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Time-Resolved Fluorescence Study of Exciplex and Triple Exciplex in 1,4-Dicyanobenzene and Alkylnaphthalenes

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Exciplex (DA)* and triple exciplex (DDA)* formation between 1,4-dicyanobenzene (DCB) and alkylnaphthalenes was investigated by steady-state and nanosecond time-resolved fluorescence spectroscopies at room temperature. Typical two-component decay of the exciplex and the fluorescence rise of the triple exciplex were observed in dioxane solutions of DCB and several alkylnaphthalenes. The results imply a significant dissociation process of (DDA)* to (DA)*. Triple exciplex formation *via* excimer (DD)* was proposed to be significant in a concentrated solution of alkylnaphthalene ($>10^{-1}$ M), while the triple exciplex was formed *via* the exciplex in a dilute solution of the electron donor.

Triple exciplex formation was reported first by Beens and Weller in the 1,4-dicyanobenzene (DCB) and naphthalene system. They reported the fluorescence lifetime of the exciplex (≈ 30 ns) and an extraordinary rate constant (1.8×10^{8} s^{-1}M^{-1}) of triple exciplex formation from the exciplex.2) Recently, Saltiel *et al.* reported triple exciplex emission in the system of 9,10-dichloroanthracene and 2,5-dimethyl-2,4-hexadiene in a polar solvent such as acetonitrile.3) On the other hand, Grellmann and Suckow have reported triple exciplex formation in the anthracene–diethylaniline system in the temperature region of ≈ 230—180 K and discussed its intersystem crossing to the triplet state of anthracene.4) More recently, Mimura and Itoh reported an intramolecular triple exciplex formation between two naphthyl moieties of 1,3-dinaphthylpropane (DNP) and DCB, and they suggested that the triple exciplex was not formed *via* intramolecular excimer of DNP, but *via* exciplex (DA)* formed between DCB and DNP.5) Preliminary results of the exciplex and the triple exciplex were also reported for the DCB and alkylnaphthalene system. The dissociation process from the triple exciplex to the exciplex was so significant that this system exhibits typical two-component decay of the exciplex and fluorescence rise of the triple exciplex.6) Although two-component decay of D*(or A*) and also fluorescence rise of (DA)* has been reported,7) there are no reports of lifetime measurements which bear on the transformation between the exciplex, (DA)*, and the triple exciplex, (DDA)*.

This paper reports steady-state and nanosecond time-resolved fluorescence studies of the triple exciplex as well as the exciplex in several solvents of the DCB and several alkylnaphthalene systems at room temperature. Typical two-component decay of the exciplex fluorescence and the fluorescence rise of the triple exciplex were observed in the dilute solution of alkylnaphthalenes and DCB in dioxane. Concentrated solutions ($>10^{-1}$ M) of acenaphthene (AcN) and DCB in dioxane or THF exhibit fluorescence rise of the exciplex, which is not attributable to exciplex formation from DCB and AcN, but to dissociation of the triple exciplex. Since a time-dependent exciplex concentration in the system cannot show any fluorescence rise of the exciplex (see Eq. 1),7,8) the triple exciplex formation *via* the excimer is suggested not to be negligible. This is consistent with the fact that the fluorescence quenching of alkylnaphthalene by DCB depends remarkably on the concentration of alkylnaphthalene above $\approx 10^{-1}$ M. The triple exciplex formation and dissociation in the intermolecular system of alkylnaphthalene and DCB are discussed in comparison with the results of the intramolecular system of DNP and DCB mentioned above.

Experimental

Commercially available 2-methylnaphthalene (2-MN), 1,5-dimethylnaphthalene (1,5-DMN) and 2,3,6-trimethylnaphthalene (2,3,6-TMN)(Tokyo Kasei) were purified by silica gel chromatography and recrystallized from methanol (spectrograde) several times. Zone-refined acenaphthene (AcN) which was available commercially (Tokyo Kasei) was also purified in a manner similar to that described above. The fluorescence spectra were recorded with a Hitachi MPF-2A spectrophotometer with an exciting light of 310 nm. Good commercial solvents (Dotite spectrosols) were used, and chloroform was used after purification through an alumina colum (Woelm, Activity I) for removal of methanol which was present as a stabilizer. Solutions were contained in squartz cells (1 cm) equipped with graded seals, and were degassed by freeze-thaw cycles at 10^{-4}—10^{-5} Torr. Rectangular quartz cells with lightpath length 0.1 mm and 1 mm were also used for the concentrated solution. The time-resolved fluorescence spectra and the fluorescence lifetimes were determined by analyzing exponential decay curves measured by an oscilloscope (Tektronix 465), and a photomultiplier, HTV-R342 or R666, and by excitation with a coaxial N_2 gas laser which has a maximum 20-kW photon peak intensity at 3371 Å.

