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ORIGINAL ARTICLE

Inclusion complex of charge transfer probe 4-amino-3-methyl benzoic acid methyl ester (AMBME) with β-CD in aqueous and non-aqueous medium: medium dependent stoichiometry of the complex and orientation of probe molecule inside β-CD nanocavity

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Abstract The absorption and emission characteristics of donor−acceptor charge transfer system 4-amino-3-methyl benzoic acid methyl ester (AMBME), capable of dual emission, i.e., local emission (LE) and charge transfer (CT) emission, have been investigated inside the β-cyclodextrin (β-CD) nanocavity in the aqueous and non-aqueous dimethylsulphoxide (DMSO) medium. Large enhancement of both LE and CT band in aqueous β-CD medium is due to decrease in non-radiative processes in less polar and restricted environment. Whereas in non-aqueous DMSO medium the CT process is hindered as a result CT intensity decreases with enhancement of LE band. These spectral differences indicate that in aqueous medium the donor – NH_2 group sticking in the hydrophilic region of β-CD cavity whereas in non-aqueous DMSO medium it exists in the hydrophobic part of the cavity. Spectral characteristics indicate that different stoichiometry of host–guest inclusion complexes are formed in aqueous and non-aqueous β-CD medium.

Keywords
4-Amino-3-methyl benzoic acid methyl ester (AMBME) · β-Cyclodextrin · Inclusion complex · Charge transfer

Introduction

There has been a longstanding interest of developing fluorescent molecular probes to monitor the environment of macromolecules like cyclodextrin [1–4]. The cyclodextrin (CD) molecules are water soluble compounds containing hydrophobic cavity. The size of hydrophobic cavity depends on the number of glucopyranose units present in cyclodextrins. Thus, cyclodextrins are capable of incorporating a wide range of guest molecule depending upon their size, shape and hydrophobic characteristics [5, 6]. There are several ways to determine the nature of host–gust complexation between cyclodextrin and the probe molecule. Spectroflurometry [7–9], H^1 NMR spectroscopy [10–13], circular dichromisim measurements [14] helps insight understanding of stoichiometry and the stability of the inclusion complex. Simple NMR measurement can provide complexation process due to upfield shift of inner surface hydrogen of CD and downfield shift of outer surface hydrogen of CD molecule. Multi-dimensional NMR spectroscopy is very much useful to get structure and stoichiometry of the complex. Theoretical calculations based on AM1 geometry [15] and also by molecular dynamics simulations using a density functional based tight binding code [16] are very useful predictive tool for such service, even the systems are too large.

There are a class of compounds such as dimethylamino benzonitrile (DMABN) and its derivative, i.e., Donor–Acceptor (D–A) substituted aromatic systems show dual fluorescence in polar solvents [17]. In polar solvent upon photoexcitation these types of compounds emit a high energy emission from locally excited (LE) state and the low energy emission from a charge transfer (CT) state. According to Twisted intramolecular charge transfer (TICT) model by Grabowski to explain this photo induced charge transfer phenomenon between D and A substituted aromatic system, it is proposed that the intramolecular charge transfer occurs when the almost planar vertically (locally) excited state relaxes to a twisted conformer with perpendicular orientation of donor and acceptor moiety

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[18] that generates a TICT state. The degree of charge transfer and the structural change in the excited state are controlled by the local polarity and the free volume of the rotable donor moiety. Thus, the TICT molecules are excellent candidates for examining the microscopic molecular environments, such as CD nano-cavity [19, 20]. It is observed that the guest molecule can be present in the different parts of the cyclodextrin cavity depending on the type of inclusion complex formed and thus their spectral characteristics may vary due to the influence of hydrophobic interior and also due to the limitation of molecular mobility inside the CD cavity. It is reported that the increase of TICT phenomenon on complexation with cyclodextrins may be due to decrease of non-radiative rates in reduced environmental polarity [21, 22]. Some studies show that TICT process may be restricted in cavity environment [23, 24]. It is reported that 4-*N*,*N*-dimethylaminocinnamaldehyde [25] interestingly formed inclusion complex with β-cyclodextrin having a preferential orientation of the dimethylamino group sticking outside in aqueous solvent and just reversed in non-aqueous solvents. So there are several arguments whether ICT is always enhanced due to complexation with cyclodextrin or excited state geometry change is influenced by complexation with cyclodextrin.

