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Delayed Fluorescence in Mixed Crystals Due to the Direct Resonance Interaction, as Revealed by Excitation Duration and Intensity Effects on the Decay Behavior

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The decay of the temperature-independent delayed fluorescence observed in the mixed crystals of phenanthrene in the biphenyl host has been studied at 77 K. That triplet molecules are involved in the mechanism for the emission of temperature-independent delayed fluorescence has been shown by observing the intensities at the instances of the short-pulse excitations effected with different dark periods after the steady-state excitation. It has been found that both the excitation duration and the excitation light intensity affect the decay behavior of the temperature-independent delayed fluorescence. The decay after short-pulse excitation has been observed to be more rapid than the decay after prolonged excitation with the same intensity. When the excitation light intensity is increased with a fixed duration, the delayed fluorescence is observed to decay more rapidly. It is concluded that the decay behavior of the temperature-independent delayed fluorescence can be accounted for in terms of the direct-resonance-interaction mechanism.

The delayed fluorescence (DF) of organic compounds has attracted the attention of many investigators,1) and different aspects of it, such as the temperature dependence,2–6) the magnetic-field effect,7–10) and the caging effect,11) have been studied. Accordingly, the nature of DF is fairly well understood, and DF is now an important probe for studying excited states. For example, the singlet–triplet (S–T) absorption spectrum can be determined by measuring the DF excitation spectrum,12) and the Davydov splitting in a certain CT molecular crystal was measured from the doublet DF-ODMR (optically detected magnetic resonance) signals.13) However, some aspects of DF are still not understood. The existence of temperature-independent delayed fluorescence (TIDF) in organic mixed crystals, in addition to the usual temperature-dependent delayed fluorescence (TDDF), has been reported by several investigators.3b,5,14,15) The mechanism for TDDF is ascribed to the triplet–triplet (T–T) annihilation between a thermally produced triplet exciton and a guest triplet state.2–6) As for the mechanism for TIDF, though several possible mechanisms have been suggested thus far,3,15) no definite one has been proposed. Because of the lack of sufficient experimental data on the TIDF, the discussion of the mechanism for TIDF has reached a dead end, and a breakthrough has been longed for.

Decay characteristics provide further knowledge about the mechanism for DF. In view of the nonexponential decay behavior of TIDF,3,4) it was felt by the present authors that a careful study of the form of the decay curves would yield some information about the nature of TIDF. In a previous brief report on the benzo[*f*]quinoline–biphenyl mixed-crystal system, we have shown for the first time that the excitation duration markedly affects the decay behavior of TIDF at 77 K.16) In this study, it has also been found that the excitation-light intensity affects the decay behavior of TIDF. We wish here to report these new effects and to discuss the mechanism for TIDF. Technically, the measurement of the excitation-light-intensity effect has been made possible as a result of the recent advent of data-processing instruments such as microcomputers and digital memories, which enable us to measure the decay curves of intrinsically weak TIDF easily and accurately.

Experimental

Chemicals and Samples. Phenanthrene (Tokyo Kasei, EP) was subjected to the chemical treatment described previously.17) Biphenyl (Wako, EP) was twice recrystallized from ethanol and zone-refined over 200 passes. Then, a central portion of the ingot, the purest portion, was subjected to an additional 200 passes of zone refining. The polycrystalline samples were prepared between two fused-silica disks as has been described previously.14) The guest concentration has been chosen to be fairly high, that is, 1.0×10^{-2} mol/mol, since the TIDF intensity is generally low.

Apparatus. Optical measurements were made on the apparatus illustrated in Fig. 1. The analyzing system consisted of a 220-mm grating monochromator (Spex, Doublemate 1672) equipped with a photomultiplier (HTV, R106), a DC preamplifier incorporating an operational amplifier (Teledyne Philbrick, 1009), a transient converter (Riken Denshi, TCB1000S-11), and a microcomputer (Fujitsu, MB25020). As a square-wave excitation source, mechanically-chopped radiation from a 250-W high-pressure mercury lamp (Ushio Electric, USH-250D) was used, in combination with a 5-cm optical-path aqueous filter. The mechanical chopping was effected by means of an electromagnetic shutter (shutter E in Fig. 1, Vincent Associates, 26LOAOX5), operated by means of a home-made control system incorporating multivibrators (Toshiba, TC4528BP) and Darlington configurations of transistors. When the excitation-light-intensity dependence was measured, calibrated neutral filters made of brass-wire gauze were used to modify the excitation-light intensity. Another shutter of the same model (shutter A in Fig. 1) was used in order to exclude the prompt fluorescence. Shutter A was opened with a delay time of about 5 ms after the cessation of excitation. The delay time is mainly determined by the operation of the control system. The intrinsic response time of the

