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The Effect of High Density Excitation on the Fluorescence Spectrum of the Anthracene-Tetracene Mixed Crystal

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The nanosecond time-resolved fluorescence spectra of anthracene–tetracene mixed crystals were studied under low and high density excitations. By measuring the time-resolved spectra with low density excitation, the energy-transfer process in the mixed crystal was directly observed. The spectral change due to high density excitation was observed and was explained in terms of the saturation effect on energy transfer from the host to the guest. The effect was found to be related with another nonlinear phenomenon, the bimolecular deactivation of the excited state.

INTRODUCTION

Fluorescence spectra and decay curves of aromatic molecular crystals were found to change the increasing intensity of irradiation light pulse.[1-8] In the preceding paper,[9] we studied the high density excitation effect on the fluorescence spectrum of the pure anthracene crystal and found that the relative fluorescence intensity increases in the shorter wavelength region with high density excitation. This phenomenon was explained mainly in terms of the ground state depletion.

In the present paper, the effect of high density excitation on the fluorescence spectra of anthracene–tetracene mixed crystals was studied by using a nitrogen gas laser as excitation source, special attention being paid upon the saturation effect in the energy transfer from host anthracene to guest tetracene. Furthermore, the energy transfer-process from the host to the guest was directly observed by using the laser. Although the energy-transfer process has been studied extensively for anthracene-tetracene mixed crystals,[10] no direct observation of the process has been made except for the measurement by two-photon excitation.[11]

EXPERIMENTAL

An excitation source and a detection system are the same as those described in the preceding paper.[9] Mixed crystals of anthracene and tetracene were prepared from ultra-pure anthracene[12] and tetracene.

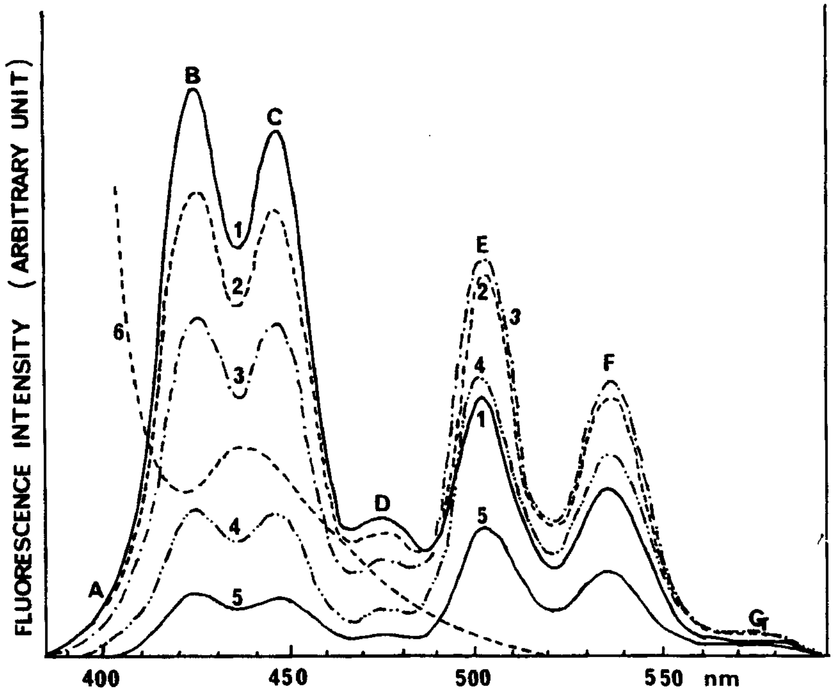

FIGURE 1 TRFS of the anthracene–tetracene mixed crystal (10^{-4} mole/mole). Curves 1, 2, 3, 4, and 5 represent the spectra 0, 6, 8, 15, and 31 ns after the anthracene fluorescence intensity becomes the highest. Curve 6 is the absorption spectrum of the evaporated thin film of anthracene–tetracene mixed crystal.

