FLUORESCENCE OF 4-DIMETHYLAMINOBENZONITRILE IN β-CYCLODEXTRIN CAVITIES: EVIDENCE FOR SELF-COMPLEXES

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الخلاصة :

يبدو إضافةً إلى طيف الفلورة المعتاد (b band) وطيف فلورة نقل الشحنة داخل الجزيء (TICT band)، أنّ جزيء ٤-دايميثل أمينوبينزونايترايل (DMABN) في بيتاسايكلو دكسترين يعطي طيف فلورة عند حوالي (٤٠٠ - ٤٢٠) نانومتر، عزيناه إلى وجود مركبات ذاتية.

وهذا النتائج مدعمّة بتجارب التحليل الوقتي وانخماد طيف الفلورة .

ABSTRACT

Besides the normal (b) and twisted intramolecular charge transfer (TICT) fluorescence bands, 4-dimethylaminobenzonitrile (DMABN) in β-cyclodextrin aqueous solution exhibits a fluorescence band at around 400–420 nm which has been attributed to self-complexes. This is supported by time-resolved and fluorescence decay results.

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INTRODUCTION

Cyclodextrins (CDs) have been shown to be interesting enclathrating agents for many molecules [1–3]. They possess hydrophobic cavities which can, in aqueous media, extract and encapsulate organic molecules of appropriate size and hydrophobicity [4–9]. The hydrophobic interior environment of the cavity affects the emission of the solute molecules [10–13]. The restricted shape and size of the cavity geometrically constrains the solute molecule and, therefore, markedly affects its properties.

The inclusion of organic and organometallic molecules within the CD hydrophobic cavity and its effect on the properties of these molecules has been the subject of many studies [14–17]. An interesting molecule is 4-dimethyl-aminobenzonitrile (DMABN). The fluorescence spectrum of DMABN in polar fluid media has two clearly different bands; namely, the normal (also called b) band and the anomalous twisted intramolecular charge transfer (TICT) band [18]. The relative positions and intensities of these two bands are sensitive to the solvent polarity and medium viscosity [18, 19].

In an earlier publication [20], we reported our analysis of the fluorescence of DMABN dissolved in an aqueous solution of α-CD. Our results indicated that DMABN in an aqueous α-CD solution exists in three different environmental conditions; polar, slightly polar, and hydrophobic. DMABN surrounded by water molecules represents the most polar and least rigid environment. The slightly rigid and slightly polar environment arises when the dimethylamino group of the DMABN molecule is headed toward the larger rim of the α-CD cavity. The least polar and most rigid environment is that when the dimethylamino group of the DMABN molecule is headed toward the smaller rim of the α-CD cavity which is, most probably, stabilized by another α-CD cup.

Nag *et al.* [21–23] have suggested that restrictions imposed by the CD cavity on the torsional motions of the dimethylamino group do not play any major role in the TICT phenomenon. According to them, the polarity of the CD cavity has the greatest influence. However, in a previous publication [20], we demonstrated that both the cavity size and polarity contribute to the TICT phenomenon.

To investigate the role of the cavity size on the TICT phenomenon further, we report our results on the behavior of DMABN in β-CD. The cavity of β-CD has a larger diameter (about 7.8 Å) than that of α-CD (about 5.7 Å). DMABN will easily fit in the cavity of β-CD with the dimethylamino group of the DMABN molecule headed either toward the larger rim or the smaller rim of the β-CD cavity. In addition, two DMABN molecules can possibly fit in the β-CD cavity and, therefore, dimers [24, 25] or self-complexes [26, 27] may be observed in this case.

EXPERIMENTAL

DMABN (Aldrich) was purified by preparative thin layer chromatography, recrystallization, and repeated vacuum sublimation. β-CD (Wako Pure Product) was kindly supplied to us by Prof. T. Azumi (Tohoku University, Sendai, Japan). A blank solution of β-CD does not show any fluorescence. Fluorescence spectra of DMABN in β-CDs from other sources are the same after equilibrium is established (usually after 2–3 days) and, therefore, we used β-CD (Wako) without further purification. A stock aqueous solution of DMABN (1.0×10^{-5} M) was prepared. Different amounts of β-CD were then dissolved in this DMABN aqueous solution to give β-CD concentrations: 0.0 M (solution 1), 1.5×10^{-4} M (solution 2), 1.0×10^{-3} M (solution 3), 5.0×10^{-3} M (solution 4), and 1.5×10^{-2} M (solution 5). In another set of solutions, a stock aqueous solution of β-CD (1.5×10^{-2} M) was prepared. Different amounts of DMABN were then dissolved in this β-CD aqueous solution to give DMABN concentrations: 1.0×10^{-5} M (solution 6), 3.0×10^{-5} M (solution 7), 6.0×10^{-5} M (solution 8), and 7.5×10^{-5} M (solution 9).

