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Some Comments on the Trap-Delayed Fluorescence of Naphthalene-Biphenyl Mixed Crystals

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Temperature and concentration dependences of the trap-delayed fluorescence observed in the naphthalene (guest)-biphenyl (host) mixed crystal system have been studied. Some remarks are made on the mechanism involved in producing the trap-delayed fluorescence.

1. Introduction

We have studied the temperature and concentration dependences of both intensity and decay of the guest-delayed luminescence (guest-phosphorescence (G_P) and guest-delayed fluorescence (G_{DF})) observed in the mixed crystals of benzo[*f*]quinoline or naphthalene guest in biphenyl host.[1-5] In those works, with lower concentrations and higher temperatures, we have detected the very weak trap-delayed fluorescence (H_{DF}) as well as a trap-fluorescence (H_F) in a shorter wavelength region than that of the guest emission (G_{DF} and guest-fluorescence (G_F)).[4] As for H_{DF}, no observation was made in the previous experiments on the mixed crystals containing biphenyl as a host.[6] On the other hand, Yee and El-Sayed reported both the guest- and host-delayed fluorescence in the anthracene-in-phenanthrene system.[7] Accordingly, the fact that we have observed both G_{DF} and H_{DF} has suggested that it is significant to study in detail their temperature dependence at the wavelengths of the main bands.

A kinetic model for the guest-trap and trap-trap annihilations has been proposed.[8] Misra has also discussed the kinetics for such a guest-trap heterogeneous triplet-triplet annihilation in some detail.[9] The kinetic model treated above, however, was the one leading to G_{DF} but not to H_{DF}.

In this paper, we will present the results of the temperature and concentration dependences of H_{DF} observed in the naphthalene-biphenyl mixed crystal system, and briefly discuss the mechanism involved.

2. Experimental

All apparatus and techniques were identical to those already reported by us.[3] Chemicals were obtained from Tokyo Kasei Kogyo Co., Ltd. Purification and preparation methods were also identical to ones already described by us.[3,5]

3. Results and Discussion

3.1. *Observations at 77 K*

Figure 1 shows a comparison of the delayed (observed by use of a phosphoroscope) and normal (so-called "fluorescence") fluorescence of a polycrystalline sample of biphenyl doped with naphthalene at 77 K with a guest concentration of 10^{-3} mol/mol, both spectra being recorded photoelectrically. It may be suggested that our biphenyl crystals are not absolutely pure, as it is the case usually. Then we have tried to obtain the luminescence of the biphenyl crystals: a typical fluorescence spectrum of the biphenyl host crystals is shown in Fig. 2, and it has been found to depend to some extent on the particular crystal specimen investigated. Detailed discussion on the luminescence of the neat biphenyl crystal will be presented elsewhere.[10]

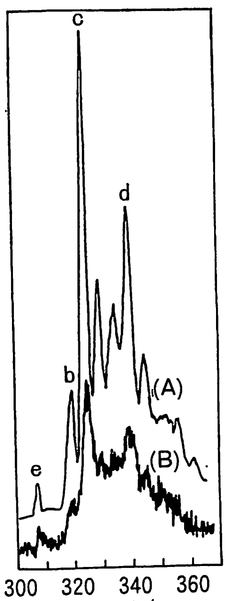

Fig. 1. Comparison of (A) normal and (B) delayed fluorescence of naphthalene-biphenyl mixed crystal system at 77 K. Concn.: 1.0×10^{-3} mol/mol. The band e and the remaining bands (bands b, c, and d inclusive) originate from the trap and the guest, respectively.

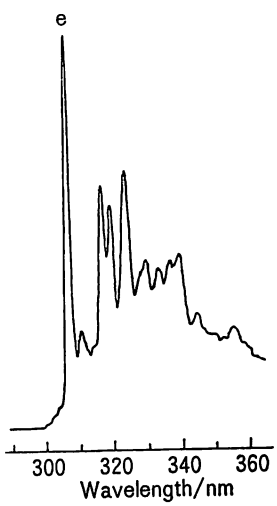

Fig. 2. Fluorescence spectrum of biphenyl host crystals at 77 K.

Now, it can be concluded that the first bands of the emission spectra shown in Fig. 1 originate from a host-associated trap (perhaps X-trap) by comparing with the first band of the host fluorescence spectrum shown in Fig. 2. The remaining bands of the spectra shown in Fig. 1 originate from the guest, as reported in Ref. 5.

As shown in Fig. 1, the normal and the delayed fluorescence spectra of both guest and trap are in good correspondence with each other, giving a confirmation that the observed G_{DF} and H_{DF} are genuine.

