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Excited-state intramolecular proton transfer coupled-charge transfer of *p-N,N*-dimethylaminosalicylic acid in aqueous β-cyclodextrin solutions

Yanghee Kim [a], Minjoong Yoon [a,*], Dongho Kim [b,1]

[a] *Department of Chemistry, Chungnam National University, Taejon 305-764, South Korea*
[b] *National Creative Research Initiatives Center for Ultrafast Optical Characteristics Control, Korea Research Institute of Standards and Science, Taejon 305-600, South Korea*

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Abstract

The single emission at 400 nm originated from mostly excited-state intermolecular hydrogen bonding has been observed for 0.05 mM *p-N,N*-dimethyaminosalicylic acid (DMAS) in aqueous solutions (pH = 1.7). Upon addition of β-CD, however, the 400 nm emission band is diminished, accompanied by a broadening of the bandwidth along with an appearance of a new band at 350 nm. According to the band analysis, the broad emission was found to be composed of two emission bands arising from the excited-state intramolecular proton transfer (ESIPT) and the excited-state intramolecular charge transfer (ICT), respectively. Being consistent with these steady-state spectroscopic results, the picosecond time-resolved fluorescence study unraveled three decay components corresponding to two different proton transfer processes and the excited ICT state with ca. 5.6 ns, 160 ps and 1.5 ns, respectively. It is noteworthy that the relative amplitude of 1.5 ns component attributable to the ICT state is enhanced in parallel with an increase of 160 ps ESIPT component. These results are interpreted in terms of the proton transfer coupled-charge transfer processes.

Keywords: *p*-Dimethylaminosalicylic acid; Excited-state intramolecular charge transfer; Excited-state intramolecular proton transfer

1. Introduction

Recently, the excited-state intramolecular charge transfer (ICT) process has been attractive topics of investigations as a primary function for basic mechanism of biological and chemical energy conversion [1–7]. The ICT process of organic molecules containing separate electron donor and electron acceptor moieties has been studied in various homogeneous and heterogeneous media, and many reports revealed that the excited-state ICT emission could be maximized by conformational change. These conformational changes are known to be affected by polarity or viscosity of the media [8–12]. In some molecules, such as dimethylaminobenzonitrile (DMABN) derivatives (I), the conformational change has been proposed to induce the twist of the whole alkylamino group with respect to the benzene ring leading to a so-called "twisted intramolecular charge transfer (TICT)" state [13,14] or the rehybridization including the nitrogen atom of the amino group leading to the "wagged intramolecular charge transfer (WICT)" state [15], respectively. According to recent theoretical calculations, besides, the bending of the cyano group of DMABN is also considered to be followed by the twisting of the dimethylamino group [16,17] and the resulting "rehybridised ICT (RICT)" has been proposed to compete with the TICT mechanism in the ICT process.

Also, it has been reported that the intermolecular hydrogen bonding process is an important factor to facilitate the ICT process by maintaining a large twist angle between the electron donor and acceptor groups in the ground state [18]. Such a hydrogen bonding effect is an interesting subject to elucidate the proton-coupled charge transfer phenomenon which has often been observed in biological assemblies including PS II systems [19]. In PS II, the photoinduced charge separation is coupled to proton motion within quinone pool. Recently, Yoon et al. investigated the intermolecular hydrogen bonding effects on ICT emission in various media, i.e. aqueous cyclodextrin solutions, SiO_2 colloidal solution and zeolites. They proposed that the intermolecular hydrogen bonding interaction between electron-withdrawing group and media plays an important role in controlling the excited-state ICT process [20–22]. However, the intramolecular hydrogen bonding effect on the ICT process has not been considered at all. Thus, further systematic studies of

* Corresponding author. Fax: +82-42-823-7008.
E-mail address: mjyoon@hanbat.chungnam.ac.kr (M. Yoon).
[1] Co-corresponding author.

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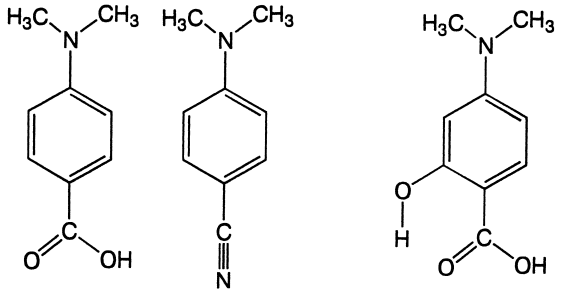
the hydrogen bonding effects on the ICT should be made to illustrate the proton transfer coupling with the ICT process.