RESULTS AND DISCUSSION

The time-resolved fluorescence spectrum of anthracene-tetracene mixed crystal at low density excitation

Figure 1 shows the time-resolved fluorescence spectrum (abbreviated hereafter to TRFS) of the anthracene–tetracene mixed crystal. The anthracene emission with four vibrational bands (400, 424, 447, and 474 nm) appears in the region of 400–480 nm and that of tetracene with three vibrational bands (500, 535, and 580 nm) in the region of 480–590 nm. Here, the seven vibrational bands are referred to as bands *A*, *B*, *C*, *D*, *E*, *F*, and *G* as shown in Figure 1. The anthracene emission decreases its intensity with time, while the intensity of tetracene emission increases until 15 nsec after the pulse irradiation. Thus, we obtained a direct evidence for the occurrence of energy transfer from the excited host molecule to the guest molecule.

Figure 2 shows the time dependence of intensity ratios of vibrational bands. Here, I_B, I_C, I_E, and I_F indicate the intensities of bands *B*, *C*, *E*, and *F*, respectively. The ratios I_B/I_E, I_B/I_C decrease monotonically with time after the excitation. Since bands *B* and *F* are almost completely due to anthracene and tetracene, respectively, the ratio, I_B/I_F, is proportional to the fluorescence-intensity ratio of anthracene to tetracene.

The effect of the excitation density on the integrated fluorescence spectrum of anthracene-tetracene mixed crystal

Integrated fluorescence spectra over the duration time (abbreviated hereafter to IFS) measured with the anthracene–tetracene mixed crystal at room temperature (296°K) with excitation sources of various intensities are shown in Figure 3. The intensity of the emission is normalized with regard to that at the peak position of band *C*. As is clearly seen from this figure, the relative intensity of emission from tetracene molecules decreases rather steeply with the increase in the excitation intensity. At the same time the relative intensity of band *B* increases with the increasing intensity of the excitation light pulse.

In Figures 4 and 5, I_B/I_C, I_E/I_F, I_B/I'_C, I_F/I'_C, I'_E/I_F, and I_e/I_F are plotted against the intensity of the excitation light source I_s. Here I'_C and I'_E are the corrected fluorescence intensity[†] of bands *C* and *E*, and I_e represents the intensity at the minimum between bands *E* and *F*.

[†] In order to investigate exactly the ratio between the intensities of the vibrational bands, the correction concerning the overlap of the emissions of anthracene and tetracene was made for the intensities of bands *C* and *E*. These correction was made with the use of the TRFS data shown in Figure 2.

Among the intensity ratios shown in Figures 4 and 5, the I_F/I'_C changes to the greatest extent. This change may be tentatively due to the following facts: (i) the decrease in the quantum yield of tetracene molecule due to the temperature increase caused by high density excitation; (ii) the saturation of the energy transfer from anthracene to tetracene; (iii) emission from tetracene

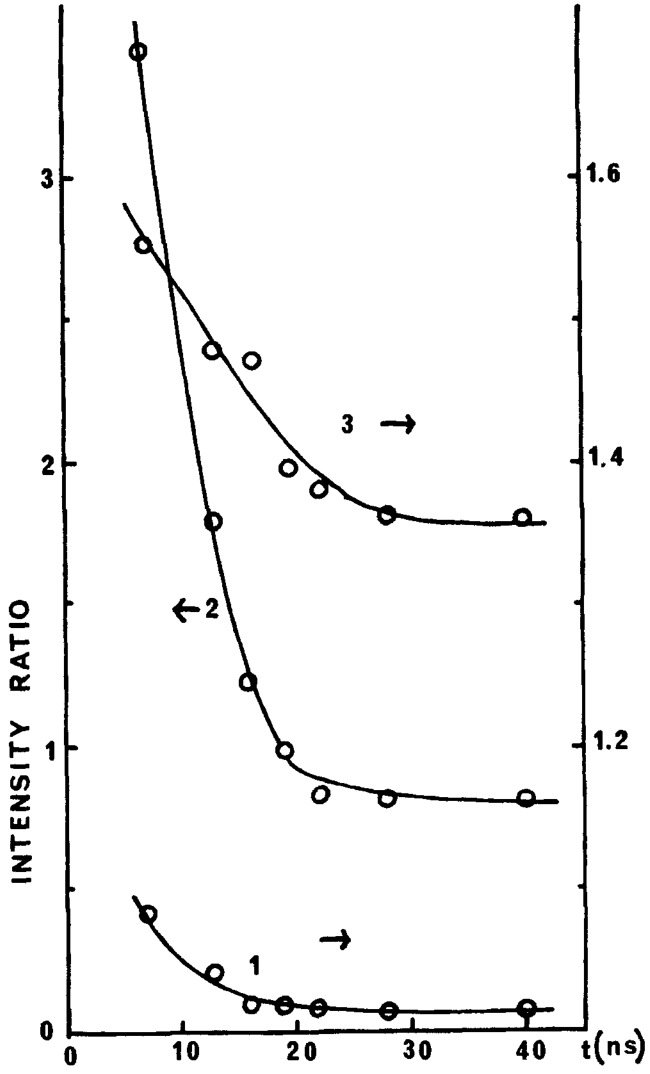

FIGURE 2 Time dependences of the fluorescence intensity ratios, I_B/I_C (curve 1), I_B/I_F (curve 2), and I_B/I_E (curve 3).

