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ORIGINAL PAPER

The Role of Normal Versus Twisted Intramolecular Charge Transfer Fluorescence in Predicting the Forms of Inclusion Complexes of Ethyl-*4*-dialkylaminobenzoate with α-Cyclodextrin in Aqueous Solution

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Abstract An evidence is introduced through the b- and the twisted intramolecular charge transfer (TICT) fluorescence of *ethyl-4-(N,N*-dimethylamino)benzoate (EDMAB) and *ethyl*-4-(*N,N*-diethylamino)benzoate (EDEAB), confirming the role of donor size on the formation and emission of various inclusion complexes formed between these probes and α-CD in aqueous solution. A large variation in the b-fluorescence band of EDEAB as compared to that of EDMAB and a large variation in the TICT-fluorescence band of EDMAB as compared to that EDEAB, as the concentration of α-CD is increased in their aqueous solutions are observed. These variations are supported by time resolved fluorescence (TRF) spectra, fluorescence decay lifetimes and red edge effect (REE) results.

Keywords Fluorescence · Twisted intramolecular charge transfer · Charge transfer · Time resolved fluorescence · Red edge effect · Ethyl-4-dimethylaminobenzoate · Ethyl-4-diethylaminobenzoate · Cyclodextrin

Introduction

The fluorescence properties of molecules undergoing twisted intramolecular charge transfer (TICT) [1, 2] have found their ways in probing various polymers [3–5] and cyclodextrins [6–23]. This is because of the relative positions and intensities of the two fluorescence bands, normal (b-band) and anomalous (TICT-band), of a certain TICT probe are sensitive to both local polarity and local micro viscosity of the medium they are present in.

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Cyclodextrins (CDs) are oligosaccharides having a shape of a two open ends truncated cone, which varies in size from 5.2 Å, 6.6 Å to 8.8 Å in α-CD, β-CD and γ-CD respectively [6]. The intensity, shape and wavelength of the fluorescence of certain probes in CD are highly dependent on their relative sizes and positioning (guest-host) inside the CD cavities [7–21]. In previous work we have suggested several types of inclusion complexes of 4-dimethylaminobenzonitrile (DMABN) in various CDs aqueous solutions. The forms of possible complexes are 1:1 and 1:2 with α-CD and also 1:1 and 2:2 inclusion complexes with β-CD. These complexes were identified by steady state fluorescence, fluorescence decay lifetime, red edge effect (REE) and time resolved fluorescence (TRF) spectra [10–12]. The formation of such complexes were confirmed by other techniques such as circular diochrism, transient triplet absorption and theoretical calculations using dynamic Monte Carlo (DMC) calculations [19, 20]. We have also found that the fluorescence properties of 4-diethylaminobenzonitrile (DEABN) to be different from that of DMABN [11] in α-CD confirming the role of donor size and CD cavity size on the formation of inclusion complexes and on their fluorescence emission [10]. An attempt therefore is presented in this study to confirm our previous observations using the fluorescence properties of ethyl-4-dimethylaminobenzoate (EDMAB) and ethyl-4-diethylaminobenzoate (EDEAB) in α-CD aqueous solutions. The fluorescence spectra of EDMAB and EDEAB in water were found to be very similar. The TICT fluorescence band was almost absent or being hidden under the tail of the normal fluorescence band. In α-CD aqueous solutions, however, both the normal and the TICT fluorescence bands undergoes changes in positions and/or enhancement of intensities with the increase in the α-CD concentration. We have also found larger variation in the TICT fluorescence of EDMAB as compared to EDEAB and larger

variation in the b-fluorescence of EDEAB as compared to EDMAB as the concentration of α-CD is increased. It is one of the goals of this study to investigate and confirm the role of the b-fluorescence band, beside the TICT fluorescence band, using various fluorescence spectroscopic techniques (excitation spectra, REE, fluorescence decay lifetimes and TRF spectra results) to predict kinds of inclusion complexes formed between these TICT probes and α-CD cavities.

Experimental

Pure, recrystallized and sublimed samples of EDMAB and EDEAB (Aldrich) were used in this study. α-CD (Wako Pure Product) was used without further purification. Stock aqueous solutions of EDMAB and EDEAB (~1.5×10^{-5} M) were prepared. Different amounts of α-CD were then dissolved in these EDMAB and EDEAB aqueous solutions to give the following α-CD concentrations: 1.0×10^{-3} M (solution # 1), 5.0×10^{-3} M (solution #2), 1.0×10^{-2} M (solution #3), 2×10^{-2} M (solution #4), 5.0×10^{-2} M (solution #5) and 0.1 M (solution #6).

Fluorescence and excitation spectra were recorded using model SPF-500C spectrofluorimeter from SLM Instruments Inc. All fluorescence spectra were corrected for lamp spectral intensity distribution and photomultiplier spectral sensitivity. Fluorescence lifetimes and time-resolved spectra were measured using a home assembled picosecond laser excited single photon counting system, Applied Photo physics. Picosecond Laser pulses (of 10 ps duration) were generated by a cavity damped dye laser Spectra Physics model 3,800 using Rhodamin 6G as the lasing medium. Light pulses were frequency doubled using frequency doubler Spectra Physics model 390. Pulse duration was checked using Spectra Physics model 490 autocorrelation system and found to be shorter than 10 ps. Monochromators excitation and emission slits were set to~2 nm wide each.

Results and Discussion

Optical Absorption and Steady State Fluorescence Spectra

Figure 1 shows no major changes in the absorption spectra of EDMAB (λ_{max}~315 nm) or EDEAB (λ_{max}~325 nm) in water and in various α-CD aqueous solutions. In contrast, Fig. 2a and b show dramatic changes in their fluorescence spectra in various α-CD aqueous solutions (#1 – #6) corresponding to changes in α-CD concentration from 1×10^{-5} M to 0.1 M. In water, the TICT fluorescence band was not observed, as this is expected and is consistent with our recent observation made for *P*-(*N*,*N*-diphenylamino)benzoic acid methyl ester DPABME [18, 23], which has been explained in terms of energy gap law [24, 25]. According to this law, stabilization of the TICT state leads to enhancement of nonradiative transitions to the ground state and therefore minimizing or preventing its fluorescence emission expected at longer wavelengths with respect to the emission from the b-state.

