Inter- and Intramolecular Exciplexes and EDA Complexes in the 9,10-Dicyanoanthracene and Alkylbenzene Systems

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The exciplex (above ~150 K) and EDA complex (below ~120 K) fluorescence were observed in the 9,10-dicyanoanthracene and several alkylbenzene systems and also in the intramolecular system of (9,10-dicyanoanthracene)-$(CH_2)_3$-(pentamethylbenzene) in the nonpolar solvents. The exciplex fluorescence lifetimes and maxima both in the inter- and intramolecular systems exhibit the continuous change to those of the corresponding EDA complex, which implies the identical fluorescent state of the exciplex and EDA complex. The fluorescence lifetimes and the fluorescence polarization suggest that the fluorescent state of both exciplex and EDA complex may be mostly locally excited state of electron acceptor.

Steady-state and transient spectroscopies, and also theoretical consideration of the electron donor-acceptor (EDA) system in the excited state suggest that the exciplex and the EDA complex may be essentially identical each other. It has been believed, however, that the EDA complex stable in the ground state can not be formed in the EDA system which exhibits the fluorescence of the exciplex stable only in the excited state.[1,2] Itoh and Mimura reported the exciplex and also the EDA complex formation in the nonpolar solution of 9,10-dicyanoanthracene (DCA) and several alkylnaphthalenes, and demonstrated a direct evidence for an identical fluorescent state of the exciplex and EDA complex.[3,4] Recently, Gaweda and Prochorow[5] reported similar evidence for the identical fluorescent state in the tetracyanobenzene and *p*-xylene system from their measurements of the decay times of fluorescence and investigation of the influence of solvent polarity on the fluorescence spectra.

On the other hand, the experimental and theoretical studies in the previous papers revealed that there are two different fluorescent state of the exciplex and EDA complex in the intramolecular system of (9,10-dicyanoanthracene)-$(CH_2)_3$-(naphthalene) (DCAN).[6,7] These two different fluorescent states were attributed to the unsymmetric property of the naphthyl moiety around the trimethylene chain in DCAN. Therefore, an intramolecular system containing an electron donor which has C_2 symmetry around the trimethylene was predicted to show the exciplex and EDA complex fluorescences from the identical fluorescent state. This paper describes further investigation of the exciplex and the EDA complex in the DCA-alkylnaphthalene system and in the intramolecular system of (9,10-dicyanoanthracene)-$(CH_2)_3$-(pentamethylbenzene).

Experimental

Materials and Measurements. Purification of materials and solvents were described in the previous papers. Commercial zone-refined samples of hexamethylbenzene were used after recrystallization (three times) from ethanol. Pentamethylbenzene and durene were recrystallized six or seven times from ethanol.

Determination of the fluorescence and absorption spectra, and the fluorescence polarization were described previously.[4,6] The fluorescence lifetimes and time-resolved fluorescence spectra were determined by analyzing exponential decay curves measured by an oscilloscope (Tektronix 465), and by a coaxial N_2 gas laser excitation (3371 Å, ~20 kW, ~5 ns width).

Synthesis of 1-(9,10-Dicyano-2-anthryl)-3-(pentamethylphenyl)-propane. The sample of *1-(9,10-dicyano-2-anthryl)-3-(pentamethylphenyl)propane* was synthesized by bromination and cyanogenation of 1-(2-anthryl)-3-(pentamethylphenyl)propane, which was prepared by the similar route to that of 1,3-dinaphthylpropane.[8] The unsaturated ketone, *1-(2-anthryl)-3-(pentamethylphenyl)-2-propen-1-one*, was prepared from 2-acetylanthracene and pentamethylbenzaldehyde: mp 214—216 °C.

Found: C, 88.22; H, 6.19%. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92%.

A solution of the unsaturated ketone (400 mg) in tetrahydrofuran (100 ml) was hydrogenated over 5% Pd/C for about 8 hr. The ketone, *1-(2-anthryl)-3-(pentamethylphenyl)-1-propanone* was obtained: mp 190 °C.

