An Interpretation of Delayed Fluorescence Behavior of Naphthalene in Biphenyl Host in the Lower Temperature Region

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Temperature and concentration dependences of the delayed luminescence observed in the naphthalene (guest)-biphenyl (host) mixed crystal system have been studied. The presence of the temperature-independent delayed fluorescence (TIDF) and its significance in the evaluation of activation energy have also been confirmed in this system as in the case of the benzo[*f*]quinoline–biphenyl system previously reported, and the generality of the existence of TIDF as well as its significance in relation to activation energy has been suggested. In addition, some remarks have been made on the nature of TIDF and the decay behavior.

We have observed TIDF of benzo[*f*]quinoline in biphenyl host in the low temperature region from 90 K down to liquid helium temperature and showed that subtraction of this temperature-independent contribution (I_{TIDF}) from the observed total delayed fluorescence intensity ($(I_{\mathrm{DF}})_{\mathrm{total}}$) above 90 K gave straight-line fits of both $\log I_{\mathrm{DF}}/I_{\mathrm{P}}{}^2$ and $\log I_{\mathrm{DF}}$ *vs.* $1/T$ plots, where I_{DF} and I_{P} stand for the delayed fluorescence (DF) and phosphorescence (P) intensities, respectively, in good agreement with the usual temperature-dependent model.[1–3] Moreover, it has been shown that the decay behavior of TIDF may be responsible for the unusual decay behavior of DF around 77 K, the decay of which deviates considerably from exponentiality in the lower temperature region where the exponential behavior is expected from the usual temperature-dependent model.[2] The investigation on the temperature and concentration dependences of both the intensity and the decay of the delayed luminescence (P and DF) of naphthalene in biphenyl host has been made in order to examine the existence and its significance of TIDF as found in the benzo[*f*]quinoline–biphenyl system. Incidentally, Misra[4] reported an observation of TIDF in the same system. In the present work, therefore, we will mainly discuss whether this temperature-independent portion of DF plays an important role for the anomaly of DF observed in the lower temperature region in the naphthalene–biphenyl system. Benzo[*f*]quinoline has overlapping phosphorescence and triplet-triplet absorption bands,[5] whereas it is not the case in naphthalene.[6] Since this type of overlapping might be significant in the triplet-triplet annihilation,[7] it seems interesting to choose naphthalene as another guest to be compared with benzo[*f*]quinoline.

Experimental

Chemicals were obtained from Tokyo Kasei Kogyo Co., Ltd. Biphenyl was recrystallized twice from ethanol, and was further purified by the method of repeated zone refining and abstraction of the non-emissive portions of the specimen. Naphthalene of the UP grade (zone refined, number of passes: 23) was used without further purification. The polycrystalline samples used were prepared from the melts between two fused-silica plates which were mounted in a brass block holder. Concentration of the samples studied ranges from 10^{-2} to 10^{-4} mol/mol. All apparatus and techniques were identical to those already described.[2]

Results and Discussion

Spectra. As shown in Fig. 1, the normal and delayed fluorescence spectra obtained at 77 K with a guest concentration of 1.0×10^{-3} mol/mol are in good correspondence with each other in any of the mixed crystal samples, giving a confirmation that the observed DF is genuine. The temperature dependence of the delayed luminescence was studied for bands b, c, and d in Fig. 1. The phosphorescence spectrum obtained at 77 K from the mixed crystals is given in Fig. 2, where "a" stands for the 0,0-band of P. The delayed luminescence spectrum of the naphthalene–biphenyl mixed crystals has been reported, particularly by Misra and McGlynn.[8] Comparing our observed spectrum with theirs, the naphthalene guest is identified to be the emitting species.

Temperature Dependence of Intensity. The results of the temperature dependence of the delayed luminescence with a guest concentration of 1.0×10^{-2} mol/mol in the

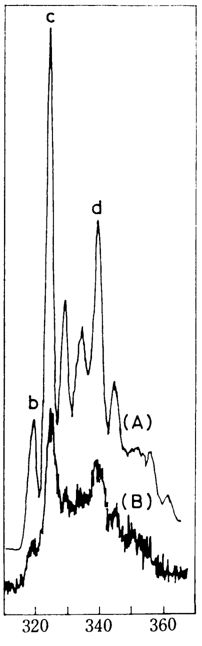

Fig. 1. Comparison of (A) normal and (B) delayed fluorescence of naphthalene in biphenyl host at 77 K. Concn: 1.0×10^{-3} mol/mol.