Fluorescence and excitation spectra were recorded with an SPF-500 spectrofluorimeter from SLM Instruments Inc. Fluorescence spectra were corrected for lamp intensity and photomultiplier sensitivity. Lifetimes were measured by using the picosecond Applied Photophysics photon counting system described elsewhere [28]. Laser pulses from a Rhodamine 6G dye laser pumped with a Spectra Physics Model 3800 Nd:YAG picosecond laser (with Model 451 mode locker) were used.

RESULTS

Absorption Spectra

Similar to the absorption spectra recorded by Nag *et al.* [22], when the concentration of β-CD is increased for a fixed concentration of DMABN (1.0×10^{-5} M) (solutions 1–5), the absorption spectrum becomes a little broader with no shift in the maximum. The effect of variation of DMABN concentration for a fixed β-CD concentration (1.5×10^{-2} M) (solutions 6–9) follows Beer–Lambert law for concentrations of DMABN upto about 7.5×10^{-5} M after which precipitation occurs; *i.e.* the solution is saturated at this temperature.

The absorption spectrum does not indicate any formation of dimers although it is possible since the β-CD cavity is big enough to accommodate two DMABN molecules if they have the right orientation. However, the probability of having two DMABN molecules in one cup is practically zero since the average population is 0.001 (about 1 DMABN molecule for 1000 β-CD cups). For the same reason, excimer fluorescence is not expected and has not been observed.

Excitation Spectra

Several excitation spectra of solution 5 were recorded by fixing the emission wavelength and variation of the excitation wavelength. These spectra are similar to the ones published by Nag *et al.* [22]. The fact that the excitation spectrum changes as the wavelength of emission is changed indicates that the absorption spectrum includes contributions from several types of DMABN; *i.e.* in different environmental conditions.

Effect of Time on the Fluorescence Spectra

While the absorption spectra of solutions 1–5 do not undergo any appreciable change with time, fluorescence spectra, on the other hand, (*a*) for freshly prepared solutions are different from (*b*) those taken after equilibrium has been established (after 2–3 days), as shown in Figure 1(*a*) and Figure 1(*b*). However, all data reported in this paper have been taken after equilibrium has been established.

Effect of the Concentration of β-CD on the Fluorescence Spectra

Both the b and the TICT fluorescence bands are blue shifted as the concentration of β-CD is increased from solution 1 to solution 5. As shown in Figure 1(*b*), the b band is enhanced about 8 times while the TICT band is enhanced about 3 times.

Fluorescence Spectra in β-CD Compared to α-CD

Figure 2(*a*) shows the steady state fluorescence spectra of DMABN in α-CD in comparison to β-CD. As can be seen, the b fluorescence band of DMABN in β-CD is broader and red shifted relative to α-CD. The TICT band is also red shifted.

Effect of the Concentration of DMABN on the Fluorescence Spectra

Fluorescence spectra of solutions 6–9 are presented in Figure 2(*b*). As can be seen, the maxima of both the b and the TICT fluorescence bands are not shifted as the concentration of DMABN is increased. However, the relative contribution of the TICT band decreases as the concentration of DMABN increases and the b-band becomes a little broader.

