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EXCITED-STATE TWISTED INTRAMOLECULAR CHARGE TRANSFER OF *p*-N,N-DIMETHYLAMINOBENZOIC ACID IN AQUEOUS CYCLODEXTRIN SOLUTIONS : TIME-RESOLVED FLUORESCENCE STUDY

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Abstract - The effects of α– and β–cyclodextrins (CD) on the twisted intramolecular charge transfer (TICT) behavior of p-N,N′-dimethylaminobenzoic acid (DMABA) in buffered aqueous solution have been investigated by examining formation and decay behaviors of the TICT-typical dual fluorescence. The ratio of the TICT emission to the normal emission (I_a/I_b) increases linearly as α–CD concentration increases, while in the presence of β–CD it shows nonlinear dependences on the CD concentration. The analysis of the CD-dependent changes of the I_a/I_b and absorption spectra demonstrates formation of 1:1 inclusion complexes between DMABA and CDs. The decay time of the normal emission (*ca.* 700 ps) is little affected by the formation of α–CD inclusion complex, whereas it increases upto *ca.* 1.6 ns upon formation of β–CD inclusion complex. The TICT emission for the β–CD inclusion complex exhibits two decay components while it shows a single component for the α–CD inclusion complex, indicating formation of one or two types of inclusion complex in the presence of α–CD or β–CD, respectively. These results are attributed to the CD cavity size dependence on patterns of complexation between CDs and DMABA. The CD size dependences of the TICT fluorescence properties with the orientation of the guest molecule demonstrate that the specific hydrogen bonding between the carboxylic acid group and water plays an important role in the excited-state TICT.

INTRODUCTION

The twisted intramolecular charge transfer (TICT) of various organic molecules has been the attractive topic of recent investigations as a model for a number of important photochemical processes.[1-3] The formation of excited TICT state is characterized by a dual fluorescence exhibiting large Stokes' shift of emission in addition to the normal emission from the locally excited state (LE), though a nonemissive TICT has been observed in some cases. This character is usually known to be brought about by a twisted conformational change of the electron donor in the excited TICT state. In some molecules such as p-N,N-dimethylaminobenzonitrile (DMABN) and its derivatives, the formation of the twist conformer is mostly controlled by the polarity of media. Thus, the relative positions and intensities of the dual emission bands are usually affected by solvent polarity and viscosity.

On the other hand, some authors have suggested that the specific hydrogen bonding between solvent and electron donor group also plays a major role to stabilize the twist conformer to facilitate the formation of the TICT state.[4,5] Such hydrogen bonding effect may be an important subject in exploring the proton-coupled charge transfer phenomena often observed in biological assemblies. From this point of view, the investigation of the hydrogen-bonding effect on TICT should be extended to other TICT molecules containing the electron acceptor to be readily hydrogen bonded with solvents. *p*-(dialkylamino)benzoic acid is an appropriate molecular system for this purpose since the carboxylic acid can form a symmetric configuration of protons to enhance the electronic coupling.

In order to distinguish the hydrogen-bonding effect from the polarity dependence of the carboxylic acid, cyclodextrin (CD) can be used to control the selective microenvironment of the functional group in aqueous solution. This is because the CD forms hydrophobic and

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‡*Abbreviations* : DMABA, 4-N,N′-dimethylaminobenzoic acid ; CD, cyclodextrin ; TICT, twisted intramolecular charge transfer; LE, locally excited state;

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 are able to accomodate the orientation of the guest molecules in their cavities.[6] In recent years, many investigators have employed the CD systems to control the TICT process of *p*-N,N-dimethylaminobenzonitrile (DMABN) derivatives.[7-12] Jiang[13,14] has already investigated the effects of α– and β–CD inclusion complex formation on the TICT fluorescence of *p*-N,N-dimethylaminobenzoic acid (DMABA) and showed that TICT is dependent on viscosity and polarity. However, the role of the hydrogen bonding of the electron acceptor with water in the formation of the TICT state has not been paid attention, even though the CD dependences of the TICT fluorescence properties of *p*-N,N-diethylaminobenzoic acid (DEABA) have demonstrated[15] that the energy barrier for the formation of the TICT state is governed by the torsion of the diethylamino group and the specific hydrogen bonding between the carboxyl group and water plays an important role in the excited state TICT. Thus, in this paper, we have extended the Jiang's investigation of the effects of α– and β–CDs on TICT emission of DMABA by examining the time-resolved fluorescence decay kinetics as well as the steady-state spectral properties. The CD cavity size dependences of the inclusion patterns of DMABA into CD cavity is established, demonstrating an important role of the hydrogen bonding effect of the carboxylic acid group with water in the formation and decay of the TICT state.