In our previous work we have synthesized a new donor−acceptor system, 4-amino-3-methyl benzoic acid methyl ester (AMBME), where intentionally we have introduced ortho methyl substitution at the donor side. The molecule is pretwisted in ground state due to steric crowding generated by ortho methyl substitution, and it shows CT emission even in nonpolar solvent [26]. However, quantum chemical calculations fail to interpret the CT phenomenon following TICT model in this molecule [26]. It is expected that as cyclodextrin generates some restricted environment around the molecule, so if the twisting motion of $-NH_2$ group coupled with methyl rotation responsible for CT emission should be affected in cyclodextrin solution. In this context, here we would like to focus on the nature of AMBME-β-CD inclusion complex both in aqueous and non-aqueous medium to explore fluorescence properties inside the cyclodextrin cavity. It is observed that in β-CD medium AMBME shows a clear dual emission [26]. It indicates that nonpolar cyclodextrin cavity is not exactly same as a non-polar organic solvent but manifests itself a microenvironment. It is reported that the measured dielectric value of β-CD cavity is 48 [27]. The reduced polarity and restricted environment in the cyclodextrin medium may tune the energy difference between locally excited state and ICT state in such way that we get two distinct bands. Jiang already studied the photophysical properties of *p*-dimethylaminobenzoic acid β-CD complex [28] and T. Stalin et al. studied *p*-amino benzoic acid [29], 2-amino benzoic acid [30] and 3-amino benzoic acid [31] in aqueous β-CD. Our system AMBME is different with respect to the above mentioned molecules as it has better acceptor group (ester group) and an ortho substitution is present in the ring. We have studied spectroscopy of AMBME β-CD inclusion complex both in aqueous and non-aqueous solution to follow the behaviour of probe in different medium.

Experimental section

The details synthetic procedure of 4-amino-3-methyl benzoic acid methyl ester (AMBME) has been reported in our previous paper [26]. Spectroscopic grade solvents from Spectrochem-UV and dimethylsulphoxide (DMSO) from E. Merck were used after vacuum distillation. β-cyclodextrin was purchased from Aldrich. All solvents were checked for any fluorescence in the desired wavelength region before any emission studies. Triple distilled water was used for making all aqueous solutions.

The absorption and emission spectra of AMBME were recorded by a Hitachi UV/VIS U-3501 spectrophotometer and Perkin Elmer LS50B fluorimeter, respectively. All the spectral measurements were done at $\sim 10^{-6}$ M concentration of solute in order to avoid aggregation and self-quenching.

The laser system used for time resolved experiment consists of a Coherent Mira 900F femtosecond laser system, the output of which was pulsed picked (Coherent 9200 pulse picker) at a rate of 3.8 MHz and then frequency tripled in an ultra fast harmonic generation system (INRAD 5-050). The fluorescence decays were recorded using a time correlated single photon counting (TCSPC) system from Edinburgh instruments (Lifespec-Red). This system has an instrument response function (IRF) of 180 ps. The fluorescence decays were deconvoluted using the iterative software provided by the manufacturer.

Results and discussions

Absorption spectra

The donor−acceptor charge transfer molecule AMBME shows a single broad absorption band with peak position at $\sim$287 nm and $\sim$300 nm in water and DMSO solvent, respectively. This absorption band corresponds to $\pi\pi^*$ transition of the aromatic benzene moiety and is resemble to that of aniline [26]. In presence of β-CD in both the medium some spectral differences are observed. Figure 1a, b shows the β-CD concentration dependent absorption spectra of AMBME in aqueous and non-aqueous DMSO

