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Journal of Photochemistry and Photobiology A: Chemistry 173 (2005) 279–286

Journal of Photochemistry and Photobiology A:Chemistry

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Effect of additives on the photophysics of 2-acetyl benzimidazole and 2-benzoyl benzimidazole encapsulated in cyclodextrin cavity

Papia Chowdhury, Tirtha Pratim Adhikary, Sankar Chakravorti *

Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

Received 2 February 2005; received in revised form 21 March 2005; accepted 31 March 2005

Abstract

Interesting excited state proton transfer photophysics of 2-acetyl benzimidazole (2ABI) and 2-benzoyl benzimidazole (2BBI) encapsulated in cyclodextrin (CD) (α and β) cavity and its modulation on addition of acid/base and inorganic salt have been delineated in this paper based on steady state and time-resolved photoemission spectroscopy. In the ground state both 2-acetyl benzimidazole and 2-benzoyl benzimidazole form complexation with β-CD, but not with α-CD. Large intensification of anion band and relatively small enhancement of neutral emission of 2BBI in β-CD points to the complex formation in the excited state with a preferential orientation of ≥N─H group in bulk water. Increased lifetime and enhancement of band intensity of 2BBI in β-CD compared to that of 2ABI indicate a definite inclusion of 2BBI inside the cavity. Base induced protons at the rims of the cavity liberated in the process of formation of anions quench the anionic species of 2BBI in β-CD solution. Cavity size of cyclodextrin influences the modulation of photodynamics of the guest. Addition of acid leads to the formation of a cationic species. Inorganic salt hinders the deprotonation and lowers the barrier for anion formation.

Keywords: Proton transfer; Anion emission; Deprotonation; Cyclodextrin; pH-variation

1. Introduction

The effects of substituents on the spectral characteristics of *N*-heterocyclic molecules in the ground and excited states have been a topic of intensive experimental investigations for a long time [1,2]. These types of molecules make inclusion complexes [3–8] with different cyclic molecules such as cyclodextrins (CDs). CDs are cyclic molecules made up of elementary glucopyaranose possessing a hydrophobic cavity and hydrophilic exterior of different sizes and they are of great importance in supramolecular chemistry. Complexation with the guest molecule occurs within the hydrophobic cavity and the glucose hydroxyl groups at both the entrances of the cyclodextrin cavity further stabilize the complex formation via hydrogen bonding [9]. The hydrophobic forces come into play to stabilize the guests in the cavity. In many ways, CDs are better systems than micelles, because they form stable structures whereas, micelles are transitory and are in dynamic equilibrium with the monomer surfactant molecules from which they are formed [11,12]. Upon complexation with CD, the photophysical properties such as fluorescence quantum yield gets greatly affected due to reduced polarity and also due to the restricted geometry provided by CDs. In recent times the CDs have received a lot of attention [1–10] as they can provide a good model for enzyme.

Since the fluorescence spectral characteristics of certain molecules are very sensitive to their surroundings [11], environments in structured micro heterogeneous systems can play a major role in the alteration of these properties, and molecules can be used as probes to study the properties of micro heterogeneous systems [13,14].

In an earlier report [15] we characterized the excited state intramolecular proton-transfer (ESIPT) photophysics of 2-acetyl benzimidazole (2ABI) and 2-benzoyl benzimidazole (2BBI) in different environments. For both the molecules in the ground state, the intramolecularly hydrogen-bonded closed-conformer (I) (Scheme 1) is the stable form

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* Corresponding author. Tel.: +91 33 24734971; fax: +91 33 24732805.
E-mail address: spsc@iacs.res.in (S. Chakravorti).

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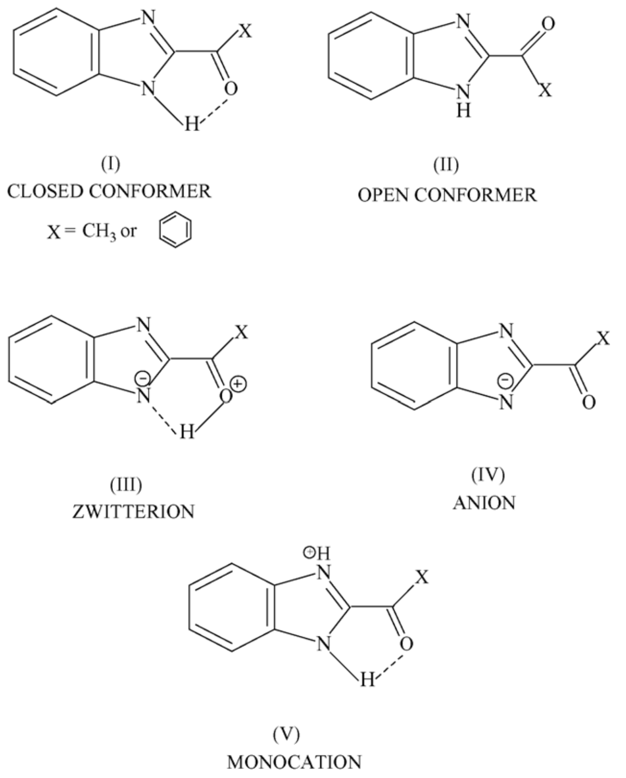
doi:10.1016/j.jphotochem.2005.03.030