Effect of the Concentration of β-CD on the Fluorescence Lifetime

Decay curves of solution 5 at 520 nm, 420 nm, and 350 nm are presented in Figure 3. The calculated lifetimes for solutions 1–5 and solutions 6–9, normalized preexponential factors, χ^2 values, and the relative quantum yields at 520 nm, 420 nm, and 350 nm are summarized in Tables 1 and 2, respectively. However, the measured decay times are dependent on the channel range used for fitting, as has also been observed by Rotkiewicz *et al.* [29] for some compounds related to DMABN in hydrocarbon solvents at low temperature. Therefore, one has to be careful in interpreting the obtained lifetime values.
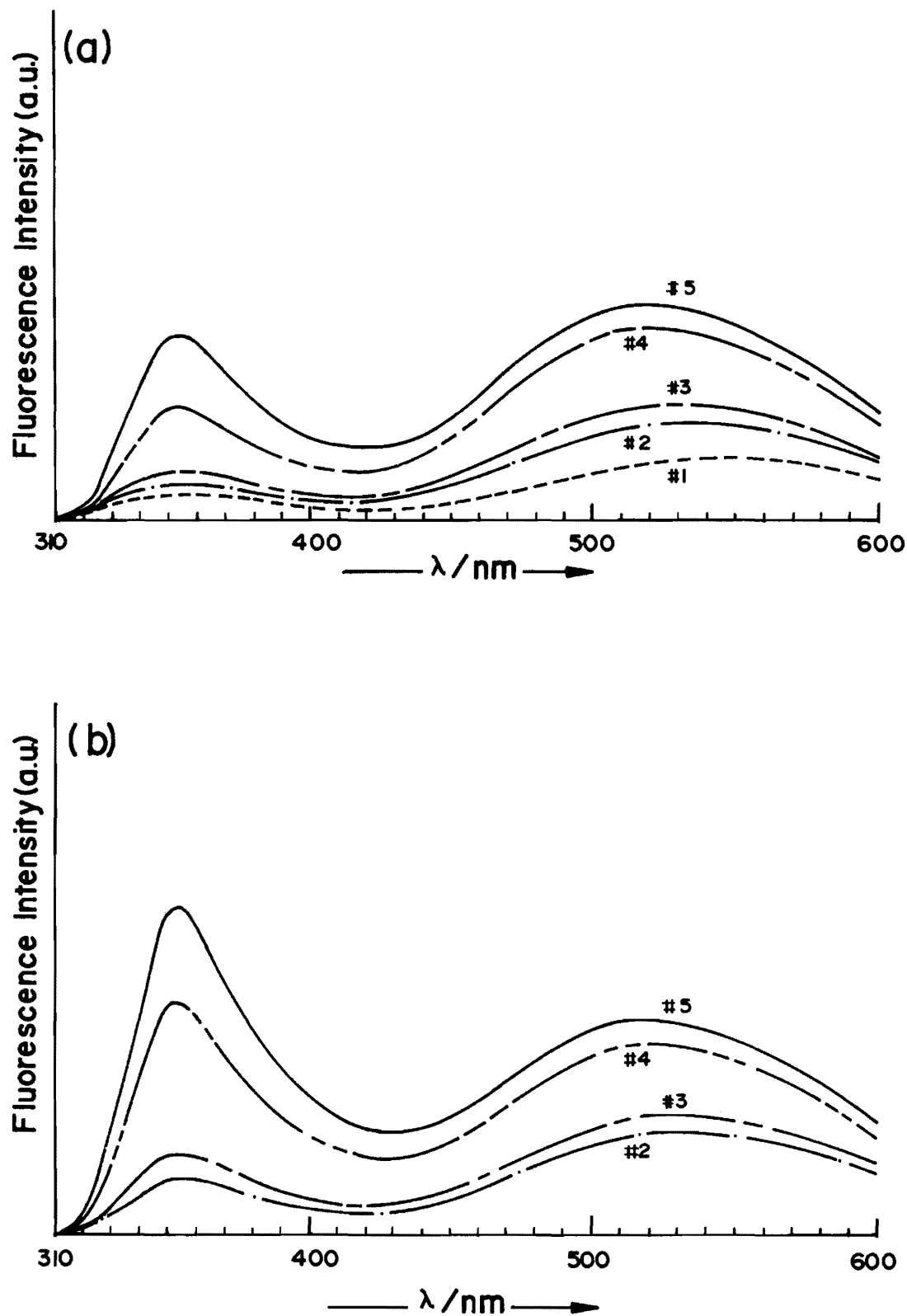
Figure 1. Fluorescence Spectra of 1.5×10^{-5} M DMABN in Water (#1) and in Aqueous Solutions of Different Concentrations of β-CD: (#2) 5.0×10^{-4} M, (#3) 1.0×10^{-3} M, (#4) 5.0×10^{-3} M, and (#5) 1.5×10^{-2} M, at Room Temperature, $\lambda_{exc} = 300$ nm. (a) Freshly prepared; (b) after equilibrium has been reached (after 2–3 days).
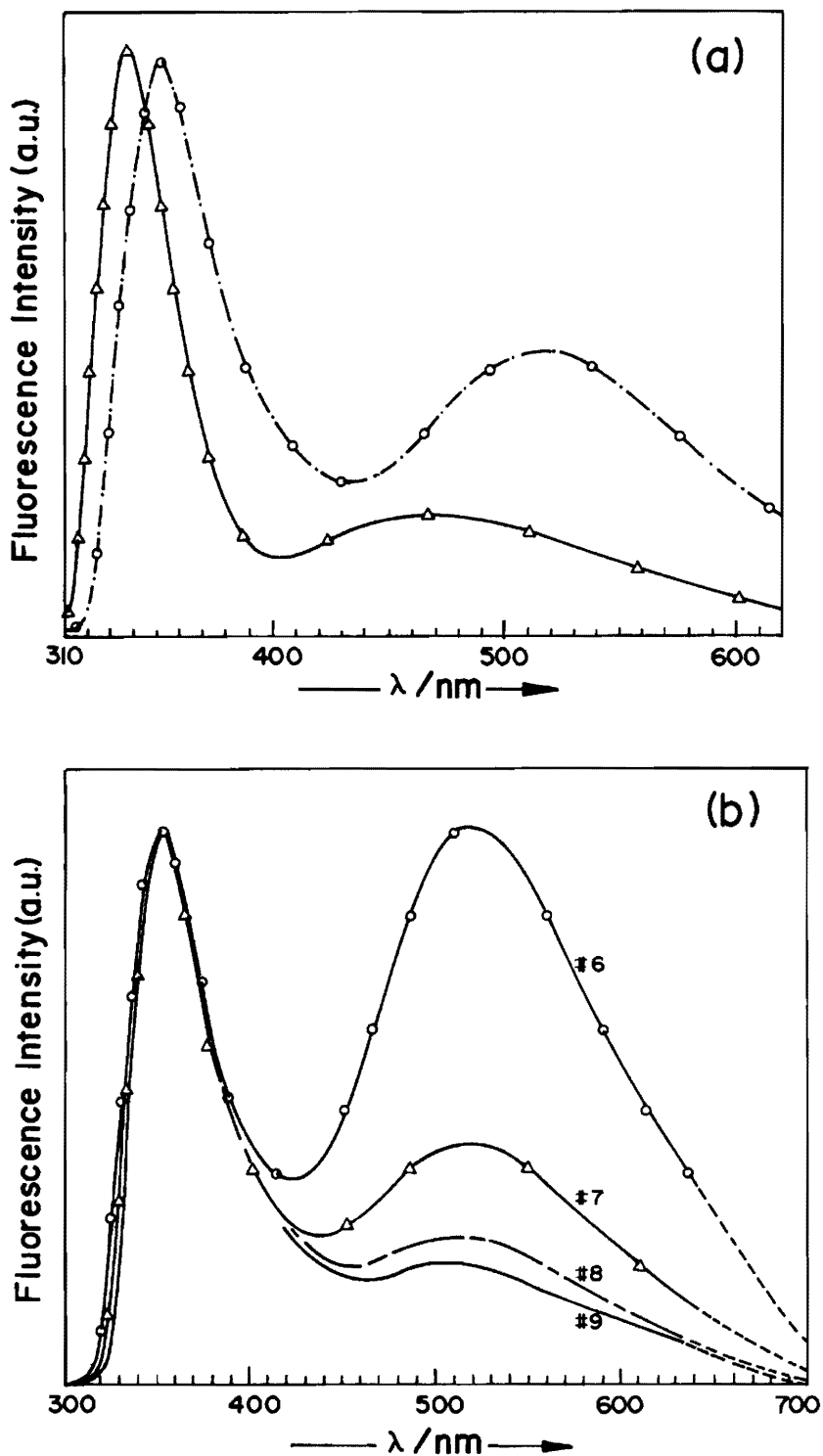
Figure 2(a). Fluorescence Spectra of DMABN in α-CD (2.0×10⁻² M) *(* —△—△— *) versus* β-CD (1.5×10⁻² M) *(* —O— · —O— *)
Aqueous Solutions;* λ_{exc} = 300 nm. *The spectra are normalized; however, the spectra in* α-CD *have much higher quantum
yields than in* β-CD.

