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Cavity Size Effect on the Excited State Dynamics of Methyl 4-(Dimethylamino)benzoate−Cyclodextrin Complexes

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The effect of cyclodextrin (CD) complexation on the fluorescence properties of methyl 4-(dimethylamino)-benzoate (MDMAB) was studied. The complex with α-, *β*-, and *γ*-CDs exhibited twisted intramolecular charge transfer (TICT) fluorescence whereas only the emission from the locally excited state was observed in aqueous solution without CD. In the case of the α-CD complex, dual TICT emission was observed, a low-energy emission was centered at 520 nm, and a higher-energy emission was centered at 450 nm. The dependence of TICT emission intensity on pH and α-CD concentration suggested that the lower and higher energy emission can be attributed to the TICT states of MDMAB in the 1:1 and 1:2 MDMAB−α-CD complexes. On the other hand, only the formation of 1:1 complex was observed in the presence of *β*- and *γ*-CDs. The cavity size effect on the fluorescence properties of MDMAB was further discussed on the basis of time-resolved laser spectroscopy.

Introduction

Cyclodextrins (CDs) are cyclic origosaccaroids composed of a hydrophilic outer surface and a hydrophilic inner cavity. The most commonly available CDs, α-, *β*-, and *γ*-CDs have six, seven, or eight glucose units for which the internal diameter of the cavity varies systematically between 0.5 and 0.8 nm. Since the hydrophobic cavity is capable of incorporating molecules of appropriate size in aqueous solution, CDs have been employed as host molecules of supramolecular photochemistry. The hydrophobic cavity interior and the confined geometry of inside of the CD nanocavities can perturb the excited-state dynamics of guest molecule.[1] Thus, increasing attention has recently been given to the study of photophysical and photochemical processes of molecules encapsulated in CD cavities. Emission properties of a guest molecule are often affected, and many important photochemical processes have been successfully examined: room-temperature phosphorescence,[2−4] dimer or excimer formation,[5−7] excited-state proton transfer,[8,9] and excited-state charge transfer,[10−13] etc.

The fluorescence properties of several classes of donor−acceptor substituted benzenes, such as 4-(dimethylamino)-benzonitrile (DMABN) is known to be strongly dependent on the solvent polarity. These molecules exhibit normal fluorescence in nonpolar solvents while anormalously red-shifted emission appears beside the normal fluorescence in polar solvents. Since the discovery of dual fluorescence from DMABN,[14] a controversial discussion has been presented for the origin of the dual fluorescence. The anormalously red-shifted emission has been attributed to excimer formation,[15] excited-state proton transfer,[16] exciplex formation with solvent,[17] and twisted intramolecular charge transfer (TICT).[18] Grabowski et al. successfully explained the dual fluorescence as occurring from two species in the excited state, differing in the dihedral angle of the dimethylamino group with respect to the rest of molecule. Since dilution studies in solution[19] and the finding that the anormal emission can still be observed in saturated hydrocarbons[20] ruled out the excimer and exciplex mechanisms as a general explanation of dual fluorescence, the TICT mechanism has been most widely accepted nowadays. The shorter wavelength fluorescence is due to a planar locally excited (LE) state, while the longer wavelength fluorescence is called a TICT emission which is due to intramolecular electron-transfer resulting from the twisting of the dimethylamino moiety to a perpendicular geometry.

The degrees of electron transfer and structural change are controlled by the local polarity in addition to the size and free volume of the rotable electron-donor moiety. Thus, the excited-state dynamics of the TICT molecules is very sensitive to the microscopic environments. Concerning TICT molecules complexed with CDs, it is quite probable that the overall effect of CD encapsulation is complicated and the size of the guest molecule relative to that of CD cavity is a critical parameter. To understand further the inclusion effect on TICT photochemistry of guest molecules, we studied fluorescence properties of 4′-(dimethylamino)acetophenone (DMAAP) and ethyl 4-(dimethylamino)benzoate in α-CD aqueous solutions. It was revealed that, in addition to the 1:1 inclusion complex, these molecules and α-CD form a 1:2 inclusion complex giving rise to the TICT emission.[21,22]

In the present paper, we describe the fluorescence properties of methyl 4-(dimethylamino)benzoate (MDMAB) in CD nanocavities. The ester derivatives of DMABN have been known to exhibit dual fluorescence in moderately polar environments. Since TICT involves the rotation of an electron donor group, CDs of different cavity size are expected to influence the TICT process differently. Time-resolved fluorescence spectra of

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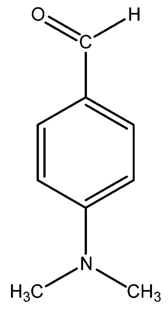
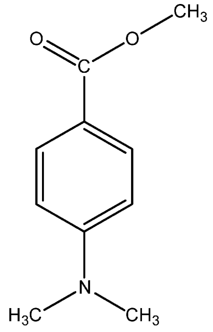


DMAAP



MDMAB

MDMAB in α-, β-, and γ-CD aqueous solutions also have examined to characterize the change on the excited-state dynamics of the TICT molecule induced by CD complexation. It was revealed that the 1:1 MDMAB−β-CD and MDMAB−γ-CD complexes exhibited dual fluorescence. The TICT emission arising from MDMAB molecule in two different environmental conditions was observed for α-CD complexes. The component ratio and the structure of the MDMAB−CD complexes were investigated. A comparison between the TICT behavior of DMAAP and MDMAB in CD cavity is also made and the cavity size effect on the excited-state dynamics of MDMAB complexes is further discussed.