(I) (II)

For this purpose, *p-N,N*-dimethylaminosalicylic acid (DMAS) (II) is an appropriate molecular system. It has two hydroxyl groups that can form two different hydrogen bondings; one is intermolecular hydrogen bonding and the other is intramolecular hydrogen bonding. It already has been reported that *p*-dialkylaminosalicylate derivatives exhibit three fluorescence bands, originating from the locally excited-state (LE), the excited-state intramolecular proton transferred (ESIPT) tautomer and the excited ICT state. Kasha et al. suggested that these three emission bands should be in competition with one another [2,23,24]. However, the inter- and intramolecular hydrogen bonding effects on the excited-state ICT process were not considered, instead only the polarity effects in aprotic solvents were investigated. They observed the proton transferred tautomer emission well separated from the ICT emission with a variation depending on solvent polarity. Furthermore, no direct evidences were found to rule out the fact that the ICT is coupled with the proton transfer. On the other hand, a recent investigation of the fluorescence properties in both protic and aprotic solvents showed the possibility that the ICT emission process in aminosalicylate is coupled with proton transfer process [25].

In this study, we have attempted to explore the hydrogen bonding effects more systematically on the excited-state processes of DMAS by observing the steady-state and time-resolved fluorescence spectral properties in aqueous cyclodextrin (CD) solutions. CD forms a hydrophobic and restrictive cavity with hydrophilic external walls in aqueous solution, providing two different microenvironments with an incorporated guest molecule. Three types of CDs are commonly available, each having a slightly different cavity diameter, and they can accommodate the guest molecules in their cavities [19]. Thus, CD is an ideal system to control the relative micro-environment of each functional group to distinguish the hydrogen bonding and polarity dependence of the electron-donating group from the hydrogen bonding effect of the carboxylic acid. Actually, many scientists have employed the CD system to control the ICT process of various ICT molecules [26–30].

2. Experimental

2.1. Materials

DMAS was purchased from Aldrich Chemical Co. and purified by triple recrystallization in ethanol until their melting points agree well with the reference values. All the solvents were obtained from Merck Chemical Co. as spectroscopic grade and used without further purification. Both α- and β-CDs were purchased from Aldrich Chemical Co. and used without further purification. The stock solutions of DMAS and CDs were prepared in pH 1.7 buffer solution (pK_a of DMAS = 3.5). In the pH 1.7 buffer solutions, the acid exists 99.5% as neutral species. The same volume of the DMAS stock solution was added to the different volume of CD stock solution, keeping the total volume constant so that the final concentration of DMAS is about 5.0×10^{-5} M. This concentration is low enough to avoid dimerization of carboxylic acids. For a comparative experiment, the aqueous CD solutions containing the related derivatives were prepared under the same condition as that for DMAS solution. Water was triply distilled in the presence of acidic dichromate and alkaline permanganate. All the solutions were degassed by the freeze-pump-thaw (three to four cycles down to ca. 10^{-4} Torr) technique before spectral measurements.

2.2. Spectroscopic measurements

Absorption spectra were measured on a Varian Cary 3 spectrophotometer. Steady-state fluorescence measurements were made on a scanning SLM-AMINCO 4800 spectrofluorometer which makes it possible to obtain corrected spectra using Rhodamine B as a quantum counter. Fluorescence lifetimes were measured by a time-correlated single photon counting (TCSPC) method, using a picosecond dual-jet dye laser (Coherent; model 702) synchronously pumped by a mode-locked Ar ion Laser (Coherent; Innova 200) as described previously [21]. The cavity-dumped beam from the dye laser has 1 ps pulse width, average power of ca. 100 mW at 3.8 MHz dumping rate, and a tunability of 560–620 nm with Rhodamine 6G as gain dye and DODCI (diethoxydicyanineiodide) as saturable absorber. To excite the sample, the dye laser pulse was frequency-doubled using a β-barium borate (β-BBO) crystal. All the standard electronics used for the TCSPC were from EG&G Ortec. This method allows a time resolution of about 10 ps after deconvolution.

3. Results

3.1. Absorption spectral properties

Fig. 1 shows the absorption spectra of DMAS (5.0×10^{-5} M) in aqueous solution containing various concentrations of β-CD. Upon increasing the concentration of β-CD, the absorption maximum was slightly red-shifted

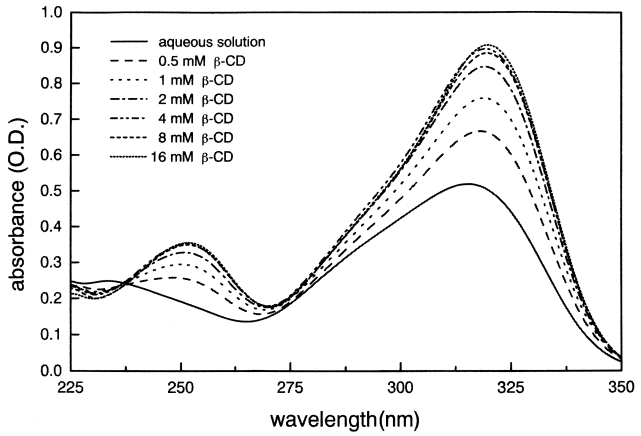


Fig. 1. Absorption spectra of DMAS (5.0×10^{-5} M) in aqueous buffer solution (pH = 1.7) containing different concentrations of β-CD.

with a gradual increase in absorbance while no spectral changes occurred with the addition of α-CD. This behavior has been attributed to the enhanced dissolution of the guest molecule through the hydrophobic interaction between aromatic-organic acid and nonpolar cavity of β-CD [21,32]. These results indicate that DMAS is entrapped in the β-CD to form DMAS:β-CD complex while no complexation with α-CD has occurred. By using the spectrophotometric titration method, the pK_a of DMAS in the presence of β-CD was determined to be 3.8 being similar to that in the absence of β-CD, implying that the acid group of the guest molecule in the CD complex is exposed to the aqueous phase. This is in a good accordance with the previous results obtained from the complexation of DMAS analog, *p*-dimethylaminobenzoic acid (DMABA), with β-CD [21,33,34].