Table 1. Values for Lifetimes (τ_i), Normalized Preexponential Factors (a_i), χ^2 Values, and Relative Quantum Yields (Q_i) from Deconvoluted Experimental Decays for the b (350 nm) and TICT (520 nm) Fluorescence Bands of DMABN in Aqueous β-CD Solutions (λ_{exc} = 300 nm). Concentration of DMABN in all solutions is constant and =1.5×10⁻⁵ M; Q_i is calculated from preexponential factors a_i as $Q_i = a_i \tau_i / \Sigma a_i \tau_i$.

[β-CD]	b Fluorescence band (350 nm)										TICT Fluorescence band (520 nm)						
	τ_1(ps)	a_1	Q_1	τ_2(ns)	a_2	Q_2	τ_3(ns)	a_3	Q_3	χ^2	τ_1(ps)	a_1	Q_1	τ_2(ns)	a_2	Q_2	χ^2
Water (Solution #1)	400	1.00	1.00	–	–	–	–	–	–	0.84	300	1.00	1.00	–	–	–	0.84
β-CD (1.5×10⁻⁴ M) (Solution #2)	250	0.91	0.68	1.2	0.09	0.32	–	–	–	0.94	260	0.93	0.73	1.30	0.07	0.27	0.88
β-CD (1.0×10⁻³ M) (Solution #3)	–	–	–	0.9	0.89	0.73	2.6	0.11	0.27	0.96	375	0.63	0.31	0.94	0.37	0.69	1.10
β-CD (5.0×10⁻³ M) (Solution #4)	–	–	–	1.0	0.86	0.71	2.6	0.14	0.29	1.10	–	–	–	0.92	1.00	1.00	1.20
β-CD (1.5×10⁻² M) (Solution #5)	–	–	–	1.0	0.78	0.58	2.7	0.22	0.42	1.10	–	–	–	0.94	1.00	1.00	1.00

Table 2. Values for Lifetimes (τ_i), Normalized Preexponential Factors (a_i), χ^2 Values, and Relative Quantum Yields (Q_i) from Deconvoluted Experimental Decays for the b (350 nm), Self-Complex (420 nm), and TICT (520 nm) Fluorescence Bands of Various Concentrations of DMABN in Aqueous β-CD Solutions (λ_{exc} = 300 nm). Concentration of β-CD in all solutions is constant and =1.5×10⁻² M; Q_i is calculated from preexponential factors a_i as $Q_i = a_i \tau_i / \Sigma a_i \tau_i$.