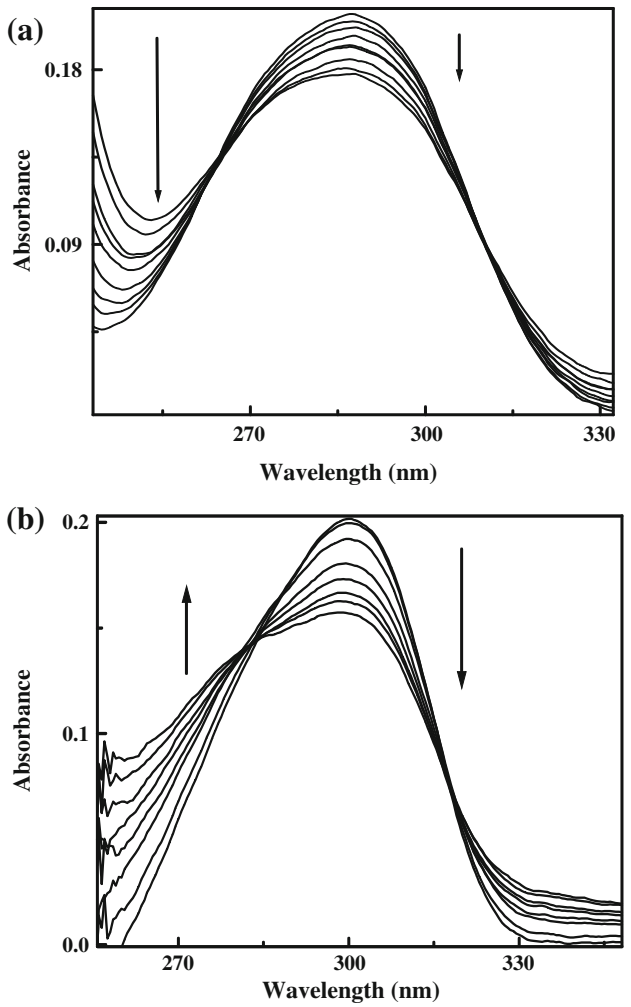


Fig. 1 (**a**) Absorption spectra of AMBME with different concentration of β-CD in aqueous solution: (1) without, (2) 0.24 mM, (3) 0.65 mM, (4) 0.90 mM, (5) 1.36 mM, (6) 1.98 mM, (7) 2.34 mM, (8) 2.91 mM, (9) 3.33 mM of β-CD concentration. (**b**) Absorption spectra of AMBME with different concentration of β-CD in non-aqueous DMSO medium: (1) without, (2) 1.41 mM, (3) 2.99 mM, (4) 3.91 mM, (5) 4.43 mM, (6) 5.23 mM, (7) 5.5 mM, (8) 5.8 mM β-CD concentration. Arrow indicates spectral trend with increase of β-CD concentration

medium, respectively, keeping the concentration of AMBME constant ($\sim 10^{-6}$ M). With increasing β-CD concentration the absorption maximum ($\sim$287 nm) in aqueous medium is slightly blue shifted with a gradual decrement of extinction coefficient up to $\sim$3.5 mM concentration range where as for non-aqueous DMSO medium the change of absorption maximum ($\sim$300 nm) is minimum with gradual decrement of extinction coefficient up to $\sim$6.0 mM concentration range. The change of optical density value may be due to the formation of inclusion complex. The clear isobestic points (265 nm and 310 nm) in aqueous β-CD medium do suggest that a single equilibrium present between bare AMBME and inclusion complex of β-CD with AMBME [32]. But in the non-aqueous β-CD medium, the isobestic point destroys at higher CD concentration. The blue shift in aqueous β-CD medium suggests that the environments around the molecule in β-CD nanocavity are different from those in the bulk aqueous medium. No significant change of the position of the absorption maxima in non-aqueous β-CD indicates that environment around the probe AMBME molecule in non-aqueous β-CD is same as that of DMSO medium and the cavity property is different from that of aqueous β-CD environment.

Emission spectra

It is pertinent to mention here that the molecule AMBME upon excitation shows dual fluorescence—one for the local and another for the charge transfer emission in different solvents [26]. The position of the charge transfer emission band shows clear dependency on both the solvent polarity and hydrogen bonding parameter indicating the presence of both dipolar and hydrogen bonding interaction. Interestingly, this molecule shows CT emission in non-polar solvent and the position of the LE and CT band in non-polar solvent merges to make a single broad band. The molecule shows dual emission in water with peaks positions at $\sim$310 nm and 370 nm for the local and CT band, respectively. In case of DMSO solvent the CT band position is found to be at $\sim$354 nm. The fluorescence characteristics of AMBME, particularly emission intensity and position of the bands, in both aqueous and non-aqueous β-CD medium are different and are shown in Fig. 2a, b. With increasing of β-CD concentration in aqueous medium the emission intensity of both the LE and CT band of AMBME increases (Fig. 2a) with a blue shifting of CT band keeping the position of LE band unaltered. The change in fluorescence intensity with increase in β-CD concentration for both LE ($\sim$310 nm) and CT ($\sim$362 nm) band is shown in Fig. 3a. It is observed that the increase of intensity is more for the CT emission band compared to that of the intensity of LE band. After 3.5 mM β-CD concentration there is no change and enhancement of fluorescence by further addition of β-CD indicates complete complexation process. The blue shifting of longer wavelength CT band indicates the inclusion of fluorophore in the non-polar cavity of β-CD. In the less polar β-CD cavity the ICT state of AMBME will be less stabilized by solvent stabilization and hence the energy gap between ICT and ground state will increase, which results the blue shifting of the CT band.