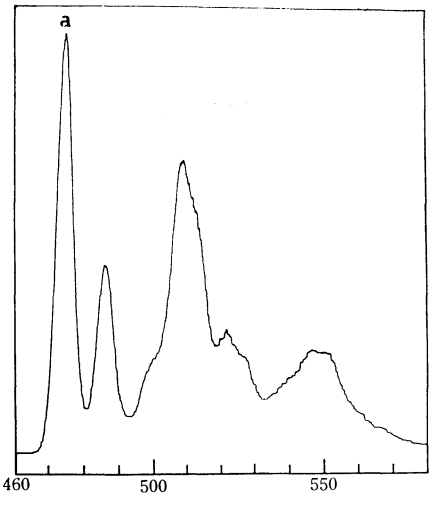

Fig. 2. Phosphorescence spectrum of naphthalene in biphenyl host at 77 K. Concn: 1.0×10^{-3} mol/mol.

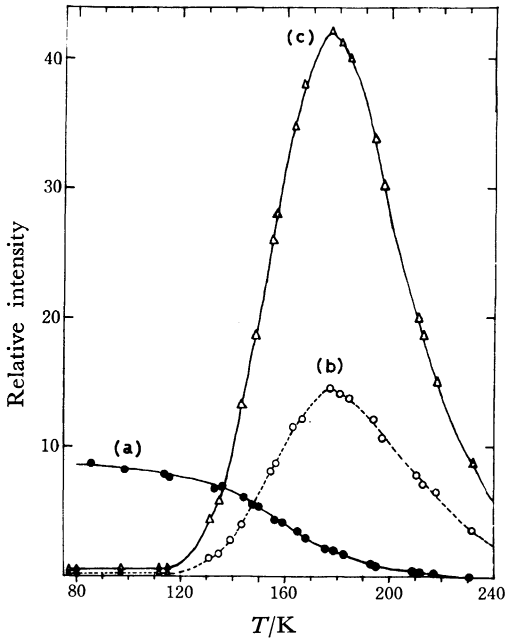

Fig. 3. Temperature dependence of the delayed luminescence of naphthalene in biphenyl host in the temperature region above 77 K. Concn: 1.0×10^{-2} mol/mol. (a): Phosphorescence intensity observed at 475 nm, *i.e.*, the 0,0-band shown in Fig. 2; (b) and (c): delayed fluorescence intensities observed at 318 nm (the 0,0-band) and the corresponding band shown in Fig. 1, respectively. No correction was made for the spectral response of the apparatus.

temperature region above 77 K are shown in Fig. 3. The results on DF observed at band d are not shown in the figure because it is similar to those of bands b and c as far as the temperature dependence is concerned. The results obtained with the guest concentrations of 1.0×10^{-3} and 1.0×10^{-4} mol/mol were also similar to those obtained with the guest concentration of 1.0×10^{-2} mol/mol just mentioned above. As can be seen in Fig. 3, the DF intensities observed at bands b and c remain constant at least in the temperature range of 77—110 K. This thermal behavior is quite similar to that in the benzo[*f*]quinoline–biphenyl system[2] except that $T_{\max}$ (the temperature at which maximum intensity of DF occurs) shifts to the higher temperature. These suggest that I_{DF} below 77 K may be independent of temperature. This system has very weak delayed luminescence at temperatures below 77 K, which we were not able to study quantitatively even by use of an NF LI-572B auto lock-in amplifier, partly because of the use of glass dewars. Incidentally, Misra[4] has reported that I_{DF} observed in the same system remains fairly constant in the temperature range from 6 to 77 K, 77 K being the highest temperature in their study. On the other hand, we also observed TIDF in the range of 77—105 K. Combining these results obtained in the different temperature regions, it may be concluded that TIDF exists over a wide range of temperature in this system just as in the case of the benzo[*f*]quinoline–biphenyl system. Hence, the important features of TIDF may be investigated in the region above 77 K. In this system, a rather peculiar temperature dependence of I_{DF}, as was already pointed out by Misra and McGlynn,[8] was found in the lower temperature region where an exponential temperature dependence is expected. This peculiarity may be correlated to the DF decay behavior at the same lower temperature region[2] and we emphasize that this peculiarity is due to the existence of TIDF over a wide range of temperature.

Evaluation of Activation Energy from Intensity Analyses. We have emphasized in the previous papers[1,2] that the peculiarity of DF in the lower temperature region can be understood well in accodance with the kinetic model if we take into consideration the temperature-independent portion of DF in a process of estimation of I_{DF}. We use the following three Arrhenius plots[2,9] in order to estimate the activation energy ΔE from the intensity analyses:

(1) In the higher temperature region, $\log I_P$ *vs.* $1/T$ (plot (1))
(2) in the lower temperature region, $\log I_{DF}$ *vs.* $1/T$ (plot (2))
(3) in the whole temperature region, $\log I_{DF}/I_P{}^2$ *vs.* $1/T$ (plot (3)).

