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TEMPERATURE-INDEPENDENT DELAYED FLUORESCENCE IN BIPHENYL HOST: A RE-EXAMINATION OF ACTIVATION ENERGY[1)]

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The delayed fluorescence observed in the mixed crystals of benzo(f)quinoline in biphenyl host has been found to be independent of temperature in the low-temperature region from 90°K down to liquid helium temperature, and subtraction of this temperature-independent contribution gave straight-line fits of the log I_{DF}/I_P^2 -vs- 1/T plots over the whole temperature range studied. In addition, some remarks have been made on the concentration effect.

We here report that the delayed fluorescence observed in the mixed crystals of benzo(f)quinoline in biphenyl host has been found to be independent of temperature over a wide range from 90°K down to liquid helium temperature,[1,2)] and that subtraction of this temperature-independent contribution gave straight-line fits of the log I_{DF}/I_P^2 -vs- 1/T plots, that is, a single activation energy to each of the plots over the whole temperature range studied, instead of two different ones as usually assumed to exist. This is a striking contrast to the results published previously, and is important in suggesting that the temperature-dependent delayed fluorescence phenomenon would thereby be interpreted generally in a more straightforward way than it has been so far.

Similar temperature-independent delayed fluorescence has been noticed by Hirota[3)] for naphthalenes and phenanthrenes in biphenyl host crystals, and by Hatch and Nieman[4)] for perprotobenzene in perdeuterobenzene host crystals, in such narrow ranges as 77 - 90°K and 4 - 8°K respectively. Very recently, Misra[5)] has reported an observation of temperature-independent delayed fluorescence in the systems similar to ours, and inferred that the direct guest triplet-guest triplet annihilation was responsible. Incidentally, we have also published a preliminary report on the same system as studied in this work, and concluded that the low-temperature delayed fluorescence improbably involved the host exciton as the transport for the triplet state energy migration.[2)] Yagi, Nagakura, and Hayashi[6)] observed for the first time the delayed charge-transfer fluorescence in the crystalline 1,2,4,5-tetracyanobenzene-biphenyl complex, and found that the delayed fluorescence was independent of temperature in the low-temperature range of 4.2 - 29°K. However, in these studies, the significance of the temperature-independent portion of the delayed fluorescence has never been explored, in particular, in relation to the thermal process of activation.

The chemicals used were obtained from Tokyo Kasei Kogyo Co., Ltd. Biphenyl was recrystallized twice from ethanol, and was zone refined over 200 passes. Benzo(f)quinoline was subjected to the same chemical treatment as described previously,7) and was finally zone refined with 250 passes.

Emission spectra were recorded with a Bausch and Lomb 500-mm grating monochromator equipped with an RCA 1P28 photomultiplier, and a Hitachi recorder model QPD-54. Exciting radiation was obtained from a 1-kW high-pressure mercury arc lamp. A rotating-disk phosphoroscope was used to exclude normal fluorescence. Temperatures were measured by means of a copper-constantan thermocouple, and a 1/8-W, 51-ohm Allen-Bradley carbon resistor, for the regions above and below 77°K respectively.

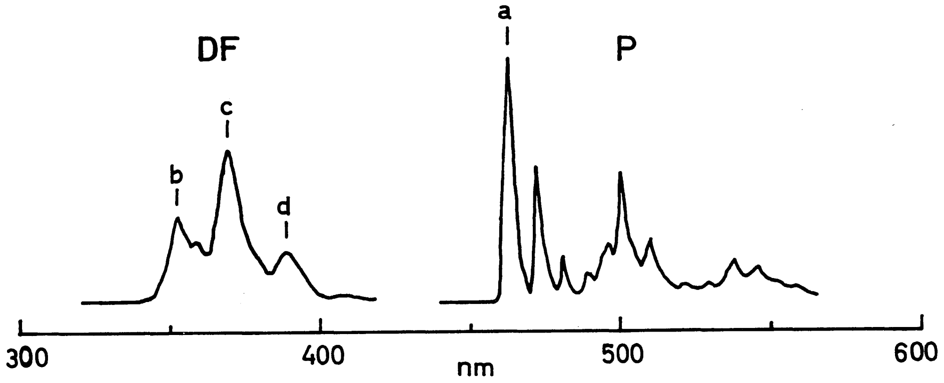

Fig. 1. The delayed fluorescence (DF) and phosphorescence (P) spectra of benzo(f)quinoline in biphenyl host at 4.2°K. Detection sensitivity was raised in the observation of delayed fluorescence. Concn.: 1.0×10^{-2} mol/mol.

Temperature dependence was studied over the range extending from 4.2°K to 230°K. Concentrations studied ranged from 10^{-4} to 10^{-2} mol/mol. Benzo(f)quinoline has been chosen as guest since it is stable to irradiation, and fluoresces efficiently as described in the previous paper.2) One of the typical observations is shown in Fig. 1 for the convenience of discussion.