3.2. Fluorescence spectral properties

Fig. 2(a) shows the fluorescence spectra of DMAS (5.0×10^{-5} M) in aqueous buffer solution (pH = 1.7) as a function of β-CD concentration, excited at 280 nm where the CD dependent absorbance change is negligible. In CD-free aqueous solution, a single fluorescence band was observed at ca. 400 nm, which is not observed in aprotic solvents. In the pH 1.7 solution, most of the DMAS exists as the neutral acid. This implies that 400 nm emission is originated partially from the anionic or neutral DMAS which is intermolecular hydrogen-bonded with water.

Upon addition of β-CD, the single emission band was gradually decreased with an appearance of dual emission bands which are similar to those observed in aprotic nonpolar solvents [23–25], indicating that a part of DMAS is entrapped in nonpolar CD cavity to form a DMAS:CD complex. Formation of the DMAS:CD complex should result in protonation of anionic DMAS, leading to produce more neutral form which permits greater hydrophobic stabilization in the interior of the CD cavity. This step decreases the amount of anionic form in solution, and thereby quenches

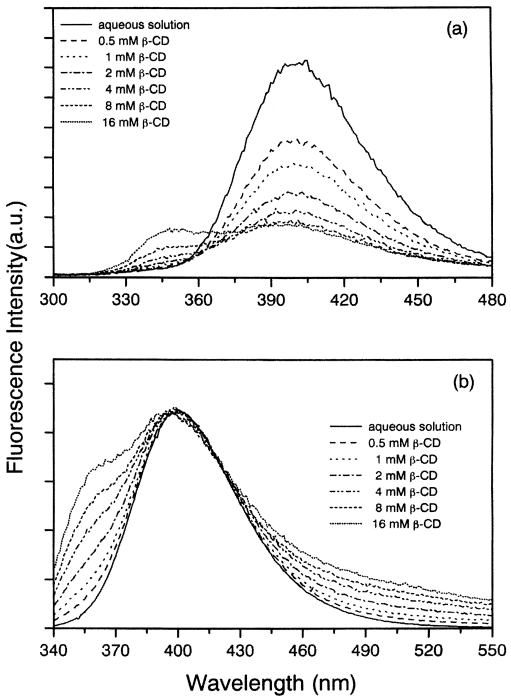


Fig. 2. (a) Fluorescence emission spectra of DMAS (5.0×10^{-5} M) in aqueous buffer solution (pH = 1.7) containing different concentrations of β-CD: the excitation wavelength was 280 nm; (b) the excitation wavelength was 320 nm and all the spectra were normalized at 400 nm.

the fluorescence, since the fluorescence quantum yield of the protonated DMAS is much smaller than that of the anion. The neutral form of DMAS in the CD cavity favor a closed conformer by intramolecular hydrogen bonding, It is well known that the closed conformer in the aprotic nonpolar solvents exhibits the excited-state intramolecular proton transfer (ESIPT) through the intramolecular hydrogen bonding [23–25]. This is why the dual fluorescence is observed for DMAS complexed by the CD. This is consistent with the fact that the dual emission of the DMAS:CD complex is similar to that observed in aprotic nonpolar solvents. Furthermore, it is noteworthy that the 400 nm emission band becomes significantly broad and slightly blue-shifted as the concentration of β-CD increases (Fig. 2(b)). These spectral changes were further confirmed by the band analysis using Gaussian distribution function (Fig. 3). Even in CD-free aqueous solution, the emission band of DMAS was found to be composed of two different bands at 390 and 420 nm, indicating that two different conformers exist in aqueous solution. One of those is an anion or a neutral open conformer formed by intermolecular hydrogen bonding of carboxylic acid and hydroxyl group with water, and the other is a closed conformer formed by intramolecular hydrogen bonding between carboxylic acid and hydroxyl group in salicylic acid [25]. The closed conformer can be tautomerized by the ESIPT, and the 420 nm emission should arise from the excited-state tautomer as observed in aprotic nonpolar solvents [23,24] while, the 390 nm emission is due to the