[DMABN]	b Fluorescence band (350 nm)							Self complex emission (420 nm)							TICT Fluorescence band (520 nm)						
	τ_1(ns)	a_1	Q_1	τ_2(ns)	a_2	Q_2	χ^2	τ_1(ns)	a_1	Q_1	τ_2(ns)	a_2	Q_2	χ^2	τ_1(ns)	a_1	Q_1	τ_2(ns)	a_2	Q_2	χ^2
5.0×10⁻³ M (Solution #4)	1.00	0.92	0.78	3.0	0.08	0.22	1.20	1.0	0.93	0.17	7.0	0.07	0.83	1.1	0.83	0.94	0.89	1.6	0.06	0.11	1.00
5.0×10⁻³ M (Solution #4)	1.00	0.89	0.74	2.8	0.11	0.26	1.10	1.0	0.91	0.58	7.6	0.09	0.42	1.3	0.82	0.49	0.32	1.7	0.51	0.68	0.92
5.0×10⁻³ M (Solution #4)	1.00	0.61	0.35	2.9	0.39	0.65	0.93	1.0	0.92	0.55	8.7	0.08	0.45	1.1	0.80	0.83	0.70	1.6	0.17	0.30	1.10
5.0×10⁻³ M (Solution #4)	1.00	0.64	0.36	3.1	0.36	0.64	1.30	1.0	0.91	0.55	8.6	0.09	0.45	1.1	0.81	0.84	0.71	1.7	0.16	0.29	1.00

Time-Resolved Spectra

Time-resolved spectra taken at different times after excitation are presented in Figure 4. Besides the b and TICT fluorescence bands, we have also observed a fluorescence band at around 400 nm which cannot be easily observed in steady state fluorescence. The fact that the steady state fluorescence of the b band of DMABN in β-CD is broader and red shifted relative to α-CD (Figure 2(*a*)) and the observation of a new fluorescence band at 400 nm in the time-resolved spectra indicates the possibility of the presence of self-complexes in the β-CD hydrophobic cavity.

DISCUSSION

In an earlier publication, we reported that there are three different types of DMABN molecules dissolved in an aqueous solution of α-CD, *i.e.* they exist in three different environmental conditions [20]. These environmental conditions are also possible in the case of β-CD. The first position could be when the dimethylamino group of the DMABN molecule is headed toward the larger rim of the β-CD cavity. This probably is the first environmental condition and these will be called Type I complexes. The second position could be when the dimethylamino group of the DMABN molecule is headed toward the smaller rim of the β-CD cavity. This probably is the second environmental condition and these will be called Type II complexes. The third type of environmental conditions is the bulk aqueous solution; *i.e.* DMABN molecules in the vicinity of water molecules.

In our discussion on the behavior of DMABN in α-CD [20], these three environmental conditions could be rationalized on the basis of fluorescence spectra, the dependence of the fluorescence spectra on the concentration of
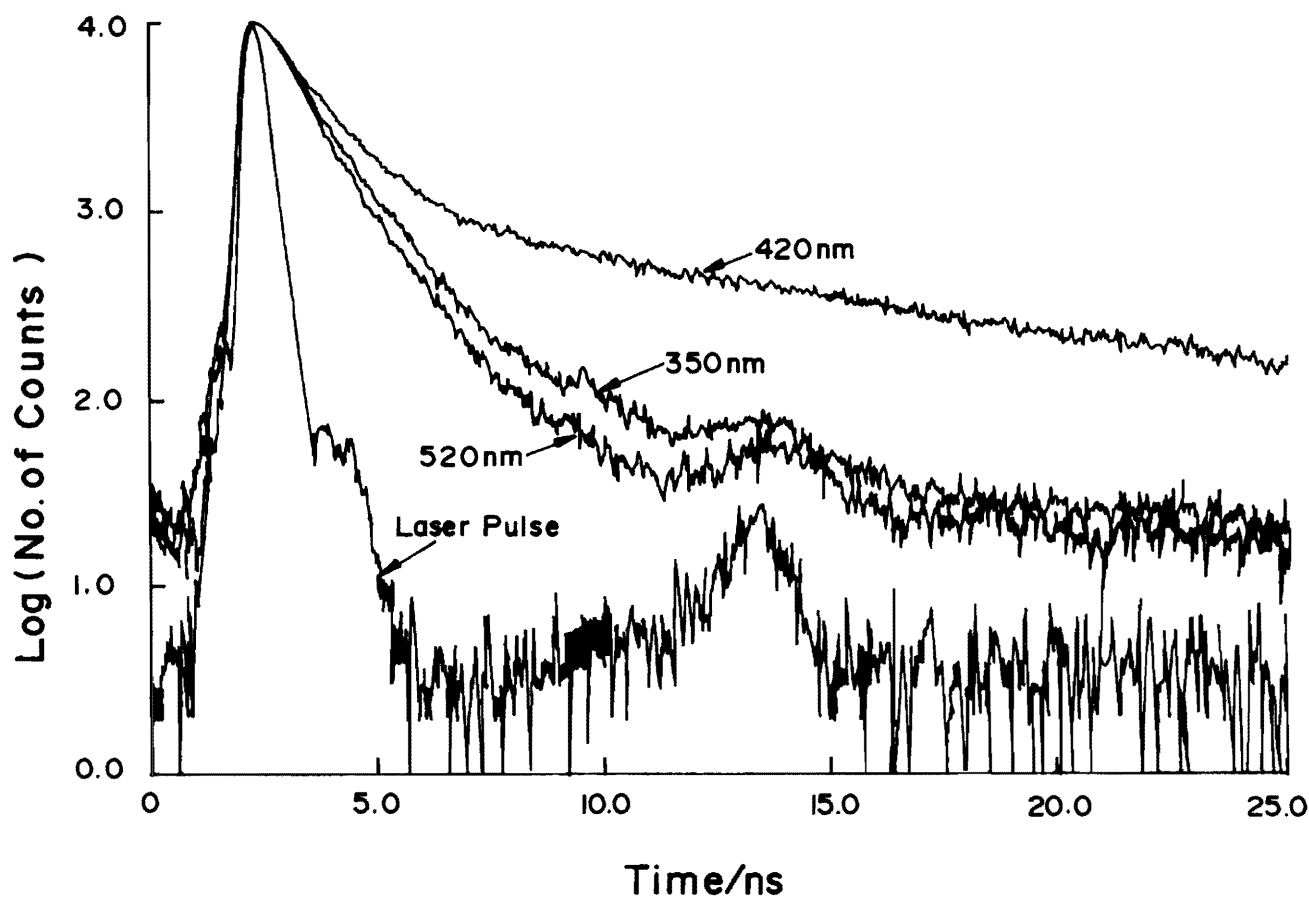