Experimental Methods

MDMAB and CDs were purchased from Tokyo Kasei Co. The concentration of MDMAB in aqueous solutions was 2.5×10^{-5} M for all measurements.

Fluorescence spectra were measured with a spectrophotometer equipped with Nikon P-250 and G-250 monochromators. Fluorescence was detected with a Hamamatsu R-585 photomultiplier by a single-photon counting method. A tunable picosecond Nd:YAG pumped OPO laser system (Continuum Mirage based custom model) was used for time-resolved emission spectra measurements. Fluorescence was detected with a streak camera (Hamamatsu Photonics C-4780), and the time resolution of the system was 100 ps. All measurements were carried out at room temperature (295 K).

Results and Discussion

The ester derivatives of DMABN, such as MDMAB, also exhibit dual fluorescence in moderately polar solvents whereas these molecules emit only the short wavelength fluorescence from the LE state in nonpolar solvents. Furthermore, it has been known that these molecules emit only the LE emission in highly polar aqueous solution due to the fast internal conversion caused by the large stabilization of TICT state.

Dispersed emission spectra of MDMAB in aqueous solution containing varying concentration of α-CD are shown in Figure 1. Addition of α-CD caused an emergence of new emission bands at 420−550 nm region while MDMAB emits only the fluorescence from the LE state with a peak position at 390 nm in aqueous solution without CD. The 420−550 nm broad emission bands can be assigned to the TICT emission of MDMAB.

The emergence of TICT emission bands of MDMAB in α-CD aqueous solutions can be explained in terms of the reduced polarity effect of CD encapsulation. The TICT state having large dipole moment interacts more strongly with the polar solvent, and its energy is expected to decrease with an increase in solvent polarity.[23] In the polar solvent, the stabilization of the highly polar TICT state results in a decrease of the energy gap between the TICT and ground states as well as the energy barrier between the initial Franck−Condon and the TICT states. Since increasing the nonradiative rates caused by the decrease in the energy gap and lowering the barrier between the Franck−Condon and TICT states tend to have opposite effects on the TICT emission yield, the overall effect of solvent polarity is probably complex. It has been known that, as increasing the solvent polarity, the TICT emission yield of MDMAB reaches a maximum in the moderately polar solvent and decreases at higher polarity. Accordingly, the emission quantum yield of MDMAB in a highly polar aqueous solution is considerably lower. In the presence of α-CD the MDMAB molecule is encapsulated by the CD cavity and in a less polar environment where the nonradiative rates decrease with increasing the energy gap between the TICT and the ground states. Consequently, the complexation with α-CD causes the enhancement in the TICT emission yield.

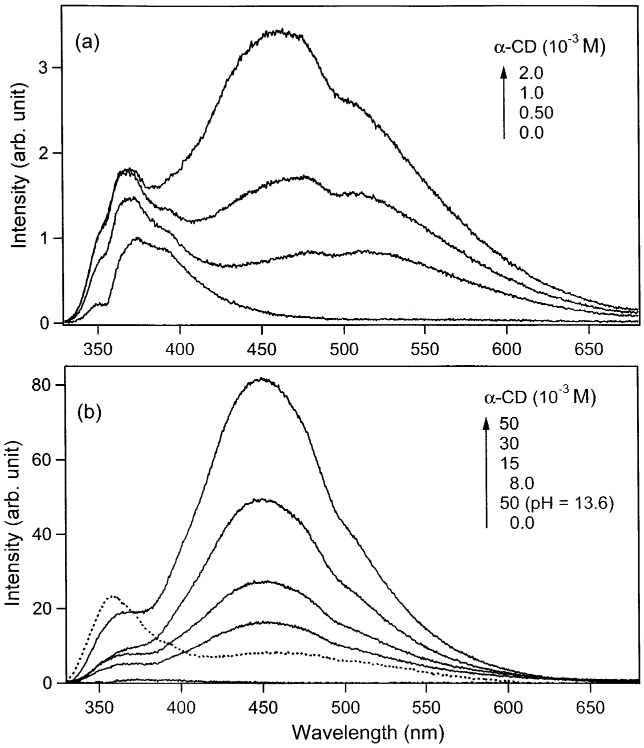


Figure 1. Dispersed emission spectra of MDMAB (2.5×10^{-5} M) in aqueous solutions in the presence of (a) 5.0×10^{-4} to 2.0×10^{-3} M, and (b) 8.0×10^{-3} to 5.0×10^{-2} M of α-CD excited at 315 nm. A spectrum recorded at pH 13.6 in the presence of 5.0×10^{-2} M of α-CD is expressed by a dashed line in part b.