Results and Discussion

Steady-State Fluorescence Study. Fluorescence spectra of dioxane solutions of alkylnaphthalene, $<10^{-4}$ M, and in the presence of several concentrations of DCB at room temperature exhibit ordinary fluorescence behavior as expected for the electron donor-acceptor system. The fluorescence intensity of alkylnaphthalene decreases and the exciplex fluorescence intensity ($\lambda_{\max}=$ 420—440 nm, $\tau = \approx 10$—15 ns) increases when the DCB concentration increases. Apparent rate constants for exciplex formation were obtained from linear Stern-Volmer plots of the fluorescence quenching of 2-MN by DCB, and found to be 1.6×10^{10} s^{-1}M^{-1} in dioxane and 2.5×10^{9} s^{-1}M^{-1} in chloroform assuming negligible reversal of exciplex formation (Scheme 1).

Excitation spectra monitored at 450 nm (concentration of electron donor $<10^{-1}$ M, where fluorescence was determined from front surface of the sample cell in the concentrated solution) and the absorption spectra of dioxane solutions of 2-MN and DCB by using 1 mm and 1 cm quartz cells indicate no complex formation in the ground state. Figure 1 shows fluorescence spectra of dioxane solutions of DCB (concentration, $\approx 10^{-2}$ M) and several concentrations of 2-MN. The fluorescence of both exciplex and alkylnaphthalene are quenched with increasing 2-MN concentration up to 10^{-3} M. In highly concentrated solution of electron donor, $> \approx 10^{-1}$ M, fluorescence intensity at the longer wavelength region increases and an isoemissive point is observed at $\approx$480 nm. The fluorescence at 490 nm region may be ascribed to the triple exciplex, as mentioned in the previous paper.[5,6] In the concentrated solution ($>10^{-1}$ M) of 2-MN, however, it is difficult to determine an exact stoichiometry of the triple complex from fluorescence intensity.

The Stern-Volmer plots of the fluorescence quenching of 2-MN show a linear relationship against DCB concentration, as mentioned above. The slope of the Stern-Volmer plots increases markedly with increasing 2-MN concentration $> \approx 10^{-1}$ M, as shown in Fig. 2. On the other hand, excimer fluorescence is known to be observed for alkylnaphthalene such as [2-MN] $> \approx 10^{-1}$ M, while excimer formation is negligible in more dilute solution of alkylnaphthalene.[9] However, unless triple exciplex formation *via* the excimer is taken into account, the fluorescence quenching of 2-MN by DCB cannot depend on the concentration of 2-MN (Scheme 1). This argument is still valid even if dissociation of the long lived excimer to D* might be significant in the concentrated solution of 2-MN. Anomalous fluorescence quenching by DCB was observed for other alkylnaphthalenes such as AcN in the concentrated solutions, [AcN] $> \approx 10^{-1}$ M. Therefore, the concentration dependence of the slope of the Stern-Volmer plot shown in Fig. 2 may be attributable to the triple exciplex formation *via* the excimer. These transformations of the excited species are shown in Scheme 1. The anomalous fluorescence quenching of alkylnaphthalene evident in this steady-state fluorescence measurement agrees well with results of the time-resolved fluorescence studies in the following section.

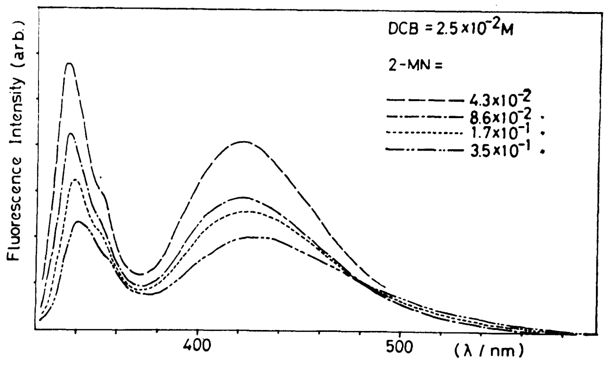


Fig. 1. Fluorescence spectra of dioxane solutions of DCB and several concentrations of 2-MN at room temperature.