Where as in non-aqueous medium, i.e., in DMSO medium with increasing of β-CD concentration the CT emission band intensity decreases with concomitant increase of intensity of the LE band. The change of emission intensity for both the bands is shown in Fig. 3b. The reduction in CT

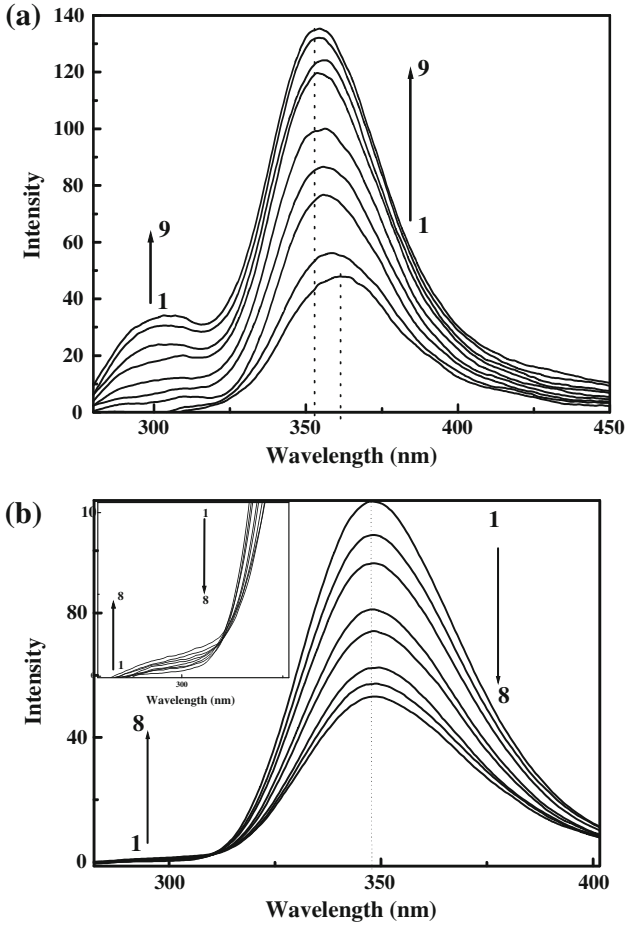


Fig. 2 (**a**) Emission spectra ($\lambda_{ext} = 270$ nm) of AMBME in the same concentration range in aqueous β-CD medium. (**b**) Emission spectra ($\lambda_{ext} = 280$ nm) of AMBME in same concentration range in non-aqueous β-CD medium

band intensity indicates that CT process is not favourable in non-aqueous β-CD medium. A clear isoemissive point ($\sim$325 nm) appeared in the emission spectrum. There is no significant change in CT band position with increase of β-CD concentration indicates that in non-aqueous β-CD medium the surrounding polarity of AMBME is almost same as that obtained in only DMSO medium.

The different behaviour of AMBME in aqueous and non-aqueous medium can be explained from the shape and stoichiometry of the inclusion complex. As clear isobestic point is observed in the absorption spectra in aqueous medium, the possibility of formation of 1:1 inclusion complex is maximum. For 1:1 complex between β-CD and AMBME, the following equilibrium can be written:

$$\text{AMBME} + \beta\text{-CD} \overset{K_1}{\leftrightarrow} \text{AMBME:}\ \beta\text{-CD}$$

$$K_1 = \frac{[\text{AMBME} : \beta\text{−CD}]}{[\text{AMBME}][\beta\text{-CD}]}$$

where K_1 is the binding constant.