In Fig. 4 are shown plots (1) and (2) obtained with three different concentrations, together with the plot obtained using corrected values of I_{DF}, *i.e.*, $[(I_{DF})_{\text{total}}-I_{\text{TIDF}}]$. Among the plots, only the latter one gave good fits to straight lines in all the concentrations studied. Figure 5 shows the results obtained with plot (3) in the three different concentrations. Here also, only the plot obtained with the corrected values of I_{DF} gave a straight line over the whole temperature range. In the naphthalene–biphenyl system, however, the effect of the correction is found to be smaller than that in the benzo[*f*]quinoline–biphenyl system, reflecting the fact that the temperature-independent fraction is much smaller, as can be seen in Fig. 3. The slopes of the straight-line portions shown in Figs. 4 and 5 give the activation energies listed in Table 1, which are comparable with the spectroscopic value[8] of 1940 cm^{-1}. Misra and McGlynn[8] obtained the ac-

TABLE 1. ACTIVATION ENERGIES[a] AND RATIOS $I_{TIDF}/(I_{DF})_m$

Guest concn (mol/mol)	Band[c]	ΔE (cm^{-1})[b]				I_{TIDF}[f] / $(I_{DF})_m$
		log I_{DF}/I_P^2 *vs.* $1/T$		log I_{DF} *vs.* $1/T$ Corrected[e]	log I_P *vs.* $1/T$	
		Uncorrected[d]	Corrected[d]			
1.0×10^{-2}	c	1755	1770	1900	1950	0.012
1.0×10^{-3}	c	1970	2040	1980	2030	0.004
1.0×10^{-4}	c	2340	2400	1910	1950	0.004

a) The spectroscopic energy gap of host triplet-guest triplet state is 1940 cm^{-1} for the naphthalene-biphenyl system.[8] b) Activation energy calculated from the temperature dependence of the delayed luminescence. See text. c) See Fig. 1. d) See text. e) Only the corrected plot gives a good fit to a straight line. See text. f) $(I_{DF})_m$ denotes the maximum I_{DF} at T_{max}.

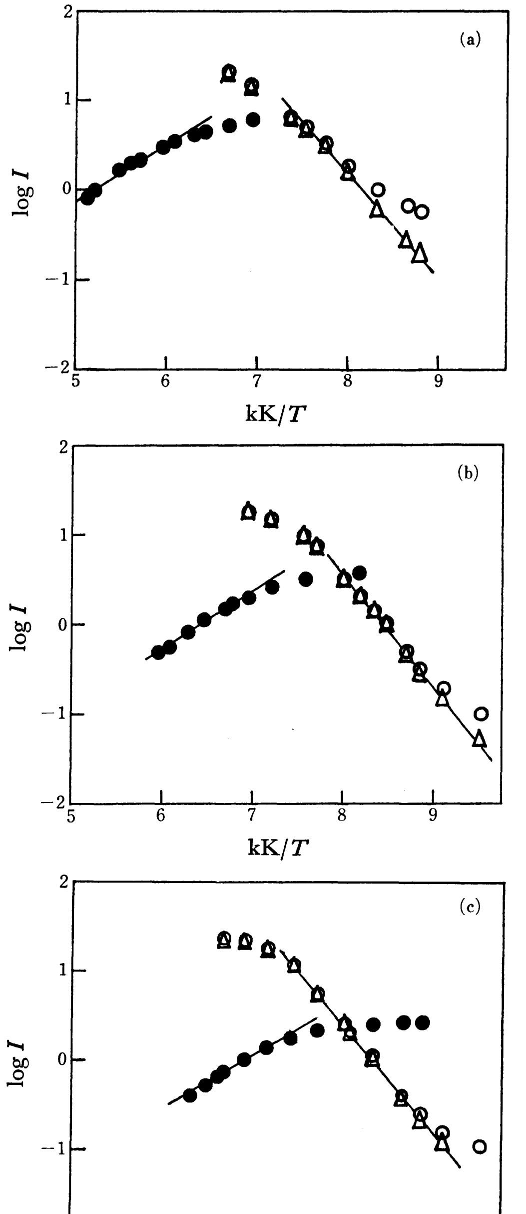

Fig. 4. Plots of log $(I_{DF})_{total}$ (○), log $[(I_{DF})_{total}-I_{TIDF}]$ (△), and log I_P (●) *vs.* $1/T$ with I_{DF} at band c shown in Fig. 1. Concn: (a) 1.0×10^{-2}, (b) 1.0×10^{-3}, (c) 1.0×10^{-4} mol/mol.

