Luminescence of anthracene molecules in single crystal matrices

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Optical properties of single fluorene/phenanthrene crystals doped with various mole fraction of anthracene, $10^{-3}$ to a few $\%$, were investigated at 10 K. In low concentration samples, sharp structures attributed to isolated anthracene molecules were observed. Inhomogeneous width in their 0-0 energy were found to be $\sim 20 \text{ cm}^{-1}$. When concentration is higher, spectral species, which are distinctly different from the isolated molecule spectrum, were observed and their origins are discussed.
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1 Introduction  Investigations on optical properties of aromatic microcrystallites embedded in poly(methylmethacrylate) (PMMA) have revealed interesting phenomena related to size confinement of Frenkel excitons, such as size dependence of exciton band width [1] and missing of self-trapped excitons [2]. For microcrystallites consisting of small number of molecules, appreciable energy gaps in the lowest electronic excitation level (0-0) are expected between crystallites consisting of $n$ and $n+1$ molecules. However, gaps are considered to be difficult to observe with PMMA as a matrix, since 0-0 energies of crystallites of the same size would have distribution width due to inevitable local inhomogeneity. In this study, to achieve uniform environment, single crystals of fluorene and phenanthrene were chosen as matrices. Optical properties were investigated for various anthracene mole fraction samples ($10^{-5}$ to a few %) to estimate inhomogeneous width in low concentration samples and to search spectral species different from the one from isolated molecules in high concentration samples.

2 Experimental  Flaky single crystals of fluorene and phenanthrene with various concentration of anthracene were grown by a sublimation method in Ar atmosphere. Starting materials are zone refined anthracene, fluorene and phenanthrene obtained from Tokyo Kasei. Concentration of anthracene in samples was deduced from the ratio of absorption intensity of anthracene to that of fluorene/phenanthrene in cyclohexane solution. Thus determined mole fraction is indicated by A/F or A/P in the figures. For luminescence measurements, a xenon lamp dispersed by a 1m monochromator (Spex, 1000M) was used as excitation light and luminescence was measured using a monochromator (ARC, SpectraPro 300i) and a liquid nitrogen cooled CCD (Roper Scientific, LN/CCD-400EB). Absorption spectra were measured using a double monochromator (SPEX, 1403) and a photomultiplier (Hamamatsu Photonics, R955). All measurements were performed at 10 K.

3 Results  3.1 Concentration dependence  Figure 1 shows absorption and luminescence spectra of three fluorene single crystals with different anthracene concentration. In the low concentration sample, Fig. 1(a), the absorption spectrum (gray curve) consists of a sharp 0-0 peak at 25980 cm$^{-1}$ and a tail to the higher en-
ergy side. The 0-0 energy is in agreement with the value, 25975 cm\(^{-1}\), reported by Bree and Katagiri [3] within experimental accuracy. Luminescence spectrum is close to a mirror image of the absorption spectrum. Structures seen above 26300 cm\(^{-1}\) and below 25600 cm\(^{-1}\) are phonon replicas associated with intra molecule vibration of anthracence [3]. All samples with anthracence concentration less than 10\(^{-3}\) show similar spectrum. We will call this type of luminescence spectrum as type A.

In the middle concentration sample, (b), relative intensity of the sharp peaks decreases. In the luminescence spectrum, humps appear at about 100 cm\(^{-1}\) lower in energy from sharp peaks.

In the high concentration sample, (c), sharp peaks are not clearly seen but type A structure is recognized in luminescence spectrum for 1410 cm\(^{-1}\) phonon replica (0-1) at around 24600 cm\(^{-1}\). Besides type A structure, two structures with lower 0-0 energies are observed. A small band at 25900 cm\(^{-1}\) and a broad band at 25200 cm\(^{-1}\) are categorized as 0-0 bands of types B and C. In luminescence spectra for high concentration samples, mixture of types A, B and C are always observed with weight dependent on samples. Spectra of samples with relatively strong type B structure showed that the 0-0 band of type B is accompanied by phonon replicas with the same phonon energies as type A structure. For type C structure, phonon replicas are not clearly seen due to broadness of the bands, but 1410 cm\(^{-1}\) phonon band was always observed. The lower energy band at 24000 cm\(^{-1}\) in Fig. 1(c) is the one which is apparently shifted to higher energy by overlapping with types A and B structures.