Temperature dependence of the delayed fluorescence intensity, I_{DF} , and the phosphorescence intensity, I_P , at various guest concentrations is shown in Fig. 2. As this figure shows, at a guest concentration of 1.2×10^{-2} mol/mol, I_{DF} was essentially independent of temperature in the range of 25-77°K, while at lower temperatures it was dependent on temperature and reached a sharp maximum around 10°K. Similar behavior was also observed at a guest concentration of 1.25×10^{-3} mol/mol. However, the maxima around 13°K are fairly lower compared to those in Fig. 2(A). On the other hand, at a more dilute concentration of 1.0×10^{-4} mol/mol, I_{DF} remained constant over a wide range of 4.2 - 77°K, showing no appreciable maximum around 10°K. This is quite different from the behavior of the other two cases of higher guest concentration just mentioned above. As for the maximum around 10°K, an empirical relation of Misra and McGlynn8) predicts an activation energy of the order of 100 cm^{-1}. This shallow depth and the disappearance of the maximum around

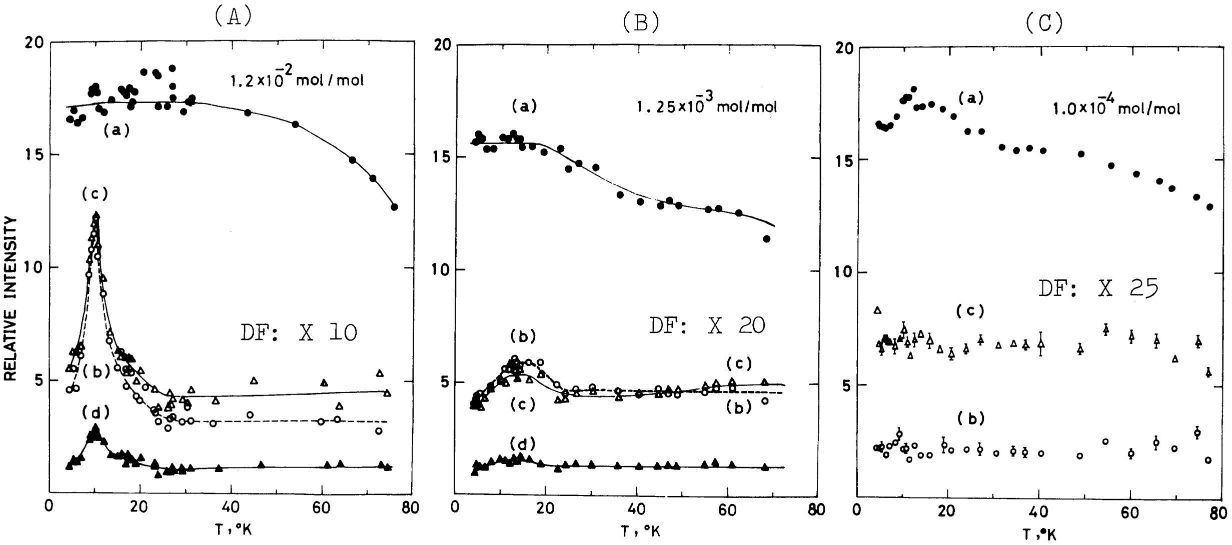

Fig. 2. Temperature dependence of the delayed luminescence of benzo(f)quinoline in biphenyl host. (a): Phosphorescence intensity observed at 464 nm, the 0,0-band; (b), (c), and (d): delayed fluorescence intensities observed at the corresponding bands shown in Fig. 1. No correction was made for the spectral response of the apparatus.

10°K in the concentration as low as 10^{-4} mol/mol lead to a conclusion that the pertinent trap is of the so-called X-trap. Moreover, it may be concluded that the mixed crystals studied in this work were sufficiently pure since this shallow depth is smaller by a factor of 10 than the depth involved in the thermal activation process to be discussed later on, and hence it is not expected to be involved therein.

As for I_P, it appears to be independent of temperature at lower temperatures, while at higher temperatures it falls off with increasing temperature, in every case shown in Fig. 2.

We have also studied the temperature dependence of I_{DF} and I_P at various guest concentrations in the temperature range above 77°K,[1,2] and have evaluated the ratio $I_{DF}(85°K)/I_{DF}(T_{max})$ since at 85°K I_{DF} approximately equals its temperature-independent contribution. Here, T_{max} is the temperature where the delayed fluorescence reaches its maximum intensity. This ratio gives an approximate value for the fraction of all triplets which decay via a second-order mechanism, namely triplet-triplet annihilation, in the temperature-independent range.[4,5] The ratios thus obtained with three different guest concentrations are listed in the last column of Table 1. It may be noted that the ratios at the guest concentration of 1.2×10^{-2} mol/mol are nearly three times as large as those at the other two lower concentrations.