We have made an experiment of temperature dependence in the delayed luminescence by observing at several bands shown in Fig. 1, where the notation is given for representative bands of the delayed fluorescence.

3.2. *Temperature Dependence of Intensity*

The results of the temperature dependence of the delayed luminescence in this mixed crystal system with two different concentrations, 1.0×10^{-3} and 1.0×10^{-4} mol/mol, are shown in Fig. 3, where the results on G_{DF} observed at band d are not shown because they

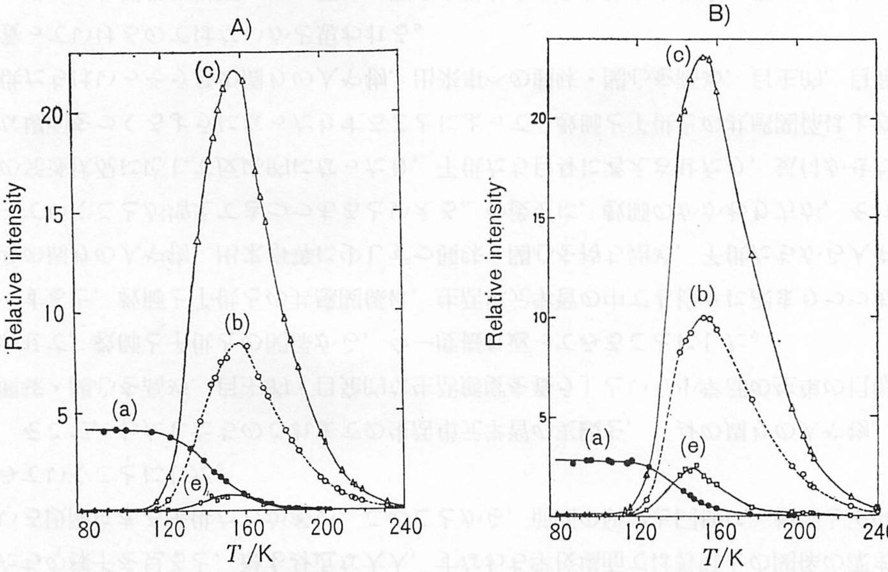

Fig. 3. Temperature dependence of the delayed luminescence of naphthalene-biphenyl mixed crystal system in the temperature region above 77 K. Concn.: A) 1.0×10^{-3}, B) 1.0×10^{-4} mol/mol. (a): G_P intensity observed at 475 nm, the 0, 0-band, see Ref. 5; (b): G_{DF} intensity observed at 318 nm, the 0, 0-band; (c) and (e): G_{DF} and H_{DF} intensities observed at the corresponding bands shown in Fig. 1. No correction was made for the spectral response of the apparatus.

were similar to those of the other bands b and c as far as the temperature dependence is concerned. In the results at a concentration of 1.0×10^{-2} mol/mol, already presented elsewhere,[5] the band e has not been observed, that is, we have not observed H_{DF}, indicating that the mixed crystals doped with the guest concentration of 10^{-2} mol/mol can essentially be regarded as the two-component system exclusively consisting of the guest and host (*i. e.*, no contribution of the trap).

As can be seen in Fig. 3, the results at the concentrations of $10^{-3}-10^{-4}$ mol/mol have two characteristics: (1) the values of T_{max} (the temperature at which maximum intensity of G_{DF} occurs) undergo considerable shifts toward the lower temperatures as compared with that (about 177 K) in the mixed crystal system doped with the high concentration of 10^{-2} mol/mol, and (2) H_{DF} (band e) is detected. Additional results *obtained from*

Fig. 3 are as follows:

(i) The samples of the mixed crystals doped with the guest concentrations of 10^{-3}–10^{-4} mol/mol may be taken as at least three-component system consisting of the guest, host, and trap.

(ii) T_{max} on H_{DF} (band e) and those on G_{DF} are not very different from one another. H_{DF} and G_{DF} seem to be similar in thermal behavior.

(iii) H_{DF} observed at band e decreases with increasing guest concentration. In addition, the ratios of both G_{DF} and H_{DF} intensities to the guest-phosphorescence (G_P) intensity at 90 K decrease with increasing guest concentration.

(iv) Judging from an empirical relation,[6b] $T_{max}=0.06\ \Delta E/k$, where ΔE is the energy separation between the host and guest (or trap) triplet states, and k Boltzmann's constant, it may follow that the trap triplet (if it exists) is higher than the guest triplet.