Upon continuous additions of α-CD to the water solutions of EDMAB and EDEAB both the b-fluorescence band, ~360 nm, and the TICT fluorescence band, above 400 nm, undergo changes in their intensities and/or positions, due to formation of inclusion complexes. The changes in fluorescence intensities and/or positions for EDMAB are quite different from those for EDEAB confirming the role of donor size (dialkylamino group) on the forms (kinds) of inclusion complexes and their corresponding fluorescence emission.

Two main differences between the fluorescence spectra of EDMAB and EDEAB could be extracted from Fig. 2a and b,

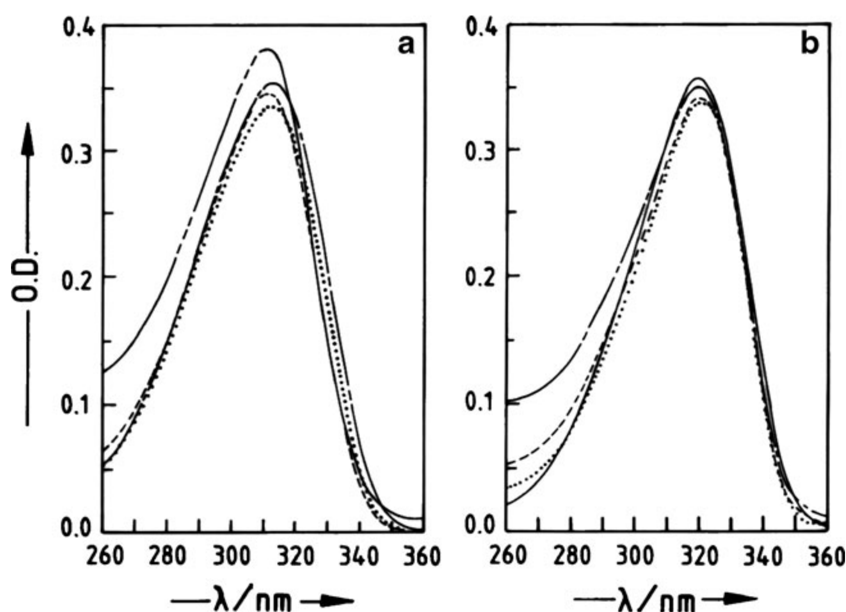


Fig. 1 Absorption spectra of EDMAB **a** and EDEAB **b** in water (••••••••••••) and in various α-CD aqueous solutions: # 2 (▬ ▬ ▬ ▬), # 4 (▬ • ▬) and # 6 (——————) and (————) respectively at 298 K