MATERIALS AND METHODS

DMABA was purchased from Aldrich Chemical Co. and purified by triple recrystallization in ethanol. α– and β–CDs were purchased from Aldrich Chemical Co. and used without further purification. The stock solutions of DMABA and CD were prepared in pH 5 buffer solution where acids exist as neutral species (pK_a of DMABA=5.2).[14] The same volume of the stock solution was added to the different volume of CD stock solution, keeping the total volume constant so that the concentration of DMABA remains constant (2×10^{-5} *M*) by adjusting the CD concentration. This concentration is low enough to avoid dimerization of the carboxylic acids. For the comparative experiments, the aqueous CD solutions containing the related derivatives were prepared under the same condition as that for DMABA solution. Water was triply distilled in the presence of acidic dichromate and alkaline permanganate. All the solutions were degassed before the spectral measurements by means of freeze-pump-thaw (3-4 cycles down to *ca.* 10^{-3} Torr) technique.

The absorption spectra were recorded on a Varian (Cary 3) spectrophotometer. The fluorescence spectra were measured on a scanning SLM-AMINCO 4800 spectrofluorometer which makes it possible to obtain corrected spectra using Rhodamine B as a quantum counter. The optical density at an excitation wavelength was held constant when different solutions were compared. Fluorescence lifetimes were measured by a time-correlated single photon counting (TCSPC) method, using a dual-jet picosecond dye laser (Coherent ; Model 702) synchronously pumped by a mode-locked Ar ion laser (Coherent ; Innova 200) as described in the previous papers.[15,16] 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 the tunablity of 560-620 nm when Rhodamine 6G for gain dye and DODCI (diethoxydicyanine iodide) for saturable absorber were used. To excite sample, the dye laser pulse was frequency-doubled by a β–BBO (β–barium borate) 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.

RESULTS AND DISCUSSION

Absorption spectral properties. Figure 1 shows the absorption spectra of DMABA in aqueous buffer solutions (pH 5.0) containing various concentrations of α–CD and β–CD. Upon increasing concentration of CD

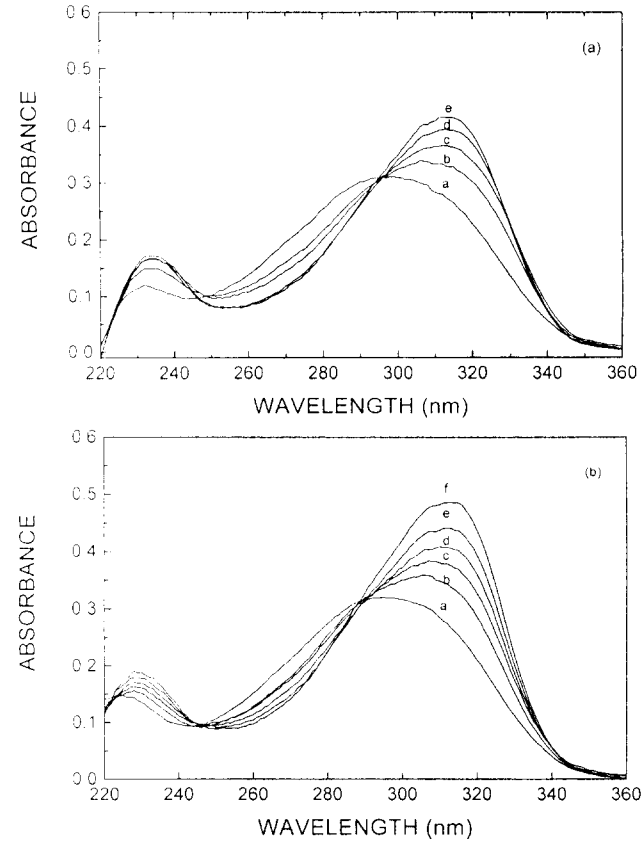

Figure 1. Absorption spectra of DMABA (2×10^{-5} *M*) in aqueous buffer solutions (pH 5.0) containing different concentration of α–CD; [CD]=(a)0, (b)4, (c)8, (d)12, (e)16 m*M* (a) and β–CD (b); [CD]=(a)0, (b)0.4, (c)0.8, (d)1.6, (e)4, (f)16 m*M*.

