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pH-Dependent excited-state proton transfer characteristics in 2-acetyl benzimidazole and 2-benzoyl benzimidazole in aqueous and non-aqueous media

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Abstract

Interesting pH-dependent excited-state proton transfer reactions in the forms of ionic species and open conformer of 2-acetyl benzimidazole (2ABI) and 2-benzoyl benzimidazole (2BBI) in hydrocarbon, aqueous and alcoholic solutions at room temperature and 77 K have been reported. Increase of acidity and basicity of solution, respectively, results in increment and decrement of emission of ionic species with shrinking and intensification of zwitterionic species. A cationic species, protonated at the benzimidazole moiety could be observed under acidic conditions in all solvents considered. Mono- and di-cation species in the excited-state were found to form in 2ABI with progressive addition of acid in methanol solution as shown by formation of a new band initially and its sharp intensification thereafter. Complete extinction of anion band along with formation of a blue-shifted band in 2BBI evince that protonation rate seems to be larger in 2BBI than in 2ABI in acidic aqueous solution. Phosphorescence for both the molecules at 77 K originates from the open conformers. It is interesting to note that less conjugation of phenyl ring with benzimidazole ring in 2BBI facilitates the benzoyl group rotation to form the open conformer compared to 2ABI.

Keywords: Proton transfer; Open conformer; Anionic species; Zwitterionic species; Mono and di-cation

1. Introduction

The pioneering work of Förster [1] and Weller [2] on the study of acid–base chemistry of electronically-excited states has blossomed into an interesting mature field with several works on the subject appearing from 1970 [3,4]. It is a well known fact that the molecules having acidic and basic groups in close proximity with suitable geometry may undergo excited-state intramolecular proton transfer (ESIPT) processes from the acidic part to the basic part as a result of the change in acidity and basicity acquired by these groups in the excited states [5–9]. Some pieces of research were done in these type of processes [6–9] and these works also focus on the utility of excited-state acid–base chemistry, i.e., how a change in acidity/basicity of a molecule in the excited-state can result in a new chemistry with examples of excited-state acid–base phenomena [4].

In an earlier communication [10], we discussed the structures and dynamical processes in the ground and excited states of 2-acetyl benzimidazole (2ABI) and 2-benzoyl benzimidazole (2BBI) in some nonpolar, polar, alcoholic and hydroxylic solvents at room temperature. Briefly, the investigation revealed that proton transfer reactions of the above-mentioned compounds undergo highly localized changes marked by the dependence on the kind of substitution on the benzimidazole ring. For both the molecules in the ground state, the intramolecularly hydrogen-bonded closed

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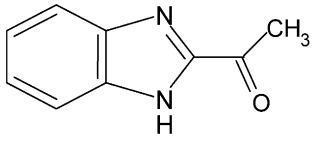
conformer (I) is the stable form in nonpolar solvents. This intramolecular hydrogen bond dissociates in polar and hydroxylic solvents due to solute–solvent interaction. The formation of zwitterionic species (III) of the closed conformer, as a result of ESIPT, is evidenced by Stokes-shifted fluorescence spectra in nonpolar solvents. In nonpolar solvent only one fluorescence band occurs due to intramolecular proton transfer. With increasing the 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. As the polarity of the solvent increases this interaction also increases, as a result the zwitterion becomes more unstable in more polar solvent. So the zwitterionic species (III) arise due to intramolecular proton transfer and another anionic species (IV) arise due to intermolecular proton transfer upon excitation of (I) [17]. The fluorescence quantum yields of both the compounds are dependent on the excitation wavelength but the fluorescence band positions are independent of it.

Solvent effects on proton transfer raise many interesting questions [11,12] concerning static and dynamic processes. Both the intermolecular and intramolecular proton transfers of aromatic molecules, which are hydrogen-bonded in the ground state, undergo significant changes depending markedly on the kind of substitution on the aromatic ring [13]. It has been noted that there are some differences in both the absorption and emission spectra of 2ABI and 2BBI depending upon the nature of the solvents in spite of the similarity in the molecular structure. There are many ESIPT processes involving the transfer of a proton from a hydrogen atom donor group (e.g. –OH, =NH, $–NH_2$ etc) to an acceptor group (=N–, .C=O etc) [14–16] but there is a significant change in the ESIPT process of heterocyclic molecules like 2-(2′-pyridyl)-benzimidazole [14], 7-azaindole [15] and 2-(2′-hydroxyphenyl)-benzimidazole [16].