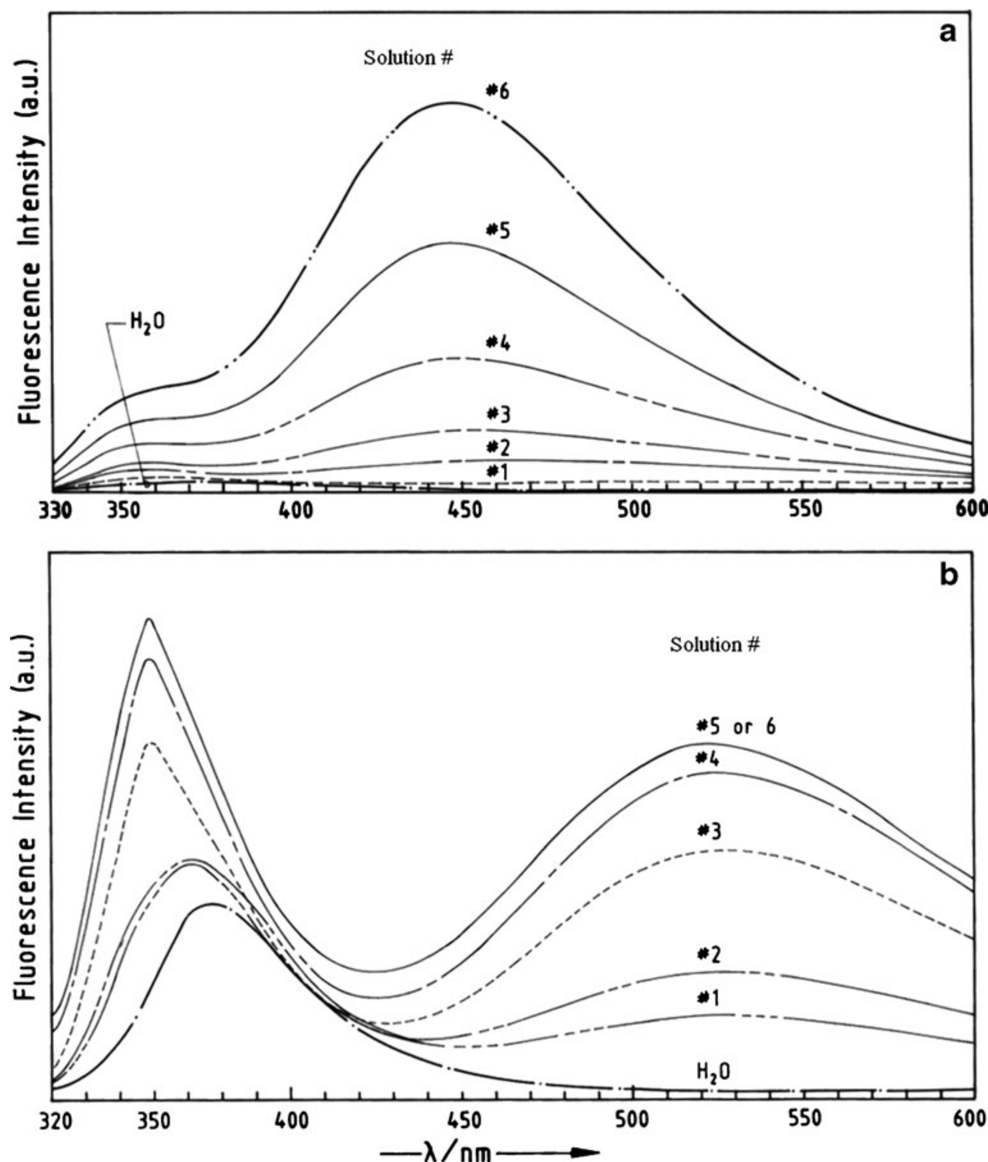
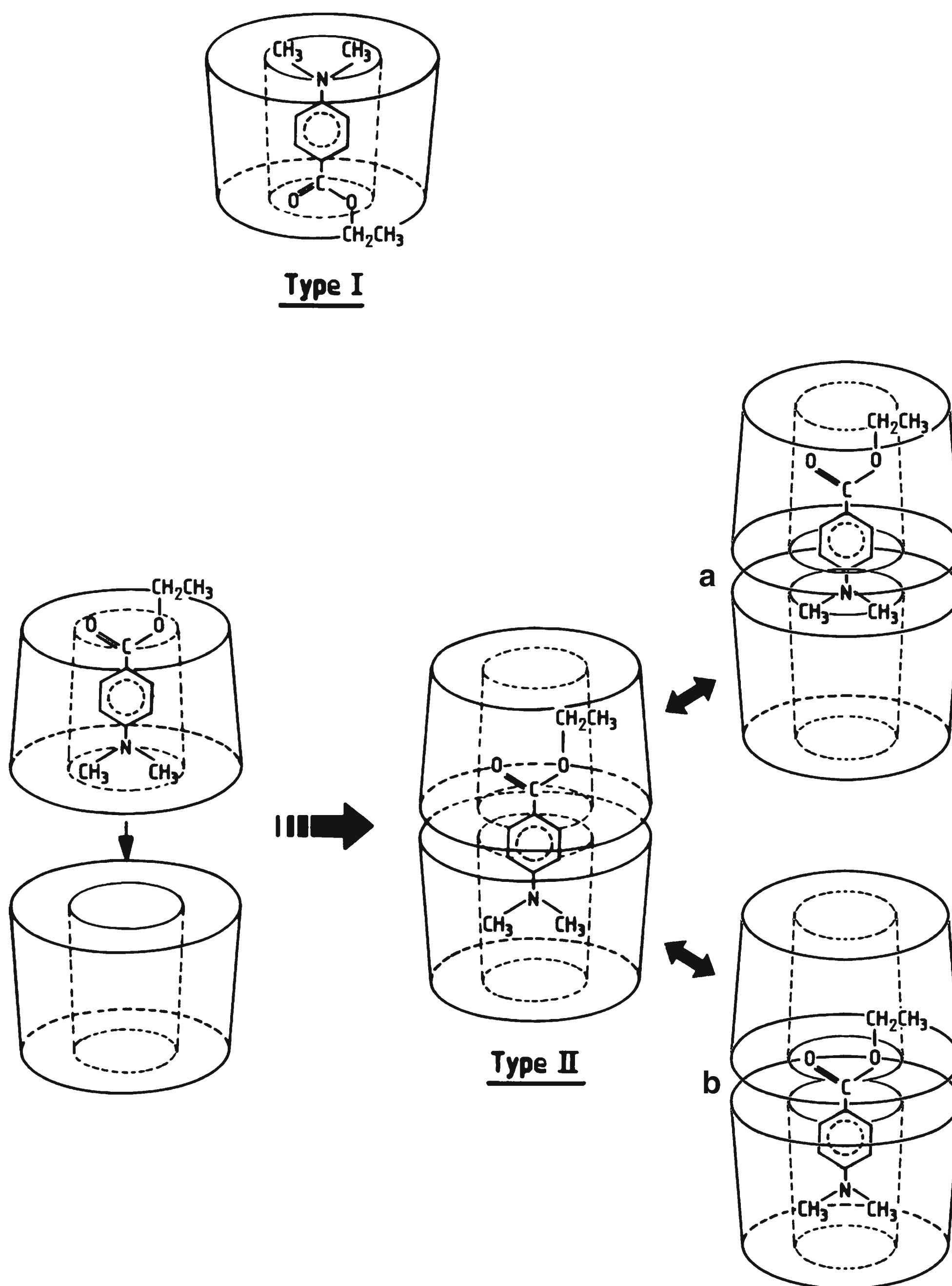


Fig. 2 Fluorescence spectra of EDMAB (**a**) and EDEAB (**b**) in water and in various α-CD aqueous solutions (# 1 – # 6) at 298 K

as well as from Fig. 4a and b. On one hand, the b-fluorescence band of EDEAB (~360 nm) is broader and undergoes a large blue shift and enhancement, as compared to the b-fluorescence band of EDMAB, with the increase of α-CD concentration. On the other hand, the TICT fluorescence band of EDMAB (~520 nm) undergoes a larger blue shift (see also Fig. 5) and enhancement as compared to EDEAB with further additions of α-CD.