At lower concentrations of α-CD, intensities of the LE emission bands were enhanced with a slight blue shift of the peak positions accompanied by the emergence of a broad emission band centered at around 520 nm. As increasing the α-CD concentration, a broad emission band centered at 450 nm appeared, and the 450 nm band was predominantly observed at higher concentration of α-CD than $\sim 2.0 \times 10^{-2}$ M. If the electronic absorption consists of contributions from MDMAB complexes in different environmental conditions, it is plausible that more than one TICT emission bands are observed. Excitation spectra of the mixed system obtained by monitoring the emission of 450 and 550 nm are shown in Figure 2. The excitation spectrum changed as the wavelength of emission monitored also indicates that at least two different type complexes coexist in the MDMAB−α-CD mixed solutions.

We made an attempt to evaluate the stoichiometry of emitting species by examining the dependence of the TICT emission

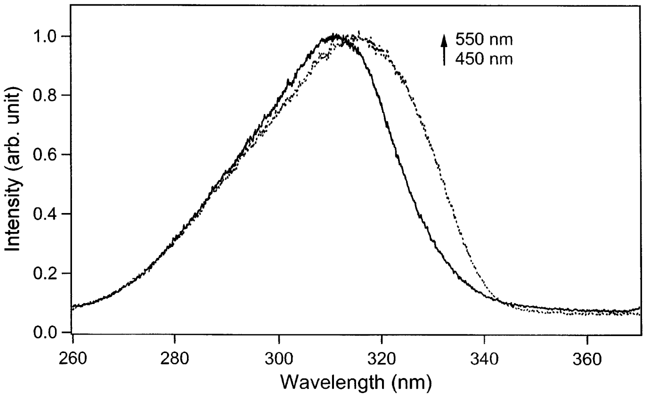


Figure 2. Excitation spectra of MDMAB (2.5×10^{-5} M) in aqueous solution containing 1.0×10^{-3} M of α-CD monitored at 450 (solid line) and 550 nm (dashed line).

intensity on the α-CD concentration. The 1:1 association between MDMAB and α-CD is described by the following equilibrium:

$$\text{MDMAB} + \alpha\text{-CD} \overset{K_1}{\rightleftharpoons} \text{MDMAB}\cdot\alpha\text{-CD} \quad (1)$$

Here, MDMAB·α-CD represents the 1:1 MDMAB−α-CD inclusion complex and K_1 is the equilibrium constant for the 1:1 complex formation. Under the assumption that the concentrations of α-CD are much higher than that of MDMAB, the Benesi−Hildebrand relation for such an equilibrium is

$$1/(I - I_0) = a\{1/[\text{MDMAB}]_0 + 1/([\text{MDMAB}]_0 K_1[\alpha\text{-CD}]_0)\} \quad (2)$$

where I stands for the TICT emission intensity with a certain concentration of α-CD, I_0 stands for initial TICT emission intensity of MDMAB without CD, $[\alpha\text{-CD}]_0$ and $[\text{MDMAB}]_0$ are the initial concentrations of α-CD and MDMAB, and a is a constant. For only the 1:1 complex to be formed, a plot of $1/(I - I_0)$ vs $1/[\alpha\text{-CD}]_0$ should yield a straight line. On the other hand, the usual Benesi-Hilderbrand double reciprocal plot of $1/(I - I_0)$ against $1/[\alpha\text{-CD}]_0$ of 450 nm emission band exhibits an upward concave curve (Figure 3a). Furthermore, the plot of 520 nm band shows a different profile providing further evidence for the presence of something other than the 1:1 inclusion complex.

Considering the very low concentration of MDMAB as compared to α-CD, we can assume the formation of 1:2 MDMAB−α-CD complex besides the normal 1:1 complex. Because of the size restriction inside the small α-CD cavity, part of a MDMAB molecule in a 1:1 inclusion complex may project out of the cavity and still be available in a bulk water environment. Accordingly, additional α-CD may accommodate the remaing part of the MDMAB molecule whose opposite end is already encapsulated in another α-CD.