Scheme 1. Different conformeric forms of the molecules 2ABI and 2BBI.

in non-polar solvents. This intramolecular hydrogen bond dissociates in polar and hydroxylic solvents due to solute-solvent interaction. The formation of zwitterionic species (III) (Scheme 1) of the closed conformer, as a result of ESIPT, is evidenced by Stokes-shifted fluorescence spectra in nonpolar solvents. In nonpolar solvent only one fluorescence band could be observed due to intramolecular proton transfer. With increasing solvent polarity this Stokes-shifted zwitterionic band intensity decreases and in aqueous medium this band intensity almost disappears with the appearance of a new anionic band. In zwitterionic structure the positive and negative charges are located very close to each other due to intramolecular interaction. The existence of zwitterionic species depends on the coulomb attraction between the charges. With the increase in polarity of solvent this interaction also increases and consequently the zwitterions become unstable in more polar solvent. So the zwitterionic species (III) arises due to intramolecular proton transfer and another anionic species (IV) arises due to intermolecular proton transfer upon excitation of (I) (Scheme 1). The effect of addition of acid, base and salt in various environments at different temperatures [15,16] has also been reported. Monocationic form exists in lower concentration of acid and for higher acid concentration formation of dication occurs due to protonation in the two sites (pyridinium type nitrogen and pyrrole type nitrogen) for both the molecules. Also we observed the existence of open conformers at low temperature [16]. In this study, we have attempted to explain the hydrogen bonding effects more systematically in the ground and excited state process of 2ABI and 2BBI by observing the steady-state and time-resolved fluorescence spectral properties in aqueous cyclodextrin solutions. CD is an ideal system to control the relative microenvironment of each functional group to distinguish the hydrogen bonding and polarity dependence of the electron-donating group from the hydrogen bonding effect of the heterocyclic groups. Many workers have employed the CD system to control the ESIPT [17–23] and different ICT process of various CT molecules [24–34].

Though many works have been done on the cyclodextrin effects on ESIPT process [35–37], but little [35] on the effects of different additives on proton transfer characteristics study could be found. Variation of pH of the solution may be conducive to increment or decrement of anionic/cationic species and the addition of inorganic salt in solution can modify electric field of the environment and also ionic excited state species. This paper reports the interesting investigation of the effect of cyclodextrin cavities (α and β) and also the addition of acid/base and inorganic salt on the ESIPT (inter or intra) photophysics of 2ABI and 2BBI.

2. Experimental details

2-Acetyl-benzimidazole or 2-(1-hydroxyethyl)-1-H-benzimidazole [38] was oxidized with pyridinium chloro chromate (PCC) and purified by column chromatography (on silica gel 60–120; 5% ethyl acetate in petrolium ether). It was crystallized from benzene [39]. The color of 2ABI crystal is white, M.P. 189 °C. 2-Benzoyl benzimidazole or 2-(α-hydroxybenzyl) benzimidazole (Scheme 1) was prepared by heating for 2 h, *o*-phenylene diamine with mandelic acid (1:1.2), in ethanol: concentrated HCl: *o*-phosphoric acid (4:1:1). The mixture was basified with Na_2CO_3 and crystallized from ether, M.P. 85 °C. The said benzimidazole was oxidized with pyridinium chlorochromate (PCC) [40]. In dry dichloro methane, activated molecular sieves (4 Å), benzimidazole, and PCC (5 equiv.) was stirred at room temperature for 4 h, monitored by TLC (dichloromethane). The mixture was diluted with ether and filtered through celite. The celite was washed with ether and dichloromethane. The filtrate was evaporated at reduced pressure. The solid was crystallized from methanol–water mixture. 2BBI is pale Yellow crystal of M.P. 210 °C. Other details of the synthesis are as reported before [15].