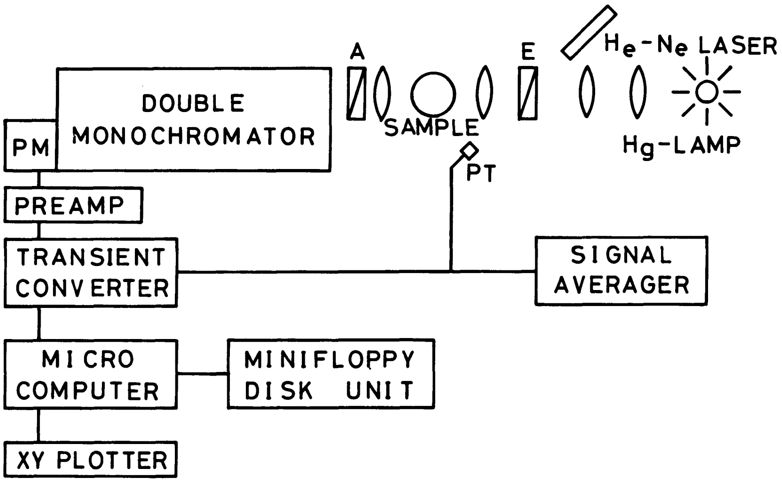

Fig. 1. A block diagram of the apparatus. A and E are electromagnetic shutters. PM and PT stand for photomultiplier and phototransistor, respectively.

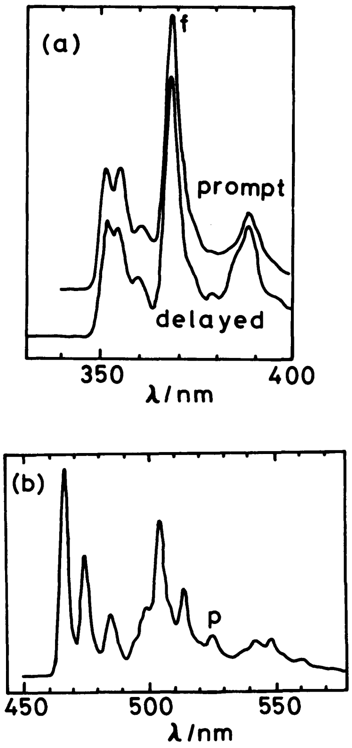

Fig. 2. Delayed luminescence and prompt fluorescence spectra. (a) Delayed and prompt fluorescence and (b) phosphorescence.

shutters is claimed to be of the order of 1 ms. The delayed luminescence decay signals were memorized on the transient converter. After a measurement run, the data were transmitted from the transient converter to the microcomputer, utilizing an RS-232C interface with 9600 bauds. This interface circuit was a home-made one incorporating a UART (Intersil 6402). The transmitted data were stored on a minifloppy disk (Epson, F100A). The analyzed results were displayed on an XY plotter (Graphtec, MP1000). The operation of the shutter E was monitored on a digital memory device (Nicolet 1170 signal averager), displaying the output of a phototransistor illuminated by a He–Ne laser (NEC, GLG5000). The output signal in turn triggered the transient converter. The delayed luminescence spectra were measured in the square-wave excitation.

Results and Discussion

General Remarks on the Spectra and the Temperature Dependence of the Spectral Intensities. Figure 2 shows the delayed luminescence spectra obtained at 77 K with a train of square-wave excitations. For comparison, the prompt fluorescence spectrum is also shown in Fig. 2, comfirming that the observed DF is genuine. As the shortest wavelength fluorescence band tends to be affected by reabsorption, the excitation-duration effect and the excitation-light-intensity effect have been studied with the f band for DF. The phosphorescence decay curve has been observed on the p band, where the T–T absorption spectrum does not overlap the phosphorescence spectrum.[18] In this paper, *t* signifies the time elapsed after the cessation of excitation.