Though all type B spectra observed have their 0-0 bands at 25900 cm\(^{-1}\), the 0-0 band of type C spectrum appeared in the energy region 25200 cm\(^{-1}\) to 25400 cm\(^{-1}\) depending on samples.

Figure 2 shows results for phenanthrene. In low and middle concentration samples, Figs. 2(a) and (b), spectra are analogous to fluorene. The 0-0 energy is at 26080 cm\(^{-1}\) in agreement with a reported value [4]. In a high concentration sample, Fig. 2(c), a band is observed at 200 cm\(^{-1}\) lower in energy from sharp peaks. Other lower energy bands can be attributed to phonon replicas of the band. This spectrum is similar to type B spectrum.

**3.2 Excitation energy dependence for the lowest concentration sample** Figure 3(a) shows an absorption spectrum of a low concentration fluorene sample around the 0-0 energy. Concentration of this sample, which has not been determined in the way described in Section 2, is estimated to be of the order of 10\(^{-4}\) judging from shape of absorption and luminescence spectra at 10 K. Figure 3(c) shows the lumines-
cence spectra, under excitation around the 0-0 energy (indicated by an arrow in Fig. 3(a)). We focus on the spectral shape around 25600 cm$^{-1}$, associated with phonon energy of 390 cm$^{-1}$. Wavenumber axis for luminescence (lower axis in Fig. 3) is shifted by 390 cm$^{-1}$ compared to that for absorption (upper axis) to compensate for energy loss in phonon emission process. Luminescence peaks which move with excitation energy (close circles) are attributed to resonantly excited anthracenes. Intensity of these peaks versus excitation energy (Fig. 3(b)) represents 0-0 energy distribution in the sample. It has a width (FWHM) of ~20 cm$^{-1}$ and tends to be larger for higher concentration samples. There are other peaks which appear at the same energy independent of excitation energy (open circles). Analogous dependence was observed for phenanthrene. The 0-0 energy distribution width was ~25 cm$^{-1}$.

4 Discussion

4.1 Low concentration sample Luminescence spectra from the lowest concentration (1.8x10$^{-5}$) fluorene sample we measured, was of type A. There is a little chance that two anthracene molecules occupy two adjacent sites with such low concentration. We assign type A luminescence to isolated anthracene molecules. The width of 0-0 energy distribution, 20 cm$^{-1}$, gives inhomogeneous width in the crystal. Since distribution function (Fig. 3(b)) is a smooth function of energy, inhomogeneity is attributed to slight difference in surroundings of anthracene molecules from site to site, strain, local anthracene concentration, etc.

In excitation energy dependence of luminescence spectrum, Fig. 3(c), two kinds of sharp peaks appear in the spectra. To clarify this behavior, spectra were simulated based on the following model. Absorption intensity at energy $E$ of each anthracene molecule is described by $f(E, E_0)$, where $E_0$ is the 0-0 energy, and distribution function of $E_0$ is described by $g(E_0)$. Luminescence intensity at energy $E$ under excitation at $E_{ex}$ is described as $I(E, E_{ex}) = g(E_0)f(E_{ex}, E)$. Here, an anthracene molecule is assumed to be excited with an efficiency proportional to absorption intensity at the excitation energy and to relax to the lowest excited level and emit luminescence at photon energy $E_0$. With this model, absorption spectrum of the sample $\alpha(E)$ is given by $\alpha(E) = \int g(E_0)f(E, E_0)\,dE_0$.