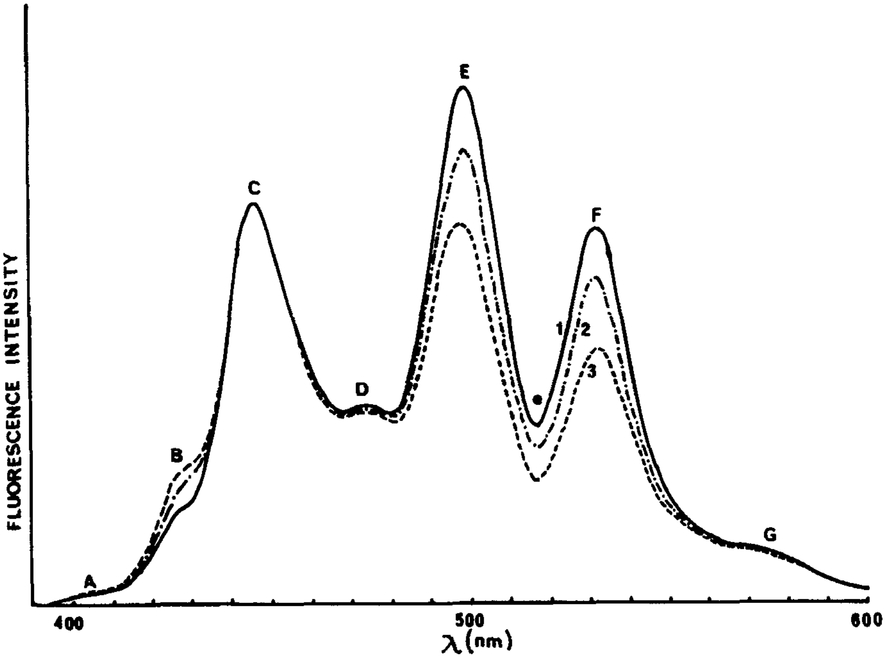

FIGURE 3 The effect on the intensity of the excitation light pulse on the IFS of the thick anthracene–tetracene mixed crystal with a tetracene concentration of 10^{-4} mole/mole. Curves 1, 2, and 3 are measured at 295°K with excitation intensities of 3.5 kW, 27 kW, and 105 kW, respectively.

molecules may be reabsorbed by excited anthracene molecules. The effects of (i) and (iii) are small for the anthracene–tetracene mixed crystal. This point will be discussed in Appendix.

The saturation effect (ii) may easily occur for the anthracene–tetracene system since the energy transfer from the host to the guest is quite efficient for this system.

The fluorescence quantum yield ratio of anthracene to tetracene may be given by the following equation:

$$Y_A/Y_T = k_1(k_4 + k_5)/k_3k_4 \ , \tag{1}$$

where Y_A and Y_T are the fluorescence quantum yields of anthracene and tetracene, respectively, and k_1, k_4, and k_5 are the rate constants for the radiative process of anthracene, the radiative and radiationless processes of tetracene, respectively. k_3 is the monomolecular rate constant of the energy transfer from anthracene to tetracene and is dependent on the concentration of tetracene. Since k_1, k_4, and k_5 may reasonably be assumed to be independent from the excitation intensity†, the increase of Y_A/Y_T with the increasing excitation density may be due to the decrease in k_3. Thus, the fluorescence intensity change with high density excitation shown in Figures 2 and 3 may be explained by the decrease in the rate constant of the energy transfer from anthracene to tetracene. This decrease is brought about by the saturation in the excitation of tetracene molecules with high density excitation.