Found: C, 87.99; H, 7.49%. Calcd for $C_{28}H_{28}O$: C, 88.38; H, 7.42%.

The ketone (300 mg) was reduced in refluxing (4 hr) diethylene glycol (5 ml) containing hydrazine (1 ml, ~95%) and sodium hydroxide (500 mg). The mixture was diluted with water and extracted with benzene. The yellow product was purified through silica gel with benzene–hexane, and recrystallized from benzene–hexane: mp 181 °C.

Found: C, 91.48; H, 7.49%. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25%.

The hydrocarbon was brominated and cyanogenated in the way described in the previous paper.

1-(9,10-Dibromo-2-anthryl)-3-(pentamethylphenyl)propane. Recrystallized from benzene: mp 157 °C.

Found: C, 64.01; H, 5.42%. Calcd for $C_{28}H_{28}Br_2$: C, 64.13; H, 5.38%.

1-(9,10-Dicyano-2-anthryl)-3-(pentamethylphenyl)propane. Purifiedaby preparative thin layer chromatography and recrystallized from hexane: mp 264 °C.

Found: C, 86.43; H, 6.75; N, 6.54%. Calcd for $C_{30}H_{28}N_2$: C, 86.49; H, 6.78; N, 6.73%.

Results and Discussion

The exciplex formation between DCA and aromatic hydrocarbons was reported first by Chandross and Ferguson.[9] The exciplex fluorescence in the 3-methylpentane (MP) solutions of DCA and several alkylbenzenes were observed at room temperature. The exciplex fluorescence was almost quenched below ~150 K, while the fluorescence due to the EDA complex was observed in the nonpolar solution of these

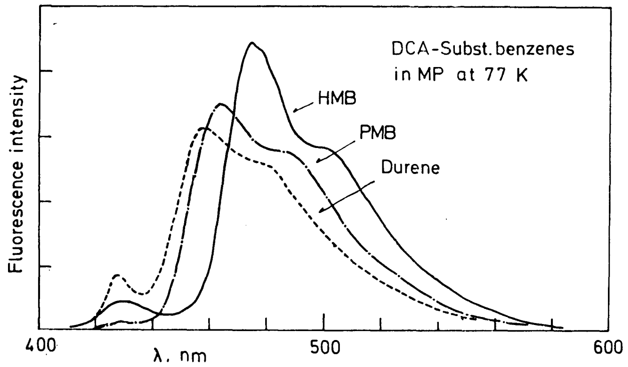

Fig. 1. Fluorescence spectra of MP solutions of DCA and several alkylbenzenes at 77 K (concentrations: DCA, 2×10^{-6} M; HMB, 6×10^{-3} M; pentamethylbenzene, 1×10^{-2} M; durene, 9×10^{-3} M).

EDA systems below ~120 K. The fluorescence spectra of the EDA complexes at 77 K are shown in Fig. 1. These exciplex and EDA complex were characterized by their fluorescence excitation and the absorption spectra at room temperature and at low temperature. The EDA complex fluorescence was observed only in the nonpolar solvents such as MP and methylcyclohexane (MC), but none in the polar solvents.[3,6] The fluorescence behavior in DCA-alkylbenzene is quite similar to the results in DCA-alkylnaphthalene reported previously.[3,4,6] Fluorescence lifetimes of these exciplex and EDA complex are considerably smaller in the DCA–alkylbenzene system (summarized in Table 1) than in the DCA-alkylnaphthalene system (~40—100 ns).

Table 1. Fluorescence maxima and life times of the exciplex (at room temperature) and the EDA complex (at 77 K) in MP solution of DCA and several alkylbenzenes, and of DCAB

DCA-alkylbenzenes and DCAB	Exciplex		EDA complex	
	λ, nm	τ, ns[a)]	λ, nm	τ, ns[a)]
Hexamethylbenzene	494	19	476	32
Pentamethylbenzene	482	21	465	34
Durene	467	21	~460	34
DCAB	501	72	~507[b)]	106

a) Errors are approximately ±1 ns. b) Determined by time-resolved fluorescence spectra.

