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Fluorescence Polarization of Intramolecular EDA Complexes in (9,10-Dicyanoanthracene)-$(CH_2)_n$-(Naphthalene)

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Synopsis. Fluorescence of the intramolecular EDA complex was observed below ~140 K in the nonpolar solution of (9,10-dicyanoanthracene)-$(CH_2)_n$-(naphthalene), $n=2$. The fluorescence and excitation polarizations of these EDA ($n=2$ and 3) complexes at 77 K were determined.

During the course of investigations of EDA complexes at low temperatures in the nonpolar solution of EDA system exhibiting exciplex fluorescence at room temperature, Itoh *et al.* reported on the intramolecular exciplex (above ~200 K) and fluorescence of the EDA complex (below ~160 K) in (9, 10-dicyanoanthracene)-$(CH_2)_n$-(naphthalene) (abbreviated as $\beta\alpha$(III) and $\beta\beta$(III), $n=3$), fluorescent states of which were found to be quite different from each other.[1,2] Recently, Itoh and Mimura reported on experimental evidence of an identical fluorescent state of the intermolecular exciplex and EDA complex between 9,10-dicyanoanthracene (DCA) and various naphthalenes;[3] CT absorption bands in these EDA systems lie in the region of the ^1L_a band of the electron acceptor with the aid of photoselection studies in 3-methylpentane (MP) solutions at 77 K.[4,5]

We have observed fluorescence of the intramolecular EDA complex in the MP solution of $\beta\alpha$(II) below ~140 K, but no exciplex formation at temperatures from room temperature to ~140 K. The fluorescence and excitation polarizations of intramolecular EDA complexes of $\beta\alpha$(II), $\beta\alpha$(III) and $\beta\beta$(III) were determined in MP solutions at 77 K.[6] The sample $\beta\alpha$(II) was synthesized and purified by preparative thin layer chromatography and recrystallized before use.

Synthesis of 1-(9,10-Dicyano-2-anthryl)-2-(1-naphthyl)-ethane. N-*(2-Anthrylmethylene)aniline (anile)*: 2-Anthraldehyde (1 mol) and aniline (1 mol) were refluxed in benzene for several hours; yellow crystals separated out from a cooled solution. Recrystallized from benzene; mp 246 °C; yield 84%; IR(KBr) 1590, 1615, 1419, 900 and 750 cm.$^{-1}$

1-(2-Anthryl)-2-(1-naphthyl)ethylene: 1-Methylnaphthalene (180 mg) and potassium *tert*-butoxide (300 mg) were dissolved in DMF, and then the anile (350 mg) was added. The mixture was stirred for 3 hr at 95 °C, and poured into water and extracted with benzene. The solvent was evaporated and extracted with warm hexane. Yellow green product was purified through silica gel chromatography (benzene–hexane); mp 235 °C; yield 12%;

Found: C, 94.36; H, 5.45%. Calcd for $C_{26}H_{18}$: C, 94.55; H, 5.45%. IR(KBr) 745, 772, 795, 895 and 957 cm^{-1}.

1-(2-Anthryl)-2-(1-naphthyl)ethane: The ethylene derivative (92 mg) was hydrogenated over 5% Pd/C for 6 hr in THF and ethanol (1 : 1). Colorless crystals were obtained. Recrystallized from benzene–hexane; mp 157 °C; yield 95%.

Found: C, 94.21; H, 6.16%. Calcd for $C_{26}H_{20}$: C, 93.98; H, 6.02%. IR (KBr) 745, 778 and 900 cm^{-1}.

The substituted ethane was brominated and cyanogenated as described previously.[1]

1-(9,10-Dibromo-2-anthryl)-2-(1-naphthyl)ethane: Recrystallized from benzene; mp 155 °C.

Found: C, 63.94; H, 3.63%. Calcd for $C_{26}H_{18}Br_2$: C, 63.67; H, 3.67%. IR(KBr) 1255, 925, 745 and 768 cm^{-1}.

1-(9,10-Dicyano-2-anthryl)-2-(1-naphthyl)ethane: Recrystallized from benzene; mp 230 °C.

Found: C, 87.92; H, 4.73; N, 7.30%. Calcd for $C_{28}H_{18}N_2$: C, 87.96; H, 4.71; N, 7.33%. IR(KBr) 2220, 772 and 760 cm.$^{-1}$

Results and Discussion

An MP solution of $\beta\alpha$(II) at room temperature shows fluorescence due to the DCA moiety alone in $\beta\alpha$(II) (quantum yield; 0.92)[7] and no fluorescence in the 500-nm region. Exciplex fluorescence in MP or 2-methyltetrahydrofuran (MTHF) solutions of $\beta\alpha$(III) and $\beta\beta$(III) was observed.[1] The electronic absorption spectrum was the sum of the each component moiety. Although a remarkable fluorescence quenching of DCA moiety and a weak structureless fluorescence in the 450—550 nm region were observed in an MTHF solution of $\beta\alpha$(II) at room temperature, no distinct exciplex fluorescence was observed in either the polar or nonpolar solutions.