As has been reported by Misra,[15] the DF and phosphorescence intensities show characteristic temperature-dependences. As the temperature is raised from 6 K, the DF intensity is constant up to about 80 K. TIDF is observed throughout this temperature range. Then it increases to reach a maximum at about 160 K and decreases thereafter. The phosphorescence intensity decreases monotonically as the temperature is raised from 6 K to 180 K, and the DF observed at 77 K consists essentially of TIDF alone.

Energy Reservoir. As the spectrum of TIDF coincides with that of the prompt fluorescence, the final process of TIDF is a transition from the lowest excited singlet state to the ground state. However, TIDF emission continues for about 2.5 s after excitation is removed. Therefore, the mechanism for TIDF must involve long-lived excited states. The most probable candidate for this energy reservoir is a triplet state. In this section, we will present experimental evidence that the guest triplet-state molecule is a constituent of the TIDF mechanism.

The phosphorescence decay is nearly exponential, with a lifetime of 3.8 s, and the TIDF intensity becomes negligible 2.5 s after the excitation light is extinguished. Consequently, that triplet molecules are involved can be shown by comparing the TIDF intensities at the instances of the short-pulse excitations effected with different dark periods after a steady-state excitation. The actual experimental procedure is as follows. The steady-state excitation is performed from −5 to 0 s, and then a 20-ms excitation is performed after a certain dark period in the course of the phosphorescence decay. The next set of 5-s and 20-ms excitations are performed after a period of darkness long enough for the triplet concentration, as estimated by monitoring the phosphorescence, to have fallen to a negligible value. The dark periods between the 5-s and 20-ms excitations have been chosen to be 0, 0.284, 0.549, 1.101, 1.616, 2.226, 2.750, 3.188, 3.750, 3.938, 4.490, 4.918, 9.740, and 60 s. The observed results are shown in Fig. 3, where, for comparison, the decay curve of phosphorescence is also shown. It may be noted that the intensities for the dark periods of 2.750 through 9.740 s are greater than that with the prolonged dark period of 60 s. Thus, it is proved that the guest triplet state is necessary for TIDF, since the excited state persisting for 10 s and disappearing at 60 s after excitation is the triplet state, as can be seen from the phosphorescence decay in Fig. 3.

The next problem to be solved is the number of triplet-state molecules which are required to produce one excited singlet state. Attempts were made to ascertain the dependence of the TIDF intensity, I_{TIDF}, on the phosphorescence intensity, I_{P}, when the excitation-light intensity, I_{exc}, was altered. The TIDF and phosphorescence intensities were measured as the integrated output obtained by the repetition of 20-ms excitations and 20-ms observations, with intervals of 10 ms between excitations and observations. The interdependence of $I_{\mathrm{TIDF}} \propto I_{\mathrm{P}}^{1.7}$ has thus been confirmed. The deviation from the square law may be brought about by the dead time of 10 ms in the operation of the two electromagnetic shutters, since the difference between the rates of disappearance of TIDF and of the phosphorescence is considerable. There are two alternative interpretations of this; *i.e.*, the above experimental facts indicate that two triplet-state molecules or one triplet-state molecule and one photon of excitation light produce one excited-singlet-state molecule, which is then responsible for TIDF. In phenanthrene, twice the energy of the lowest excited triplet state is larger than the value of the energy of the lowest excited singlet state. Consequently, both interpretations of the biphotonic nature are conceivable.

Possible Mechanisms. Here, in an effort to pick possible mechanisms for TIDF, we will list the mecha-