The fluorescence of the EDA complex in the MP solution of DCA and hexamethylbenzene (HMB) was determined at 77 K to exhibit very small positive polarization with the excitation at 360 nm, as shown in Fig. 2. In the DCA and alkylnaphthalene systems reported previously, the fluorescence polarization of the MP solution of the EDA complex at 77 K with the excitation at 370 nm (LE band in DCA) decreased from negative to more negative value, and the fluorescence lifetimes increased with decreasing ionization potential of alkylnaphthalenes.[4)] The results of these fluorescence lifetimes and polarizations in DCA-alkylnaphthalenes were attributed to the considerable charge-transfer character in the fluorescent state of the EDA complex. From the small fluorescence lifetimes and small positive polarization obtained in DCA–alkylbenzenes, the fluorescent state of the EDA complex in this system seems to consist mostly of the locally excited state of DCA. The fluorescence lifetimes in the MP or MC solution of DCA–HMB exhibit continuous variation from room temperature (exciplex) to 77 K (EDA complex) as shown in Fig. 3, which implies the identical fluorescent state of the exciplex and the EDA complex.

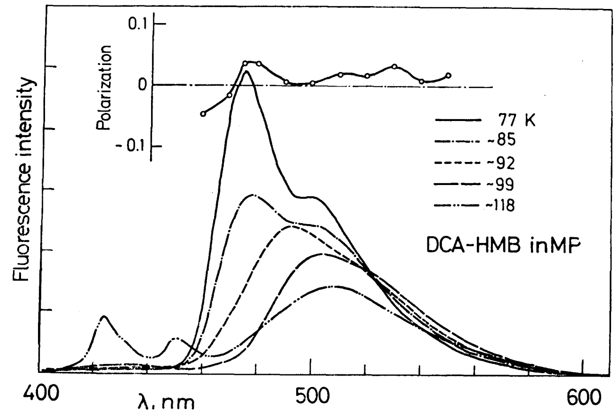

Fig. 2. Fluorescence spectra of an MP solution of DCA and HMB at several temperatures and fluorescence polarization at 77 K (excitation at 360 nm). Concentration: DCA, 5×10^{-6} M; HMB, 1×10^{-3} M.

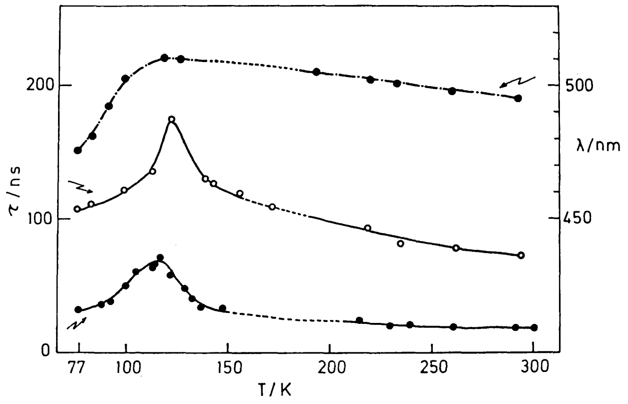

Fig. 3. Temperature dependence of fluorescence maxima and lifetimes of the exciplex and EDA complex in MP (lifetimes monitored at 540 nm); ----●----and —●— are fluorescence maxima and lifetimes in DCA–HMB, respectively, and —○— is the fluorescence lifetimes in DCAB.