If the 1:2 MDMAB−α-CD complex is thus formed in the mixed solution, the equilibrium will be expressed as

$$\text{MDMAB}\cdot\alpha\text{-CD} + \alpha\text{-CD} \overset{K_2}{\rightleftharpoons} \text{MDMAB}\cdot 2\alpha\text{-CD} \quad (3)$$

where MDMAB·2α-CD represents the 1:2 complex, and K_2 is the equilibrium constant for the 1:2 complex formation. The concentrations of the emitting species in the MDMAB−α-CD mixed system are expressed as follows:

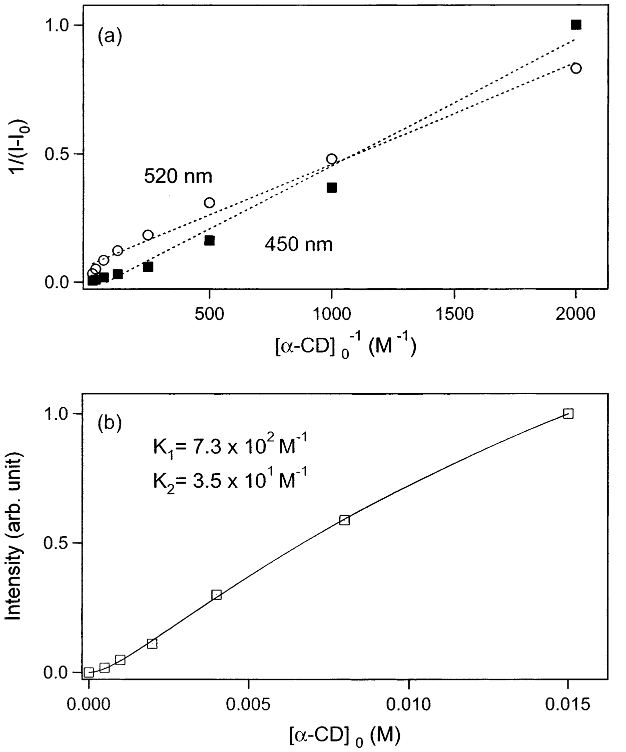


Figure 3. (a) Benesi−Hildebrand plot for the intensity of TICT emission bands centered at 450 (■) and 520 (○) nm of MDMAB in α-CD solutions. (b) Plot of the intensity of TICT emission band centered at 450 nm of MDMAB against concentration of α-CD. The best-fit curve of the concentration of the 1:2 complex simulated using eq 6 is also shown.

$$[\text{MDMAB}] = [\text{MDMAB}]_0/(1 + K_1[\alpha\text{-CD}]_0 + K_1K_2[\alpha\text{-CD}]_0^{\,2}) \quad (4)$$

$$[\text{MDMAB}\cdot\alpha\text{-CD}] = K_1[\text{MDMAB}]_0[\alpha\text{-CD}]_0/(1 + K_1[\alpha\text{-CD}]_0 + K_1K_2[\alpha\text{-CD}]_0^{\,2}) \quad (5)$$

$$[\text{MDMAB}\cdot 2\alpha\text{-CD}] = K_1K_2[\text{MDMAB}]_0[\alpha\text{-CD}]_0^{\,2}/(1 + K_1[\alpha\text{-CD}]_0 + K_1K_2[\alpha\text{-CD}]_0^{\,2}) \quad (6)$$

The α-CD concentration dependence of the TICT emission intensities observed at 450 nm is shown in Figure 3b. The concentration curves of emitting species were simulated using the above equations. Only the curve for the 1:2 complex reproduced the observed data, evidently indicating that the 1:2 complex is responsible for the 450 nm TICT emission. The best-fit curve for the concentration of 1:2 complex with $K_1 = 7.3 \times 10^2$ M^{-1} and $K_2 = 3.5 \times 10^1$ M^{-1} is also shown in Figure 3b.

The most probable structure of the 1:2 inclusion complex is a barrel-type, in which the larger rims of α-CDs face each other as shown in Figure 4. Cyclodextrins have secondary hydroxy groups on their larger rim, and the pK_a value of the hydroxy groups is reported to be 12.1.[24] At a pH above the pK_a value, the deprotonation of a neutral α-CD molecule is occurred to form an anion. Thus, the barrel-type complex dissociates owing to the electronic repulsion forces between two associating α-CD molecules.[4,5] The spectrum indicated with a dashed line in Figure 1b is the emission of the MDMAB−α-CD mixed system in a solution of 0.4 M NaOH, where the strong TICT emission band at around 450 nm vanished while the band at the longer wavelength remained. Thus, disappearance of the 450 nm TICT

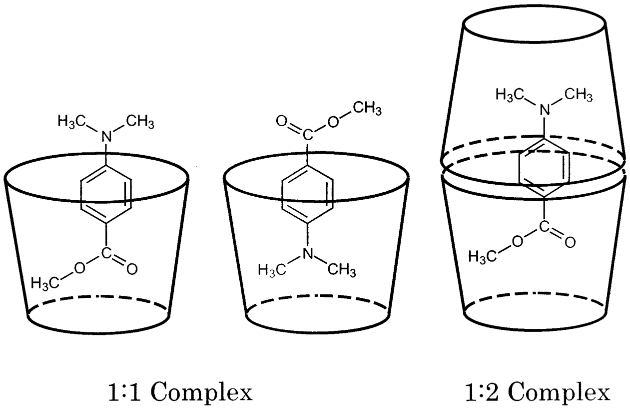


Figure 4. Possible structures of the MDMAB−α-CD complex.