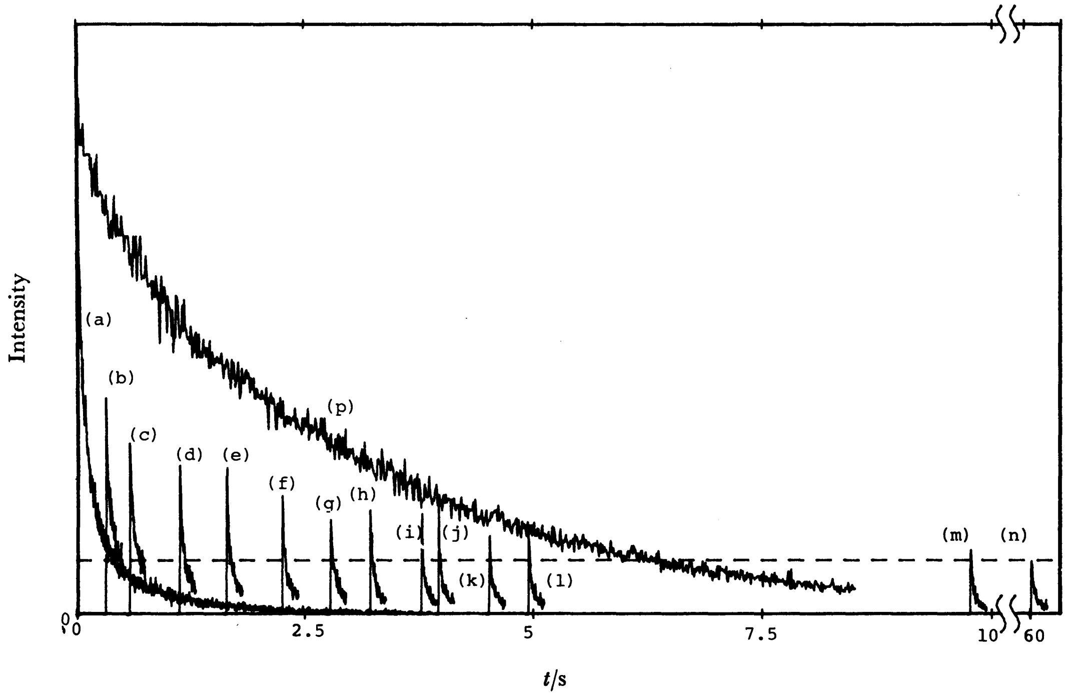

Fig. 3. Decay curves of delayed fluorescence and phosphorescence. (p) Phosphorescence decay after 5 s excitation. (a—n) TIDF decays by successive double pulse excitations. The excitation durations of the first and second pulses are chosen to be 5 s and 20 ms, respectively. The dark periods between the first and the second pulses are (a) 0, (b) 0.284, (c) 0.549, (d) 1.101, (e) 1.616, (f) 2.226, (g) 2.750, (h) 3.188, (i) 3.750, (j) 3.938, (k) 4.490, (l) 4.918, (m) 9.740, and (n) 60 s, respectively.

nisms proposed thus far for DF. The E-type,[1a] Williams-Stevens,[1a] exciton-splitting,[19] recombination,[20] trap,[4] P-type,[1a] exciton-migration,[2–6] direct-resonance-interaction,[3,4,19] double-excitation,[1a] and reabsorption mechanisms[1a,3,19] have all been proposed in the literature. According to the preceding discussion, the mechanism for TIDF must involve two triplet-state molecules or one triplet-state molecule and one photon of excitation. Then, the possible mechanisms for TIDF are the direct-resonance interaction, double-excitation, and reabsorption mechanisms.

In the case of the direct-resonance-interaction mechanism, two separately produced guest triplet molecules interact with each other and energy transfer occurs from one triplet-state molecule to the other. A highly excited state will eventually be produced, and once produced it will revert to the lowest excited singlet state or the triplet state with a significantly higher probability than excitation back to the initial state. The excited singlet state thus produced emits TIDF.

In the case of the double-excitation mechanism, a guest molecule is first excited to a triplet state, and then this triplet-state molecule is excited to a higher excited state X by a second quantum of light. The excited state X thereafter reverts partially to the lowest excited singlet state.

In the case of the reabsorption mechanism, one triplet molecule reaches a higher triplet/singlet state by reabsorbing the energy that another triplet radiates as phosphorescence.