3.3. *Concluding Remarks on H_{DF}*

In Table 1 are collected the values of T_{max} on H_{DF}, and the host-trap triplet separations ΔE deduced from T_{max} through the above-mentioned empirical relation.[6b] The values of T_{max} seem to be in agreement with each other within the experimental error, and hence so seem the corresponding values of ΔE. As mentioned in section 3.2, it is found that the values of ΔE estimated on H_{DF} are smaller by about 80 cm^{-1} than the corresponding ones on G_{DF} in Ref. 4. The difference between ΔE on H_{DF} and that on G_{DF}, however, may fall within the experimental error.

TABLE 1. VALUES OF T_{max} AND ACTIVATION ENERGIES ON H_{DF} (BAND e)

Guest concn. (mol/mol)	T_{max}/K[b)]	ΔE[a)]/cm^{-1} From T_{max}[c)]
1.0×10^{-3}	150	1740
1.0×10^{-4}	147	1700

a) The spectroscopic energy gap of host triplet-trap triplet state is unknown because H_P has not been detected. That of host triplet-guest triplet state is 1940 cm^{-1}. See Ref. 6b. b) T_{max} is the temperature at which maximum intensity of H_{DF} occurs. c) Calculated from an empirical relation, $T_{max}=0.06\ \Delta E/k$. See Ref. 6b.

The ratio of the G_P intensity to the G_{DF} intensity at T_{max} decreases with decreasing guest concentration, as can be seen in Fig. 3. In addition, the ratio of the H_{DF} intensity to the G_{DF} intensity at T_{max} increases with decreasing concentration. Then, in the present stage of knowledge we would like to make some remarks on the origin of H_{DF}.

(1) With decreasing concentration, the ratios of both G_{DF} and H_{DF} intensities to the G_P intensity increase, as mentioned above. Accordingly, it may be suggested that the process

$$T_{1G} \rightsquigarrow T_{1G}^{*} \rightsquigarrow T_{1H} \rightsquigarrow T_{1D},$$

where subscripted letters G, H, and D signify guest, host, and trap molecules, respectively, and T^*_{1G} denotes a guest triplet in higher vibrational state, giving rise to H_{DF}, and decreasing G_P might be operative although we have detected no trap-phosphorescence (H_P). In the comparatively lower guest concentrations of $10^{-3}-10^{-4}$ mol/mol, the trap concentration becomes relatively higher. In such a case, the following process might also be possible: the process

$$T_{1D} \rightsquigarrow T^*_{1D} \rightsquigarrow T_{1H} \rightsquigarrow T_{1D} \quad \text{and} \quad T_{1G},$$

where T^*_{1D} denotes a trap triplet in higher vibrational state, contributing to the production of H_{DF} and G_{DF}. The process

$$T_{1G} \rightsquigarrow T^*_{1G} \rightsquigarrow T_{1H} \rightsquigarrow T_{1G},$$

leading to the guest triplet-guest triplet annihilation, may also play an important role in producing G_{DF}. The above-mentioned two processes, *i.e.*, the processes $T_{1G} \rightsquigarrow T^*_{1G} \rightsquigarrow T_{1H} \rightsquigarrow T_{1D}$ and T_{1G}, and $T_{1D} \rightsquigarrow T^*_{1D} \rightsquigarrow T_{1H} \rightsquigarrow T_{1D}$ and T_{1G}, seem to be operative at the same time.

(2) As mentioned in section 1, Yee and E1-Sayed[7] reported both the host- and the guest-delayed fluorescence from the anthracene guest-phenanthrene host mixed crystal system characterized by an added impurity (guest) in low concentrations and of large triplet trap depth. Incidentally, in the previous reports[6] on the thermally activated delayed fluorescence due to heterogeneous annihilation, only G_{DF} was observed. Following interpretation can be given to this phenomenon. Owing to the relatively high guest concentrations used in the previous experiments,[6] any singlet host excitation created by the annihilation process would have been quenched efficiently by the singlet-singlet energy transfer to the guest singlet manifold, and hence, only G_{DF} resulted. Above interpretation may be applied to our mixed crystal system with the relatively high guest concentrations. That is, the fact that H_{DF} decreases with increasing guest concentration (In fact, H_{DF} was not observed for the mixed crystals doped with the high guest concentration of 10^{-2} mol/mol, as mentioned in section 3.2.) would be interpreted as due to the quenching by the singlet-singlet energy transfer from the trap to the guest.

The experiments made so far are not enough to elucidate the nature and origin of H_{DF}. Further detailed experiments, particularly on decay behavior of H_{DF}, are required to clarify this question fully.

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