[October, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (10), 2509—2511 (1977)

Exciplex and EDA Complex Fluorescence in 1,4-Dicyanonaphthalene with Alkylbenzenes and Alkylnaphthalenes

Michiya Itoh,*[1] Shu-ichi Furuya, and Toshihiko Okamoto
*Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920
Faculty of Pharmaceutical Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received January 17, 1977)

The exciplex (at room temperature) and EDA complex (at low temperature) fluorescence was observed in 3-methylpentane solution of 1,4-dicyanonaphthalene with several alkylbenzenes and alkylnaphthalenes. The fluorescence behavior provides evidence for an identical fluorescent state of the exciplex and EDA complex.

Intermolecular electron donor-acceptor (EDA) interaction leads to the formation of molecular complexes stable in the ground state and also the exciplexes stable only in the excited state. Formation of an exciplex can be observed in the fluorescence quenching of the component molecule and/or in the appearance of a new red-shifted fluorescence band. By transient absorption spectroscopy both the singlet excited states of the EDA complex and the exciplex are seen to show absorption bands of cation and anion radicals of the electron donor and acceptor, which indicates their strong charge transfer (CT) character in the excited state.[2]

Itoh and Mimura[3] and others[4,5] reported on the exciplex and EDA complex formation in the nonpolar solution of 9,10-dicyanoanthracene (DCA) and several naphthalene and benzene derivatives, demonstrating an experimental evidence for an identical fluorescent state of the exciplex and EDA complex. Similar evidence was reported for the identical fluorescent state in the tetracyanobenzene and *p*-xylene system by Gaweda and Prochorow.[6] This paper describes further examples of evidence for their identical fluorescent state in the simple EDA system of 1,4-dicyanonaphthalene (DCN) and alkylbenzenes (alkylnaphthalenes).

Experimental

1,4-Dicyanonaphthalene was prepared from naphthalene by bromination and cyanogenation, and purified several times by silica gel chromatography (solvent; benzene–hexane) and recrystallization. The sample has no fluorescent impurity in solution as verified by thinlayer chromatography. Purification of alkylbenzenes, alkylnaphthalenes, and solvents was carried out as reported.[4,5]

Measurement of fluorescence spectra was carried out with Hitachi MPF-2A and MPF-4 spectrophotometers, and that of absorption spectra with Cary 11 and Hitachi 323 spectrophotometers. Determination of fluorescence polarization was described previously.[4] The fluorescence lifetimes and time-resolved fluorescence spectra were determined by analyzing exponential decay curves measured with an oscilloscope and a coaxial N_2 gas laser.

Results and Discussion

The exciplex fluorescence in the 3-methylpentane (MP) solution of 1,4-dicyanonaphthalene (DCN) and alkylbenzenes was observed at room temperature. Figure 1 shows the fluorescence and fluorescence excitation spectra of MP solution of DCN and pentamethylbenzene (PMB) at room temperature. The fluorescence maxima and lifetimes of the exciplexes in

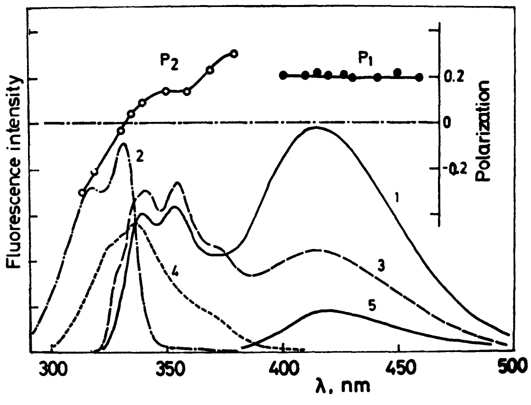

Fig. 1. Fluorescence and fluorescence excitation spectra, and their polarizations of MP solutions of DCN and PMB. *Spectra* 1 (excited at 310 nm) and 2 (monitored at 450 nm) are fluorescence and excitation spectra at room temperature, respectively (Concentration: DCN, 3×10^{-6} M: PMB, 1.5×10^{-2} M). *Spectra* 3 (excited at 310 nm) and 5 (excited at 370 nm) are fluorescence spectra at 77 K, and 4 (monitored at 450 nm) is a fluorescence excitation spectrum. P_1 (excited at 370 nm) and P_2 (monitored at 420 nm) are fluorescence and excitation polarizations at 77 K, respectively (Concentration: DCN, 9×10^{-7} M; PMB, 1×10^{-3} M).