the absorption maximum around 296 nm shifts to longer wavelength with a gradual increase in the absorbance. The absorption spectral changes are accompanied by the isosbestic points, indicating formation of a well defined 1:1 inclusion complex between DMABA and CDs. This is also supported by the fact that the absorbance changes are well fitted to the equilibrium equation[39] for the formation of 1:1 complex as expressed in the following equation 1,

$$\frac{1}{A_o - A} = \frac{1}{A_o - A'} + \frac{1}{K(Ao - A')[\alpha\text{–CD}]} \qquad (1)$$

where K is the association constant, A_o and A are the observed absorbances in the presence and absence of CD, respectively, and A′ is the intrinsic absorbance of the inclusion complex. The association constants derived from this equation are 320 M^{-1} and 1258 M^{-1} for the α–CD and β–CD complexes, respectively, indicating that the β–CD complex is more stable than the α–CD complex. By using the spectrophotometric titration method the pK_as of DMABA in the presence of α–CD and β–CD were determined to be 5.75 and 5.98, respectively, which are slightly larger as compared with that for CD-free solution. This is in good accordance with the Jiang's results,[13,14] implying that the orientation of the carboxylic acid group of the guest molecule in the α–CD and β–CD complexes is the same and the carboxylic acid group is exposed to aqueous phase.

Fluorescence spectral properties. Figure 2 shows the fluorescence spectra of DMABA in aqueous solution as a function of α–and β–CD concentration, excited at 295 nm, the isosbestic point. In the CD-free aqueous solution the TICT-typical dual fluorescence is observed with normal emission around 350 nm and TICT emission around 500 nm even though the quantum yield of the TICT emission is very low. The extremely weak TICT

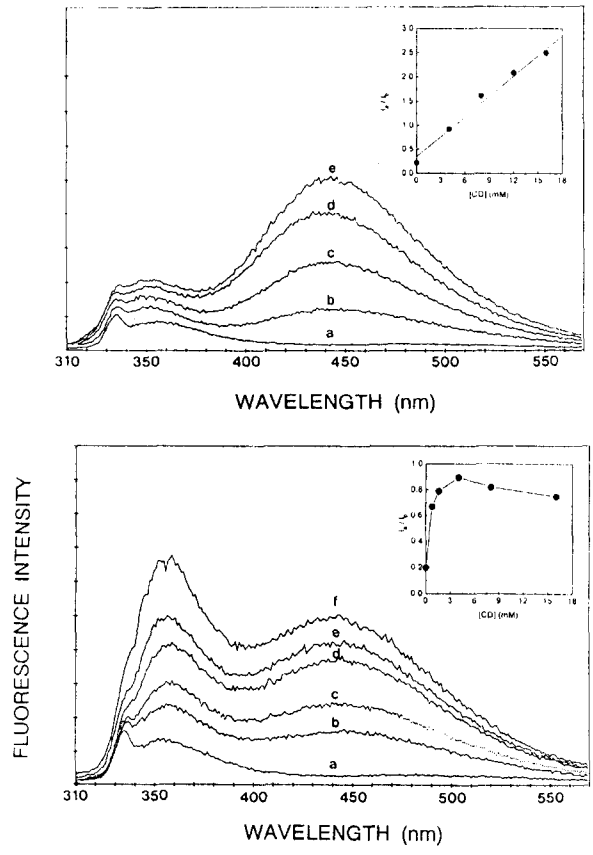

Figure 2. Influence of α–CD (a) and β–CD (b) concentration on the fluorescence emission spectra of DMABA (2×10^{-5} *M*) in aqueous solution at pH=5. (a) α–CD; [CD]=(a)0, (b)4, (c)8, (d)12, (e)16 m*M* and (b) β–CD; [CD]=(a)0, (b)0.4, (c)0.8, (d)1.6, (e)4, (f)16 m*M*.