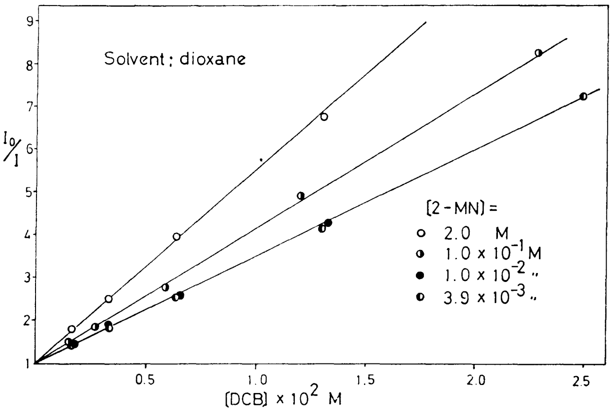


Fig. 2. Stern-Volmer plots of fluorescence quenching of 2-MN by DCB in several concentrations of 2-MN at room temperature.

Time-Resolved Fluorescence Study. Figure 3 shows time-resolved fluorescence spectra of a dioxane solution of DCB and 2-MN. The fluorescence spectra cen-

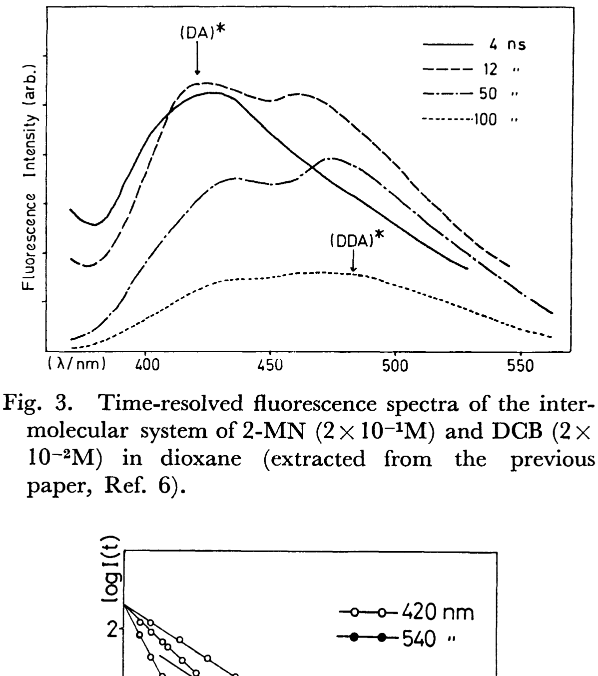


Fig. 3. Time-resolved fluorescence spectra of the intermolecular system of 2-MN (2×10^{-1}M) and DCB (2×10^{-2}M) in dioxane (extracted from the previous paper, Ref. 6).

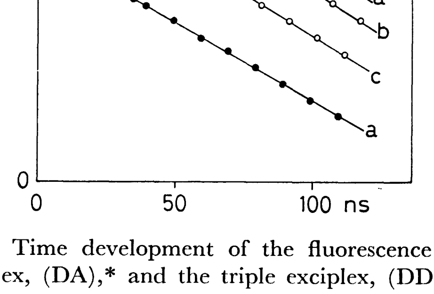
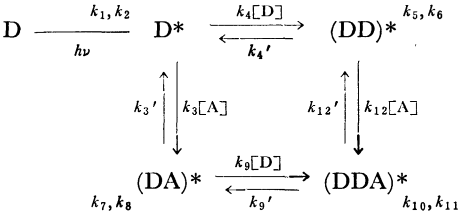


Fig. 4. Time development of the fluorescence of the exciplex, (DA),* and the triple exciplex, (DDA),* in dioxane solutions of 2-MN and DCB (2×10^{-1}M). The concentrations of 2-MN are 2.0×10^{-1}M (a), 3.5×10^{-3}M (b), and 8.8×10^{-4}M (c), respectively.

tered at 420 and 490 nm are ascribed to the exciplex and the triple exciplex, respectively. The fluorescence spectrum of the exciplex with a maximum at the 420—430 nm region was observed at 4 ns after laser pulse, while the fluorescence spectra of the exciplex as well as the triple exciplex were observed at 50—100 ns after a laser pulse. Figure 4 shows semilogarithmic plots of the fluorescence decay monitored at 420 nm in dioxane solutions of DCB and several concentrations of 2-MN. The fluorescence at 420 nm shows a single exponential decay in a high concentration of 2-MN, while the fluorescence at 420 nm exhibits a double exponential decay with decreasing concentration of 2-MN. On the other hand, fluorescence rise when the emission is monitored in the 470—580 nm region was observed from a concentrated solution of 2-MN and DCB (Fig. 4).