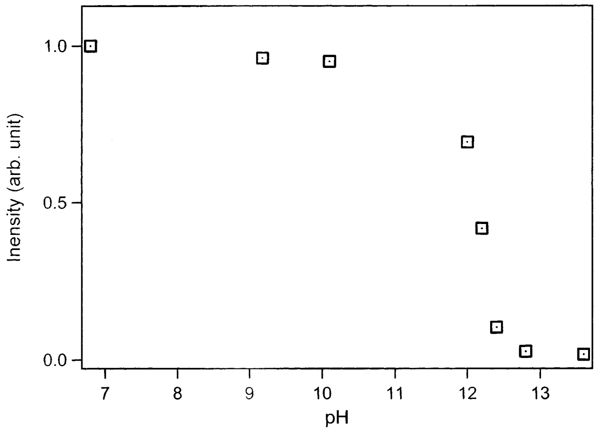


Figure 5. Plot of TICT emission intensity of MDMAB (2.5 × 10^{-5} M) against pH in the presence of α-CD (5.0 × 10^{-2} M) in KH_2PO_4−NaOH buffer (pH = 6.8), boroic acid−KCl−NaOH buffer (pH = 9.2), $NaHCO_3$−Na_2CO_3 buffer (pH = 10.1), KCl−NaOH buffer (pH = 12.1−12.7), and 0.4 M NaOH solution (pH = 13.6).

emission in the alkaline solution is consistent with the assumption that the TICT emission band is due to the 1:2 barrel-type complex. Furthermore, the longer wavelength emission band can be attributed to a 1:1 complex for which the concentration may not have such drastic pH dependence.

The observed blue shift of the TICT emission maximum indicates that the molecular environment of MDMAB is less polar where the stabilization of TICT state is insufficient due to the poor solvation. This finding is consistent with the assumption that the TICT emission centered at around 450 nm arises from a 1:2 barrel type complex where MDMAB molecule must be totally encapsulated in the CD cavities.

The pH dependence of the TICT emission intensity was investigated to further examine the formation and structure of the 1:2 complex. Figure 5 displays the TICT emission intensity of MDMAB (2.5 × 10^{-5} M) in buffer solutions of α-CD (5.0 × 10^{-2} M) monitored at 450 nm. The TICT emission intensity decreased drastically in the pH range from 12.0 to 12.4 while the intensity remains constant in the pH range below 10. The pH range of the drastic change on the TICT emission intensity is identical to the pK_a of the secondary hydroxy groups of α-CD, further indicating that the TICT fluorescence is due to the 1:2 barrel-type complex.

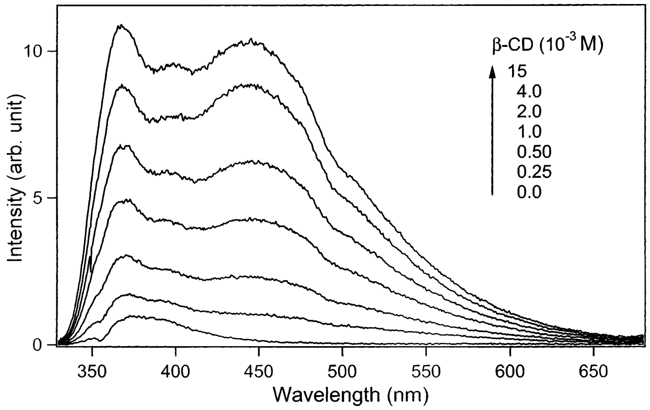


Figure 6. Emission spectra of MDMAB (2.5 × 10^{-5} M) in aqueous solutions in the presence of β-CD excited at 315 nm.

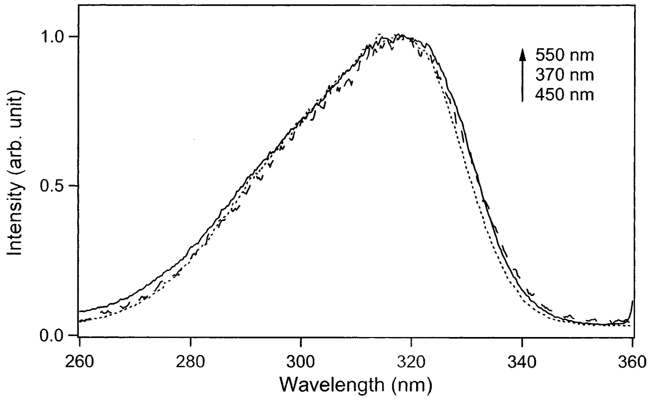


Figure 7. Excitation spectra of MDMAB (2.5 × 10^{-5} M) in aqueous solution containing 2.0 × 10^{-3} M of β-CD monitored at 370 (dotted line), 450 (solid line) and 550 nm (dashed line).