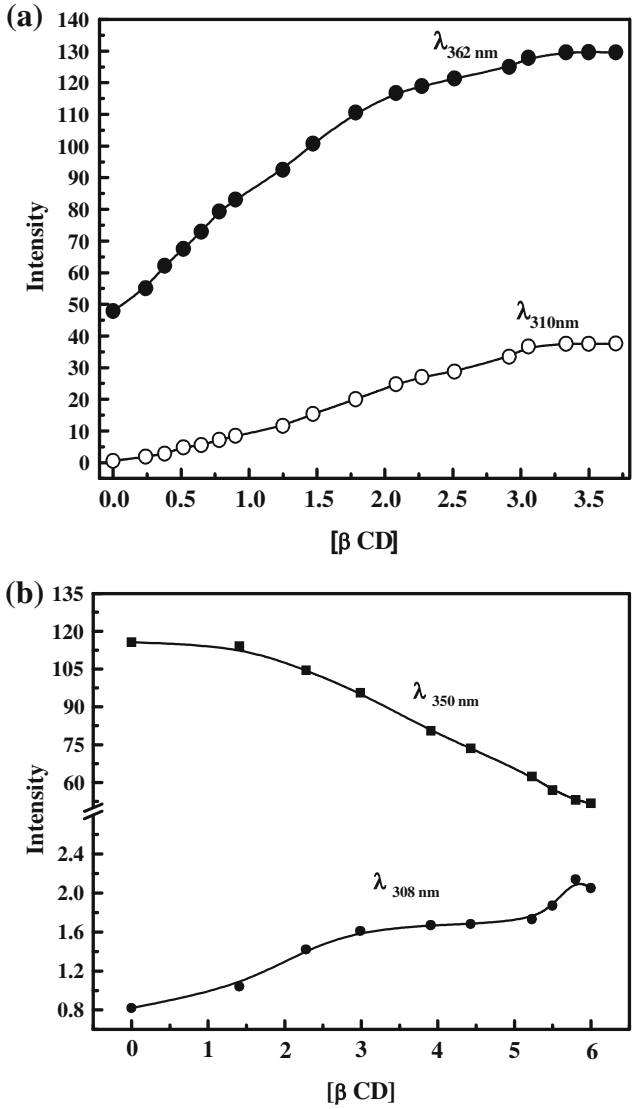


Fig. 3 (**a**) Plot of fluorescence intensity (-•-) for $\lambda_{em} = 362$ nm, (-○-) for $\lambda_{em} = 310$ nm band with different aqueous β-CD concentration. (**b**) Plot of fluorescence intensity (-■-) for $\lambda_{em} = 350$ nm, (-•-) for $\lambda_{em} = 308$ nm band with different non-aqueous β-CD concentration

The binding constant (K_1) and stoichiometric ratios of the inclusion complex can be determined according to the Benesi–Hildebrand relation assuming the formation of 1:1 host–guest complex. Considering the concentration of the complex is less compared to the free CD concentration, i.e., free CD concentration is equal to total CD concentration, Benesi–Hildebrand relation can be written as follow.

$$\frac{1}{(I - I_0)} = \frac{1}{(I_1 - I_0)} + \frac{1}{(I_1 - I_0)K_1[\beta\text{-CD}]}$$

where I_0, I and I_1 are the emission intensities in absence of β-CD, in presence of β-CD and when AMBME totally solubilized in β-CD, respectively. A linear $1/(I - I_0)$

versus 1/[β-CD] plot in aqueous β-CD medium (Fig. 4a) confirms the formation of 1:1 inclusion complex in aqueous β-CD medium. The calculated equilibrium constant K_1 is 1,579 M^{-1}. Where as in non-aqueous β-CD medium the similar $1/(I - I_0)$ versus 1/[β-CD] plot shows nonlinearity (Fig. 4b (inset)). Assuming 1:2 host–guest complex formations the following equilibrium can be established between AMBME and β-CD in non-aqueous medium:

$$\text{AMBME} + 2\beta\text{-CD} \overset{K_2}{\leftrightarrow} \text{AMBME: } 2\beta\text{-CD}$$

$$K_2 = \frac{[\text{AMBME} : 2\beta\text{-CD}]}{[\text{AMBME}][\beta\text{-CD}]^2}$$

where K_2 is the binding constant.