Table 1. Fluorescence Decay Time (τ_i), Preexponential Factors (a_i) and Relative QuantumYields (Q_i)* for the TICT (450 nm) and Normal (350 nm) Fluorescence Bands of DMABA in α–CD Solutions

solvent	λ_{flu} (nm)	τ_1 (ps)	a_1	Q_1	τ_2 (ns)	a_2	Q_2	τ_3 (ns)	a_3	Q_3
water	350	15	0.98	0.57	0.7	0.02	0.43			
	450	9	0.68	0.07	0.26	0.32	0.93			
α–CD	350	14	0.98	0.49	0.7	0.02	0.51			
(1 m*M*)	450	13	0.64	0.04	0.27	0.33	0.44	3.7	0.03	0.52
α–CD	350	10	0.98	0.52	0.6	0.02	0.48			
(2 m*M*)	450	13	0.6	0.02	0.28	0.32	0.21	4.0	0.08	0.77
α–CD	350	15	0.98	0.48	0.7	0.02	0.52			
(8 m*M*)	450	20	0.51	0.006	0.19	0.08	0.09	4.1	0.17	0.93
α–CD	350	10	0.99	0.56	0.8	0.01	0.44			
(10 m*M*)	450	15	0.6	0.007	0.12	0.03	0.003	4.2	0.37	0.99
α–CD	350	10	0.99	0.58	0.7	0.01	0.42			
(12 m*M*)	450	15	0.54	0.004				4.2	0.46	0.996
α–CD	350	10	0.99	0.55	0.7	0.01	0.45			
(16 m*M*)	450							4.2	1	

* $Q_i = \dfrac{a_i \tau_i}{\sum_i a_i \tau_i}$

Table 2. Fluorescence Decay Time (τ_i), Preexponential Factors (a_i) and Relative Quantum Yields (Q_i) * for the TICT (450 nm) and Normal (350 nm) Fluorescence Bands of DMABA in β-CD Solutions

solvent	λ_{flu} (nm)	τ_1 (ps)	a_1	Q_1	τ_2 (ns)	a_2	Q_2	τ_3 (ns)	a_3	Q_3	τ_4 (ns)	a_4	Q_4
Water	350	15	0.98	0.51	0.72	0.02	0.49						
	450	10	0.68	0.06	0.26	0.315	0.86						
β-CD	350	15	0.98	0.52	1.17	0.008	0.33						
(0.4 m*M*)	450	15	0.39	0.001	0.25	0.34	0.014	2.53	0.12	0.53	1.3	0.14	0.31
β-CD	350	15	0.98	0.53	1.2	0.01	0.40						
(0.8 m*M*)	450	26	0.41	0.001	0.26	0.17	0.5	2.85	0.15	0.49	1.4	0.27	0.45
β-CD	350	15	0.98	0.56	1.1	0.01	0.37						
(1.6 m*M*)	450	17	0.4	0.00	0.2	0.07	0.014	2.7	0.22	0.58	1.4	0.3	0.4
β-CD	350	20	0.97	0.38	1.4	0.02	0.55						
(2.0 m*M*)	450	30	0.2	0.004	0.15	0.08	0.008	2.9	0.26	0.52	1.5	0.45	0.46
β-CD	350	17	0.97	0.34	1.5	0.02	0.61						
(4.0 m*M*)	450	30	0.1	0.002				3.2	0.25	0.44	1.6	0.62	0.56
β-CD	350	15	0.94	0.18	1.45	0.04	0.74						
(8.0 m*M*)	450							3.0	1	1			
β-CD	350	18	0.93	0.16	1.6	0.05	0.79						
(16 m*M*)	450							3.0	1	1			

$$* Q_i = \frac{a_i \tau_i}{\sum_i a_i \tau_i}$$

emission has been ascribed to the large stabilization of the highly polar TICT state through maintaining stable twist conformation of amino group by strong dipole-dipole interaction with water and consequent rapid nonradiative transition to ground state and/or low lying triplet state.[10,15] However, the intensity of TICT emission increases dramatically upon addition of α-CD while the normal emission is only slightly increased (Figure 2a). It can be seen that the fluorescence intensity ratio of the TICT band to the normal band (I_a/I_b) of DMABA increases linearly as the concentration of α-CD increases (inset in Figure 2a). On the other hand, upon addition of β-CD to the aqueous solution of DMABA, both normal and TICT emissions are enhanced and the fluorescence intensity ratio, I_a/I_b shows nonlinear dependence on the β-CD concentration (inset in Figure 2b). It is also noteworthy that the TICT emission maxima are blue-shifted to 450 nm along with the change of the I_a/I_b upon addition of α-CD and β-CD, indicating the formation of inclusion complexes with same orientation of DMABA in the CD cavity. The difference in the CD concentration-dependent changes of I_a/I_b implies that the inclusion pattern of the guest molecule into CD cavity for α-CD complex is different from that for β-CD complex.