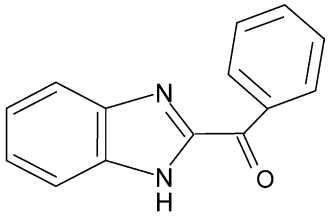
Even though ESIPT processes have extensively been investigated but most of the studies focus on proton transfer in non-aqueous non-alcoholic solvents. Photophysics and photochemistry of ESIPT in aqueous and alcoholic solvents are in general more interesting and complicated than in the other solvents [17,18]. 2ABI and 2BBI are the striking examples of such molecules showing different behavior in hydroxylic solvents from that in the other solvents [10]. To understand this different behavior of ESIPT in different environments, we will attempt in the present paper to get information on the photochemistry of 2ABI and 2BBI in basic and acidic solutions. It would be interesting to investigate the type of cation formed in the ground and excited states upon protonation since the molecules contain two basic nitrogen sites, the pyridinium type nitrogen atom and the pyrrole type nitrogen atom. The present work will also highlight the low temperature (77 K) study in order to identify the species responsible for low temperature emission for the two compounds and the substitution effect (ketomethyl and ketophenyl) in benzimidazole in the formation of such species.

2. Experimental details

The samples 2ABI and 2BBI were synthesized as reported before [10].



2-Acetyl-benzimidazole



2-Benzoyl benzimidazole

Methyl cyclohexane (MCH) (Fluka) was purified by nitration and sulfonation, dried over anhydrous sodium sulfate and distilled at 101 °C. Ethanol (EtOH), methanol (MeOH) and acetonitrile (ACN) (E. Merck, spectroscopic grade) were used as supplied but only after checking the purity fluorimetrically in the wavelength range of interest. Sodium ethoxide (NaEtH) was prepared in our laboratory with ethanol and sodium pellets. For aqueous solution, we used deionized Millipore water. β-cyclodextrin (β-CD) from Aldrich Chemical Company and H_2SO_4 (E. Merck, spectroscopic grade) were used as received.

The absorption spectra were taken with a Shimadzu UV–vis absorption spectrophotometer model UV-2401PC. The fluorescence and phosphorescence 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. The fluorescence lifetime measurement was done by time-correlated single photon counting coupled to a micro-channel plate photomultiplier (model 28090, Hamamatsu, Edinburgh Instrument). The phosphorescence lifetime (>μs) measurement was done by Hitachi F-4500 fluorescence spectrophotometer with chopper arrangement.