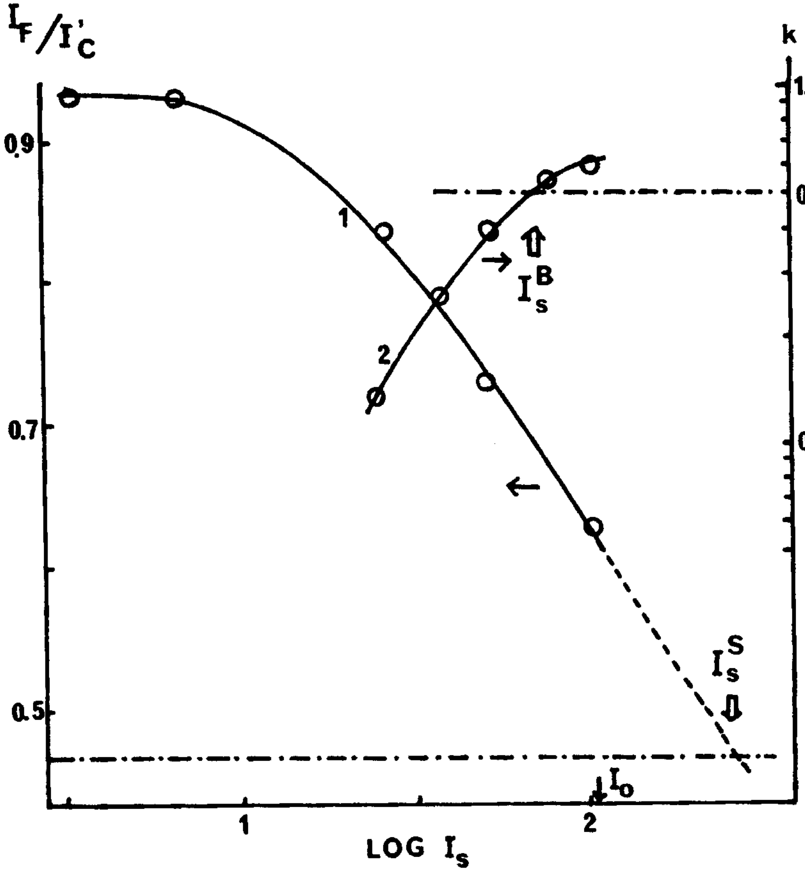

FIGURE 4 The I_s dependences of I_F/I'_C (curve 1) and k (curve 2) measured at 293°K with the anthracene crystal containing 10^{-4} mole/mole tetracene.

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† As seen in Figure 5, the spectral shape changes only slightly, except for I_B/I_C and I_E/I_F, by excitation light intensity. This shows that the induced emission or the new emission caused by the exciton-exciton interaction is very weak for anthracene and tetracene, even if it takes place. Therefore, k_1 and k_4 may be considered to be independent from the intensity of the excitation pulse.

The saturation effect may conceivably be caused by the double excitation of the acceptor tetracene molecule leading to a highly excited state. This type of excitation transfer, conceptually quite similar to the biexcitonic quenching[6,7] as is shown schematically in Figure 6. This figure shows that the saturation effect occurs by the heterogeneous bimolecular quenching.

According to the above-mentioned mechanism, the saturation of the energy acceptor fluorescence becomes conspicuous when more than a half of the total numbers of tetracene molecules encounter with anthracene excitons during their lifetimes. This condition is given by the following equation:

$$\frac{\mu'}{\lambda+\mu'} n_A \lambda\tau \frac{N_T z_n{}^T}{N_A} \geqslant \frac{1}{2} N_T \tag{2}$$

where N_A and N_T represent the numbers of anthracene and tetracene molecules in the laser irradiated volume V_{tot} in the mixed crystal, respectively, and n_A, τ, and λ are the density, lifetime with high density excitation, and migration rate of anthracene exciton, respectively. $z_n{}^T$ is the number of the sites of the anthracene molecule in the nearest neighbours of a tetracene molecule. $\mu'$is the monomolecular rate of the energy transfer from the excited anthracene to the excited tetracene molecules in the nearest neighbour. If we assume $\mu' \gg \lambda$, the condition is rewritten in the following way,

$$\frac{\tau\lambda n_A z_n{}^T}{N_A} \geqslant \frac{1}{2} \tag{3}$$

Comparison of energy transfer saturation with another nonlinear phenomenon: Bimolecular quenching