α-Cyclodextrin and β-cyclodextrin (Aldrich) were used as received. Triethylamine (TEA) (E. Merck, spectroscopic grade) were used as supplied but only after checking the purity fluorimetrically in the wavelength range of interest. For aqueous solution, we used deionized Millipore water. H_2SO_4 (E. Merck, spectroscopic grade) was used as received.

The absorption spectra were taken with a Shimadzu UV–vis absorption spectrophotometer model UV-2401PC. The fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer. For emission measurements, the sample concentration was maintained at $\sim 10^{-5}$ M in each case in order to avoid aggregation. Quantum yields were determined by using secondary standard method ($\phi_f = 0.23$) with recrystalized β-naphthol in MCH (methylcyclohexane), details of the process are described elsewhere [36,37]. For lifetime measurement the sample was excited (at 405 nm; o.d. ∼0.15) with pico-second diode (IBH Nanoled-07). The emission was detected by a magic angle polarization using two polarisers coupled with Hamamatsu MCP photo multiplier (2809U). The time correlated single photon counting (TCSPC) set up consists of an Ortec 935 QUAD CFD and a Tennelec TC 863 TAC. The data were collected with a PCA3 card (Oxford) as a multichannel analyzer. The typical FWHM of the system response is about 80 ps. Typical slit width ∼30 nm, monochromator type Jobin-Yvon (MCH 910), number of channels 4096 (6 ps per channel), window width ∼24.5 ns and number of counts ∼3000 were used in taking decay profiles. The lifetime data were analysed considering them as multi-exponential decay. Mean lifetime data have been put in the table taking the amplitude of the components into account.

3. Results

3.1. Absorption spectra

In aqueous solution 2BBI shows absorption maximum around 321 nm but with addition of β-cyclodextrin it shows a decrease in absorbance along with a negligible red shift (∼4 nm), Fig. 1. The presence of an isosbestic point (∼300 nm) indicates the formation of single type of equilibrium in the mixed system. Addition of α-cyclodextrin does not show much effect as with β-CD. Same type of results were obtained in 2ABI in α-CD and β-CD solutions. In presence of cyclodextrins addition of different additives shows some interesting results in both the molecules. For 2BBI in β-CD medium addition of base (TEA) shows decrease in absorbance with a red shift but addition of acid (H_2SO_4) shows a blue shift. The absorption spectra of 2ABI show same kind of results on addition of acid/base in cyclodextrin solution.

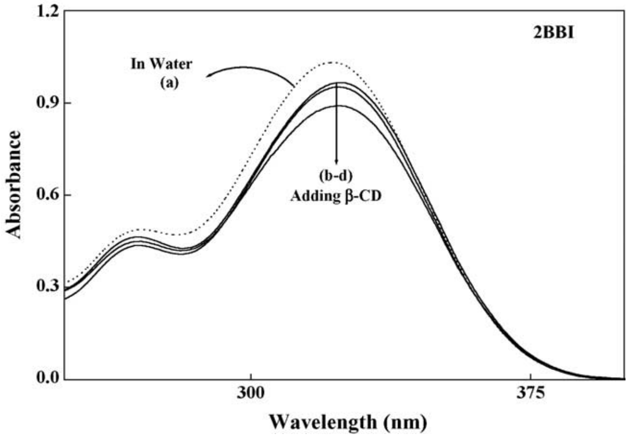


Fig. 1. Electronic absorption spectra of 2BBI in different β-CD concentration. [2BBI] = 20 mM. (a) pure water, (b–d) 5.2, 7.3, and 12.7 mM of β-CD concentration.

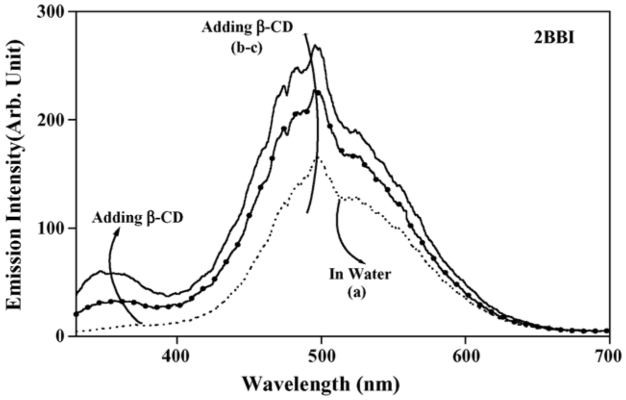


Fig. 2. Fluorescence emission spectra of 2BBI in different β-CD concentration. Excitation wavelength = 300 nm [2BBI] = 20 mM. (a) pure water, (b and c) 5.2 and 12.7 mM of β-CD concentration.