The fluorescence intensity due to the DCA moiety of an MP solution of $\beta\alpha$(II) decreased markedly at 77 K, a new broad fluorescence spectrum (λ_{max} 540 nm) being observed as shown in Fig. 1. The fluorescence excitation spectrum (monitored at 560 nm) and the absorption spectrum of an MP solution of $\beta\alpha$(II) differ from those of the DCA moiety at room temperature, and are very similar to the fluorescence excitation spectra and also the absorption spectra of MP solutions of $\beta\alpha$(III) and $\beta\beta$(III).[1] Fluorescence maximum and lifetime (540 nm, 100 ns) of an MP solution of $\beta\alpha$(II) at 77 K show similar values to those of $\beta\alpha$(III) (540 nm, 125 ns) and $\beta\beta$(III) (540 nm, 150 ns). The intramolecular EDA complex might be formed in an MP solution of $\beta\alpha$(II) below ~140 K, while no exciplex was detected at room temperature.

In intermediate temperatures, ~140—240 K, an MP solution of $\beta\alpha$(II) shows also a long wavelength fluorescence spectrum (500—600 nm), its excitation spectrum differing somewhat from that of the DCA

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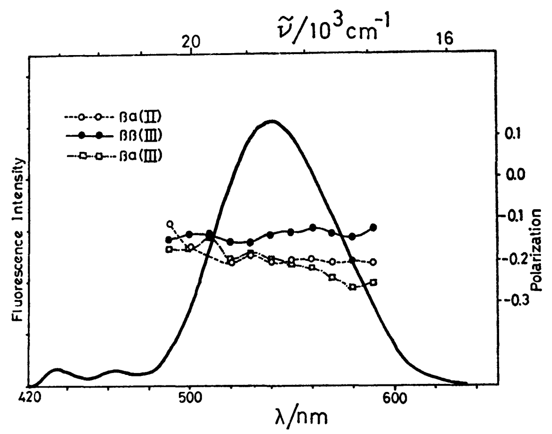

Fig. 1. The fluorescence spectrum of $\beta\alpha$(II) and the fluorescence polarizations of $\beta\alpha$(II), $\beta\alpha$(III) and $\beta\beta$(III) in MP at 77 K (excited at 360 nm; concentration: $\sim 10^{-6}$ M) The fluorescence intensity is in an arbitrary unit.

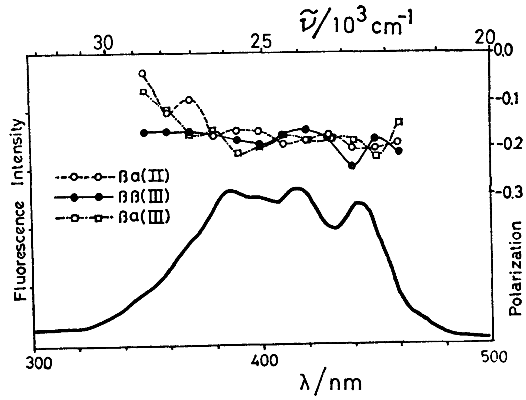

Fig. 2. The excitation spectrum of $\beta\alpha$(II) and the excitation polarizations of $\beta\alpha$(II), $\beta\alpha$(III) and $\beta\beta$(III) in MP at 77 K (monitored at 550 nm; concentration: $\sim 10^{-6}$ M) The fluorescence intensity is in an arbitrary unit. The excitation spectrum is not corrected for the intensity.

moiety (room temperature) and the EDA complex (77 K). An absorption spectrum corresponding to the excitation spectrum was also detected at almost the same intermediate temperature. These fluorescence and absorption spectra at $\sim$140—240 K suggest an intramolecular electronic interaction in the ground state, geometrical and electronic structures of which seem to differ from those of the EDA complex at 77 K.

The fluorescence and excitation polarizations of MP solutions of $\beta\alpha$(III), $\beta\beta$(III) and $\beta\alpha$(II) were determined at 77 K by the photoselection method. Figure 1 shows negative polarization of these three compounds with excitation at 360 nm. Excitation polarization monitored at 550 nm exhibits negative values almost flat in the 440—360 nm range, as shown in Fig. 2. It is therefore unlikely that CT absorption bands in these intramolecular EDA complexes lie in this region. CT absorption bands in the EDA complexes between DCA and various naphthalenes lie in the wavelength region.[4,5] Since the electronic absorption band in the range 350—440 nm was ascribed to a local excitation (mostly ^1L_a transition) in the EDA complex, the negative fluorescence polarization by the excitation at 360 nm suggests that the long wavelength fluorescence (λ_{max} 540 nm) in these compounds is the CT fluorescence between DCA and naphthalene moieties,[8] if it is mixed with local excitations.

The average distance between the electron donor and acceptor seems to be larger in the intramolecular interaction than in the intermolecular interaction of DCA and naphthalene by a steric factor of the trimethylene chain in $\beta\alpha$(III) and $\beta\beta$(III). This is consistent with the results of the dipole moments in the fluorescent state of the exciplex, which are larger in $\beta\alpha$(III) and $\beta\beta$(III) (8.7—9.5 D)[1] than in the intermolecular systems of DCA and naphthalenes (5.9—8.6 D).[5] Thus, the CT state in the EDA complex may be higher in the former, and the CT band seems to shift to the shorter wavelength region than the first excited state of DCA by mixing with local excitations.

References

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

4) M. Itoh, *ibid.*, **26** 505 (1974).

5) M. Itoh, *J. Amer. Chem Soc.*, **96**, 7390 (1974).

6) Determination of fluorescence and absorption spectra, and fluorescence (excitation) polarizations was made according to the method described previously. (See Ref.1)

7) The fluorescence quantum yield was measured as in the previous paper.

8) M. Chowdhury and L. Goodman, *J. Amer. Chem. Soc.*, **86**, 2777 (1964).