In order to further characterize the cause of the difference in the CD concentration-dependent changes of I_a/I_b, we measured the decay behaviors of normal (350 nm) and TICT emission (450 nm) of DMABA in aqueous buffer solution (pH 5.0) containing different concentration of α-and β-CD by using the time-resolved fluorescence apparatus based on a picosecond pulse laser. Figure 3 depicts the typical TICT emission decay profiles in the absence or presence of α-and β-CD. Their analysis with the normal emission decay is listed in Table 1 and 2. The normal emission decay in the CD-free solution exhibits a fast decay component (15 ps) as a major decay component with a slow decay component (700 ps), indicating two different normal emitting species from the LE; one is the prompt emission and the other is the delayed emission generated through the equilibration achieved between the LE state and the TICT state.[15] The decay times of the normal emission and their relative quantum yields stay the same within experimental error even with increasing α-CD concentration. However, upon addition of β-CD the decay time and its relative quantum yield of the slow component increase upto 1.6 ns while the quantum yield of the fast component decreases. The CD-dependent

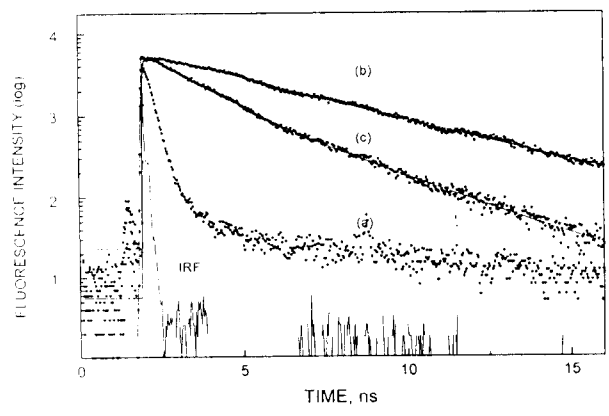

Figure 3. Fluorescence decay profiles of DMABA in the absence (a), and presence of 16 m*M* α-CD (b) and β-CD (c).

decay behavior of the normal emisssion is consistent with the enhancement of the normal emission intensity upon addition of β-CD in contrast to the little change in the presence of α-CD. This indicates that the formation of TICT state of DMABA is more or less inhibited upon complexation with β-CD while it is little affected upon complexation with α-CD. This might be due to the differences between the inclusion pattern of the guest molecule into CD cavity for α-CD complex and that for β-CD complex.

The decay time of the TICT emission was analyzed to be 260 ps in the CD-free aqueous solution in addition to partial contribution of the short decay component of the normal emission. Upon addition of CD, the two decay components disappear and consequently new decay components become dominant (see Tables 1 and 2), exhibiting much longer decay times (*ca.* 1.3 – 4.2 ns). This is also consistent with the enhancement of TICT emission intensity as the CD concentration increases. It is important to note that the TICT emission for the α-CD complex has one decay component (*ca.* 4 ns) while that for β-CD complex has two decay components (*ca.* 1.5 and 3.0 ns) with a very short rise time (15 ps). Again this indicates that there exist two different species of β-CD complex in contrast to a single species of α-CD complex.