TABLE 1. FLUORESCENCE MAXIMA AND LIFETIMES OF THE EXCIPLEX (AT ROOM TEMPERATURE) AND THE EDA COMPLEX (AT 77 K) IN MP SOLUTION OF DCN AND ALKYLBENZENES AND ALKYLNAPHTHALENES

Donor	Exciplex		EDA complex	
	λ, nm	τ, ns[a]	λ, nm	τ, ns[a]
Hexamethylbenzene	430	86	430	71
Pentamethylbenzene	416	69	415	66
Durene	413	69	405[b]	50
Mesitylene	390	43	400[b]	40
p-Xylene	390	38	400[b]	37
Toluene	376[c]	15[c]	—	—
1,5-Dimethylnaphthalene	440	59	434	58
2-Methylnaphthalene	436	52	430	50
Naphthalene	430	51	427	48

a) Errors are approximately ± 1 ns. b) Determined by time-resolved fluorescence spectra. c) Determined in the concentrations of DCN $=6\times10^{-6}$ M and toluene $=1.1$ M.

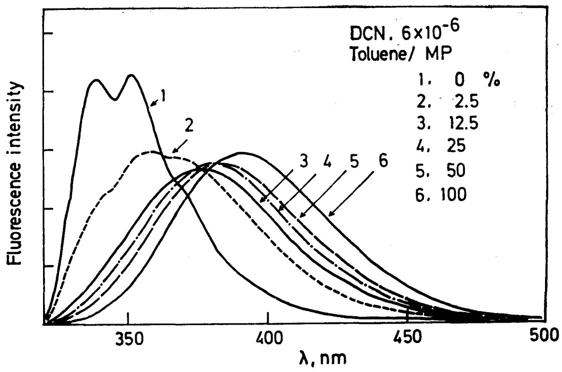

Fig. 2. Fluorescence spectra of MP solutions of DCN and toluene at room temperature.

MP, summarized in Table 1, show a slight concentration dependence of the electron donor. In the DCN and toluene system, however, the fluorescence maxima and lifetimes show remarkable concentration dependence (Fig. 2). Data of these exciplexes determined in almost the same concentrations of electron donor ($\approx 10^{-1}$ M) and acceptor ($\approx 10^{-6}$ M) are given in Table 1. The concentration dependence is due to the increasing solvent polarity with donor concentration.[7]

The exciplex fluorescence was gradually quenched with decrease in temperature. Almost the same fluorescence band as that of exciplex increases in intensity with further decrease in temperature. The temperature region of the decrease and increase of the long wavelength fluorescence is dependent on the concentrations of donor and acceptor. The fluorescence spectra of the MP solution of DCN with low concentration of alkylbenzene show no exciplex fluorescence band at room temperature but a similar fluorescence to that of the exciplex at low temperature. The fluorescence and excitation spectra of MP solution of DCN and PMB at 77 K are also shown in Fig. 1. The absorption spectra of the MP solution of DCN–alkylbenzene system at room temperature are completely superimposed by those of the component molecules, while the spectra show the EDA complex formation at low temperature as shown in Fig. 3 (DCN–PMB). The electronic absorption spectra at 77 K are similar to the corresponding excitation spectra monitored at long wavelength fluorescence (Fig. 1). From the absorption and fluorescence excitation spectra in the MP solutions of DCN–alkylbenzenes, the long wavelength fluorescences at room temperature and at low temperature are ascribed to the exciplex and to the EDA complex, respectively. The absorption and excitation spectra indicate a small absorption band in the EDA complex at 350—400 nm as will be mentioned later. The fluorescence maxima and fluorescence lifetimes of the EDA complex in the MP solution at 77 K are summarized in Table 1. In the EDA complexes of DCN with durene, mesitylene and *p*-xylene, fluorescence maxima were determined with time-resolved fluorescence spectra because of their low solubility in MP at 77 K. The DCN–toluene system shows no detectable EDA complex formation.