This follows the following Benesi–Hildebrand relation:

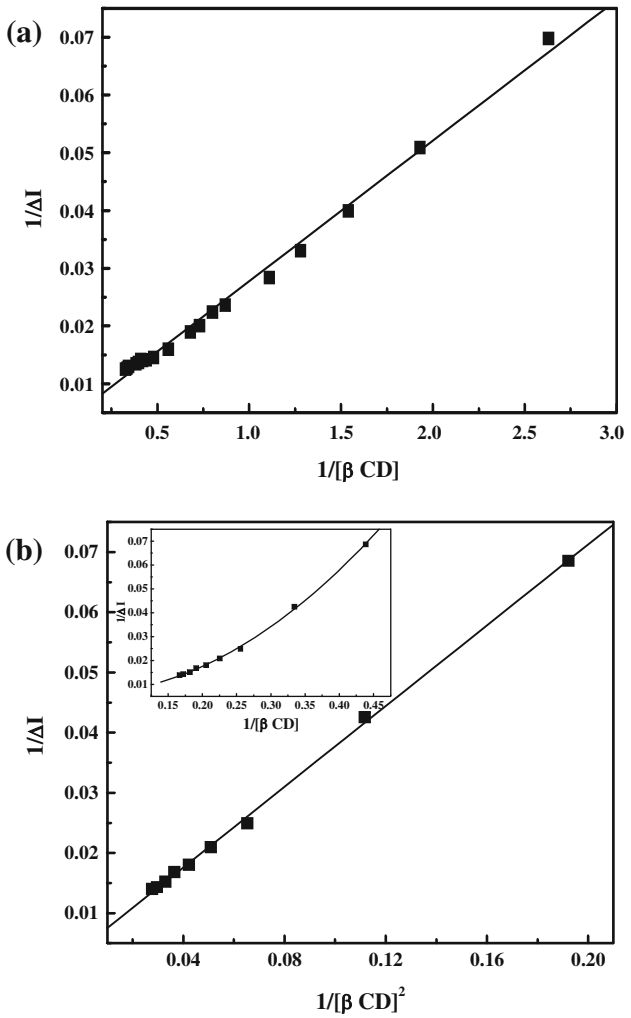
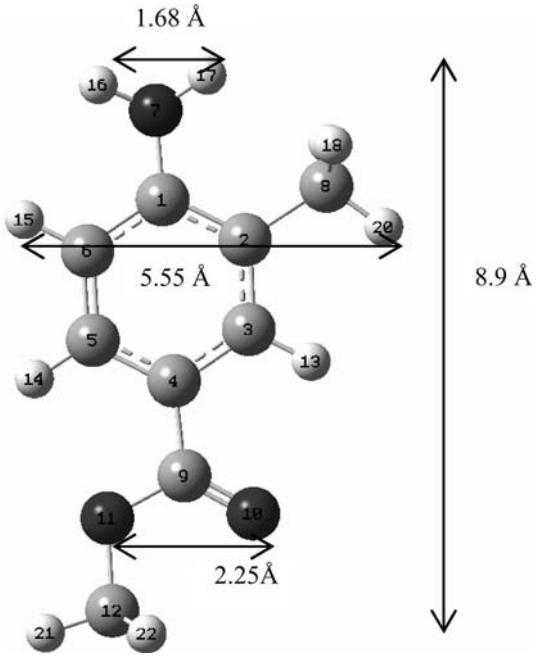


Fig. 4 (**a**) The Benesi–Hildebrand plot for 1:1 complexation of AMBME with different concentration of β-CD in aqueous medium. (**b**) The Benesi–Hildebrand plot for 1:2 complexation of AMBME with different concentration of β-CD in non-aqueous medium. Inset: Non-linear curve obtained for 1:1 complex formation

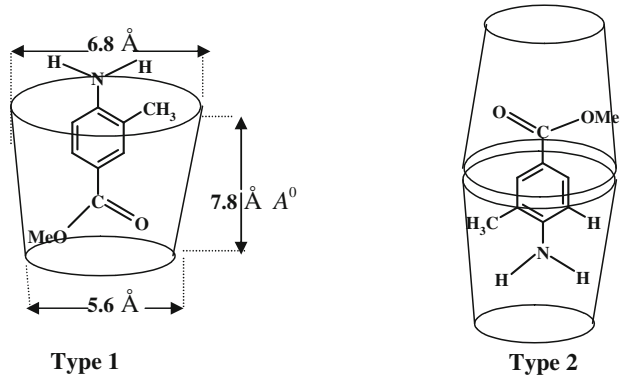
$$\frac{1}{(I - I_0)} = \frac{1}{(I_1 - I_0)} + \frac{1}{(I_1 - I_0)K_2[\beta\text{-CD}]^2}$$

where I_0, I and I_1 are same as mentioned above.