The bimolecular quenching process in pure anthracene crystal under high density excitation becomes predominant[1,5] when the density of anthracene exciton satisfies the following relation:[6,7]

$$\gamma n_A \geqslant \alpha \tag{4}$$

where α and γ are the monomolecular and bimolecular rate constants, respectively. γ is given by the following equation.[6,7]

$$\gamma = (2-A)\frac{V_o z_n^A}{V_{\text{tot}} z_u^A}\frac{\lambda\mu}{\lambda+\mu} \tag{5}$$

Here A, $z_n{}^A$, and $z_u{}^A$ are the quantum yield of the formation of the lowest excited singlet state from the higher excited singlet state, number of the nearest neighbours and the number of molecules in a unit cell of anthracene crystal with volume V_o, respectively, and μ represents the monomolecular rate of the quenching for a pair of two nearest neighbouring excitons.

Equation (4) can be rewritten in the following way.

$$(2-A)\,\frac{V_o z_n^A}{V_{\text{tot}} z_u^A}\,\frac{\lambda\mu}{\lambda+\mu}\,n_A \geqslant \alpha \qquad (6)$$

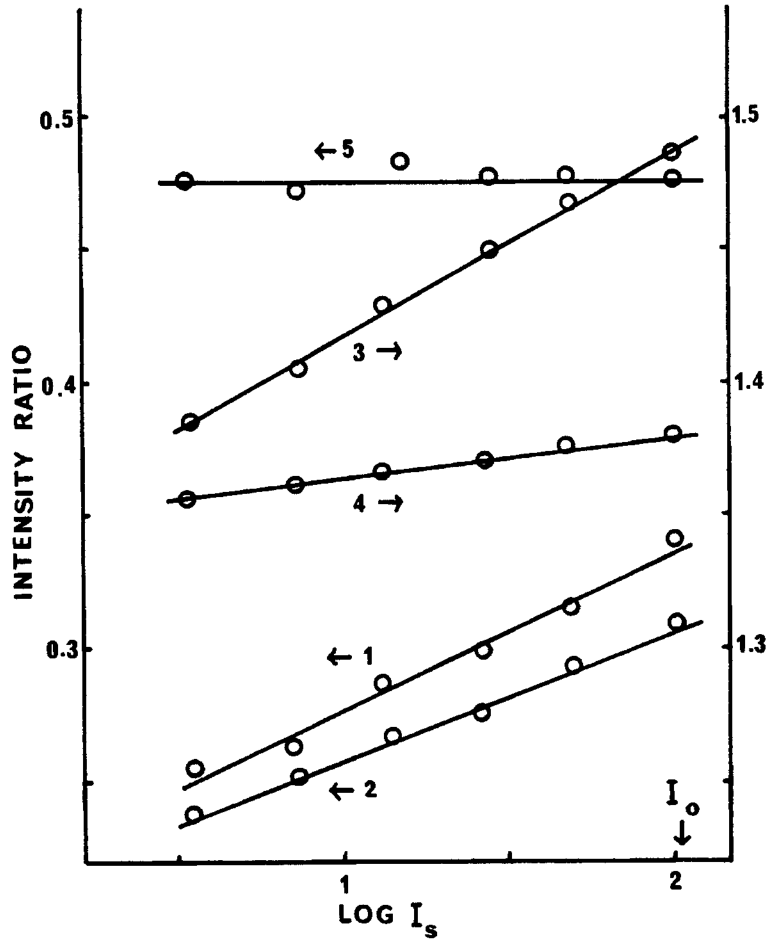

FIGURE 5 The I_s dependence of the fluorescene intensity ratios, I_B/I_C (curve 1), I_B/I'_C (curve 2) I_E/I_F (curve 3), I'_E/I_F (curve 4), and I_e/I_F (curve 5) measured at 295°K with anthracene crystal of 10^{-4} mole/mole tetracene. I_o is the maximum power of the laser used in the present study.