Inspection and following up the growth and the blue shift of the TICT fluorescence band of EDMAB, Fig. 2a, lead us to suggest that a 1:1 inclusion complexes, type I (Scheme 1), are formed and dominant in dilute α-CD aqueous solution. For type I inclusion complexes, the dimethyl amino group of EDMAB is oriented toward the larger rim of α-CD giving rise to fluorescence ~520 nm, solution #1 Fig. 2a. With further additions of α-CD, type II complexes become interlocked in a two CD cavities and become dominant in concentrated, 5×10^{-2} M or 0.1 M, α-CD aqueous solutions, and give rise to TICT fluorescence ~450 nm, solutions #5 or #6 of Fig. 2a. This is consistent with our previous observations and interpretation made for DMABN in α-CD aqueous solutions [10]. Type II complexes represent the most rigid and least polar environment and type I complexes represent a less rigid and more polar, relative to type II, environment. The relative contributions of type I and type II complexes for the TICT fluorescence of EDMAB in α-CD at ~450 nm and 520 nm is therefore controlled by the amount (concentration) of α-CD present in their aqueous solutions.

In contrast, the growth of the TICT-fluorescence band (~520 nm) of EDEAB, with further additions of α-CD, Fig. 2b, leads us to conclude that only 1:1 (type I) inclusion complexes could be formed. The absence of the TICT-fluorescence band ~450 nm for the case of EDEAB could be either due



Scheme 1 Possible positions of EDMAB in α-CD cavity: type I (1:1) is dominant in diluted α-CD aqueous solution and type II (1:2) is dominant in concentrated α-CD aqueous solution. The two possible forms of type II inclusion complexes (IIa and IIb) between EDMAB and α-CD in concentrated α-CD aqueous solution, are shown at lower right

to formation of type II complexes, (for which the diethylamino group is interlocked in the double cups of 1:2 inclusion complex and therefore unable to undergo twisting during the excited state lifetime) or due to the absence of type II inclusion complex at all. In both cases only the TICT fluorescence ~520 is observed. This is similar to our previous observations and interpretation made for DEABN in α-CD aqueous solutions [11].

The judgment on the models as a good representation of the spectral results presented in this study needs to be justified or confirmed by previous investigations [16, 17] and by various fluorescence spectroscopy results: excitation spectra, REE, fluorescence decay lifetimes and TRF spectra presented below:

Excitation Spectra

Inspection of Fig. 3a or b shows two groups of excitation spectra corresponding to the b-fluorescence band (340–370 nm) and to the TICT fluorescence band (420–520 nm) of

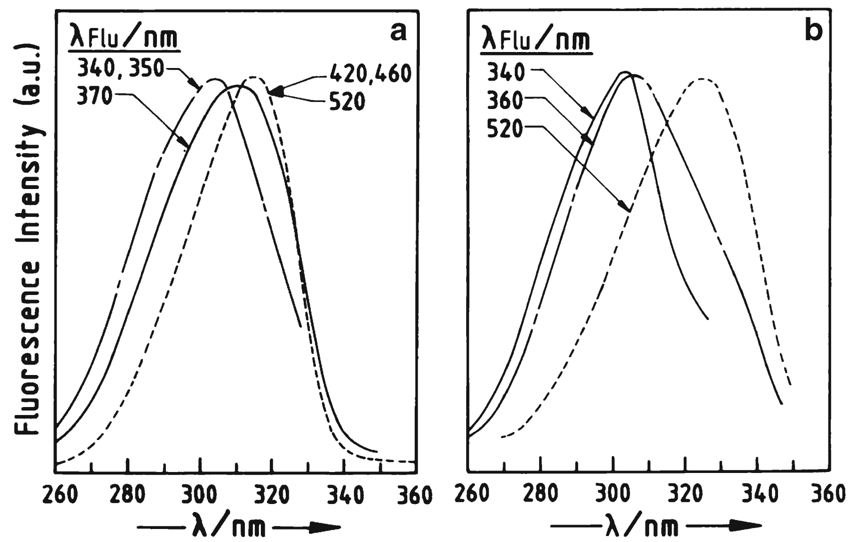


Fig. 3 Excitation spectra of EDMAB (**a**) and EDEAB (**b**) in α-CD aqueous solution # 6 at 298 K