Of these three mechanisms, the first, the direct-resonance interaction mechanism, is the most probable, because this is simply a special case of the mechanism for TDDF, as will be detailed below. The mechanism for TDDF may be summarized as follows:[4]

$$S_0 + h\nu \rightarrow S_1 \qquad \text{(absorption)} \tag{1}$$

$$S_1 \rightarrow S_0 + h\nu \qquad \text{(fluorescence)} \tag{2}$$

$$S_1 \rightarrow S_0 \qquad \text{(relaxation)} \tag{3}$$

$$S_1 \rightarrow T_1 \qquad \text{(intersystem crossing)} \tag{4}$$

$$T_1 \rightarrow S_0 + h\nu \qquad \text{(phosphorescence)} \tag{5}$$

$$T_1 \rightarrow S_0 \qquad \text{(relaxation)} \tag{6}$$

$$T_1 + T_1 \rightarrow S_1 + S_0 \qquad \text{(annihilation)} \tag{7}$$

$$T_1 + T_1 \rightarrow T_1 + S_0. \qquad \text{(annihilation)} \tag{8}$$

TDDF is ascribed to the fluorescence emitted by the S_1 state produced in the process of Eq. 7. Equation 7 is an abbreviated representation of thermal excitation, exciton migration, and annihilation and is realized as follows;

$$T_1 \rightleftarrows T_1^* \qquad \text{(thermal excitation)} \tag{9}$$

$$T_1^* + S'_{0H} \rightleftarrows S_0 + T'_{1H} \qquad \text{(energy transfer from guest to exciton)} \tag{10}$$

$$T'_{1H} + S_{0H} \rightleftarrows S'_{0H} + T_{1H} \qquad \text{(exciton migration)} \tag{11}$$

$$T_{1H} + S_{0H} \rightleftarrows S_{0H} + T_{1H} \qquad \text{(exciton migration)} \tag{12}$$

$$T_{1H} + S''_{0H} \rightleftarrows S_{0H} + T''_{1H} \qquad \text{(exciton migration)} \tag{13}$$

$$T''_{1H} + T_1 \rightarrow S''_{0H} + S_1, \qquad \text{(annihilation)} \tag{14}$$

where the subscript H identifies the host species; the primed symbols identify host molecules which are adjacent to guest molecules, and T_1^* is a vibrationally excited triplet state of the guest with an energy comparable to the host triplet-exciton band. (For more detailed information, Ref. 4 can be referred to.) Equation 9 represents a thermal excitation of the guest triplet state. As the mechanism for TDDF involves the thermal excitation of Eq. 9, TDDF can be said to depend on the temperature. Equation 12 stands for one-step migration or many-step migration, as the case may be. Equation 14 represents the process of energy transfer from a host triplet-state molecule to a guest triplet-state molecule. Kinoshita and McGlynn[4] assumed that the energy transfer of Eq. 14 was operative between adjacent molecules and explained the behavior of TDDF satisfactorily. However, we assume that energy transfer by long-range interaction can also be operative with a relatively small probability. This process may be rendered undetectable by competing fast exciton diffusion and process of Eq. 14 at high temperatures where TDDF is intense. At low temperatures where the process of Eq. 9 is ineffective, long-range direct-resonance interaction between guest molecules is predominant to give rise to DF, which is here called TIDF, because the fast, competing process favoring TDDF is absent. Therefore, Eqs. 9 through 13 do not apply at low temperatures; now, Eq. 7 represents not a sequence of processes, but really a one-step process. This mechanism does not need thermal excitation and is compatible with the experimental results described thus far. This mechanism for TIDF is the same as that proposed by Azumi and McGlynn in rigid glass.[19] The validity of their proposal has partly been proved by the experimental results of Nakashima *et al.*[21] According to Kellogg,[22] the necessary conditions for this type of energy transfer to occur are satisfied in phenanthrene.

Excitation-duration and Excitation-light-intensity Effects. In this section, we will show the experimental results of excitation-duration and excitation-light-intensity effects on TIDF decay. These two effects have been observed under exactly the same conditions except for the excitation duration and the excitation light intensity.

Figure 4 shows the observed TIDF decay curves. The excitation durations are chosen to be (a) 4.25, (b) 0.257, (c) 0.102, (d) 0.050, and (e) 0.021 s. It can easily be seen that shortening the excitation duration makes not only the TIDF intensity weak, but also the decay steep. The TIDF decay curves with excitations of more than 5 s are essentially the same as that with the excitation of 4.25 s.