With the aid of the condition $\lambda \ll \mu$ satisfied for the anthracene crystal[13] and of relation (7), relation (8) can be obtained.

$$V_{\text{tot}} = N_A V_o / z_u^A \tag{7}$$

$$(2-A)\frac{\tau_o \lambda \eta_A z_n^A}{N_A} \gg 1 \tag{8}$$

Here τ_o is the lifetime of anthracene exciton with low density excitation and is given by the inverse of α. This condition is similar to that for the saturation effect given by relation (3), only with the difference between $(2-A)$ to z_n^A and $2\tau\, z_n^T$. Here we define the critical concentration for the bimolecular quenching, n_A^B, and the saturation of the energy transfer from donor to acceptor, n_A^S, as follows:

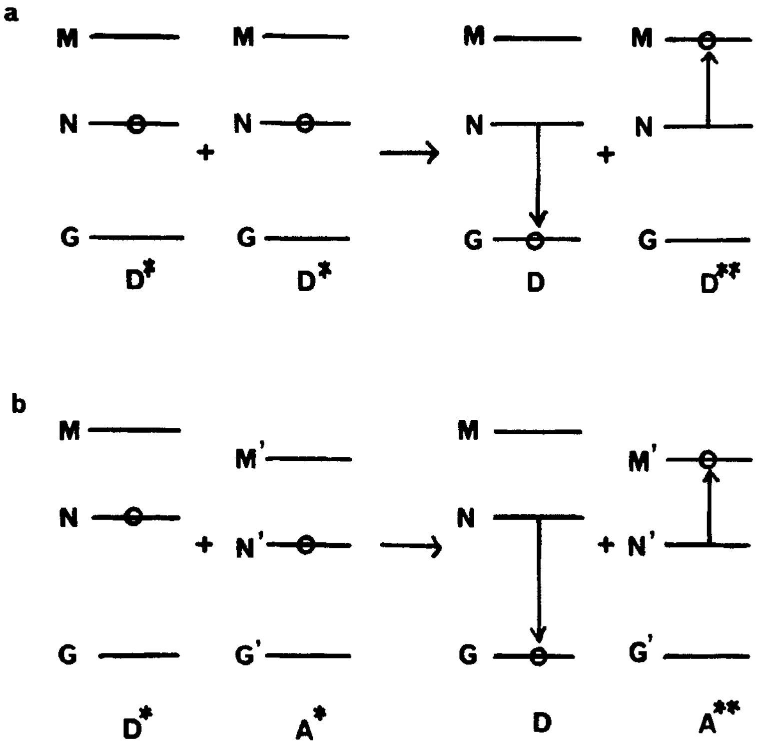

FIGURE 6 The schematic diagrams representing (a) the bimolecular quenching process and (b) the saturation process of the energy transfer. D, D^*, and D^{**} represent the energy of donor molecule in the ground state (G), in the lowest excited state (N) and in the higher excited state (M), A, A^*, and A^{**} represent the energy of acceptor molecules in the ground state (G'), in the lowest excited state (N') and in the higher excited state (M').

$$n_A{}^B = \frac{N_A}{\tau_o \lambda z_n{}^A} \frac{1}{2 - A} \tag{9}$$

$$n_A{}^S \doteq \frac{N_A}{\tau \lambda z_n{}^T} \frac{1}{2} \tag{10}$$

On the assumptions of $z_n{}^T = z_n{}^A$ and $A = 0$, $n_A{}^B/n_A{}^S = \tau/\tau_o$ was obtained.

The following equation can be obtained for the system where both monomolecular and bimolecular quenching processes take place:[1,4-8]

$$\frac{1}{n_A} = e^{\alpha t}\left(\frac{1}{n_A{}^o} + \frac{\gamma}{\alpha}\right) - \frac{\gamma}{\alpha}, \tag{11}$$

where $n_A{}^o$ is the initial value of n_A. The linear relationship between $1/n$ and $e^{\alpha t}$ is satisfied as is shown in Figure 7. Here we define k to be the intercept of the horizontal axis in the plot of $1/n_A$ versus $e^{\alpha t}$. There is a following relationship among k, $n_A{}^o$, α, and γ.

$$\frac{1}{1 - k} = \frac{n_A{}^o \gamma}{\alpha} \equiv k' \tag{12}$$

The value of k' defined in Eq. (12) is a measure for determining whether or not the initial concentration of the excited anthracene molecule, $n_A{}^o$, exceeds the critical concentration for the bimolecular quenching, $n_A{}^B$. The criterion for determining which is predominant, the monomolecular (case (a)) or bimolecular (case (b)) decay process, is represented in terms of k, k', or $n_A{}^B$ as follows:

$$\begin{array}{ll} \text{case (a)} & 0 \leqslant k \leqslant \frac{1}{2};\ k' \leqslant 1;\ n_A{}^o \leqslant n_A{}^B \\ \text{case (b)} & \frac{1}{2} \leqslant k \leqslant 1;\ k' \geqslant 1;\ n_A{}^o \geqslant n_A{}^B \end{array} \tag{13}$$

When $n_A{}^o$ is equal to $n_A{}^B$, k has the value of 1/2.