Figure 3. Fluorescence Decay Curves of 3.0×10⁻⁵ M DMABN in β-CD (1.5×10⁻² M) Aqueous Solutions at Room Temperature, Monitored at 520 nm, 420 nm, and 350 nm; λ$_{exc}$ = 300 nm.

α-CD and DMABN, and the lifetime analysis. The three environmental conditions can be rationalized in β-CD in the same way. Two fluorescence bands of the DMABN molecules in β-CD solutions are observed in the case of the third environmental condition; *i.e.*, the polar environment, namely the normal band at around 330 nm and the TICT band at around 530 nm. In the case of Type II complexes, the dimethylamino groups experience the least polar and most rigid environment and, therefore, give rise to a TICT fluorescence band which is blue shifted as compared to Type I complexes where the dimethylamino groups experience an environment of higher polarity and larger free volume because they are directed towards the water.

We also believe that some DMABN molecules exist in a fourth environmental condition in β-CD solutions. Interaction between unoccupied β-CD cups and occupied ones is, of course, possible. Unoccupied β-CD cups will probably stabilize Type II complexes since the fluorescence spectrum continues to change upon further addition of β-CD and the fluorescence decays, shown in Figure 3, indicate that no DMABN is present in water any more. Moreover, interaction between two occupied β-CD cups (a 2:2 complex), as shown in Figure 5, is also possible. It will result in some interaction between the two DMABN molecules probably forming a self-complex, during the excited state lifetime, representing the fourth environmental condition.

Dimers, self-complexes, and aggregates have been suggested by several investigators [24–27] to be responsible for the appearance of a fluorescence band at around 400 nm for DMABN and related compounds in nonpolar solvents at low temperature. Nakashima and Mataga [26] reported such a band for DMABN in cyclohexane at higher DMABN concentration and low temperature with λ_{max} around 400 nm. Nakashima *et al.* [27] found that the lifetime of this
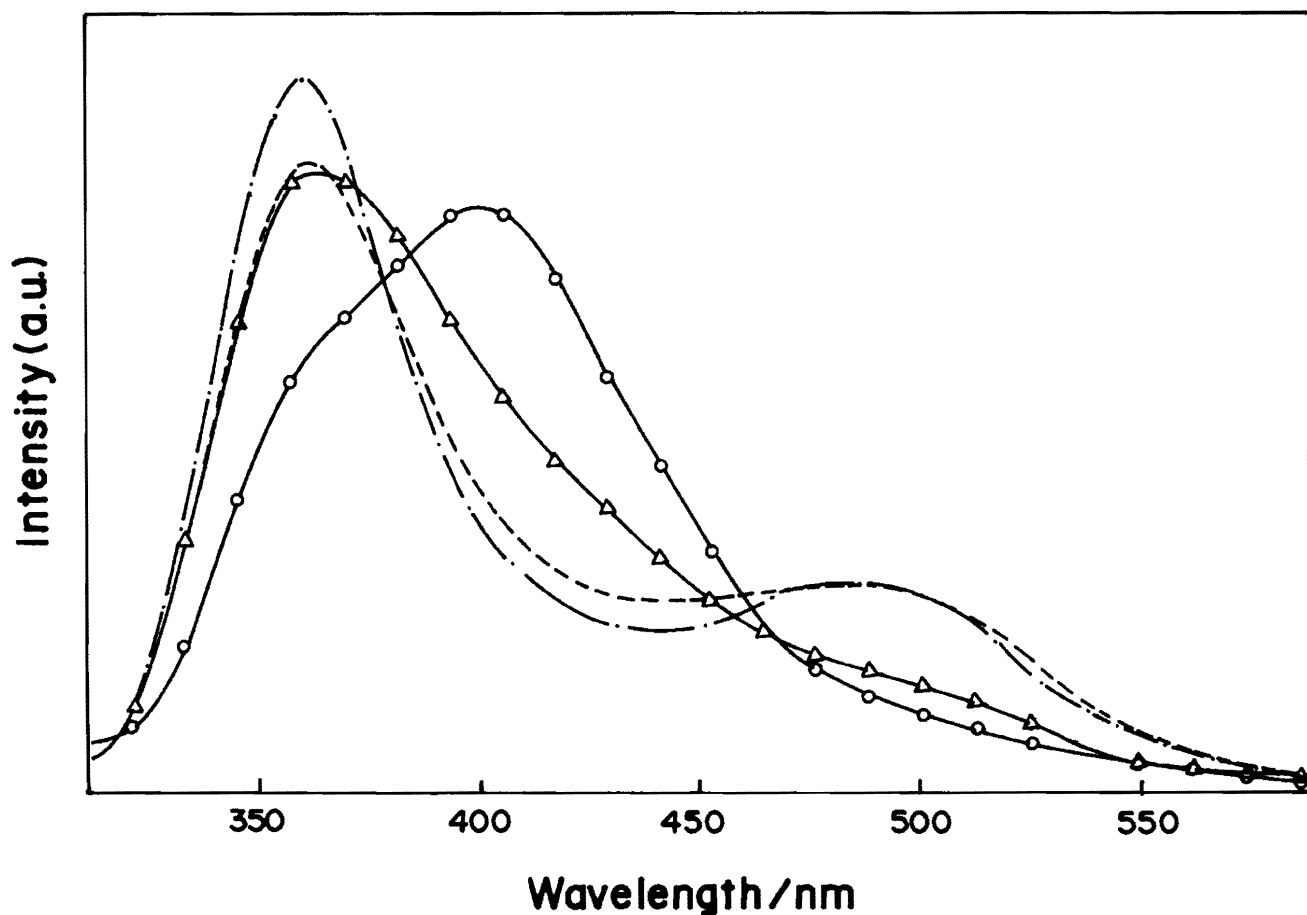