3.1.1. Emission and excitation spectra

2BBI shows distinct dual fluorescence in all polar solvents [15,16]. The higher energy emission (∼360 nm) has been assigned to be arising out of the neutral form of the molecule. The other emission band in the lower energy side (∼500 nm) arises from the anionic state, which is due to intermolecular proton transfer between solute and solvent in the excited state. This anionic state is the most polar state of 2BBI and the band position is very much solvent sensitive. In pure water the anionic band intensity is more prominent than the neutral one as depicted in Fig. 2. When α-CD is added to 2BBI in aqueous solution, this peak intensity increases slightly, whereas, for addition of β-CD, it increases significantly (almost double the peak intensity observed for only aqueous solution of 2BBI) (Fig. 2). Addition of β-CD in 2BBI solution shows a small increase in peak at ∼360 nm (neutral emission) in addition to anion-peak, but with addition of α-CD no such change in normal band intensity could be observed. With 2ABI a different type of result is obtained in presence of α-CD or β-CD. Not much change in band position or intensity is observed in 2ABI on addition of α-CD. It is observed that, as the β-CD concentration is increased in the aqueous solution of 2BBI, the intensity of both the bands increase (Fig. 2). Different excitation spectra corresponding to aqueous solution of 2BBI with fixed concentration of α-CD or β-CD, by monitoring at different emission wavelength, have been recorded (Fig. 3). The fluorescence excitation spectrum in α-CD or β-CD monitored at 500 nm clearly reflects the absorption spectrum. It shows that the excitation band position remains unaltered with varying emission wavelength, which clearly points out that only one type of complex contributes to the absorption spectrum.

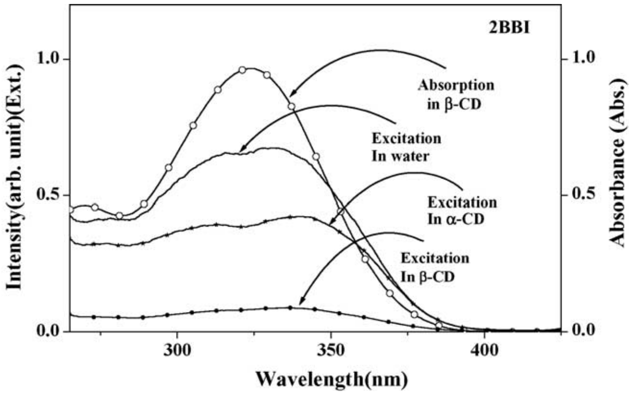


Fig. 3. Fluorescence excitation spectra of 2BBI in both CDs (monitoring wavelength 500 nm.) and absorption spectrum of 2BBI in aqueous β-CD solution.

3.1.2. *Effects of additives in emission spectra*

In restricted geometry of β-CD with progressive addition of acid (varying pH), the band intensity and position of the two emission bands show interesting changes (Fig. 4). The lower energy anion-band (∼500 nm) intensity is found to decrease with a negligible blue shift after adding H_2SO_4 to it; while the intensity of higher energy band (∼360 nm) increases with a small red shift. It is important to note that addition of acid to the aqueous β-CD solution of 2BBI, an isoemissive point is observed at ∼448 nm. In sufficiently higher concentration of H_2SO_4 (pH ∼ 1.5), a high intense new band appears at ∼380 nm with comparatively higher quantum yield along with a low intensity band at ∼500 nm. In the acid induced emission, the spectral changes of the molecule accompanied by the appearance of isoemissive point and the formation of 380 nm band for 2BBI confirm the exclusive formation of the corresponding cation. The changes in the emission as a function of acid concentration ($[H_2SO_4]$, pH 6.5–1.5), where $[H_2SO_4]$ refer to the initial concentration of H_2SO_4, can be related to Eq. (1) which is frequently utilized as the Benesi–Hildebrand expression [41]. The appearance of isoemissive point indicates the formation of 1:1 complex between 2BBI in β-CD and acid contrary to the excited state picture [15]. In the event of formation of the 1:1 complex in the excited state, the Benesi–Hildebrand relation must be satisfied,

$$\frac{1}{I - I_0} = \frac{1}{K_1(I_1 - I_0)\,[H_2SO_4]} + \frac{1}{I_1 - I_0}, \tag{1}$$

where I_0 and I_1 denote fluorescence intensity of the probe molecule in β-CD solution and in the complex, respectively, I is the fluorescence intensity at a given H_2SO_4 concentration and K_1 is the association constant. If only the 1:1 inclusion complex exist in the system in the excited state, the plot

$$\left\{\frac{1}{I_0 - I}\right\} \text{versus} \left\{\frac{1}{H_2SO_4}\right\}$$

should yield a straight line [16,34]. Fig. 5 shows the plot for the complexation of 2BBI with acid, which confirms the 1:1 complexation between anionic and protonated form in the excited state. From the intercept and slope values of the plot K_1 is evaluated to be ∼570 M^{-1}.