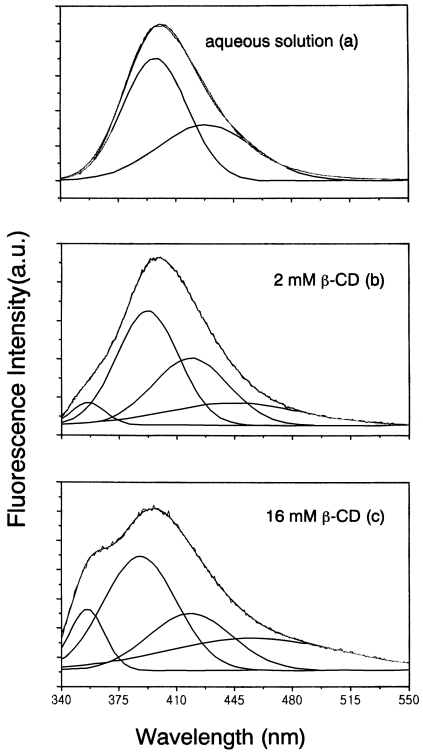


Fig. 3. Band analysis of fluorescence emission of DMAS: (a) aqueous buffer solution (pH = 1.7); (b) 2 mM β-CD; (c) 12 mM β-CD. The excitation wavelength was 280 nm.

locally excited-state of the anion or the neutral open conformer. According to the band analysis, as the concentration of β-CD increases, two additional emission bands were observed at 350 and 460 nm. This indicates that two corresponding excited species in addition to the locally excited

Table 1
Fluorescence maxima and bandwidth of DMAS in aprotic solvents[a]

Solvent	λ_{max}(nm)	Bandwidth (cm^{-1})
n-Hexane	454	4361
Tetrahydrofurane	460	4607
Acetonitrile	498	5079

[a] Excitation wavelength is 320 nm.

species of open and closed conformers are formed by the CD complex formation (Fig. 3(b) and (c)). Actually, in aprotic nonpolar solvents, the 350 nm emission which is attributed to the locally excited-state of the closed conformer is usually observed along with the 420 nm emission [23,24]. Moreover, the 460 nm emission was greatly enhanced by increasing the concentration of β-CD. Thus, it can be suggested that the 460 nm emission band is related to the formation of β-CD inclusion complex.

To characterize the new emission band at 460 nm, the fluorescence properties of DMAS were studied in various aprotic solvents (Fig. 4). In nonpolar solvents, such as *n*-hexane, the fluorescence spectra exhibit dual emission originated from the locally excited singlet state (LE) and the ESIPT state [23,24]. It is known that a large Stokes' shift of ESIPT emission is further red-shifted as the solvent polarity increases, so that the ICT emission is rather competitive [23,24]. However, in the present results, it was found that the large Stokes' shifted emission is not only further red-shifted, but also broadened as the solvent polarity increases (Table 1), indicating that the large Stokes' shifted emission in aprotic polar solvents is composed of two emitting species. Actually, the band analysis of the large Stokes' shifted emission in acetonitrile shows two emission bands. Especially, the sec-

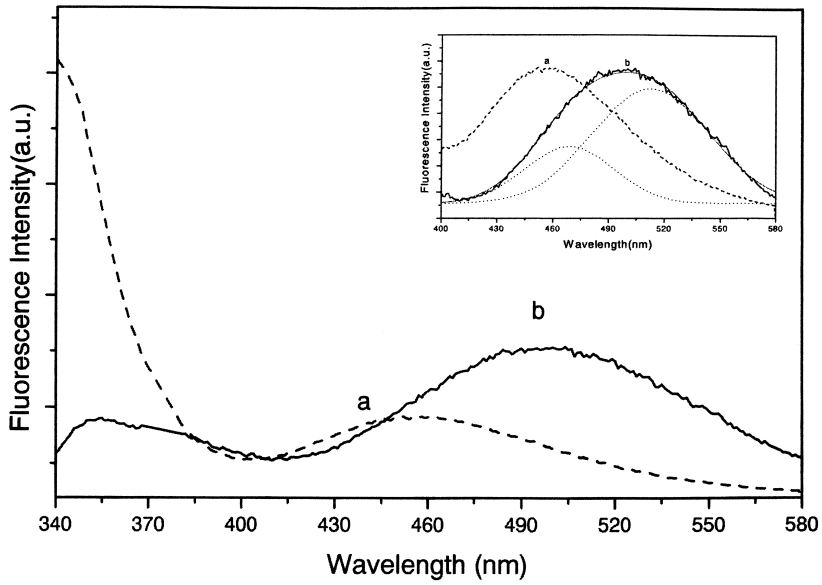


Fig. 4. The large Stokes' shifted emission in the dual fluorescence spectra of DMAS in hexane (a) and acetonitrile (b). The inset shows the band analysis of the large Stokes' shifted emission band in acetonitrile. The excitation wavelength was 320 nm.

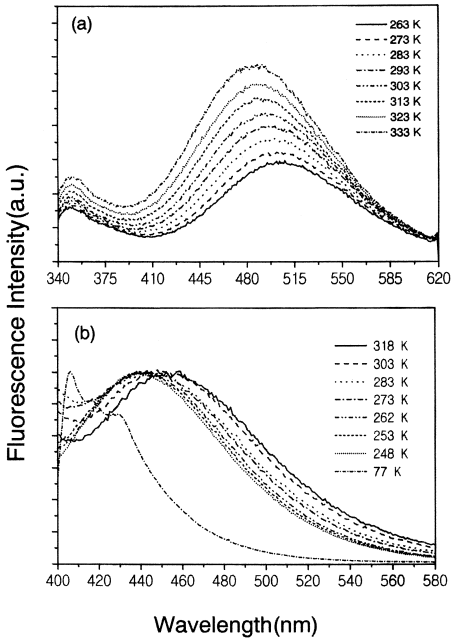


Fig. 5. The fluorescence emission spectra of DMAS as a function of temperature: (a) acetonitrile and (b) hexane.