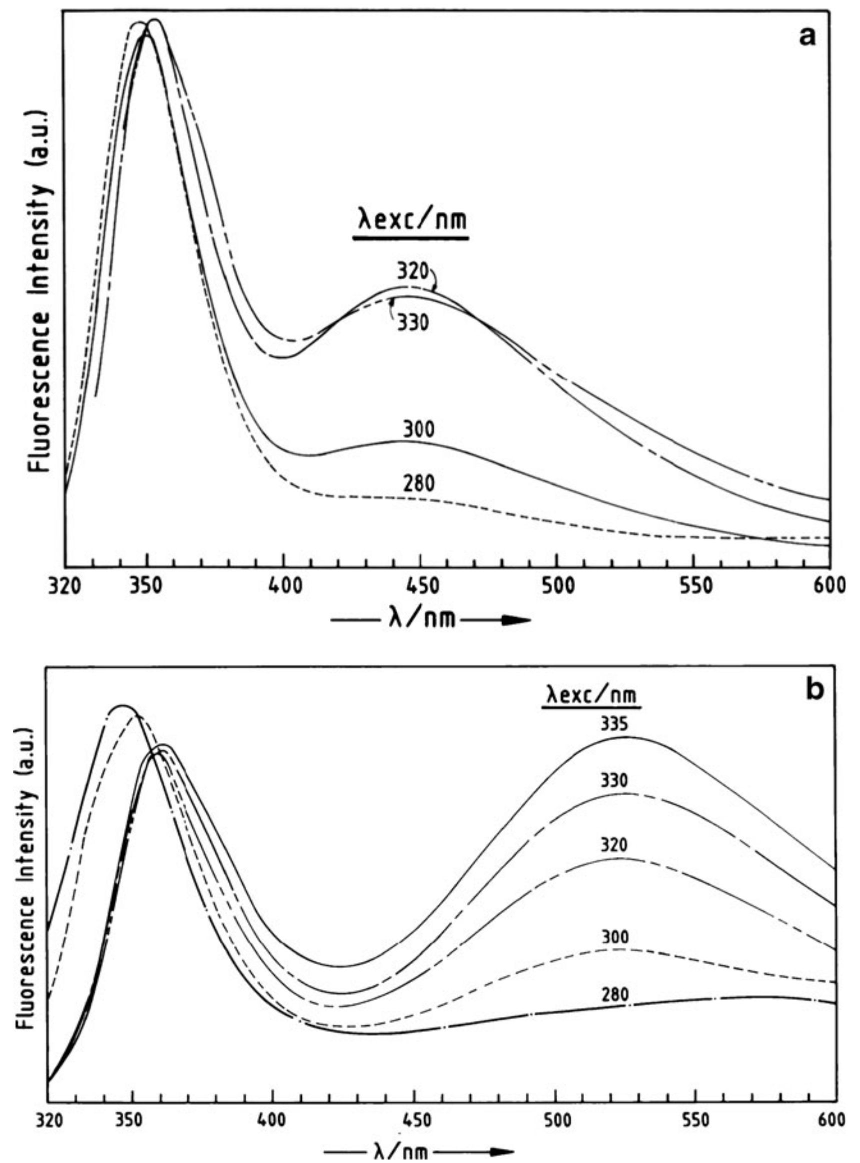


Fig. 4 Fluorescence spectra of EDMAB (**a**) and EDEAB (**b**) in α-CD aqueous solution # 6 as a function of $\lambda_{exc.}$ (280 nm – 335 nm) at 298 K

EDMAB and EDEMB, in α-CD aqueous solution #5, respectively. Those correspond to EDMAB Fig. 3a, are narrower $\left(\Delta\overline{\nu}_{1/2}\approx 5000\ \mathrm{cm}^{-1}\right)$ as compared to the broader ones correspond to EDEAB, Fig. 3b $\left(\Delta\overline{\nu}_{1/2}\approx 6000\ \mathrm{cm}^{-1}\right)$. Moreover, the excitation spectra group of EDEAB undergo larger red shift, (~2,100 cm^{-1}), as compared to the excitation spectra group of EDMAB (~1,500 cm^{-1}). These results are indication for the presence of more than one kind of inclusion complexes for either EDMAB or EDEAB with α-CD in aqueous solution and focus attention to the complementary role of the b-fluorescence band, along with the TICT-fluorescence band, in predicting the forms of their inclusion complexes.

Red Edge Effect (REE)

Three main variations can be predicted from the fluorescence spectra of EDMAB and EDEAB, in various α-CD aqueous solutions, as function of excitation wavelength, shown in Figs. 4 and 5 ($1_{exc.}$=280−330nm)

1. Variation in the relative intensity of the TICT- fluorescence band with respect to the b-fluorescence band of EDEAB as function of $\lambda_{exc.}$: Fig. 4b shows a large variation in the TICT-fluorescence as $\lambda_{exc.}$ is changed from 280 nm to 335 nm. This is quite general observation for most TICT-fluorescent probes as it has been the case for DMABN and DEABN in various α-CD aqueous solutions [10, 11]. Exciting at the red edge of the absorption band (λ_{exc}=320–335 nm) selectively excite the more polar and less rigid, type I (1:1) inclusion complexes which absorb at longer wavelength, as compared to type II (more rigid and less polar) complexes which absorb and emit at shorter wavelengths. Therefore exciting at the red edge of the absorption band of EDEAB enhances emission from type I inclusion complexes, ~520 nm, leading to an increase in the intensity of the TICT-fluorescence band with respect to the b-fluorescence band. The TICT emission of type II complexes for EDEAB could not be observed at any exciting wavelength.
2. Variation in position of the TICT fluorescence as function of λ_{exc}: Fig. 5 shows large variation in the position of the TICT fluorescence band of EDMAB in various α-CD aqueous solutions (#1 – #6) using λ_{exc}=335 nm (the red edge of the absorption band). On one hand, in the dilute α-CD solution #1, the TICT emission, ~520 nm, corresponding to type I (1:1) inclusion complexes is dominant. On the other hand, in the concentrated α-CD aqueous solution #6, the TICT emission, ~450 nm, corresponding to type II (1:2) inclusion complexes is dominant. This is consistent with the steady state fluorescence results presented in Fig. 2a and in line with the excitation spectra results presented in Fig. 3a.

In contrast as mentioned above, Fig. 4b, EDEAB in α-CD aqueous solution, don't show such variation in position of

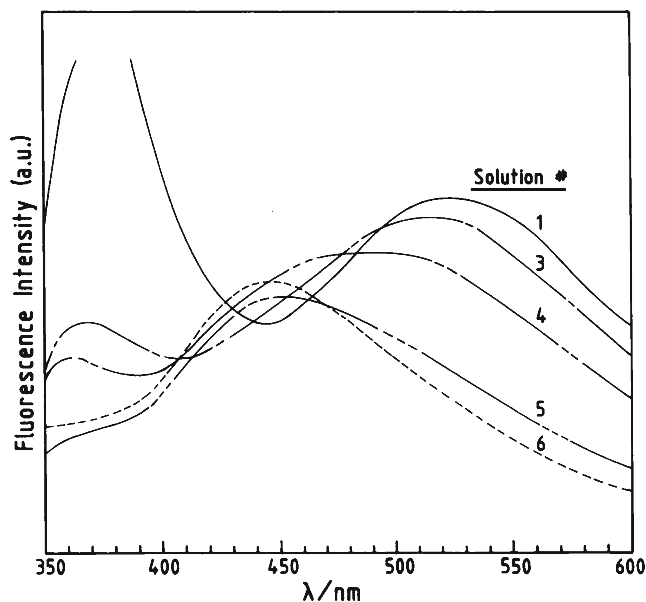


Fig. 5 Fluorescence spectra of EDMAB in various α-CD aqueous solution # 1 to # 6 using $\lambda_{exc.}$ = 335 nm at 298 K