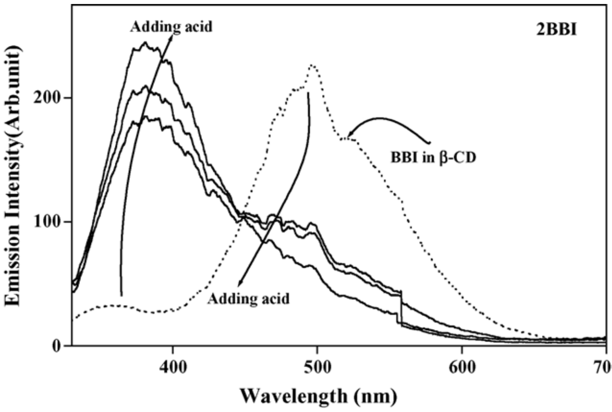


Fig. 4. Fluorescence emission spectra of 2BBI in β-CD by increasing acid-concentration (varying pH from 6.5 to 1.5) [2BBI] = 20 mM.

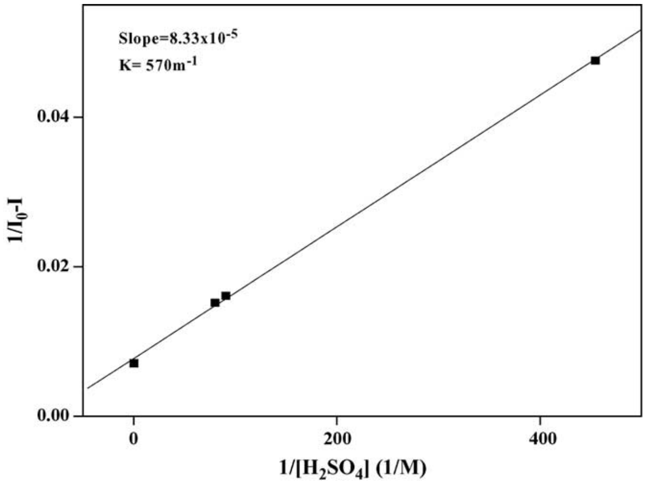


Fig. 5. Plot of $1/I_0 - I$ vs. $(H_2SO_4)^{-1}$ for finding K_1 (association constant) of Benesi–Hildebrand equation (Eq. (1)).

We got almost similar results in the case of 2ABI also, the only difference being the position of the lower energy band at ∼470 nm. Also the intensity of the higher energy band is very poor and sometimes we could not observe this band in the spectrum of 2ABI either in α-CD or β-CD on addition of acid or base. The computed equilibrium constant is found to be ∼649 M^{-1} for the inclusion complex of 2ABI and β-CD.

Now if we continue to add base in the aqueous β-CD solution of 2BBI, the lower energy (∼500 nm) band starts to decrease in intensity. The higher energy (∼370 nm) band remains nearly the same with a small red shift. If we change the restricted environment of the molecule by some other type of cyclodextrin, α-CD, in the aqueous solution of 2BBI, the results seem to be almost same, but, the band intensities are much more stronger in case of β-CD compared to that in α-CD. Adding acid or base here also increases the higher

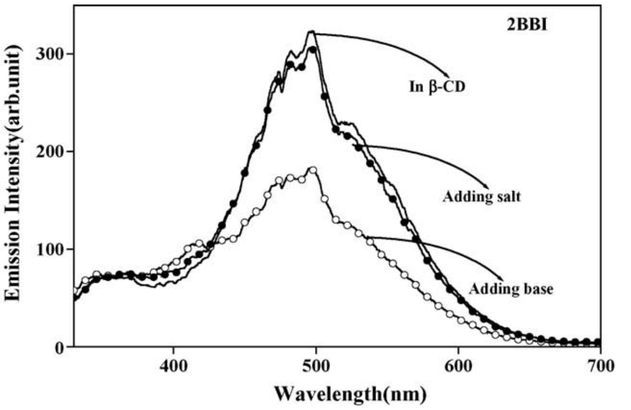


Fig. 6. Fluorescence emission spectra of 2BBI with addition of base and salt. Excitation wavelength = 300nm.

energy band with a small red shift and the lower energy bands starts to disappear.