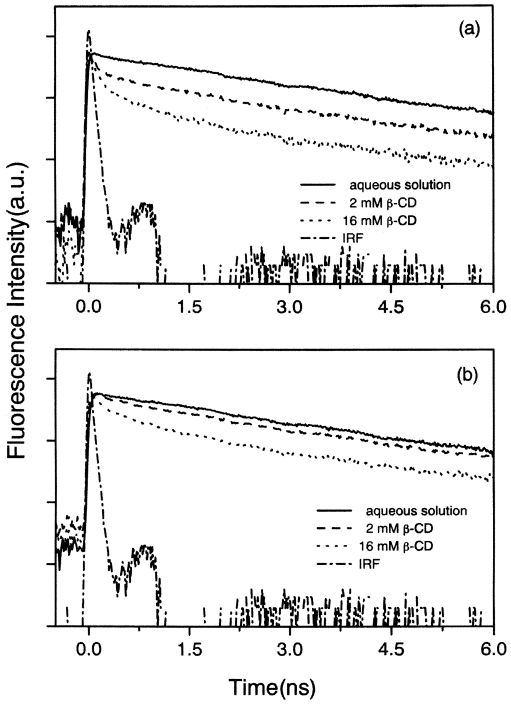


Fig. 6. The fluorescence decay profiles of DMAS monitored at (a) 365 and (b) 440 nm as a function of β-CD. The excitation wavelength is 300 nm.

ond emission band at longer wavelength is greatly reduced and blue-shifted as the solvent polarity decreases, suggesting that this emission band is originated from the excited ICT state. Thus, it is concluded that the appearance of the ICT emission is associated with the ESIPT emission. Moreover, upon increasing the temperature in acetonitrile, the emission band became greatly enhanced and blue-shifted as usually observed for the typical temperature-dependence of the ICT emission arising from the conformational changes (Fig. 5(a)) [36]. It is noteworthy that in nonpolar solvents at 77 K only the ESIPT emission was observed at ca. 410 nm (Fig. 5(b)). Upon increasing the temperature, the emission band was greatly red-shifted and broadened, indicating the appearance of new emission band that could be originated from the ICT state. From these results, one can again exclude the possibility that DMAS exhibits only the ESIPT emission without the ICT emission in nonpolar solvents and the ESIPT and excited-state ICT are competitive processes [23,24]. Therefore, our observations suggest that the large Stokes' shifted emission band of DMAS in β-CD aqueous solutions should have complicate origins.

To further characterize, the CD-induced changes in the fluorescence spectra of DMAS, the fluorescence lifetimes were measured. Fig. 6 shows the typical temporal profile of the DMAS emission in aqueous β-CD solutions, demonstrating that the fluorescence decay is significantly affected by the concentration of β-CD. The fluorescence lifetimes are summarized in Table 2. In CD-free aqueous solution, the 365 nm emission decay exhibits a slow decay (5 ns) as a major decay component with a small contribution of a fast decay component (60 ps). The fast decay component could be originated from the locally excited-state. The amplitude of the slow component is reduced upon addition of β-CD. Thus, this component is considered to arise from the intermolecular hydrogen bonding because the contribution of the intermolecular hydrogen bonding is reduced due to the entrapment of DMAS into the CD cavity. In the presence of CD, the large Stokes' shifted emission band decayed with three time constants: ca. 160 ps, 1.5 and 5 ns. This behavior matches well with the band analysis of the steady-state emission spectra. The fast time (160 ps) constant corresponds to the decay of intramolecular hydrogen bonding species. In accordance with this interpretation, as the concentration of β-CD increases, the relative amplitude of this component increases at the expense of 5 ns component. Concomitantly, ca. 1.5 ns component is newly observed in addition to 5 ns and 160 ps components corresponding to the hydrogen bonding species upon addition of β-CD. It is noteworthy that the 1.5 ns component is dominantly observed in aprotic polar solvents, indicating that this component in the presence of β-CD should be originated from the excited-state ICT. These results support that DMAS is entrapped in the nonpolar CD cavity and the ESIPT through the intramolecular hydrogen bonding is accessible along with the ICT process.