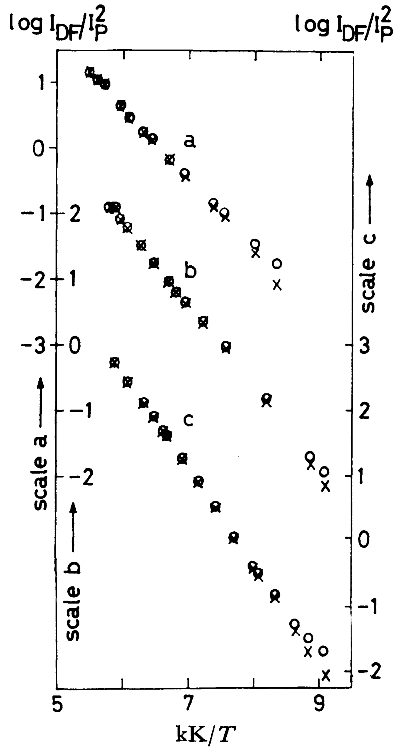

Fig. 5. Plots of log $(I_{DF})_{total}/I_P^2$ (○) and log $[(I_{DF})_{total}-I_{TIDF}]/I_P^2$ (×) *vs.* $1/T$ with I_{DF} at band c. Concn: (a) 1.0×10^{-2}, (b) 1.0×10^{-3}, (c) 1.0×10^{-4} mol/mol.

tivation energy of 1760 cm^{-1} from the "uncorrected" part of plot (3) and 175 K for T_{max}. Our uncorrected results are in good agreement with theirs. We would like to emphasize here that, according to our results, the existence of shallow traps in host crystal lattices suggested by Misra and McGlynn[8] as an interpretation of DF in the lower temperature region is in doubt and that it should be re-interpreted as due to the existence of TIDF as has been detailed on the benzo-[*f*]quinoline–biphenyl system.[1,2] The activation energies obtained from plot (3) with a very low guest concentration of 10^{-4} mol/mol seem too large to fall within the experimental error in either of the spectroscopic value or the other thermal activation energies. As was already suggested in the previous paper,[2] this may be due to an influence of a very weak trap-DF observed at such a very low concentration. Judging from the thermal values obtained from the other sources (*i.e.*, plots (1) and (2)) and from the discussion in the previous paper,[2)] it may be concluded that the thermal activation energy is independent of concentration.

Decay Behavior. We have observed exponential or nearly exponential decays of DF of naphthalene in biphenyl host crystals in the temperature range of 120—130 K,[3)] just as have been reported by Hirota[9)] and by McGlynn *et al.*[8,10,11)] in the vicinity of the so-called characteristic temperature (*i.e.*, the temperature at which deviations from exponential decay behavior of P begin to occur). These experimental observations indeed seem to be in accordance with our suggestion[2)] that when the contribution of TIDF is negligible and the decay of temperature-dependent DF remains exponential, the exponential decay behavior of DF to be observed will be expected at least in the vicinity of the characteristic temperature. Detailed results on the decay behavior will be presented elsewhere.

Some Remarks on the Nature of TIDF. In the last column of Table 1 are given the ratios of I_{TIDF} to I_{DF} at T_{max}, that is, $I_{\mathrm{TIDF}}/(I_{\mathrm{DF}})_{\mathrm{m}}$. For naphthalene in biphenyl host, Misra obtained a value of 0.12 for the above ratio from the temperature dependence of I_{DF},[4)] while our values are lower by one order as listed in Table 1. These ratios seem to exhibit the concentration dependence, as have already been suggested by us, and are much smaller than those obtained in the benzo[*f*]quinoline–biphenyl system.[1,2)] In any event, considering the fact that we have observed TIDF, it may be concluded that the overlap of the P and T-T absorption bands is not necessarily significant for the occurrence of TIDF. Recently, Gondo *et al.*[12)] have suggested, on the sound basis of the results on the concentration depolarization in P and normal fluorescence of some aromatic compounds in ethanol glass at 77 K, that formation of the molecular complexes might be responsible for the energy transfer observed in the benzophenone–naphthalene-in-rigid-glass system by Terenin and Ermolaev.[13)] Namely, the experimental results that the triplet-triplet energy transfer is inefficient and is of the short range phenomenon,[12)] and that TIDF has been observed at the low concentrations of the order of 10^{-4} mol/mol, suggest that the formation of molecular aggregates in mixed crystals may be responsible for the existence of TIDF.[2,14)]

Similar TIDF has also been observed for naphthalenes and phenanthrenes in biphenyl host crystals,[4,9)] for perprotobenzene in perdeuterobenzene host crystals,[15)] and in the crystalline 1,2,4,5-tetracyanobenzene–biphenyl complex,[16)] as well as for the naphthalene- and benzo[*f*]quinoline–biphenyl systems. Very recently, in the benzo[*h*]quinoline–biphenyl system, TIDF has also been observed and the above-mentioned correction has been carried out successfully.[17)] Therefore, it may be allowed to state that the existence of TIDF in organic mixed crystals is a general phenomenon and the correction should be carried out in those systems where TIDF is observed.

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