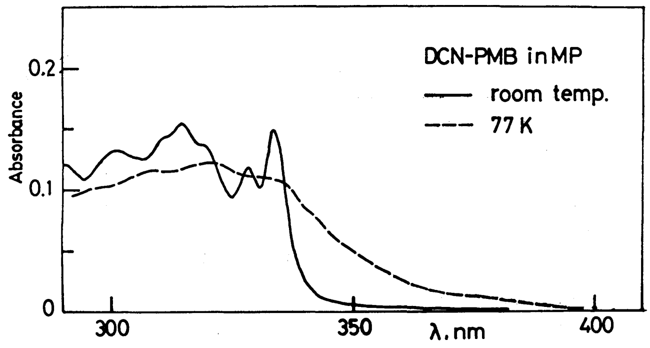

Fig. 3. Electronic absorption spectra of an MP solution of DCN and PMB at room temperature and 77 K (Concentration: DCN, 1.6×10^{-5} M; PMB, 7.5×10^{-3} M). Volume change at 77 K was corrected.

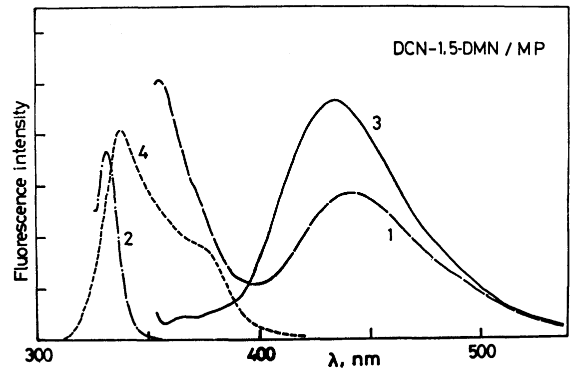

Fig. 4. Fluorescence and excitation spectra of MP solutions of DCN and 1,5-dimethylnaphthalnene. *Spectra* 1 (excited at 335 nm) and 2 (monitored at 450 nm) are fluorescence and excitation spectra at room temperature, respectively (Concentration: DCN, 2×10^{-6} M; 1,5-DMN, 2.2×10^{-2} M). *Spectra* 3 (excited at 340 nm) and 4 (monitored at 450 nm) are fluorescence and excitation spectra at 77 K, respectively (Concentration: DCN, 2×10^{-6} M; 1,5-DMN, 3.4×10^{-3} M).

The DCN and methylnaphthalene system shows exciplex formation at room temperature with the excitation of DCN and the EDA complex formation at low temperature, spectra of which are shown in Fig. 4 (DCN–1,5-dimethylnaphthalene). With the excitation of electron donor, however, no exciplex fluorescence but only alkylnaphthalene fluorescence was observed. The excitation spectra monitored at long wavelength fluorescence of the EDA complex of DCN–DMN (Fig. 4) give a similar absorption band at 350—400 nm to that in DCN–PMB.