Here we examine the above-mentioned relationship, $n_A{}^B/n_A{}^S = \tau/\tau_o$. In actuality, instead of $n_A{}^B/n_A{}^S$, we take the irradiation light intensity ratio $I_s{}^B/I_s{}^S$. Here $I_s{}^B$ and $I_s{}^S$ are the intensities of the laser beam corresponding to $k = 1/2$ and $I_F/I'_C = 0.47$ as is shown in Figure 4 and may be considered to be proportional to $n_A{}^B$ and $n_A{}^S$, respectively. From the data shown in Figure 4, $I_s{}^B$ and $I_s{}^S$ are estimated to be 0.55 I_o and 2.70 I_o, respectively, I_o being the maximum intensity of the laser beam focused. Hence $I_s{}^B/I_s{}^S$ is ~0.2. This value is consistent with the τ/τ_o value which was estimated to be about 0.3†. Therefore the relationship, $n_A{}^B/n_A{}^S = \tau/\tau_o$, is found to be satisfied for the pure anthracene and anthracene–tetracene mixed crystals.

Spectral change in the fluorescence of anthracene and tetracene

Let us consider the effect of high density excitation on the spectral shape of the fluorescence from the host in the anthracene–tetracene mixed crystal. As is clearly seen in Figure 5 the fluorescence intensity ratio I_B/I'_C increases with I_s. The feature is similar to that of pure anthracene crystal and may be caused by the depletion of the ground state anthracene molecules. The other reasons like the appearance of fluorescence due to the exciton-exciton interaction or of induced emission may be conceivable.[9]

Let us turn to the change in the tetracene emission due to high density excitation. As is seen in Figure 5, the ratio, I'_E/I_F, increases with the increasing excitation light intensity. This may be caused partly by the reabsorption effect due to the excited anthracene molecules. The appearance of the induced emission may be another reason for the occurrence of the phenomenon.

The peak positions of bands C, E, and F are independent from I_s while band D slightly shifts to the shorter wavelengths with the increasing I_s. The halfwidth increases for band E with the increasing I_s and is independent from I_s for bands C and F. These phenomena are explainable by the increase in the mixing of anthracene emission with band E and the decrease of the overlap of tetracene emission to band D with the increase of I_s, since when the intensity of excitation laser pulse was increased the relative intensity of anthracene to tetracene increases.

As concluding remarks, we list up the effects of high density excitation upon the fluorescence spectra of the anthracene–tetracene mixed crystal and their possible causes as follows:

1) The remarkable decrease in the relative intensity of tetracene emission. – This is mainly caused by the saturation effect of the energy transfer and partly by the temperature elevation and the reabsorption by the excited anthracene molecule.

2) The increase in I_B/I'_C. – This is partly explained in terms of the ground state depletion caused by high density excitation. The exciton-exciton interaction and the induced emission may also be other causes.

3) The increase in I'_E/I_F. – This is caused partly by the reabsorption effect due to the excited anthracene molecule. The appearance of the induced emission may conceivably contribute to the phenomenon.

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† The apparent lifetime of exciton in the pure anthracene crystal at high density excitation is given by $\tau = (\tau_0{}^{-1} + (\gamma_n)^{-1})^{-1}$ and is estimated to be $\sim 1/3\tau_0$ at $n_A = n_A{}^A$. In this estimation of τ, the excitation saturation effect of anthracene molecules is considered.