The photochemical interactions in the excited states are as follows:



Scheme 1.

where D and A are alkylnaphthalene and DCB, respectively. The rate constants k_1,k_5,k_7, and k_{10} are the radiative rate constants of each excited species, and k_2, k_6,k_8, and k_{11} are nonradiative rate constants. The rate constants k_3,k_4,k_9, and k_{12}, and their primed counter parts are for the association and dissociation of the excimer, the exciplex and the triple exciplex, respectively. If excimer formation is neglected in a dilute concentration of alkylnaphthalene,[2] the time dependent concentrations of the exciplex (DA)* and the triple exciplex (DDA)* are expressed by the following well known equations:[4,8]

$$[(DA)^*] = c_1 \exp(-\lambda_1 t) + c_2 \exp(-\lambda_2 t), \tag{1}$$

$$[(DDA)^*] = c_3\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\}, \tag{2}$$

where

$$\lambda_{1,2} = 1/2[k_7+k_8+k_9[D]+k_9'+k_{10}+k_{11}+k_{12}' \mp\{(k_9'+k_{10}+k_{11}+k_{12}'-k_7-k_8-k_9[D])^2 +4k_9k_9'[D]\}^{1/2}]. \tag{3}$$

The time lag (t_L) between a response curve of the triple exciplex fluorescence and the exciting laser pulse is given by[8]

$$t_L = \ln(\lambda_2/\lambda_1)/(\lambda_2-\lambda_1). \tag{4}$$

The value of λ_2 was obtained from t_L and decay of the triple exciplex for several concentrations of the electron donor in dioxane solution. The association rate constant (k_9) was obtained from a slope of $\lambda_1+\lambda_2$ against alkylnaphthalene concentration, and the dissociation rate constant (k'_9) was obtained from λ_2 and fluorescence lifetimes of the exciplex, $(k'_3+k_7+k_8)^{-1}$, in a very dilute solution of electron donor compared with that of DCB. The rate constant k_9 and k'_9 obtained here for the 2,3,6-TMN and DCB system are 2.1×10^9 s^{-1}M^{-1} and 1.5×10^7 s^{-1}, respectively as reported in a previous paper.[5] These rate constants demonstrate a significant dissociation process of the triple exciplex to the exciplex, which are in good agreement with results obtained from the typical two-component decay of the exciplex fluorescence. However, the values of k_9 determined in the concentrated solutions of alkylnaphthalene, $>\approx10^{-1}$ M, appear to be considerably smaller than those determined in dilute solution. This is attributed to formation of the triple exciplex *via* the excimer as well as the exciplex in concentrated solutions of alkylnaphthalenes.

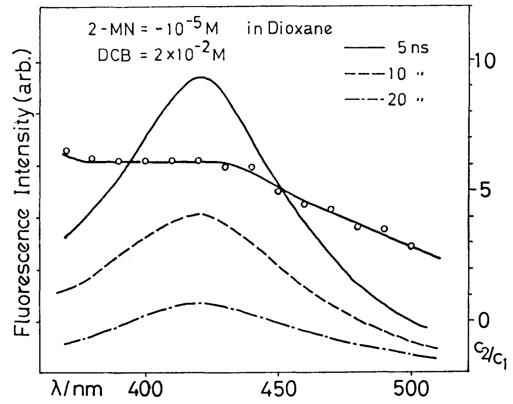


Fig. 5. Time-resolved fluorescence spectra of the intermolecular system 2-MN ($\approx10^{-5}$M) and DCB (2×10^{-2}M) in dioxane at room temperature and plots of c_2/c_1 at several wavelengths.

In order to exclude the ambiguity that the double-exponential decay curve of the exciplex may overlap the decay of the triple exciplex, ratios of c_2 and c_1, in Eq. 1, were plotted *vs.* the wavelength. The values of c_1 and c_2 were obtained by a deconvolution method from the decay curves of the exciplex. Figure 5 shows these plots and time-resolved fluorescence spectra in the dilute solution of 2-MN and DCB. The ratio of c_2/c_1 does not depend on the wavelength in the 380—440 nm region in dioxane solution. The fact implies real two-exponential decay of the exciplex fluorescence. Time-resolved fluorescence spectra in dilute solution shown in Fig. 5 reveal no significant triple exciplex but two-component decay of the exciplex fluorescence. Similar behavior of the fluorescence decay of the exciplex was observed for DCB associated with other alkylnaphthalenes. The results are summarized in Table 1.

The AcN–DCB system in a polar solvent such as THF does not exhibit triple exciplex fluorescence in either steady-state fluorescence or in time-resolved fluorescence spectra. The plots of c_2/c_1 also indicate no triple exciplex fluorescence even in 500—590 nm. Nevertheless, the double exponential decay of the exciplex fluorescence was observed at low concentration of the electron donor ($<10^{-5}$ M). A short lifetime component in the double exponential decay decreased and a long lifetime component increased with increasing AcN concentration. Furthermore, the fluorescence rise of the exciplex was observed in concentrated solutions of AcN $>\approx10^{-1}$ M. Semilogarithmic plots of these exciplex fluorescence decay for several concentrations of AcN are shown in Fig. 6.