4. Discussion

Naturally, two different types in the inclusion complex formation between DMAS and β-CD are available. One is the molecular conformation with the amine group captured

Table 2
Fluorescence lifetimes (τ_i), and relative amplitudes (a_i) for DMAS in β-CD aqueous solutions (pH 1.7) and aprotic solvents[a]

Solvent	Wavelength (nm)	τ_1 (ns)	a_1	τ_2 (ps)	a_2	τ_3 (ps)	a_3	τ_4 (ns)	a_4
Water	365	4.6	0.64	60	0.36	–	–	–	–
	400	5.3	0.99	–	–	160	0.01	–	–
	440	5.5	0.95	–	–	155	0.05	–	–
β–CD (2 mM)	365	4.2	0.18	50	0.65	170	0.15	–	–
	400	5.5	0.60	–	–	160	0.26	1.5	0.14
	440	5.6	0.47	–	–	155	0.32	1.5	0.20
β-CD (16 mM)	365	4.2	0.12	50	0.70	220	0.18	–	–
	400	5.6	0.24	–	–	155	0.49	1.5	0.26
	440	5.6	0.14	–	–	160	0.51	1.5	0.35
Hexane[b]	440	–	–	–	–	398	0.94	1	0.06
	510	–	–	–	–	390	0.91	1	0.09
Acetonitrile[b]	440	–	–	–	–	110	0.35	2	0.65
	510	–	–	–	–	150	0.14	1.7	0.86

[a] Excitation wavelength is 300 nm. Measurement error limits are <10% of the listed values.
[b] The wavelength 360 nm emission could not be measured because of its low quantum yield.

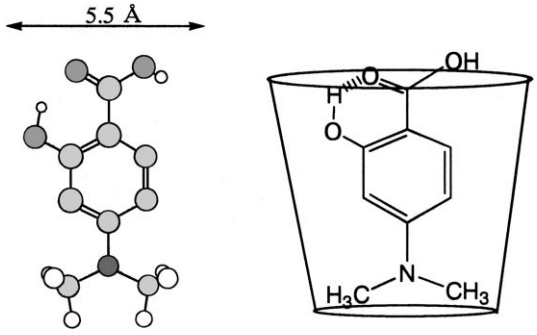
in CD cavity and the other is with salicylic acid group captured, depending on the internal diameters of CD cavities as well as the molecular size of DMAS. To determine the dimensions of DMAS, the geometry in the ground state was optimized by using the 6–31G* program. This calculation revealed that the diameter of the intramolecular hydrogen bonded salicylic acid group is about 5.5 Å which is much bigger than that of the α-CD cavity (4.5–5 Å) [21]. However, salicylic acid and amine group is likely to be inserted into the β-CD cavity which is much bigger than the α-CD cavity. Since the pK_a of DMAS remains unchanged in β-CD solution, the carboxylic acid group is exposed to aqueous phase, and DMAS should be encapsulated into the β-CD cavity as shown in Scheme 1.

In general, the existence of an isosbestic point in the absorption spectra is indicative of the formation of well-defined 1:1 complex. However, for the DMAS/β-CD complex the detergent action of CD is so strong that no isosbestic point was observed in the absorption spectra. Thus, it is difficult to estimate the stoichiometry of the complex formation based on the absorption spectral changes. We attempted to evaluate the stoichiometry and association constant of the DMAS/β-CD complex by monitoring the I_a/I_b ratio, where I_a and I_b are the intensity of LE and the intensity of Stokes' shifted emission, respectively, using the following Eq. (1) proposed by Jiang [33].

$$\frac{1}{[(I_a/I_b)_0 - (I_a/I_b)]} = \frac{1}{[(I_a/I_b)_0 - (I_a/I_b)']} + \frac{1}{K[(I_a/I_b)_0 - (I_a/I_b)][\mathrm{CD}]} \quad (1)$$

Where K is the association constant, $(I_a/I_b)_0$ is the initial intensity ratio of free DMAS, (I_a/I_b) and $(I_a/I_b)'$ are the observed and intrinsic intensity ratios of the inclusion complex, respectively. Fig. 7 shows a straight line from the plot of the reciprocal of $(I_a/I_b)_0 - (I_a/I_b)$ versus the reciprocal of the β-CD concentration for the present system, indicating 1:1 stoichiometry in the DMAS/β-CD complex. From the slope and intercept, the formation constant was determined to be 870 M^{-1}.

The formation constant is so small compared with other guest molecule/CD complexes such as dialkylaminobenzonitrile and its derivatives [21,32–34]. This is probably because the intramolecular hydrogen-bonded DMAS entrapped in the β-CD cavity is so bulky that encapsulation cannot easily occur. Nevertheless, the inclusion complex seems to favor the intramolecular hydrogen bonding instead of the intermolecular hydrogen bonding, and consequently the ESIPT state is easily formed. This is supported by the fact that the 5 ns decay component originated from the excited-state intermolecular proton transfer becomes dramatically reduced upon addition of β-CD, followed by the enhancement of the ESIPT emission decay component. Concomitantly, a new emission component (1.5 ns) from the ICT state is enhanced, suggesting that the ICT state is induced by the formation of the excited-state intramolecular hydrogen bonding.



Scheme 1. The optimized structure of DMAS and the proposed structure of inclusion complex with β-CD.