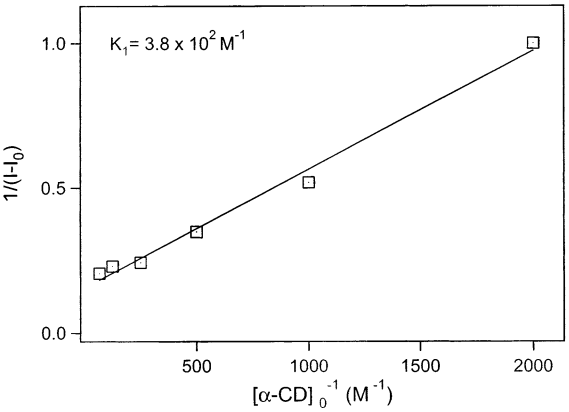


Figure 8. Benesi−Hildebrand plot for the intensity of TICT emission bands of MDMAB in β-CD solutions.

Figure 6 indicates the emission spectra of MDMAB (2.5 × 10^{-5} M) in aqueous solutions containing varying concentration of β-CD excited at 315 nm. With an increase in the concentration of β-CD, intensities of the LE emission band were enhanced, accompanied by an emergence of shoulder band at around 480 nm, which can be assigned to the TICT emission band. Excitation spectra of MDMAB (2.5 × 10^{-5} M) in aqueous solution containing 2.0 × 10^{-3} M of β-CD monitored at 370 (dotted line), 450 (solid line), and 550 nm (dashed line) are shown in Figure 7. In contrast to the case of α-CD, no significant difference of the spectral shapes was observed when the monitoring wavelength of the emission was changed. Furthermore, as shown in Figure 8, the Benesi−Hildebrand double reciprocal plot of $1/(I - I_0)$ vs $1/[\beta\text{-CD}]_0$ yields a straight line, indicating the 1:1 stoichiometry of the emitting species. The equilibrium constant for the 1:1 complex formation was obtained as 3.2 × 10^2 M^{-1}. Steady-state emission spectra of MDMAB−β-CD mixed system have been reported by Jiang,[25] and he also concluded that only the 1:1 inclusion complex was formed.

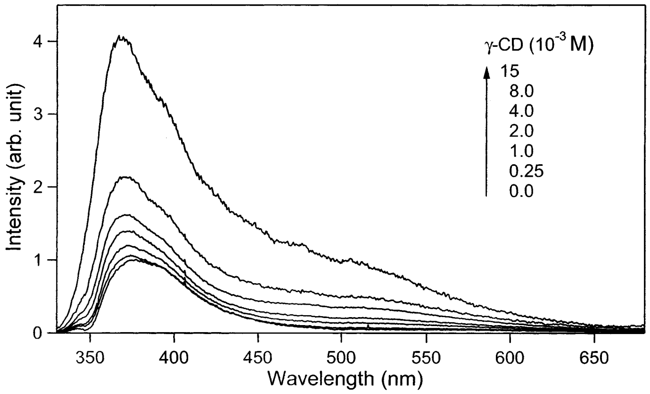


Figure 9. Emission spectra of MDMAB (2.5×10^{-5} M) in aqueous solutions in the presence of γ-CD excited at 315 nm.

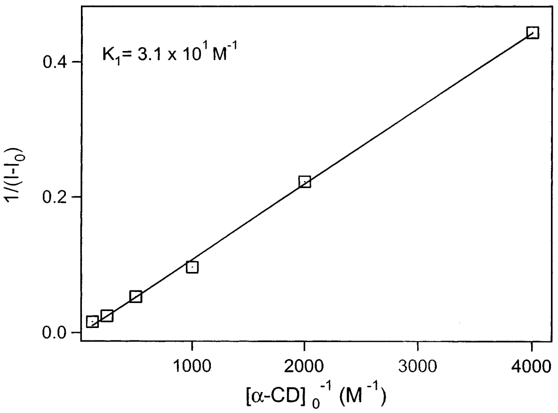


Figure 10. Benesi−Hildebrand plot for the intensity of TICT emission bands of MDMAB in γ-CD solutions.

Because of the larger cavity size of β-CD as compared with α-CD, a MDMAB molecule in a 1:1 inclusion complex should penetrate the CD cavity deeply and an additional β-CD may not be able to accommodate another part of MDMAB whose opposite end is already in the CD cavity.

Figure 9 shows the emission spectra of MDMAB (2.5×10^{-5} M) in aqueous solutions in the presence of γ-CD excited at 315 nm. Though an emergence of emission band in the TICT emission region also observed as increasing the γ-CD concentration, the intensity of the band was very weak. The result can be interpreted that a fast nonradiative decay channel is exist due to the large stabilization of the TICT state with highly polar water environment. The Benesi−Hildebrand double reciprocal plot of the TICT emission intensity yielding a straight line (Figure 10) indicates the 1:1 stoichiometry of the γ-CD complex. The equilibrium constant for the 1:1 complex formation was obtained to be 3.1×10^1 M^{-1}. To further characterize the cavity size effect on the excited-state dynamics of MDMAB, emission decay profiles of these complexes were examined in the following section.