With a view to study the effect of modulated electric field in cyclodextrin cavity on the proton transfer photophysics and also to get an idea about the position of molecules 2ABI and 2BBI inside different cavity, inorganic salt was added in cyclodextrin solution. The anion band intensity decreases with increase of KNO_2 concentration along with total disappearance of neutral band intensity of 2BBI in β-CD (Fig. 6). We have observed similar type of phenomena in the case of 2ABI also.

3.2. *Time-resolved emission*

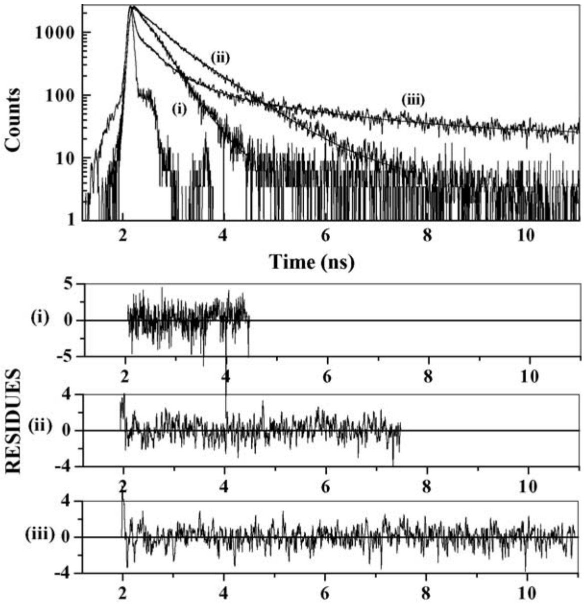


Fig. 7. Typical decay profile of 2BBI {excitation at 405 nm and emission monitored at 500 nm (curve-i and ii) and 425 nm (curve-iii)} in aqueous and CD solutions. Curve (i) is single exponential ($\chi^2 = 1.196$), Curve (ii) is double exponential ($\chi^2 = 1.103$), Curve (iii) is triple exponential ($\chi^2 = 1.003$).

Table 1
Values of k_r and k_{nr} for 2ABI and 2BBI computed from ϕ_{fl} and τ_{fl}

Sample	Additives	ϕ_{fl}	τ_{fl} (ps.)	k_r (10^8 s^{-1})	k_{nr} (10^8 s^{-1})
2BBI	Water	0.05	340	1.522	28.32
Aqs. 2BBI	β-CD	0.08	520	1.528	17.81
Aqs. 2BBI	α-CD	0.055	380	1.447	24.87
2BBI + β-CD	Acid	0.09	120	12.48	127.8
2BBI + β-CD	Base	0.055	<10	>200	>200
2ABI	Water	0.31	3420	0.910	2.017
Aqs. 2ABI	β-CD	0.35	3310	1.046	1.978
Aqs. 2ABI	α-CD	0.36	3305	1.086	1.939
2ABI + β-CD	Acid	0.24	20	81.89	511.6
2ABI + β-CD	Base	0.30	720	4.176	9.791