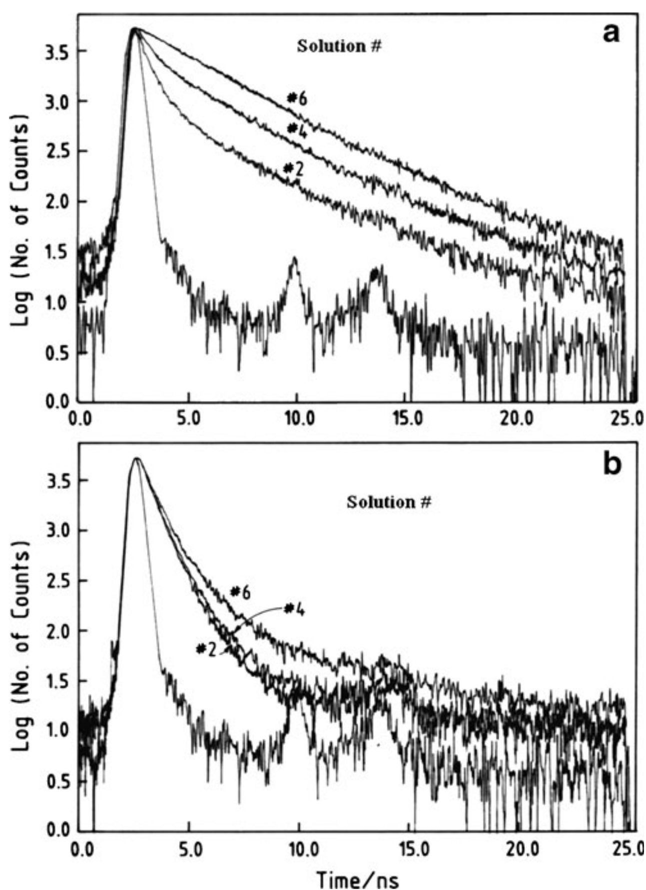


Fig. 6 Fluorescence decay of TICT fluorescence band, ~ 520 nm of (**a**) EDMAB and (**b**) EDEAB in α-CD aqueous solutions # 2, 4 and 6 at 298 K

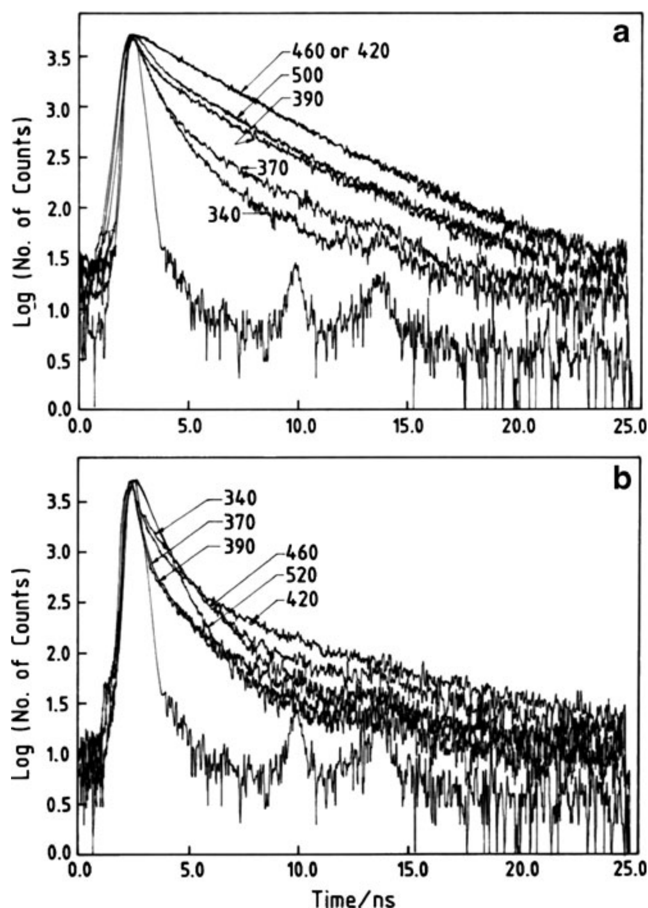


Fig. 7 Fluorescence decay of (**a**) EDMAB and (**b**) EDEAB in α-CD aqueous (solution #4) at various wavelengths of emission at 298 K

TICT fluorescence (~520 nm) as function of $\lambda_{exc.}$. This is because the TICT emission ~450 nm is absent for EDEAB in α-CD aqueous solution. This apparently leads one to suggest that only 1:1 inclusion complexes are formed for the case of EDEAB in α-CD aqueous solutions. However, this is inconsistent with the excitation spectra results of Fig. 3b which reflects more than one kind of inclusion complexes to be formed. Therefore we could suggest, as it has been suggested earlier, for DEABN in α-CD aqueous solution [11] that 1:2 inclusion complexes are also formed between EDEAB and α-CD, however inemissive due to limitation imposed by the size of the double α-CD cavities, making the diethylamino group interlocked and unable to twist during the excited state lifetime. This suggestion is confirmed by the red edge effect results of the b-fluorescence band, ~360 nm, presented below.

3. Variation of position and shape of the b-fluorescence band as function of $\lambda_{exc.}$: Fig. 4b shows a large red shift (1,030 cm^{-1}) for the b-fluorescence band of EDEAB in α-CD aqueous solution #6 as $\lambda_{exc.}$ changed from 280 nm to 320 nm. In contrast, the corresponding red shift for the b-fluorescence band of EDMAB is much smaller (400 cm^{-1}) as shown in Fig. 4a. Moreover the b-fluorescence band of EDEAB is broader ($\Delta\bar{\nu}_{1/2} \approx$ 4,300 cm^{-1}) as compared to the narrower b-fluorescence band of EDMAB ($\Delta\bar{\nu}_{1/2} \approx$ 3,500 cm^{-1}). The broad nature of the b-fluorescence band of EDEAB implies on us to suggest that EDEAB constitute a larger number of sites as compared to EDMAB when complexed with α-CD in aqueous solution.

