lapse time before it is casted. When it was short,

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say 3 min, the average crystallite size was smaller compared to that which was left aside longer. We used the specimen that has a smallest average size to see the quantum effect in small MCs.

We have measured luminescence spectra to inspect the crystallite form. Sharp luminescence lines are observed and are located at (0–0)–350 cm^{-1} and at (0–0)–1400 cm^{-1}. We will use these symbols throughout this report. The transition (0–0)–350 cm^{-1} implies the transition from the lowest singlet excited state to the state located 350 cm^{-1} above the ground state. Observation of such sharp line spectrum indicates that the specimen includes exclusively β-perylene. The line spectra shift according as the shift of excitation photon energy. This means that the specimen includes MCs with various sizes.

The MC absorption spectra were measured, using a monochromator, Acton Spectra Pro 300i. The light from tungsten lamp was used as the light source. The light that goes through the specimen was detected with a liquid-nitrogen-cooled CCD (Roper Scientific, LN/ccd-400EB). The measurement was done 100 times and the signal was accumulated. However, due to the scattered light the absorption spectrum was dim. We therefore used excitation spectrum instead of absorption spectrum in this report. The measurements of the excitation spectrum were carried out in a back scattering arrangement. In order to yield persistent hole-burning, a Ti: sapphire laser (Spectra Physics, Tsunami) was used for the excitation. The pulse width was 4 ps and the repetition rate was 82 MHz. All the optical measurements were done at 10 K.

3. Result and discussion

3.1. Persistent hole-burning

Fig. 1 shows three excitation spectra, which are used alternatively to absorption spectra. The spectrum with open squares is the excitation spectrum before persistent hole-burning. The spectrum with solid line is the excitation spectrum after laser irradiation at 22,535 cm^{-1}. The spectrum with solid triangles is the annealed spectrum after laser irradiation. The luminescence was monitored at (0–0)–350 cm^{-1} lines. In order to observe luminescence we applied line (0–0)–350 cm^{-1}, which shifts according to the (0–0) excitation shift.

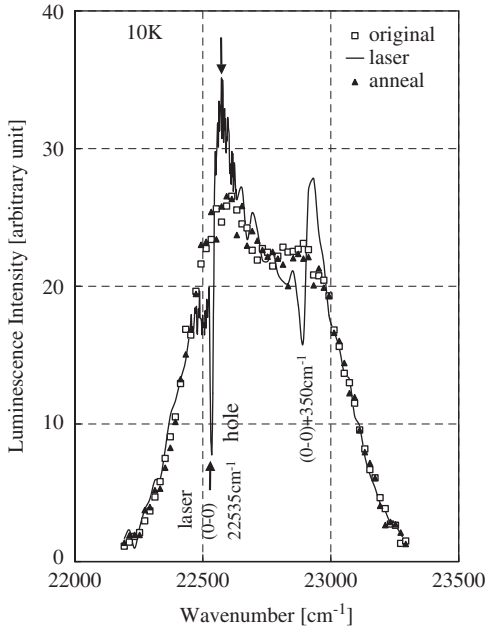

Fig. 1. The excitation spectra measured at 10 K. The spectrum given in solid line shows the persistent hole-burning at 22,535 cm^{-1}. The spectrum shown by open squares is the spectrum before laser irradiation (before persistent hole-burning), while the solid triangles show the spectrum measured after annealing applied on the specimen shown in solid line. A Xe lamp was used as a light source to measure those spectra.

We have resolved the excitation (absorption) spectrum that was measured before the laser excitation. The spectrum can be resolved into two Gaussian curves, the 0–0 absorption band and the (0–0)+350 cm^{-1} absorption band. Both of them had a half-width of about 330 cm^{-1}, which is appropriate to study persistent hole-burning. Here the symbol (0–0)+350 cm^{-1} implies the transition from the ground state to the state that is located 350 cm^{-1} above the lowest singlet state.

In the spectrum (solid line) measured after laser beam irradiation, one finds a sharp dip at 22,535 cm^{-1} whose width was 20 cm^{-1}, indicating the occurrence of the persistent hole-burning. The width of the persistent hole-burning amount is in general approximately twice of the laser light width, because optical absorption (excitation) tails of adjacent MCs are overlapped with the hole. The measurement of the laser light width is now on the way and will be found in a little while.

On the high energy side of the 0–0 dip, we observed a bump, which is indicated by a downward arrow. Since this bump is located on the high energy side of the hole (dip), the presence of this bump suggests the resolution of MCs into smaller MCs by laser irradiation.

The spectrum measured after annealing (solid triangles in Fig. 1) accords with the spectrum measured before laser excitation (open squares in Fig. 1). This fact strongly suggests that the MCs that were destructed are located close to each other so that they can combine again to the old MC by annealing.

The destructions occur in MC itself and contribute to form a bump. The molecule that was excited by laser beam loses their energy radiatively or non-radiatively. In the molecules which loose energy by non-radiative process, the lost energy becomes heat and the molecules become hot. This causes instability of MC, which leads MC to destruction.

On the low energy side of the sharp dip (hole), one finds another dip whose width is larger than the hole at 22,535 cm^{-1}. The origin of this dip is not clear at the moment.

3.2. Fill in back

A schematic diagram of persistent hole-burning is shown in Fig. 2. Top diagram Fig. 2(a) shows an MC before persistent hole-burning occurs. Bold solid curves show PVA molecules. The MC is located in a space where it is surrounded by PVA molecules. A small MC that is removed from the old MC is probably located near but separate position in a PVA matrix. Fig. 2(b) shows the diagram where a persistent hole-burning occurred. A small MC is separated from the original MC. Fig. 2(c) shows the MC after annealing. It is depicted so that it looks the same as that shown in Fig. 2(a), because in Fig. 1 the spectrum (solid triangle) of the annealed specimen after laser light excitation looks very similar to the spectrum (open square) measured before persistent hole-burning occurred. This observation shows that the holes produced were filled in back by annealing. For annealing, the specimen was held at elevated temperatures for 15 min.

3.3. Microcrystallites consisted of small number molecules

We will discuss the spectrum (solid line), which shows persistent hole-burning in Fig. 1. In Fig. 3 the spectrum that is shown is copied from Fig. 1. The vertical solid lines are drawn to demonstrate peaks and dips, which we will discuss. The numbers from 6 to 9 indicate