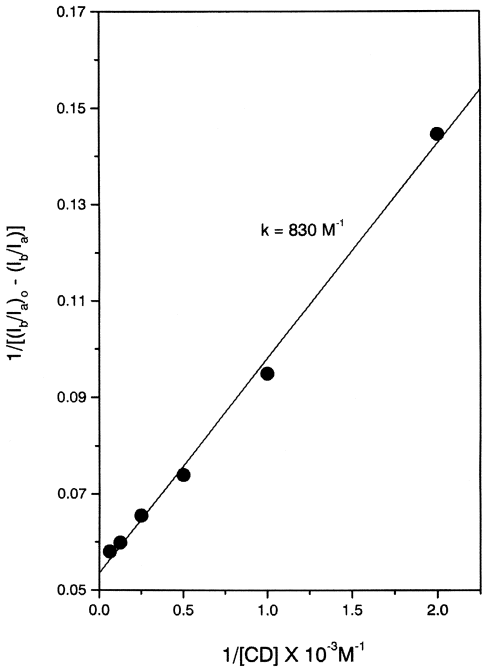
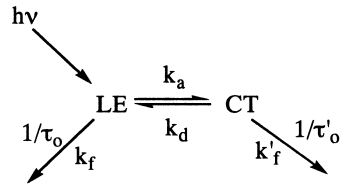


Fig. 7. Plot of the reciprocal of $(I_a/I_b)_0 - (I_a/I_b)$ vs. the reciprocal of β-CD concentration for DMAS/β-CD system.

It is well known that dimethylaminobenzoic acid (DMABA) does not exhibit the excited-state ICT emission in nonpolar solvents because of a weak dipole–dipole interaction between solute and solvent and a fast back charge transfer. However, our present work demonstrated that DMAS exhibits the excited-state ICT emission in addition to the ESIPT emission even in nonpolar solvents, even though the lifetime of the ICT emission was ca. 1 ns, which was slightly shorter than that in polar solvents such as acetonitrile, ca. 2 ns (Table 2), due to less stabilization of the excited ICT state by a weak dipole–dipole interaction. The difference in structure between DMAS and DMABA is just 2-hydroxy



Scheme 2.

group, which has an ability to form the intramolecular hydrogen bonding and the existence of the ICT emission of DMAS in nonpolar solvents indicates the important role of the intramolecular hydrogen bonding in the ICT emission. Then, a question arises why the intramolecular hydrogen bonding is important in the formation of ICT state. At present no unambiguous answer is available, but it is possible to postulate that the excited-state proton transfer through the intramolecular hydrogen bonding lowers the activation energy of the forward ICT process. In order to check this assumption, we attempted to calculate the activation energies of DMAS and DMABA between locally excited-state (LE) and ICT state using the temperature dependent fluorescence spectra and the Stevens-Ban plot which is plotted as $\ln(\Phi'(\mathrm{CT})/\Phi(\mathrm{LE}))$ against the reciprocal absolute temperature.

For a reaction described in Scheme 2, the following expression (Eq. (2)) holds

$$\frac{\Phi'(\mathrm{CT})}{\Phi(\mathrm{LE})} = \frac{k'_f[\mathrm{CT}]}{k_f[\mathrm{LE}]} = \frac{(k'_f k_a)}{(k_f(k_d + 1/\tau'_0))} \tag{2}$$

where [CT] and [LE] are, respectively, the photostationary concentrations of CT and LE [35]. Two limiting conditions can be distinguished between a high-temperature limit (HTL) with $k_d \gg 1/\tau'_0$, and a low-temperature limit (LTL) with $k_d \ll 1/\tau'_0$ [35] where k is $(k'_f/k_f)\tau'_0$.

$$\frac{\Phi'(\mathrm{CT})}{\Phi(\mathrm{LE})} = \frac{k'_f k_a}{k_f k_d} \tag{3}$$

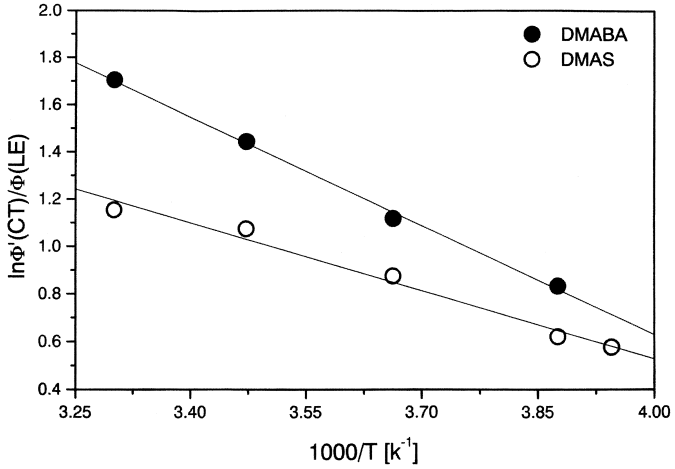


Fig. 8. Stevens-Ban plot: the ratio of $\ln(\Phi'(\mathrm{CT})/\Phi(\mathrm{LE}))$ to the reciprocal temperature for 0.05 mM DMAS and DMABA in acetonitrile.