Our suggestion that the TICT fluorescence of EDMAB in α-CD is due, at least, to two kinds of inclusion complexes 1:1 and 1:2 follows our previous proposal made for DMABN [10,

Table 1 Values for fluorescence lifetimes (τ), relative quantum yields (Φ), χ^2 and average lifetimes ⟨τ⟩ from deconvoluted experimental decays for the b-(340 and 370 nm), and TICT-(460 and 520 nm) fluorescence bands of EDMAB (left) and EDEAB (right) in α-CD aqueous solutions # 2, 4, and 6 (λ_{exc}=310 nm). Concentration of EDMAB or EDEAB in all solutions is ~1.0×10^{-5} M

Compound		EDMAB							EDEAB						
Solution #		λ/nm	τ_1/ns	ϕ_1	τ_2/ns	ϕ_2	$\langle\chi^2\rangle$	⟨τ/ns⟩	λ/nm	τ_1/ns	ϕ_1	τ_2/ns	ϕ_2	$\langle\chi^2\rangle$	⟨τ/ns⟩
2	b-Band	340	0.57	0.77	2.5	0.23	1.0	1.0	340	0.28	0.9	1.4	0.1	1.1	0.39
		370	0.56	0.76	3.4	0.24	0.95	1.2	370	0.25	0.96	1.2	0.04	1.6	0.29
4		340	0.67	0.71	2.7	0.29	1.0	1.3	340	0.2	0.25	1.5	0.75	1.2	1.2
		370	0.58	0.58	2.9	0.42	1.1	1.6	370	0.26	0.88	1.7	0.12	1.3	0.43
6		340	0.76	0.45	1.9	0.55	1.1	1.4	340			1.6	1.0	1.0	1.6
		370	0.74	0.47	2.8	0.53	0.94	1.8	370	0.16	0.48	1.6	0.52	1.2	0.91
2	TICT-band	520	0.52	0.56	3.1	0.44	1.0	1.7	520	0.51	0.6	1.1	0.4	0.91	0.75
		460	0.46	0.16	3.4	0.84	1.0	2.9	460	0.62	0.75	2.2	0.25	1.2	1.0
4		520	0.5	0.22	3.3	0.78	1.0	2.7	520	0.39	0.33	0.93	0.77	0.85	0.85
		460			3.4	1.0	0.94	3.4	460	0.59	0.65	1.9	0.35	0.91	1.1
6		520			3.5	1.0	1.0	3.5	520	0.68	0.74	2.2	0.26	1.1	1.1
		460			3.6	1.0	1.1	3.6	460	0.73	0.57	2.9	0.43	1.1	1.7

11] which was confirmed later by other investigators [19, 20] and is consistent with the results obtained by Matsushita et al. [17]. Their investigation [17] however was extended to find the stability constants K_1 and K_2 to be 211 M^{-1} and 35 M^{-1} respectively. These suggestions were later confirmed by other investigators [22]. For the case of EDEAB, we also could suggest that it forms two kinds of inclusion complexes with α-CD as shown by the results of the excitation spectra and the b-fluorescence band spectra, Figs. 3b, and 4b respectively. These suggestions are quite consistent with previous investigation made by M. Yoon et al. on the acid derivative, namely, 4-diethylaminobenzoicacid (DEAB) [16]. They suggested that there are two kinds of inclusion complexes between DEAB and α-CD, however 1:1 in both forms were the diethylamino group, in both complexes, being (little in and little out respectively) toward the larger rim of α-CD cavity. Their suggestions were based on the relative widths of diethylamino group (6.2 Å) to that of α-CD cavity (�much 5.2A) that do not allow the diethylamino group toward the smaller rim of CD cavity. The difference between the two proposals [11, 16] needs further investigations.

To explain the observed small red shift in the b-fluorescence band of EDMAB: α-CD complexes, as function of $\lambda_{exc.}$, Fig. 4a, we like to propose the possibility of presence of two forms of (a & b) 1:2 inclusion complexes as shown in Scheme 1, where the dimethylamino group of EDMAB lies closer to the smaller rim or closer to the middle of the double cups of α-CD cavities. This dynamic nature of motion of EDMAB in the bi-α-CD channel, can also be proved through TRF spectra of Fig. 8a.

Fluorescence Decay Lifetimes

Figure 6a and b show the decays of the TICT fluorescence band, ~520 nm of EDMAB and EDEAB in α-CD aqueous solutions (# 2, 4 and 6) respectively. The decays of their