The CD-dependent differences of the inclusion complexation could be explained in terms of difference in the internal diameters of the α- and β-CD cavities. As shown in Figure 4, the size of the dimethylamino group of DMABA fits to the internal diameter of the α-CD cavity to form the type I complex, in which the carboxylic acid group of the guest molecule is mostly exposed to aqueous phase with the amino group emtrapped into the cavity. However, the internal diameter of the β-CD cavity is larger than that of the α-CD cavity. Thus, it is possible for the guest molecule to be located more deeply and consequently form the type II complex in addition to type I complex, in which the carboxylic acid group is less exposed to aqueous phase as compared to the type I complex. Considering that only type I is available for the α-CD complex and its TICT emission decay time is *ca.* 4.0 ns, the *ca.* 3.0 ns component and 1.5 ns component for the β-CD complex are attributable to the type I and type II, respectively. As the β-CD concentration increases, the DMABA seems to have more chances to be entrapped deeply into the nonpolar CD cavity to from the type II complex so that all the part of guest molecule face nonpolar environment. This is the reason why contribution of the 1.5 ns component was detected in the presence of highly concentrated β-CD. Supporting this, only normal emission of DMABA was observed without the TICT emission in the aqueous solution of γ-CD which has the cavity size much larger than that of β-CD (data not shown).

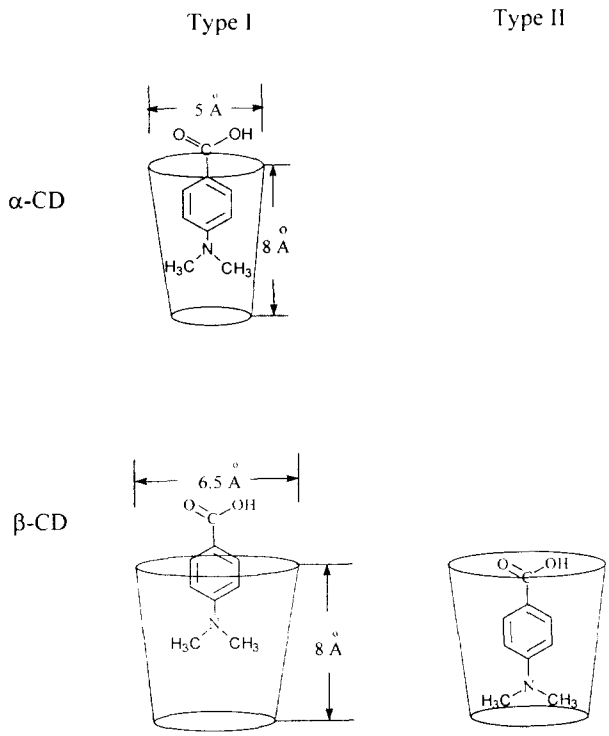

Figure 4. The proporsed structures of the DMABA/CD complexes.

In aqueous solution the strong dipole-dipole interaction of the amino group with water is known to stabilize the TICT state so that the TICT emission is extremely weak.[10,13] However, upon addition of CD the intensity of TICT emission increases dramatically. This is due to destabilization of the TICT state by entrapment of the dimethylamino group in nonpolar CD cavity as demonstrated by the blue-shift of the TICT emission in the presence of CD. According to the energy gap law, destabilization of the TICT state causes the reduction of the nonradiative transition. Of course, this is under the condition that the carboxylic acid group is interacting with water[15]. However, if the carboxylic acid group is also entrapped in the CD cavity as in case of γ-CD complex or type II species of the β-CD complex, the formation of TICT state is even inhibited as discussed above. These results indicate that the intermolecular hydrogen-bonding between the carboxylic acid and water plays an important role in the formation of TICT state. In aqueous solution the strong hydrogen bonding would be formed between water and carboxylic acid group in addition to the polarization interaction so that the carboxyl group becomes coplanar with benzene ring. Thus, a migration of electron density can occurr easily from benzene to carboxyl group so that the formation of TICT state is facilitated. In the type I complex, the intermolecular hydrogen-bonding of the carboxylic acid is still accessible to facilitate the forward TICT process. This is the reason why the decay time of the normal emission is little affected by the addition of α-CD. On the other hand, in type II complex, the

intermolecular hydrogen bonding between the carboxylic acid group with water would be inhibited. Thus, the forward TICT process is inhibited as demonstrated by the β-CD-dependent increase of the longer decay time of the normal emission.

CONCLUSION

The ratio of the TICT emission to normal emission of DMABA increases linearly as the α-CD concentration increases while it shows nonlinear dependance on β-CD concentration. The β-CD effect on the decay time of TICT and normal emission is quite different from the α-CD effect, indicating that complexation pattern of β-CD/DMABA is different from that of α-CD/DMABA. These results demonstrate that a hydrogen bonding interaction of the electron with drawing group with water plays an important role in controlling the TICT process.

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