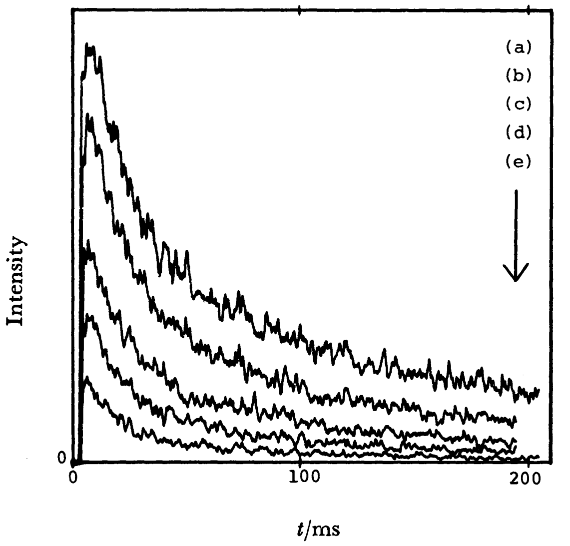

Fig. 4. Excitation duration effect on the delayed fluorescence decay at 77 K. Excitation durations are (a) 4.25 s, (b) 257 ms, (c) 102 ms, (d) 50 ms, and (e) 21 ms, respectively.

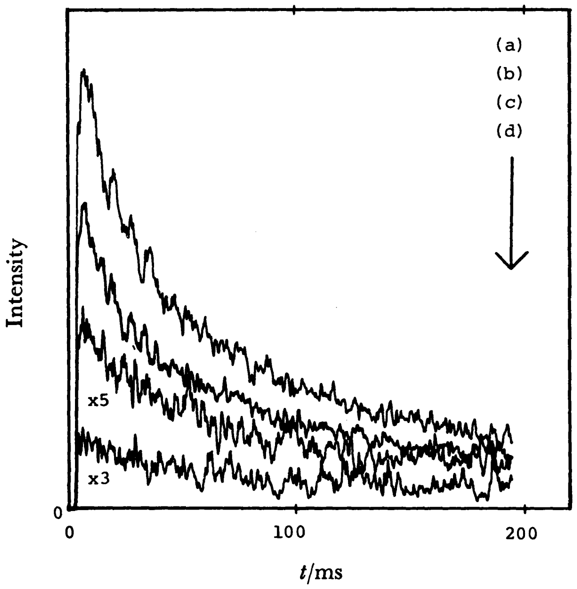

Fig. 5. Excitation light intensity effect on the delayed fluorescence decay observed at 77 K with a fixed excitation duration of 8.6 s. Relative excitation light intensities are (a) 1, (b) 0.6, (c) 0.1, and (d) 0.02, respectively.

Figure 5 shows the results of the observation of the excitation-light-intensity effect. The relative excitation light intensities are chosen to be 1, 0.6, 0.1, and 0.02.

When the excitation duration or excitation-light intensity are altered, the amount of light energy which is stored in the guests is changed. The TIDF intensities thus observed are greatly different from each other, as is shown in Figs. 4 and 5; in consequence, it is desirable to normalize the TIDF decay curves for the convenience of comparison. Figure 6 shows the normalized TIDF decay curves. The experimental conditions are as follows: (a) The excitation duration is 8.62 s; the relative excitation-light intensity is 1. (b) The excitation duration is 8.62 s; the relative excitation-light intensity is 0.02. (c) The excitation duration is 21 ms; the relative excitation-light intensity is 1. We can clearly see from this figure that (b) and (c) show opposite tendencies when we choose (a) as a reference.