The fluorescence maxima and lifetimes of both exciplex and EDA complex increase with decreasing ionization potential of alkylbenzene (alkylnaphthalene), indicating an increase of CT character of their fluorescent state with decreasing ionization potential of the electron donor. The fluorescent behavior in DCN–alkylbenzene (alkylnaphthalene) is similar to that in the DCA–alkylbenzene (alkylnaphthalene).[4,5] The fluorescence of the EDA complex in the DCN–alkylbenzene system at 77 K shows positive polarization with excitation at 370 nm, and negative with excitation at 320 nm. On the other hand, the electronic absorption spectra

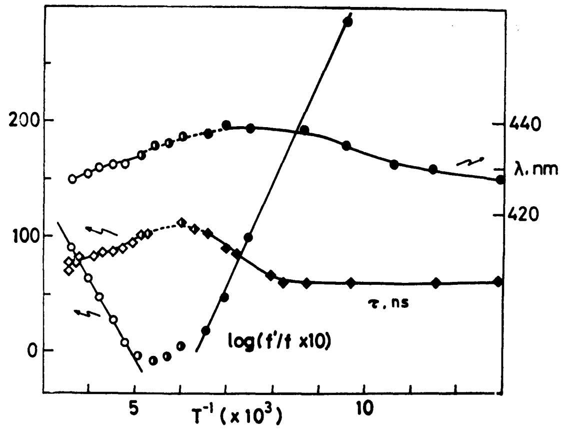

Fig. 5. Temperature dependence of fluorescence maxima (—○— exciplex and —●— EDA complex) and lifetimes (—◇— exciplex and —◆— EDA complex) in MP solutions of DCN and PMB, and of intensity ratio of the long wavelength fluorescence (f′ at λ_{max} 415 nm) and DCN fluorescence (f at λ_{max} 355 nm); —◐—, —◈— and —◐— are fluorescence indistinguishable from each other between exciplex and EDA complex.

and the excitation spectra of the EDA complex give a small absorption band at 350—400 nm. The results indicate that the absorption is a CT band between DCN and the electron donor. In the DCA–alkylbenzene system reported previously, small positive polarization with the local excitation of DCA and rather small fluorescence lifetimes of the EDA complex as well as the exciplex suggest that the fluorescent states mostly consist of the locally excited state of DCA.[5] The results of the EDA complex and the exciplex in DCN–alkylbenzene (alkylnaphthalene) show marked CT character in their fluorescent states.

The fluorescence maxima and lifetimes of the long wavelength fluorescence of MP solution of DCN–PMB at serveral temperatures, plotted in Fig. 5, both show continuous variation from room temperature to 77 K. On the other hand, the temperature dependence of intensity ratio of the long wavelength fluorescence to the DCN fluorescence completely differ between exciplex and EDA complex.[4] If the exciplex and EDA complex have different fluorescence behavior, different fluorescence should be observed in the intermediate temperature (200—140 K). However, no distinguishable fluorescence is observed between exciplex and EDA complex in DCN–HMB system at ≈205 K, the fluorescence being observed in the excitation of DCN absorption band and CT band of the complex (Fig. 6). Appearance of one fluorescence species in this temperature region and the continuous change in fluorescence maxima and lifetime indicate an identical fluorescent state of the exciplex and EDA complex.[3]

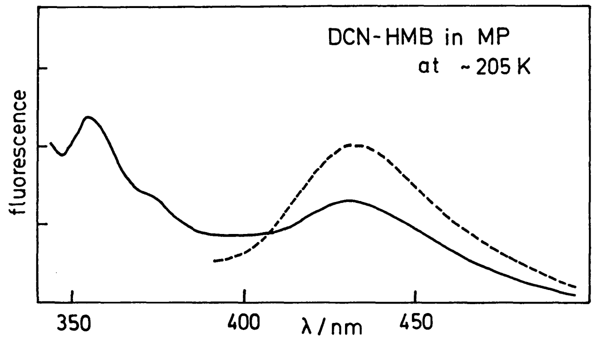

Fig. 6. Fluorescence spectra of an MP solution of DCN and HMB at 205 K in the excitations at 320 nm (———) and at 380 nm (------), (concentration; DCN, 3×10^{-6} M and HMB, 6×10^{-3} M).

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1) To whom correspondence should be addressed at Kanazawa University.

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