Misra and McGlynn[8] have found that the plot of log I_{DF}/I_P^2 -vs- $1/T$ gives a good fit to a straight line in the high-temperature region, whereas in the low-temperature region such a plot deviates considerably from that straight line, showing a much smaller slope. They have also suggested on the basis of the smaller

Table 1. Guest-concentration dependence of the ratio $(I_{DF})_c/(I_{DF})_m$ and the activation energies.[a]

Guest concn. (mol/mol)	Band[c]	T_{max}(°K)[d]	$\Delta E(cm^{-1})$[b]			$(I_{DF})_c/(I_{DF})_m$[g]
			From T_{max}[e]	Uncorrected[f]	Corrected[f]	
1.2×10^{-2}	b	129	1495	1630	1700	0.2
	c	130	1507	1640	1680	0.2
	d	132	1530	....	....	0.25
1.25×10^{-3}	b	125	1450	1950	1900	0.07
	c	124	1437	1920	1900	0.06
	d	124.5	1443	....	....	0.07
1.0×10^{-4}	b	129	1495	2000	2080	0.07
	c	128	1484	2090	2160	0.08
	d	128.5	1489	....	....	0.06

[a] The spectroscopic energy gap of host triplet-guest triplet state is 1395 cm^{-1} for the benzo(f)quinoline-biphenyl system.[2)] An alternative value of 1465 cm^{-1} is obtained by adopting a value of 23010 cm^{-1} for the triplet state of biphenyl.[3,9)]

[b] Activation energy calculated from the temperature dependence of delayed fluorescence. For detail, see text.

[c] For notation, see Fig. 1.

[d] T_{max} is the temperature at which maximum intensity of delayed fluorescence occurs.

[e] Calculated from an empirical relation, $T_{max} = 0.06\Delta E/k$. See Ref. 8.

[f] See text.

[g] $(I_{DF})_c$ denotes the intensity of delayed fluorescence at 85°K, where I_{DF} approximately equals the temperature-independent contribution. $(I_{DF})_m$ refers to T_{max}.

activation energy obtained from this smaller slope that the delayed fluorescence observed in the vicinity of 77°K may well be due to the annihilation involving thermal depopulation of defect states. However, as Fig. 2 shows, the delayed fluorescence around 77°K was independent of temperature in our cases. Moreover, as mentioned above, the delayed fluorescence was independent of temperature in a wide range below 90°K.

In this connection, it is significant to re-examine the log I_{DF}/I_P^2 -vs- 1/T plots, since I_{DF} in the ratios I_{DF}/I_P^2 should duly be the temperature-dependent portion of the delayed fluorescence. As Fig. 3 shows, subtraction of the temperature-independent contribution gave straight-line fits of the semilog plots over the whole temperature region studied. The thermal activation energies thus obtained are listed in Table 1 under the heading of "corrected", together with the corresponding "uncorrected" values. It should be noted that an indisputable manifesta-

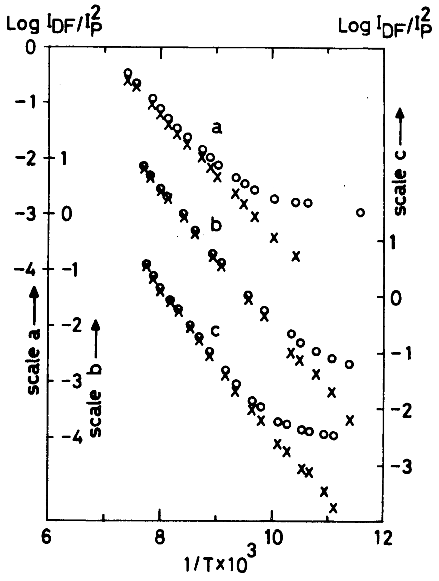

Fig. 3. Plot of log I_{DF}/I_P^2 as a function of 1/T with I_{DF} obtained at band (b) shown in Fig. 1.
Concn.: a) 1.2×10^{-2} mol/mol,
b) 1.25×10^{-3} mol/mol,
c) 1.0×10^{-4} mol/mol.
O: Uncorrected; X: corrected.

tion of the existence of the temperature-independent delayed fluorescence, as shown in Fig. 2, has encouraged us to attempt this kind of correction. The activation energies obtained from the semilog plots are comparable with the corresponding spectroscopic value of 1395 cm^{-1} , as far as the concentration of 1.2×10^{-2} mol/mol is concerned. However, those for the other two lower concentrations are too large. This concentration effect is not clear at present.

For comparison, we have also applied this type of correction to the experimental results on the phenanthrene-biphenyl system published by Misra and McGlynn,[8] obtaining a straight line which covers the whole temperature range studied. Accordingly, the suggestion made by McGlynn et al.[8,10] on the delayed fluorescence observed in the low-temperature region, in particular, in the vicinity of 77°K is hardly convincible.

In Table 1 are also collected the T_{max} values and the host-guest triplet separations ΔE deduced from T_{max} through the empirical relation mentioned above. The values of T_{max} seem to be in agreement with one another within the error of experiment, and hence so seem the corresponding values of ΔE. It may also be noted that the decay behavior of the delayed fluorescence and phosphorescence was observed to remain constant at least in the temperature range of 4.2 - 77°K.

Detailed description of the experimental results and discussion will be presented elsewhere.

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