The plot of $1/(I - I_0)$ versus $1/[\beta\text{-CD}]^2$ in non-aqueous β-CD shows a linear relationship, which confirms the formation of 1:2 inclusion complex in non-aqueous β-CD medium. The binding constant (K_2 = 11,940 M^{-2}) is quite larger than K_1. The possible orientation of AMBME in aqueous and non-aqueous β-CD medium can be interpreted from the spectral observations. The probe AMBME is in the less polar and restricted environment in aqueous β-CD medium, which may be responsible for the enhancement of both the emission bands with increasing β-CD concentration. It is to point out that H-bonding acts as a non-radiative deactivation path for CT emission of AMBME where the protic solvents stabilised the CT state of AMBME by forming H-bonding with the carbonyl group [26]. It is known that in aqueous β-CD solution hydrophobicity is the driving force for encapsulation of the molecule inside the cavity and the hydrophobic C=O part would like to go inside the deep core of the cavity and the amine group is projected in bulk water medium [25]. Therefore, in aqueous β-CD medium, AMBME orients in such a way that no water molecule is available to the ester group of AMBME (Type 1). So the absence of non-radiative deactivation paths by H-bonding is responsible for emission enhancement of both LE and CT bands in aqueous CD environment. Any factor such as low-frequency large-amplitude motions that favour ICT process may be hindered in restricted CD cavity and hence CT emission may decrease inside the CD nanocavity. But here as the $-NH_2$ group sticking towards the larger rim of the β-CD, so such hindrance is not affected the CT emission. In non-aqueous medium it is observed that the intensity of CT band decreases with increasing β-CD concentration. So AMBME oriented in non-aqueous β-CD medium in such a way that its ICT formation is hindered causing an enhancement of LE band. It is possible if the amino group goes to the interior part of the β-CD cavity. The proposed orientation of the inclusion complex in non-aqueous β-CD medium is like of Type 2, i.e., the 1:2 inclusion complex is most probably assigned to a barrel-type complex with larger rims of β-CD facing each other. However, it is suggested that 2D NMR may provide far better understanding about the stochiometry and exact depth of the inclusion complexes. The possibility of formation of 1:2 or higher complex can also be supported from the optimized structure of AMBME at DFT level using B3LYP hybrid functional and 6-311++g (d,p) basis set (Schemes 1, 2). It shows that the horizontal distance between H16 and H17 atoms is 1.68 Å and the distance between H15 and any of the H18/19/20 atoms are 4.9, 4.92, 5.55 Å. Similarly, the



Scheme 1 Optimised geometry of minimum energy conformer of 4-amino-3-methyl benzoic acid methyl ester (AMBME) at DFT level using 6-311 ++g(d,p) basis set with B3LYP hybrid functional



Scheme 2 Possible inclusion complex of AMBME with β-CD in different environment: Type 1: In aqueous medium, Type 2: In non-aqueous medium