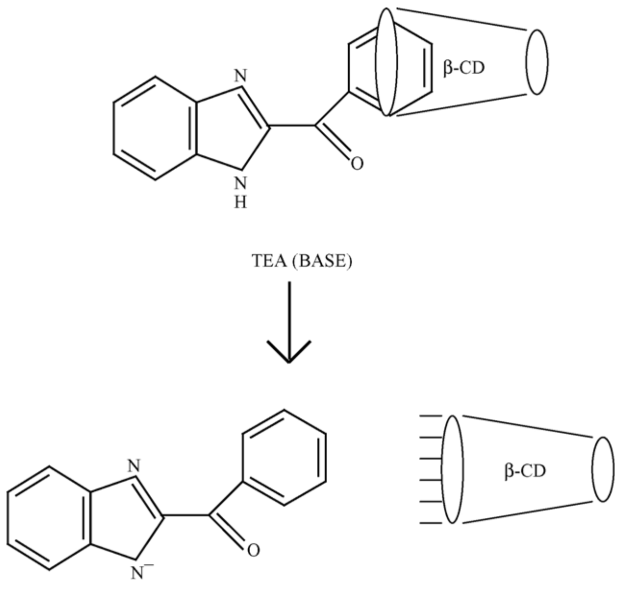
The lifetimes of freshly prepared solutions of 2ABI and 2BBI at two different concentrations of α-CD and β-CD were measured by exciting the solutions at 375 nm and monitoring at 470 nm. The lifetime of 2BBI in hydroxylic solvent water is found to be 340 ps. Adding α-CD (concentration = 20 mM) to this solution this lifetime increases to 380 ps. Upon addition of β-CD (concentration = 20 mM) in the aqueous solution of 2BBI this lifetime further increases to 520 ps, shown in the representative plot (Fig. 7). This lifetime datum confirms that β-CD is more tightly bound with 2BBI than with α-CD, i.e., the complexation with the CD cavity in more favorable in β-CD. In the case of 2ABI we got the lifetime in aqueous solution to be ∼3.5 ns. Very little change in lifetime was observed with addition of β-CD or α-CD (∼3.3 ns) (Table 1). This result concludes that almost no complexation occurs with CDs and 2ABI in hydroxylic solvents. Now a different type of behavior of lifetime occurs with the addition of different additives like acid or base in the CD medium for both the molecules. In the case of 2BBI in the β-CD medium with the addition of acid (H_2SO_4) the lifetime decreases to 120 ps (Fig. 7). Same type of decrease in lifetime (nanosecond to picosecond) ∼20 ps could be observed in 2ABI with addition of acid. From the above mentioned lifetime data we may conclude that in the acidic medium for both the molecules the anion formation is severely hindered. Acid opposes the deprotonation process, so the lifetime decreases. The values of the radiative (k_r) and non-radiative (k_{nr}) decay rate constants were calculated using the following equations

$$k_r = \frac{\phi_{fl}}{\tau_{fl}}; \quad k_{nr} = \left\{ \frac{1}{\tau_{fl}} \right\} - k_r$$

The values obtained are given in the Table 1. These data show that the values of k_{nr} decrease with increasing the concentration of α-CD or β-CD.

4. Discussion

We reported the formation of excited state intramolecular proton transfer ($ESI_{ra}PT$) species (III) (Scheme 1) and formation of anion (IV) (Scheme 1) in the excited state of 2ABI and 2BBI having preexisting hydrogen bonding between acidic part (N–H group) and basic part (C=O group)



Scheme 2. Inclusion of 2BBI (both neutral and anionic form) inside β-CD and base induced exclusion of anionic form from host β-CD.

in ground state [15,16]. In the presence of CD the stoichiometry of the formed inclusion complex depends on the nature and size of the cage. We know that in aqueous solutions cyclodextrins (CD) form a well-defined hydrophobic cavity and encapsulate molecules of suitable sizes and the resulting supramolecules often exhibit properties drastically different from those of the free guest molecules in aqueous solutions. Due to large rim diameter of β-CD (8.5 Å) than α-CD (5.7 Å) the encapsulation of the molecule inside β-CD cavity is more favorable than α-CD so we get the larger change in emission intensity with addition of β-CD. The effects of α-CD or β-CD on 2ABI are small compared to 2BBI. We know there are two types of conjugations formed between benzimidazole group and the substituents ($-CH_3$, $-C_6H_6$) in 2ABI and 2BBI. The conjugation of $-CH_3$ group with benzimidazole ring is more than the conjugation of phenyl ring with benzimidazole [15]. Due to the presence of this greater conjugation the -CH_3 group and the keto moiety will rotate slowly in 2ABI [15,16] and in 2BBI the phenyl ring can rotate around the C-C single bond freely and can form open conformer (II) (Scheme 1), consequently it will no longer be in the plane of benzimidazole ring. So the tendency of the molecule to go inside the cavity is more in 2BBI (at least partly) than 2ABI. From this type of experimental data we may say that β-CD binds more tightly with 2BBI than α-CD.