The fluorescences of an MP solution of (9,10-dicyanoanthracene)-$(CH_2)_3$-(pentamethylbenzene) (abbreviated to DCAB) at several temperatures are shown in Fig. 4. The exciplex fluorescence (λ_{max} ~500 nm) was completely quenched below ~150 K, and no fluorescence maximum in this wavelength region was detected at 77 K. However, the time-resolved fluorescence spectra of this solution at 77 K revealed that the fluorescence with a maximum at ~510 nm was hidden by a strong fluorescence of the DCA moiety in DCAB, as shown in Fig. 5. The fluorescence excitation spectrum of this

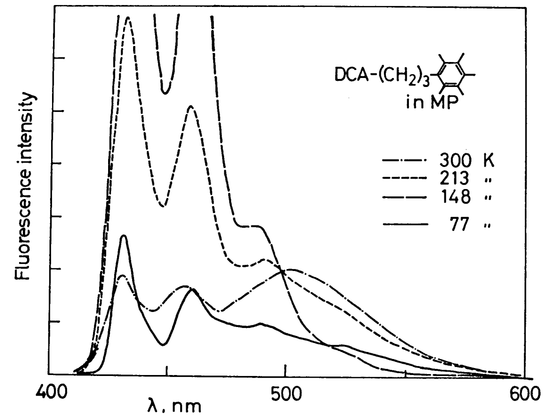

Fig. 4. Fluorescence spectra of an MP solution of DCAB at several temperatures (concentration: $\sim 4\times 10^{-5}$ M).

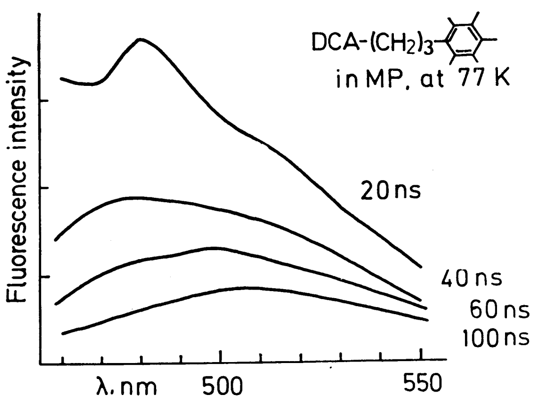

Fig. 5. Time-resolved fluorescence spectra of an MP solution of DCAB at 77 K.

solution (77 K) monitored at 530 nm showed significantly different from the spectrum monitored at 430 nm. Furthermore, the absorption spectrum of DCAB in dilute solution of MP ($\sim 10^{-5}$ M) demonstrated considerable EDA complex formation at 77—140 K. Therefore, the weak fluorescence of an MP solution of DCAB shown in Fig. 5 may be ascribed to the fluorescence of the intramolecular EDA complex.

The rise and decay curves of the exciplex fluorescence were observed in a dioxane solution of DCAB at room temperature by nanosecond laser excitation, while neither rise time of the exciplex fluorescence was detected in less viscous solution such as MP or 2-methyltetrahydrofuran at room temperature, nor rise time was detected in the viscous solution of DCAB in MP at ~100 K where the intramolecular EDA complex was formed. Similar time-development of the exciplex fluorescence was also observed in the intermolecular system of DCA–HMB. They are shown in Fig. 6. These results suggest that the fluorescence in the ~500 nm region at room temperature is ascribed to the exciplex different from the EDA complex at low temperature, though the characterization of the exciplex and the EDA complex was already suggested by the absorption and fluorescence excitation spectra, as mentioned above.