Typical time-resolved emission spectra of MDMAB in aqueous solutions in the presence of CDs are indicated in Figure 11. The decay profiles could be fitted to the sum of two exponential functions while the LE fluorescence of MDMAB decays monoexponentially with a rather short decay time (∼230 ps) in aqueous solution without CD. The fluorescence lifetimes of MDMAB are summarized in Table 1.

The decay profiles were examined based on the kinetics scheme of TICT process proposed by Kajimoto et al. in Scheme 1,[26] where k_1 and k_2 are the rate constants of forward and backward charge-transfer processes, and k_{LE} and k_{CT} indicate the sum of the radiative and nonradiative decay rates of the S_1 (LE) and TICT states, respectively. According to the above kinetics scheme, both the S_1 and TICT fluorescence profiles follow double-exponential decay.

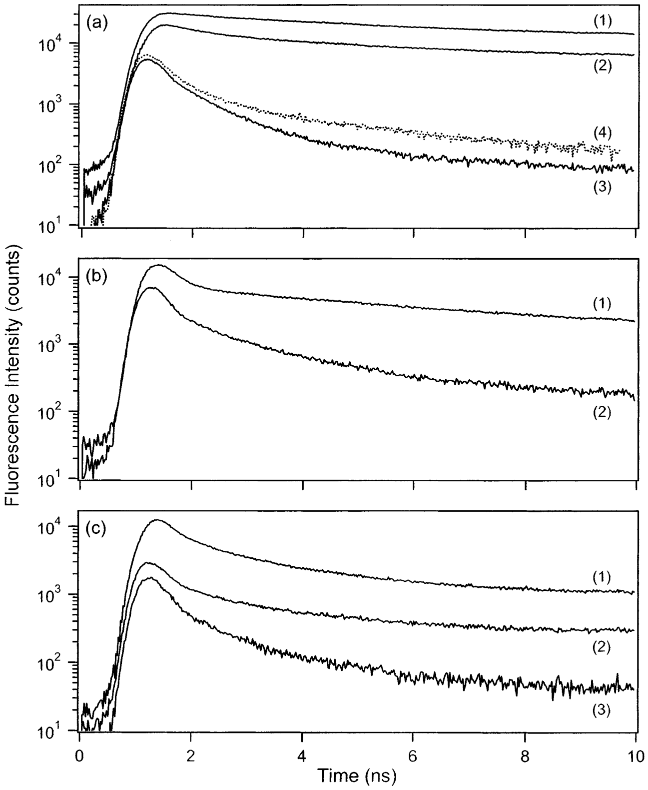
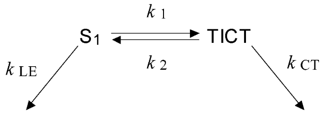


Figure 11. Emission decay traces of MDMAB (2.5×10^{-5} M): (a) (1) 5.0×10^{-2} M α-CD, (2) 1.5×10^{-2} M α-CD, and (3) 5.0×10^{-4} M α-CD neutral solutions and (4) 5.0×10^{-2} M α-CD alkaline solution at a pH of 13.6 (dashed line) obtained by monitoring total fluorescence; (b) 1.5×10^{-2} M β-CD neutral solution obtained by (1) monitoring total fluorescence and (2) the TICT emission region ($\lambda_{obs} > 460$ nm); (c) 5.0×10^{-2} M γ-CD solution obtained by (1) monitoring total fluorescence and (2) the TICT emission region ($\lambda_{obs} > 460$ nm), and (3) 1.5×10^{-2} M γ-CD solution obtained by monitoring TICT emission region ($\lambda_{obs} > 460$ nm).

TABLE 1: Fluorescence Lifetimes (τ_i), and Ratios of Preexponential Factors (A_2/A_1) for MDMAB in CD Solutions Obtained by Monitoring LE (370 nm) and TICT (460 nm) Band Regions

solution	band	τ_1 (ns)	τ_2 (ns)	A_2/A_1
α-CD (5.0×10^{-4} M)	LE	0.24	2.1	0.14
α-CD (1.5×10^{-2} M)	TICT	0.31	7.8	1.1
α-CD (5.0×10^{-2} M)	TICT	0.28	9.0	4.6
α-CD (5.0×10^{-2} M, pH 13.6)	LE	0.29	2.9	0.10
α-CD (5.0×10^{-2} M, pH 13.6)	TICT	0.28	2.8	0.12
β-CD (1.5×10^{-2} M)	LE	0.26	7.1	0.28
β-CD (1.5×10^{-2} M)	TICT	0.26	2.6	0.15
γ-CD (1.5×10^{-2} M)	TICT	0.24	2.1	0.14
γ-CD (5.0×10^{-2} M)	TICT	0.26	3.7	0.23
γ-CD (5.0×10^{-2} M)	LE	0.26	3.4	0.35