Figure 4. Time-Resolved Fluorescence Spectra of 3.0×10^{-5} M DMABN in β-CD (1.5×10^{-2} M) Aqueous Solutions at Room Temperature with Different Delay Times (Δt) after the Laser Pulse: Δt = 100 ps (— · — ·), Δt = 2.5 ns (———), Δt = 5.0 ns (—△—△—), and Δt = 10 ns (—O—O—).

fluorescence band was about 9 ns. From their analysis, it was concluded that this band was due to an electrostatic self-complex. Later, Peng *et al.* [30] observed a broad emission centered at 385 nm for DMABN in the supersonic jet when the temperature was raised especially at higher backing pressure. They assigned this fluorescence to aggregates of DMABN itself. Rotkiewicz *et al.* [24, 29] studied the fluorescence of DMABN and some derivatives at low temperature. In the case of DMABN they measured a lifetime of about 5 ns for the long wavelength fluorescence band at around 400 nm which they attributed to the formation of aggregates of DMABN. Dähne *et al.* [31] have also observed a fluorescence band at 400 nm for *p*-dimethylaminobenzaldehyde in nonpolar solvents at low temperature which was explained by the formation of aggregates, mostly dimers. Recently, Howell *et al.* [25] observed a fluorescence band for DMABN in supersonic jet at about 390 nm with a lifetime of 12.5 ns which was attributed to dimeric or higher stoichiometric self-complexes.

Besides the b and TICT fluorescence bands, we have also observed a fluorescence band at around 400 nm, clearly visible in the time-resolved spectra, with a lifetime of about 8 ns which we assign to emission from self-complexes. Geometric constrains and low probability for the formation of aggregates of DMABN in β-CD cups suggest the formation of dimeric self-complexes rather than higher aggregates.

As presented in Table 1, a single exponential decay is observed when the fluorescence is monitored at 520 nm in an aqueous solution with no β-CD. The lifetime is about 300 ps, which represents the TICT fluorescence lifetime of the DMABN in the polar environment. When β-CD is added, the three environmental conditions are expected: the pure water, Type I complexes, and Type II complexes. Of course, the concentration of the DMABN molecules in the aqueous medium will decrease as the concentration of β-CD is further increased. TICT fluorescence monitored at 520 nm shows three lifetimes of about 300 ps, 0.83 ns, and 1.3 ns corresponding to pure water, Type I complexes, and Type II complexes, respectively.