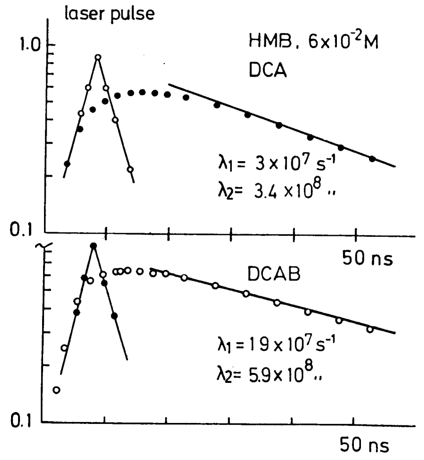

Fig. 6. Time-developments of the exciplex fluorescence (monitored at 560 nm) in the dioxane solutions of DCA–HMB and DCAB at room temperature. Time dependent exciplex concentration is expressed as a following equation; $[(DA)^*]=\frac{C}{\lambda_2-\lambda_1}\left\{\exp(-\lambda_1 t)-\exp(-\lambda_2 t)\right\}$. The time constant, λ_1 was obtained from the decay curve, and λ_2 was obtained from λ_1 and the time lag between the maxima of [(DA)*] and the exciting laser pulse; $t_1=\frac{\ln(\lambda_2/\lambda_1)}{\lambda_2-\lambda_1}$.

The fluorescence liferimes of the exciplex (room temperature) in the MP solution of DCAB were observed to vary continuously to that of the EDA complex (77 K). This temperature dependence of the fluorescence lifetimes in DCAB is almost same as that in the DCA–HMB system, as shown in Fig. 3. The continuous change of the fluorescence lifetimes means that there is no different fluorescent state in the exciplex and the EDA complex.[3,4] This fact seems to be attributable to the C_2 symmetry of the pentamethylphenyl moiety around the trimethylene chain in DCAB as metnioned in the introductory section.

As seen in Fig. 3, it is noteworthy that a remarkable temperature dependence of the fluorescence lifetimes of the EDA complex at ~120—77 K. The solvent viscosity increases markedly below ~120 K to make a rigid glass at 77 K.[10] Decrease of fluorescence lifetimes both in the inter- and intramolecular EDA complexes from ~120 K to 77 K are ascribed to the solvent viscosity, and this is consistent with the remarkable temperature dependence of the fluorescence spectra of DCA–HMB shown in Fig. 2. The solvent viscosity reduces the extent which molecular reorientation can occur during the excited state, and as the results the fluorescence lifetime of the EDA complex is reduced. Therefore, the fluorescence emmits from near Franck-Condon excited state of EDA complex at 77 K,[11] which seems to be almost locally excited state of DCA. It is because the fluorescence of the EDA complex of DCA–alkylbenzenes at 77 K has a vibrational progression ($\tilde{\nu}=\sim 1260\ \mathrm{cm}^{-1}$) and positive polarization with the local excitation in the EDA complex, as mentioned above.

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References

1) For comprehensive books: (a) R. S. Mulliken and W. B. Person "Molecular Complexes, A Lecture and Reprint Volume," Willy-Interscience, New York, N.Y., 1969; (b) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York, N. Y. 1970.

2) See references Ref. (1).

3) M. Itoh and T. Mimura, *Chem. Phys. Lett.*, **24**, 551 (1974).

4) M. Itoh, *J. Amer. Chem. Soc.*, **96**, 7390 (1974); *Chem. Phys. Lett.*, **26**, 505 (1974).

5) E. Gaweda and J. Prochorow, *Chem. Phys. Lett.*, **30**, 155 (1975).

6) M. Itoh, T. Mimura, H. Usui, and T. Okamoto, *J. Amer. Chem. Soc.*, **95**, 4388 (1973).

7) T. Mimura, M. Itoh, T. Ohta, and T. Okamoto, This Bulletin, **48**, 2245 (1975).

8) E. A. Chandross and C. J. Dempster, *J. Amer. Chem, Soc.*, **92**, 3586 (1970).

9) E. Chandross and J. Ferguson, *J. Chem. Phys.*, **47**. 2557 (1967).

10) T. Kobayashi, K. Yoshihara, and S. Nagakura, This Bulletin, **44**, 2603 (1971).

11) N. G. Bakshiev, *Opt. Spectrosk.*, **16**, 821 (1964); *Opt. spectrosk.*, **16**, 446 (1964); **20**, 542(1966).