TABLE 1. FLUORESCENCE MAXIMA OF EXCIPLEX (DA)* AND TRIPLE EXCIPLEX (DDA)*, THEIR LIFETIMES AND TIME LAGS t_L

Electron donor	Fluorescence maxima		Fluorescence lifetimes		
	(DA)* (nm)	(DDA)* (nm)	t_L [a] (ns)	(DA)* [b] (ns)	(DDA)* [a] (ns)
2-MN	425	480	6	10 (49)	56
1,5-DMN	435	490	8	6 (40)	38
2,3,6-TMN	440	510	12	8 (49)	55

Concentration of DCB is constant (2×10^{-2} M). Concentrations of electron donors are $10^{-1}\approx10^{-2}$ M (a) and $\approx10^{-4}$ M (b), respectively. Values in parentheses are long lifetime components in exciplex fluorescence decay curves.

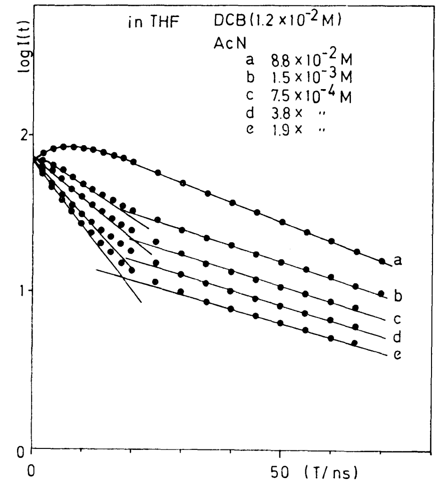


Fig. 6. Time developments of the fluorescence of the exciplex in the DCB-AcN system at room temperature.

In the dioxane solution of AcN and DCB, slope of Stern–Volmer plots of the AcN fluorescence against DCB concentration increased with increasing AcN concentration, $>\approx10^{-1}$ M, as mentioned for the 2-MN and DCB system. The experimental fact was accounted for by a postulate of significant triple exciplex formation *via* excimer and dissociation to the exciplex in high concentration of AcN, as mentioned above. This is consistent with the observation of fluorescence rise for the exciplex in a concentrated solution of AcN, as shown in Fig. 6. The excimer is implicated in the triple exciplex formation because the time dependent exciplex concentration as expressed by Eq. 1 cannot show any fluorescence rise, nor is fluorescence rise from the direct formation of exciplex between excited AcN and DCB molecules detected.

In the DCB and 1,3-dinaphthylpropane (DNP) system, the absence of concentration dependence of the fluorescence lifetimes of the excimer on the DCB concentration suggested that the intramolecular triple exciplex is not formed *via* excimer but formed *via* exciplex, as reported in the previous papers.[5,6] However, similar concentration dependence of the excimer fluorescence lifetimes was difficult to determine in the DCB and alkylnaphthalene systems. This is because the weak excimer fluorescence (lifetime $\tau=\approx35$ ns) was hardly distinguishable from the emission of the exciplex ($\tau=\approx10$ and ≈45 ns). In the concentrated solution of alkylnaphthalene where the excimer formation occurs,[9] the triple exciplex formation *via* the excimer as well as the exciplex was suggested in this paper. On the other hand, the intramolecular excimer formation is well known in symmetric DNP ($\beta\beta$- and $\alpha\alpha$-DNP).[10] Therefore, if the triple exciplex formation from the excimer and DCB is significant as mentioned above, the triple exciplex formation *via* the excimer can be also observed in the DNP and DCB system. The results of no triple exciplex formation *via* excimer in the DCB and DNP systems were ascribed to the different geometrical arrangement of two naphthyl moieties in the triple exciplex from that of the excimer. The favorable intramolecular excimer of DNP was regarded as a parallel sandwich structure of the long axis in the naphthyl moiety,[10] while two naphthyl moieties were regarded to be twisted in the molecular plane by a small angle around an axis perpendicular to the plane (a twisted model[6]). These two models cannot be transformed into each other while retaining the distance between the two aromatic moieties which is imposed by the steric requirements of the trimethylene chain. In the formation of the triple exciplex from the excimer of alkylnaphthalene and DCB which is suggested here, no steric hindrance in the transformation between a parallel sandwich model and a twisted model is anticipated.

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