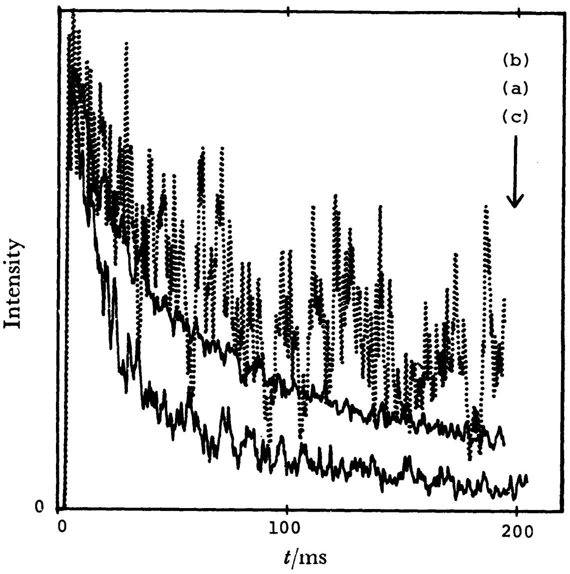

Fig. 6. Comparison between the excitation duration and excitation light intensity effects. Excitation durations are (a) 8.62 s, (b) 8.62 s, (c) 21 ms, respectively. Relative excitation light intensities are (a) 1, (b) 0.02, (c) 1, respectively.

The Mechanism for TIDF. In the foregoing sections, we have discussed the mechanism for TIDF and shown that the possible mechanisms for TIDF are the direct-resonance-interaction, double-excitation, and reabsorption mechanisms. In this section, we will consider the types of TIDF decay to be expected for the three possible mechanisms when the excitation duration and the excitation-light intensity are altered and will compare them with the experimental results shown in the preceding section.

If TIDF is caused by the direct-resonance-interaction mechanism, the energies from the two seperate guest triplet molecules are concentrated in a single guest molecule by the long-range direct interaction. Part of the resultant highly excited guest molecules are degraded into the lowest excited singlet state and then emit TIDF. We can now postulate that this interaction depends on the distance between the two interacting triplet molecules; the closer these two molecules, the higher the transfer probability. A triplet-state molecule far apart from other triplet-state molecules obeys the exponential decay law with the intrinsic transition probability. If another triplet-state molecule lies near the triplet-state molecule, this molecule obeys an exponential decay with an enhanced transition probability.

Therefore, the spatial distribution of the triplet-state molecules is important in this mechanism. In the case of the delta-pulse excitation, the distribution of the triplet-state molecules may be random at the moment of excitation. Consequently, the distances between triplet-state molecules are various and the decay laws to be obeyed are different for triplet-state molecules in different environments. As we observe the total TIDF intensity, the observed decay is a sum of the TIDF decays with different transition probabilities. In the case of the steady-state excitation, the situation is different from the case of the delta-pulse excitation. The distribution of the triplet-state molecules may be random at the initial stage of excitation, while interaction between triplet-state molecules is occurring. As pairs with shorter distances are annihilated with higher probabilities, pairs with longer distances survive with relatively higher probabilities. Therefore, the observed TIDF decay is a sum of the TIDF decays weighting slower components; *i.e.*, the TIDF decay after steady-state excitation contains more of the slowly decaying components than that after a delta-pulse excitation. In other words, a short excitation duration increases the relative number of pairs of triplet-state molecules with short distances. Contrary to this, decreasing the excitation-light intensity reduces the relative number of pairs of triplet-state molecules with short distances. Therefore, shortening the excitation duration quickens the TIDF decay, while decreasing the excitation light intensity makes it slower.

If the double-excitation mechanism is valid, the interaction between the excited states X is negligible. If X is confined within a molecule, the decay law is exponential. As a nonexponential decay is a necessary condition to observe the effect of excitation duration, the effect of excitation duration is not expected to appear in this case. If X is associated with more than one molecule, like an excimer and an exciplex, or with an electron-cation pair, TIDF will decay nonexponentially, and the effect of excitation duration may appear. When the excitation-light intensity is decreased, the total intensity of TIDF decreases, but the form of the decay curve does not change.

If the reabsorption mechanism is operative, a triplet-state molecule absorbs a photon of phosphorescence emitted by another triplet-state molecule and then undergoes the same processes as those in the direct-resonance-interaction mechanism. The effects of excitation duration and excitation-light intensity can be detected easily, judging from the fact that the triplet-state concentration is the major factor in the reabsorption and is affected both by the excitation duration and by the excitation-light intensity. Either shortening the excitation duration or decreasing the excitation-light intensity should have the same effect on TIDF decay.

Figure 6 shows the observed decay type, which is in accord with the prediction by the direct-resonance-interaction mechanism. Consequently, the observed effects of the excitation duration and excitation-light intensity can be reconciled only by adopting the direct-resonance-interaction mechanism for TIDF.

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