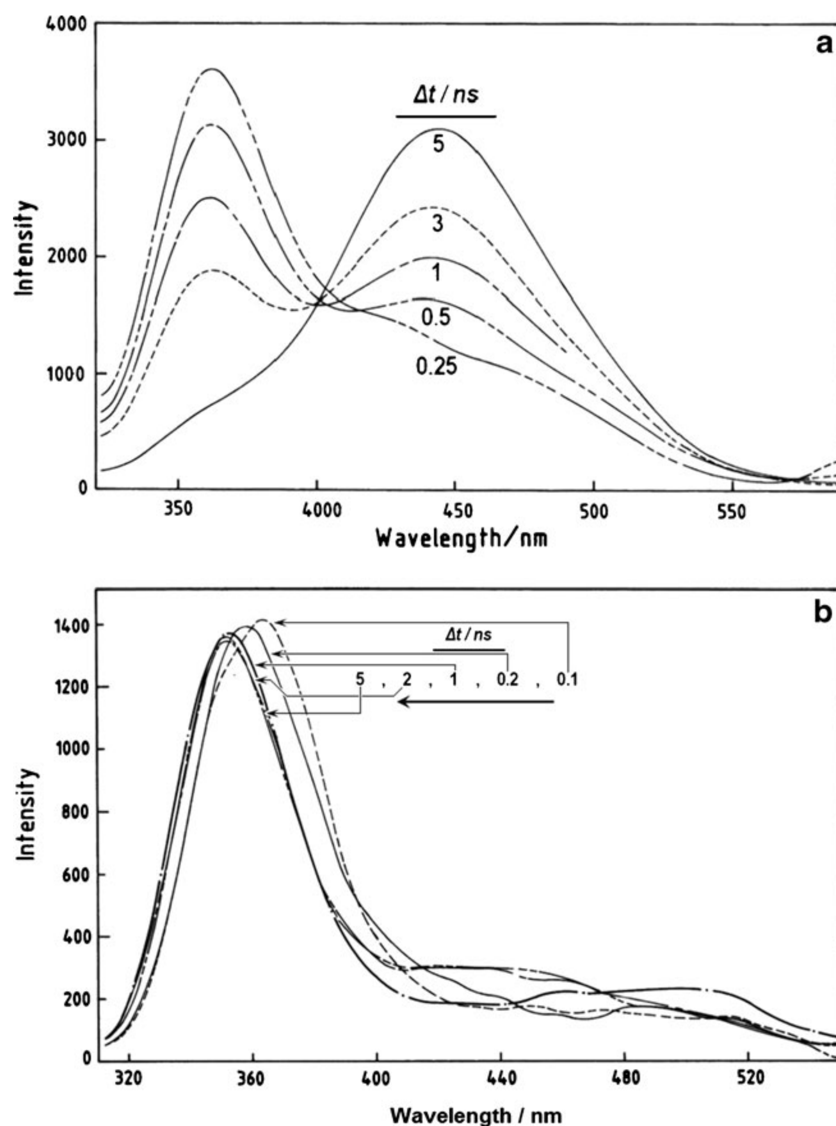


Fig. 8 Time resolved fluorescence spectra of (**a**) EDMAB and (**b**) EDEAB in α-CD aqueous solution (# 6) using different time windows at 298 K

fluorescence (b- and -TICT bands) in α-CD aqueous solution (# 4) at 340, 370, 460 and 520 nm are shown in Fig. 7a and b respectively. Their corresponding lifetimes are presented in Table 1.

The decays are biexponential for the TICT fluorescence (at 460 and 520 nm) of EDMAB in dilute α-CD aqueous solutions (# 2) with average lifetimes ~1.7 ns and ~2.9 ns corresponding to 1:1 and 1:2 inclusion complexes respectively. The decay of the TICT of EDMAB became monoexponential in highly concentrated α-CD aqueous solutions (# 6) with lifetime ~3.6 ns corresponding to the dominant 1:2 inclusion complexes. In contrast the decays of the TICT fluorescence of EDEAB also biexponential, however closer to monoexponential in either dilute or concentrated α-CD aqueous solutions with average lifetime ~1.0 ns corresponding to 1:1 inclusion complexes.

On the other hand the decays of the b-fluorescence of EDEAB in either dilute or concentrated α-CD aqueous solutions is biexponential with life time ~0.3 ns in dilute α-CD solutions (# 2) and becomes ~0.91 and ~1.6 ns in concentrated α-CD solutions (# 6) corresponding to 1:1 and 1:2 inclusion complexes, respectively. In contrast the decays of the b-fluorescence of EDMAB are biexponential, however closer to monoexponential decay in either dilute or concentrated α-CD aqueous solutions with average lifetime vary from 1.0 – 1.2 ns in dilute α-CD solutions (# 2) to 1.4 – 1.8 ns in concentrated α-CD solutions (# 6). The longer lifetime, (~1.8 ns), corresponds to 1:2 type II inclusion complexes. The large variation of the lifetimes for the TICT fluorescence of EDMAB and of the lifetimes for the b-fluorescence of EDEAB in α-CD aqueous solutions are consistent with the variation observed in their steady fluorescence, excitation spectra and REE results.

Time Resolved Fluorescence (TRF) Spectra

The time resolved fluorescence (TRF) spectra, taken at different gating times, after excitation, for EDMAB and EDEAB in concentrated α-CD aqueous solution (# 6) are presented in Fig. 8a and b respectively.

For EDEAB the TRF spectra of the b-fluorescence band, Fig. 8b show two kinds of fluorescence emissions, one ~350 nm gated at longer times (1–5 ns) and another ~365 nm gated at shorter times (< 1 ns) corresponding to type II (1:2) and type I (1:1) inclusion complexes respectively. This leads us to conclude that type II inclusions complexes are also dominant in highly concentrated α-CD aqueous solutions of EDEAB, however unable to lead to TICT-fluorescence ~460 nm due to restriction imposed by the size of the donor (diethylamino group) and the size of α-CD cavities. This is reflected on the negligible TRF spectra of EDEAB at 460 nm and 520 nm at different gating times. This confirms the role of b-fluorescence band in predicting the forms of inclusion complexes for TICT-probes in CD aqueous solutions.

In contrast, the TRF spectra of EDMAB in concentrated α-CD aqueous solution (# 6) (Fig. 8a) shows almost a mother-daughter relationship due to isosbestic point between the b-fluorescence band ~360 nm (being dominant at shorter gating times, 0.25-1.0 ns) and the TICT fluorescence band ~450 nm (being dominant at longer gating times, 3.0 – 5.0 ns) corresponding to type II (1:2) inclusion complexes. The two forms IIa and IIb suggested in Scheme 1 couldn't be identified under the conditions of our experiment, however they need faster techniques to be identified. Moreover, these forms are under our attention for further investigation using, as well, molecular dynamics calculation.

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