Absorption spectrum in Fig. 3(a) has humps in the higher energy side of the 0-0 peak. This is due to fluorene lattice phonons [3]. To represent the 0-0 band and a tail consisting of phonon bands, $f(E, E_0)$ was assumed to be a sum of four Lorentzian functions with peak energies at, $E_0$, $E_0 + 30$ cm$^{-1}$, $E_0 + 70$ cm$^{-1}$ and $E_0 + 100$ cm$^{-1}$. Gaussian distribution was assumed for $g(E_0)$. We first simulated absorption spectrum as in Fig. 3(a) to find suitable parameters, such as intensity

![Fig. 3](image-url) Absorption spectrum (gray curve) and simulated one (black curve) (a), resonance luminescence peak intensity (b) and luminescence spectra at various excitation energies for a low anthracene concentration fluorene crystal at 10 K.

![Fig. 4](image-url) Simulation of excitation energy dependence of luminescence spectra using $g(E_0)$ and $f(E_0, E)$. See text for details.
and width of each Lorentzian function and width of \( g(E_0) \), and used those parameters to simulate luminescence spectra. Adopted \( g(E_0) \) and \( f(E, E_0) \) are shown in Fig. 4(a). In Fig. 4(b), the simulated luminescence spectra are shown. When excited at a higher energy, a small peak at the excitation energy (indicated by a short vertical line) and a band at the peak energy of distribution function \( g(E_0) \) are observed (open circle). The former is due to resonantly excited anthracene molecules and the latter due to anthracene molecules with lower 0-0 energies than \( E_{ex} \), which are excited into higher energy tail. Since, tail shape is rather flat, anthracene molecules with different 0-0 energies are uniformly excited and resultant luminescence reflects \( g(E_0) \). When excitation energy is lower, fraction of the resonantly excited anthracene increases and its peak becomes the main component.

4.2 Higher concentration samples In higher concentration fluorene samples, as shown in Fig. 1(c), type B and type C structures appear. Thus, as concentration increases, two kinds of luminescence centers distinctly different from the ones responsible for type A should be formed. It is natural to consider two or more anthracene molecules located at adjacent lattice positions as luminescence center candidates for these structures.

The fact that the 0-0 energy of type B structure is always at the same energy suggests that it is from well-defined luminescence centers. With one-dimensional energy-transfer model [5] and exciton band width of 300 cm\(^{-1}\) for anthracene bulk crystals [1], the energy gap of 75 cm\(^{-1}\) is expected between the lowest excitation level of single anthracene molecule and that of two anthracene molecules. The energy difference 100 cm\(^{-1}\) between the 0-0 energies of type B and type A structures is comparable to 75 cm\(^{-1}\). Thus type B structure is tentatively assigned to two-molecule centers. As for type C, judging from variation in 0-0 energy from sample to sample and its wide width, we speculate that it is from the amorphous region with high anthracene concentration.

Parallel discussion can be made for concentration dependence in phenanthrene but for high concentration sample where type C spectrum was absent different from fluorene. Anthracene and phenanthrene are known to form solid solutions over the entire concentration range [6]. It is expected that anthracene is more uniformly distributed in phenanthrene than in fluorene, so that amorphous region with high anthracene concentration.

5 Conclusion Optical properties of single fluorene/phenanthrene crystals doped with various concentration of anthracene were investigated at 10 K. With low concentration samples, inhomogeneous width of 0-0 energy was found to be \( \sim 20 \) cm\(^{-1}\). Coexistence of resonant and non-resonant peaks in luminescence was reproduced by a simulation assuming a narrow inhomogeneous width and absorption spectrum of each anthracene molecule consisting of a sharp 0-0 peak and a tail. When concentration is higher, two spectral species distinctly different from that observed at low concentration were observed. They were assigned to two anthracene molecules situated at adjacent lattice positions and the amorphous region with high anthracene concentration.

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References