distance between O11 and O10 atoms is 2.25 Å and the vertical distance between H17 and H21/22/23 atoms are 8.9, 8.76, 8.7 Å, respectively. It is known that the internal diameter of the hydrophilic side of β-CD is 6.65 Å and that of hydrophobic side is 5.6 Å, and its height is 7.8 Å. As the distance between H15 and H20 is 5.55 Å, so if the amino group goes inside the β-CD cavity, i.e., in the hydrophobic region, it does not totally enter into the cavity and the rotation of amino group coupled with ortho methyl torsional motion should be hindered due to geometrical restrictions. Therefore, ICT band intensity decreases with enhancement of LE emission band. Again as the height of AMBME is larger than the height of β-CD cavity the formation of 1:2 inclusion complexes is possible. In aqueous β-CD medium as the –COOMe group goes inside the hydrophobic cavity and it does not feel any steric effect as the distance between O10 and O11 = 2.25 Å, i.e., smaller than β-CD hydrophobic cavity diameter and molecule can go more inside the β-CD cavity with the formation of 1:1 complex. For more accurate interpretation it is necessary to perform structural calculation of inclusion complexes of AMBME with β-CD at the same level. Theoretical calculation of the global system may provide more information about the inclusion depths, different thermodynamical parameters of the system, polarity or pH of the medium etc. But all these are very heavy theoretical works so we try to make this simplified calculation about the guest molecule AMBME which also can interpret our experimental findings. The similarity of the fluorescence excitation spectra recorded at different detection wavelengths for both local and ICT bands and their resemblances with the absorption spectra indicates the formation of one kind of inclusion complex in each case. Again a clear isobestic point (in aqueous β-CD medium) and isoemissive (non-aqueous β-CD medium) point supports this fact. In both case high binding constant values imply AMBME tightly encapsulated in β-CD nanocavity. Higher binding constant in non-aqueous β-CD indicates that AMBME strongly bounds within two β-CD molecules.

Fluorescence lifetime measurements

Fluorescence lifetime measurements provide useful information about the properties of the fluorescence probe. The excited state lifetimes of AMBME–β-CD inclusion complex were measured at 3.5 mM β-CD concentration for aqueous medium and 4 mM β-CD concentration for non-aqueous medium. Fluorescence lifetime values are presented in Table 1. In our previous publication [26] we have

Table 1 Fluorescence lifetime of AMBME molecule in different solvents at room temperature

Medium	Fluorescence lifetime (ps)		χ^2
	τ_1 (a_1)	τ_2 (a_2)	
Water (λ_{em} = 360 nm)	Similar to IRF		
3.5 mM β-CD in water (λ_{em} = 360 nm)	29 (67%)	110 (32%)	1.2
DMSO (λ_{em} = 350 nm)	470 (12%)	1000 (88%)	1.3
4 mM β-CD in DMSO (λ_{em} = 350 nm)	9300 (5%)	570 (95%)	1.1

τ is the lifetime value; a_1, a_2 represent corresponding relative amplitudes of different components in bi-exponential fitting of the temporal profile

Decay monitored at emission maximum

reported that due to the presence of hydrogen bonding as non-radiative channel, the fluorescence lifetime of AMBME in water is found to be below the instrument resolution. In aqueous β-CD medium fluorescence lifetime value increases as the hydrogen bonding C=O of ester group goes inside the hydrophobic β-CD cavity which deactivates non-radiative channel. The fluorescence lifetime of the probe in aqueous β-CD medium is found to be $\sim$27 ps for normal emission and $\sim$110 ps for CT emission. In non-aqueous medium with increasing β-CD concentration intensity of the quantum yields of CT band decreases with continuous increases of LE band. Fluorescence lifetime values also reflect the same results (Table 1). In the pure DMSO medium, fluorescence lifetimes for the LE and CT states are found to be $\sim$470 ps and $\sim$1,000 ps, respectively. In DMSO-β-CD medium fluorescence lifetime of the LE species increases to $\sim$9,300 ps (LE of 1:2 complex), and for the CT species decreases to $\sim$570 ps.

Conclusion

Based on the absorption and emission spectra it is found that the charge transfer fluorescence probe AMBME formed 1:1 and 1:2 stoichiometric complex β-CD in aqueous and non-aqueous medium, respectively. The binding of the probe with β-CD in non-aqueous medium is stronger than that of aqueous medium. It is found that the orientation of the donor and acceptor groups of the probe inside the β-CD nano-cavity is different in the two mediums. The enhancement of both LE and CT band in aqueous medium is due to less polar interaction of highly polar ICT state of AMBME with less polar β-CD cavity. In aqueous medium as the ester group goes to the hydrophobic part of the cavity, so H-bonding does not play as non-radiative deactivation path leading to the increase of intensity and fluorescence lifetime of the CT band. But in the non-aqueous medium spectral data indicate that the amino group goes inside the hydrophobic cavity of β-CD and now free rotation of amino group which may coupled with the ortho methyl group is hindered resulting the reduction of CT emission intensity.

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