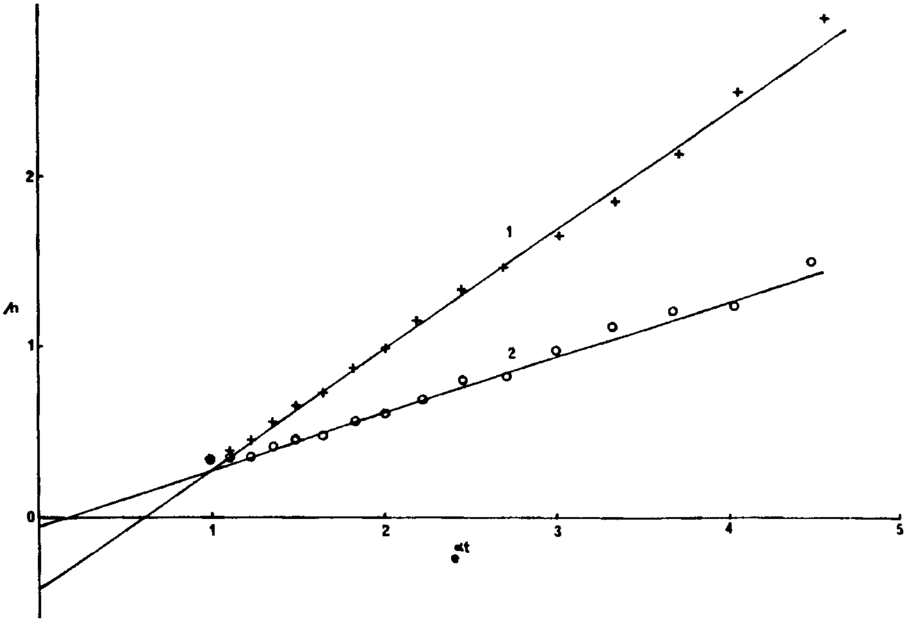

FIGURE 7 The plot of $1/n_A$ versus $e^{\alpha t}$ for the thick anthracene crystal at room temperature. Curves 1, and 2 are for the excitation by the laser at 21 kW and 105 kW peak intensities, respectively.

Appendix

To check the possibility of (i), the IFS of the anthracene–tetracene mixed crystal was observed at various temperatures at low density excitation and the intensity ratio of I_F/I_C was obtained, the result being shown in Figure 8. As the ratio I_F/I_C is nearly proportional to the intensity ratio of tetracene to anthracene, the figure shows that the relative intensity of tetracene decreases with the increasing temperature.

Next let us estimate temperature elevation due to high density excitation. Since the fluorescence quantum yield of anthracene crystal is nearly equal to 1, the temperature elevation due to the radiationless transition from the fluorescent state to the ground state is negligibly small. Therefore temperature increase, ΔT, at high density excitation is caused by the radiationless transition from the Frank-Condon state to the fluorescent state and can be evaluated by $dc_p \Delta T = N_0 \Delta E$ where d, c_p, N_0, and ΔE are the density, specific heat, number of photons absorbed, and the energy difference between the levels of excitation and emission. With the aid of the experimental values of N_0 and ΔE and the values of d and c_p in literature, ΔT was obtained to be 17°C at the highest excitation density in the present work. This value gives the upper limit of temperature elevation because of the probable escape of anthracene excitons from the irradiated volume. According to the data given in Figure 8, the temperature elevation of 17°C reduces I_F/I_C from 0.93 to 0.92. The decrease is too small to explain the observed change in I_F/I_C (0.93 to 0.63).

Let us consider the possibility of (iii). From the estimation by the case of the absorbance of the excited anthracene molecule, I_E/I_F is changed from 0.356 with low density excitation to 0.430 with high density excitation on the assumption that the decrease in the relative intensity of tetracene emission is due to the reabsorption by the excited anthracene molecules. The estimated I_E/I_F value, 0.430, is considerably larger than the observed value, 0.380. Therefore the decrease in I_F/I_C is only partly explained by (iii).

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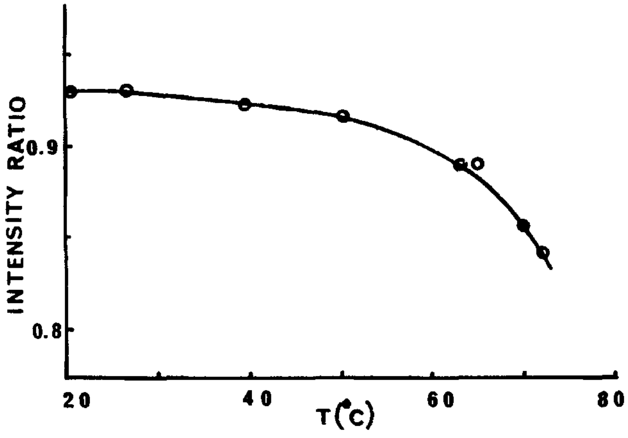

FIGURE 8 Temperature dependence of I_F/I_C for the anthracene–tetracene mixed crystal.

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