On the other hand, when the fluorescence is monitored at 350 nm in an aqueous solution with no β-CD, a single exponential decay is observed with a lifetime about 400 ps, representing the b fluorescence lifetime in water. Upon
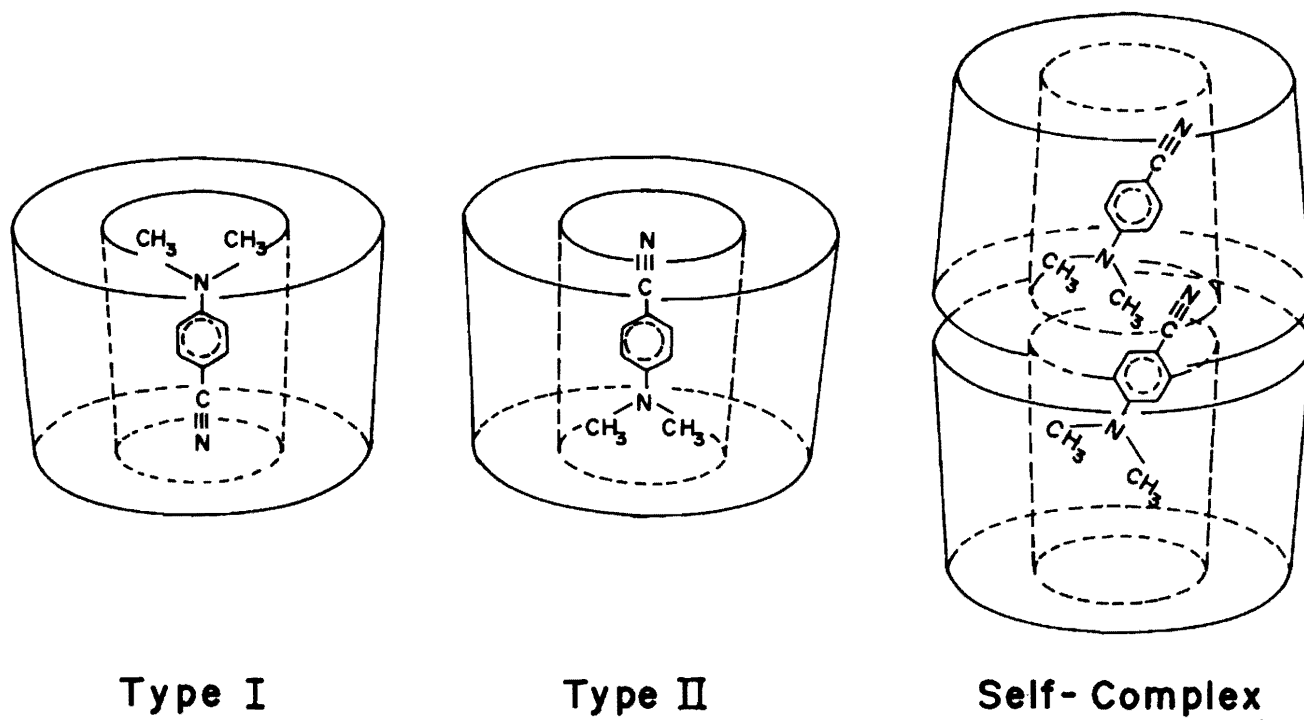

Type I   **Type II**   **Self-Complex**

Figure 5. Possible Positions of DMABN in β-CD Cavity: Type I: Dimethylamino Group Towards The Larger Rim,
Type II: Dimethylamino Group Towards the Smaller Rim, and a Self-Complex.

addition of β-CD, b fluorescence from Type I and Type II complexes is also observed, giving lifetimes of about 1.0 ns and 2.6 ns, respectively.

When the concentration of DMABN is increased, more β-CD cups will now be singly occupied since absorption spectra do not indicate that dimers are present and no excimer fluorescence has been observed. Thus, in addition to the stabilization of occupied cups by unoccupied ones, it is now more probable for two singly occupied cups to stabilize each other; *i.e.* a 2:2 complex is formed. The other possibility that the reaction of two singly occupied cups leads to the formation of a 2:1 complex; *i.e.* one doubly occupied cup and an empty cup, will have the same concentration dependence of the fluorescence of the singly occupied cups (TICT band at 520 nm). However, as already mentioned the formation of a 2:1 complex is unlikely because such complex should affect the absorption spectrum and should also show excimer fluorescence. There will be some interaction between DMABN molecules and self-complexes will then be possible. Fluorescence monitored at 420 nm shows that this is actually the case since fluorescence from a long lived species with a lifetime of about 8.0 ns is observed. This is supported by the time resolved spectra presented in Figure 4. At short times after excitation (100 ps–2.50 ns), only the b and TICT fluorescence bands are dominant. At longer times after excitation (5 ns–8 ns), self-complexes emission at about 400 nm is clearly enhanced.

CONCLUSION

Fluorescence and excitation spectra as well as fluorescence decays and time resolved spectra of DMABN in β-CD are presented. DMABN molecules in β-CD aqueous solution experience four different environmental conditions. These are: (*a*) the bulk water, (*b*) when the DMABN molecule is inside the β-CD cavity with its dimethylamino group headed towards the smaller rim of the β-CD cup and is probably stabilized by another unoccupied β-CD cup, (*c*) when the DMABN molecule is inside the β-CD cavity with its dimethylamino group headed towards the larger rim of the β-CD cup, and (*d*) when two DMABN molecules in two β-CD cavities interact with each other. The last environment allows the formation of self-complexes in β-CD.

ACKNOWLEDGMENT

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