$$\frac{\Phi'(\mathrm{CT})}{\Phi(\mathrm{LE})} = \left(\frac{k'_\mathrm{f}}{k_\mathrm{f}}\right) k_\mathrm{a}\tau'_0(\mathrm{LTL}) \quad (4)$$

$$\ln\left[\frac{\Phi'(\mathrm{CT})}{\Phi(\mathrm{LE})}\right] = \ln k + \ln k_\mathrm{a} \quad (5)$$

The activation energy E_a of forward ICT reaction is obtained from the LTL slope of $-E_\mathrm{a}(\mathrm{SB})/\ln \Phi'(\mathrm{CT})/\Phi(\mathrm{LE})$ (Eq. (4)), when k is temperature independent. Fig. 8 shows the Stevens–Ban plot and the E_a's are 812 J/mol for DMABA and 522 J/mol for DMAS. Thus, DMAS molecule more easily forms the excited ICT state than DMABA, indicating that ESIPT through the intramolecular hydrogen bonding lowers the activation energy for the ICT state formation. We attempted to calculate the excited-state energy of aminosalicylic acid (AS), an analog of DMAS, using the CASSCF(6,6) method. The AS molecule is known to have only the ESIPT state because the amine group is a weak electron donating group [1,2]. However, if the ESIPT through the intramolecular hydrogen bonding lowers the activation energy for the formation of the ICT state, the ICT state would be formed even in AS. As a matter of fact, the preliminary calculation revealed the existence of the ICT state as well as the ESIPT state in AS (to be published), indicating the feasible formation of the ICT state by way of the ESIPT state. Actually, we observed the ICT emission from AS in acetonitrile [25] even though the lifetime is very short.

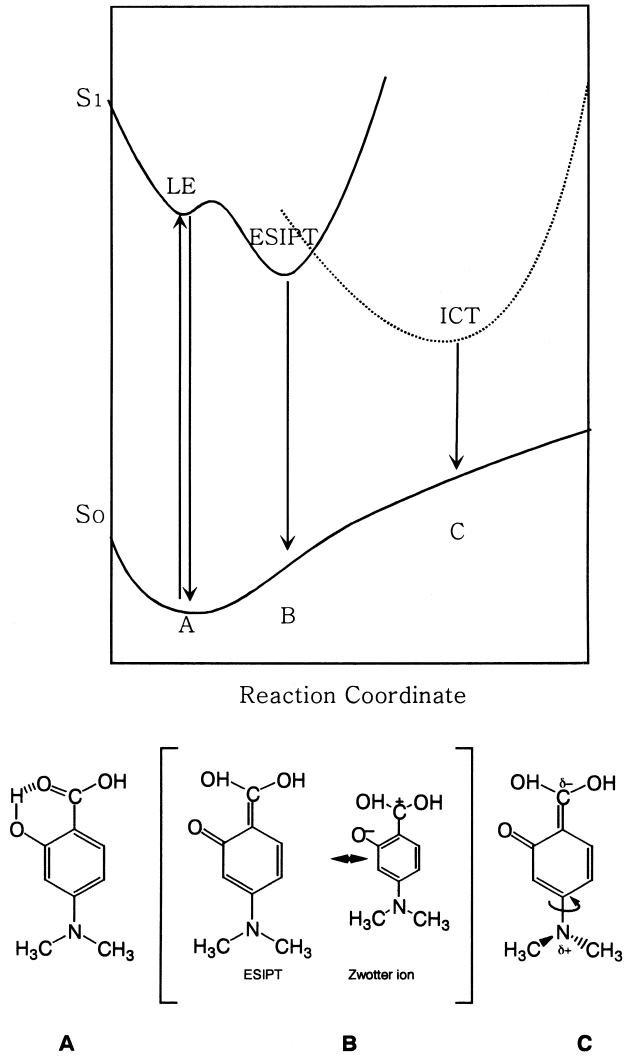


Fig. 9. Proposed potential energy surface diagram for the proton transfer coupled intramolecular charge transfer of DMAS/ß-CD system.

Based on the experimental and theoretical observations, the excited-state potential surface for the reaction of DMAS in β-CD is suggested in Fig. 9. It should be noted here that the LE-CT reaction barrier is relatively low through coupling the ICT state with the ESIPT state, which is lowered in energy, since no rise time was observed in contrast to the clear observation of the rise time for DMABA (40 ps) [20]. However, as the temperature is lowered, the ICT formation is inhibited with increasing the activation energy as well as the inhibition of the conformational change. This is consistent with the fact that the sharp ESIPT emission is only observable in aprotic nonpolar solvents at 77 K (Fig. 5(b)).

5. Conclusion

The fluorescence spectroscopic studies demonstrate that the hydrogen bonding has a significant fluorescence on the excited-state intramolecular charge transfer process of DMAS in aqueous cyclodextrin solutions. The ICT emission of DMAS arises from the intramolecular hydrogen bonding upon addition of β-CD, while no such emission is observed in aqueous solution. It is proposed that the ESIPT through the intramolecular hydrogen bonding plays an important role in the excited-state ICT.

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