SCHEME 1



$$I_f(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \qquad (7)$$

When the rate constants k_1 and k_2 are large enough compared with k_{LE} and k_{CT}, namely, in the case of fast equilibration between the LE and CT states, the short lifetime component can be approximated as

$$\lambda_1 \approx k_1 + k_2 \tag{8}$$

In addition, if λ_1 is much larger than λ_2, the ratio of the preexponential factors of the LE fluorescence can also be simplified as

$$A_2/A_1 = k_2/k_1 \tag{9}$$

Because of the overlapping of the emission from the LE and TICT states and the complexed and uncomplexed molecules, it was not possible to determine the values of k_1 and k_2 from the fast decay component of LE or the rise component of TICT fluorescence. However, the component ratio of the slow decay, the A_2/A_1 value, generally increased as the CD concentration increased, indicating that the backward charge-transfer process was enhanced by the CD complexation. This could be due to the lowering of the activation barrier for the backward TICT process caused by the destabilization of the TICT state in the less polar hydrophobic cavity environment

If a 1:2 barrel-type complex is formed, the MDMAB molecule in the complex should be well isolated from the highly polar water environment and the TICT state is destabilized. In an alkaline solution at a pH value larger than pK_a of CD, the 1:2 barrel-type complex should dissociate leading the stabilization of the TICT state and the increase of the activation energy for the backward charge-transfer process. As shown in Figure 11a and Table 1, the A_2/A_1 value is considerably larger for the neutral solution at higher concentration of α-CD, and the ratio drastically decreased in the α-CD alkaline solution. This result also indicates that the 1:2 barrel-type complex should be formed at higher α-CD concentrations.

The TICT photochemistry of DMABN and its derivatives in CD complexes have been studied by several groups and the effect of CD complexation has been interpreted in terms of restriction on molecular motion or the polarity effect introduced by the hydrophobic cavity.[27−29] However, most of these studies consider only the 1:1 complex formation. Few studies which take account of the higher order complexes have so far been made, such as the speculation of the formation of 1:2 complex by Al−Hassan[30] and Nag et al.[31] and very recent reports by Panja and Chakravorti[32] and by Das.[33] In a previous work,[22] we confirmed the formation of the TICT state in the 1:2 DMAAP−α-CD complex. In the present study, the formation of the TICT state was observed even in the 1:2 barrel-type complex of MDMAB which has a bulky alkoxy−carbonyl group as compared to DMAAP. The result indicates that the polarity effect introduced by the hydrophobic cavity, instead of the restriction on molecular motion, plays a major role in controlling the TICT process.

In the case of DMAAP, the 1:2 α-CD and 1:1 β-CD complexes exhibited dual fluorescence while no TICT fluorescence attributed to the 1:1 complex of α- or γ-CD was observed. In contrast, the MDMAB 1:2 complex with α-CD and the 1:1 complexes with α-, β-, and γ-CDs exhibited dual fluorescence. It has been reported that the initial Franck−Condon and TICT states correlate without excited-state crossing in the case of the alkoxy−carbonyl derivatives while they correlate with crossing in the case of cyano derivatives as a result of the substituent-induced level reversals.[34] Thus, some carbonyl derivatives of dimethylaniline exhibit strong TICT emission as compared to DMABN. On the other hand, DMAAP should have a fast nonradiative decay cannel via nπ* states while the nπ* states of MDMAB are high in energy and do not lead to fast nonradiative decay in both the polar and nonpolar environments. Thus, the TICT emission of 1:1 complex with α- and γ-CDs must be observed only in the case of MDMAB solutions.

Conclusions

Dual fluorescence of MDMAB complexed with α-, β- and γ-CDs was observed. Benesi−Hildebrand double reciprocal plot for β- or γ-CD solutions yielded a straight line, indicating the 1:1 stoichiometry of the complex. Two different type complexes which have TICT emission bands at around 450 and 520 nm were formed in α-CD solutions. The dependence of TICT emission intensity on pH and α-CD concentration suggested that the lower and higher energy emission can be attributed to the TICT states of MDMAB in the 1:1 and 1:2 barrel-type α-CD complexes. Though the effect of CD complexation on TICT photochemistry has been interpreted in terms of the restriction on molecular motion and the reduced polarity effect introduced by CD cavities, these effects tend to have opposite effects on the TICT emission yield. Thus, the overall effect of CD encapsulation is probably complex and the problem still causes controversy. Our results indicate that the polarity effect introduced by the hydrophobic cavity is the dominant factor in the controlling the photochemistry of ester derivatives of dimethylaniline in α-CD complexes. Time-resolved emission spectra also indicate the formation of a 1:2 complex with α-CD and faster backward electron transfer from the TICT state for 1:1 complexes.

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