Inside β-CD cage the intensity of anionic emission increases to double the initial value, Fig. 2. This may be due to encapsulation by β-CD cavity and a possible lowering of barrier between neutral and anionic form. The orientation of encapsulation of 2BBI inside β-CD may be such that the proton in the ≥N–H group may still be available for intermolecular hydrogen bonding in the bulk water and hence the increase in anion band (Scheme 2). Addition of base in 2BBI in β-CD solution marks progressive quenching of anion band along with a little increase in neutral band (Fig. 6). It is known that cyclodextrins contain secondary hydroxyl groups on their larger rim and these may form anion by deprotonation in basic medium [34,42,43]. On addition of base the protons liberated in the process of anion formation at the rim might land up in the molecule 2BBI and thereby quenching the anion formation of 2BBI (Scheme 2). This is also reflected in negligible lifetime (below detection limit of the instrument) of anion emission and a depletion of lower energy band due to addition of base, Table 1. The addition of acid in β-CD solution of 2BBI helps the formation of cation. The lifetime of this band also increases in the restricted cavity (Table 1). For 2BBI the lifetime in β-CD cage is around 520 ps. For 2ABI, due to greater conjugation, the –COX (X=CH_3 group) remains in the plane of benzimidazole group and it is less likely to enter inside the cavity of CDs and so emission intensity possibly does not increase rather it is little less compared to that of water. For larger cage in β-CD the molecule 2BBI enter into the cage of host β-CD at least partly, (Scheme 2) and internal molecular rotation in the trapped guest is restricted inside the cage and as a result its lifetime becomes longer than in α-CD or in water solution. So as expected the overall lifetime of the complex (2BBI·CD) increases with the size of caging entity, i.e., 520 ps and 380 ps for β-CD and α-CD complexes, respectively. In pure solvents such as water, the lifetime is 35 ps. So the results clearly indicate that the size, that is space domain of the nanocavity of the host (α- or β-CDs) governs the photodynamics and emission spectroscopy of the nanostructure of 2BBI from the picosecond to nanosecond regime. For 2BBI the rate of the intermolecular proton transfer reaction from water to CD is found to increase upon CD addition. To explain this observation we may propose a geometrical structure (Scheme 2) for the confined system. For this particular geometry where the phenyl ring of the molecule is found near the hydroxyl rim of β-CD, the rate of proton transfer is directly affected by the microenvironment due to the cage to the extent it is enhanced by the factor of two. For α-CD the molecule possibly cannot go inside the cavity so much due to smaller cavity, the rate of proton transfer reaction is not affected by complexation and it is nearly similar to the uncomplexed 2BBI. For 2ABI as the substituted –CH_3 group remains in the plane of benzimidazole group it cannot rotate inside the cavity of CDs. Though 2ABI does not enter into the CD cavity and can not form 1:1 complex but due to some sort of association, the intensity of the anionic emission band increases in case of 2ABI inside the cavity of CDs.

Due to addition of inorganic salt, a decrease in anion emission with total disappearance of neutral band intensity of 2BBI and 2ABI may be explained in terms of modified electric field. Actually the formation of NO_2^- in aqueous solution of β-CD has lot of influence on the structure of water in the form of increased aqueous solubility of both the guest and CDs or may form ternary complex leading to more stabilization of inclusion complex [44]. In β-CD due to addition of salt the molecule possibly cannot go inside the cavity region of β-CD and consequently the local hydroxyl concentration around the cavity decreases and causes suppression of the deprotonation process, leading to lowering of intensity of anion emission band (Fig. 6). Simultaneously with salt addition the modified electric field possibly decrease the barrier of formation of anionic state from neutral species—thus a total disappearance of neutral band. In the absence of CDs, KNO_2 has no effect on the emission spectra of guest.

5. Conclusion

We have investigated the excited state proton transfer characteristics of 2ABI and 2BBI in two types of cyclodextrin cavities (α-CD and β-CD) and also modulation of these properties on addition of different additives like acid, base and salt. In the ground state 2BBI forms inclusion complex with β-CD and addition of base causes decrease in absorbance with a red shift, whereas on addition of acid a blue shift was observed. This effect is less pronounced in α-CD. 2ABI shows similar result. In emission, both the anionic and neutral band increase with β-CD addition, which points the availability of proton of ≥N–H group in bulk medium. But with α-CD addition both the bands show little effect. In the β-CD encapsulated 2BBI solution with addition of acid an increase in neutral band with simultaneous decrease in anion band was observed. With progressive addition of acid a new band at 380 nm due to protonated form is found and 1:1 complex formation between this protonated form and neutral form could be observed. In 2ABI similar result is obtained. An interesting thing could be observed on addition of base in 2BBI/β-CD solution, the anion band is quenched with a very small increase in neutral band. Base induced anion formation in hydroxyl groups in the β-CD rim helps to replenish the liberated protons in already formed anions of 2BBI—thus a quenching of anionic state of 2BBI. The salt addition in 2BBI/β-CD solution possibly influences the barrier between neutral and anionic form heavily due to modified electric field and causes the neutral band to disappear.

Acknowledgements

The authors thank Prof. Kankan Bhattacharya, Department of Physical Chemistry, IACS Kolkata for kindly allowing them to use the picosecond lifetime measurement instrument procured under DST project no. IR/1-1/CF-01/2002. The authors also thank Dr. Pranab Bhattacharya, IICB, Kolkata for kindly synthesizing the molecules, 2ABI and 2BBI.

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