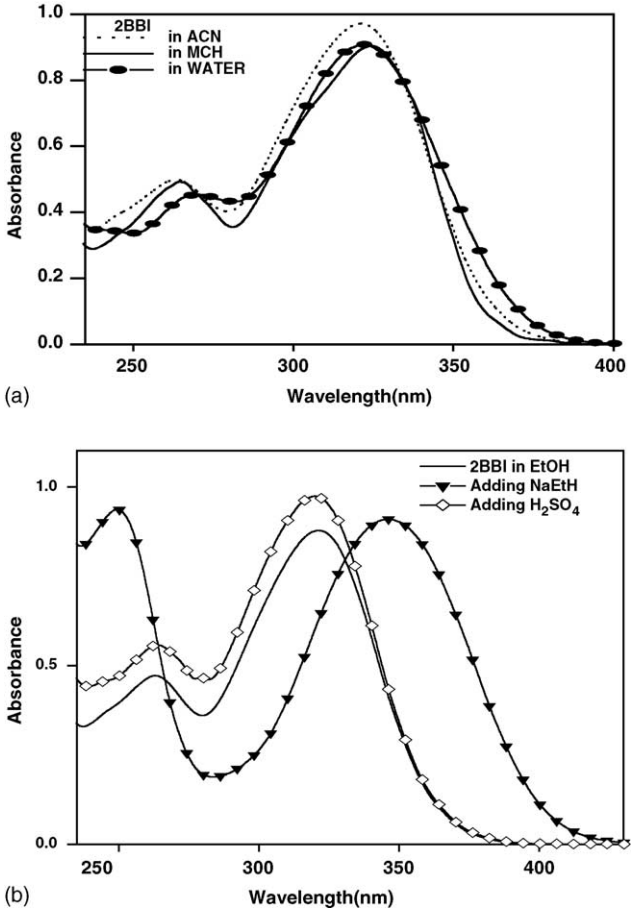


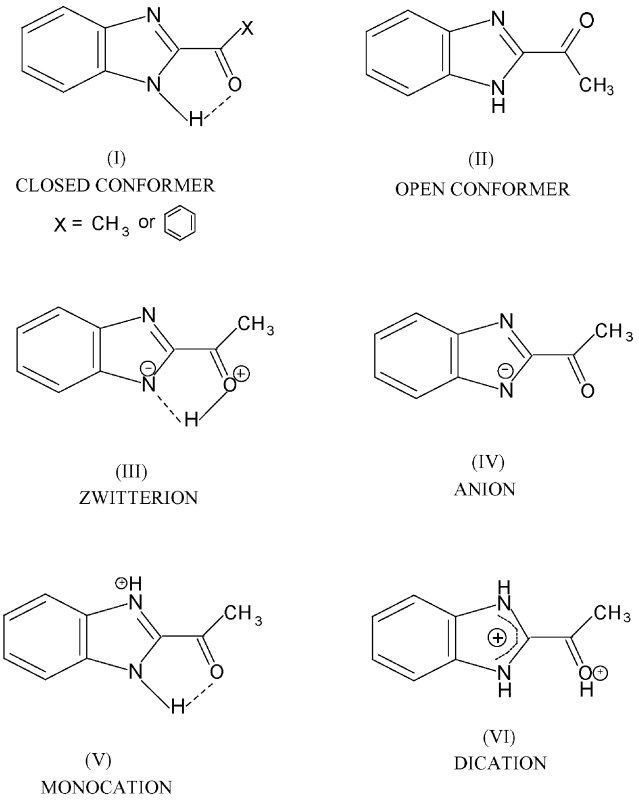
Fig. 1. (a) Electronic absorption spectra of 2BBI in various solvents (2BBI = 5×10^{-5} mol dm^{-3}), (b) electronic absorption spectra of 2BBI and in the presence and absence of base (NaEtH) and acid (H_2SO_4) in EtOH.

3. Results and discussion

3.1. Absorption

2BBI shows three band systems: one at 270 nm, another around 320–330 nm, and a shoulder at 370 nm (Fig. 1(a)) similar to 2ABI [10], The spectral change and presence of lower-energy shoulder in hydrocarbon solvents are due to ketophenyl (benzoyl) substitution as well as intramolecular hydrogen bonding between acid and base groups of the benzimidazole molecule [10,13,17–19]. Also it is important to note here that the red-shifted shoulder in hydrocarbon solvent and structureless tail possibly account for the ground state closed conformeric form (I) (Scheme 1). In alcoholic and aqueous solution, the lower-energy shoulder vanishes for both the molecules due to solute–solvent interaction and the spectrum consists of only two bands system.

The absorption spectrum of 2BBI in EtOH solution over a wide range of acidity is shown in Fig. 1(b). With the increase of acid (H_2SO_4) concentration, the lower-energy absorption band of 2BBI is shifted slightly towards higher wave numbers. So the acid dependent blue-shifted structure (Fig. 1(b))

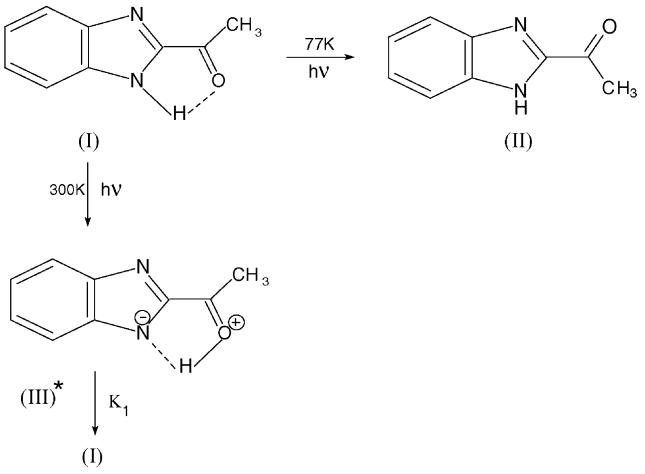


Scheme 1.

in the absorption band could be due to the formation of monocation (V) [20,21]. On further increasing the hydrogen ion concentration, no change occurs in the position and shape of the band. So we could not find any formation of dication in the ground state. The same type of effect was observed in the case of 2ABI where only band intensity decreases with increasing acid concentration. When the base concentration is increased in the EtOH solution of 2ABI and 2BBI, the lower-energy absorption band of both the molecules shifts considerably towards red. This red-shifted band system is due to the anion formation (IV). The pK_a's have been calculated using Förster cycle [19–21] with the wavelength at maximum absorption λ_{max} of 2ABI, 2BBI, their anion and their cation. In the case of 2ABI, the values of pK_a are 2.09 (from neutral to anion) and 1.04 (from neutral to cation) and those values for 2BBI are 3.27 and 1.13. These changes in the pK_a values in the ground state for the two molecules indicate the existence of two types of species. In aqueous solution for both the molecules with addition of β-CD, any change in the band position and intensity of the absorption spectra were negligible. So this confirms non-formation of inclusion complex with β-CD in the ground state.

3.2. Emission at room temperature

In hydrocarbon solvent, the fluorescence spectrum of 2ABI shows one distinct band peaking around 340 nm with a bathochromic shift (red shift) with solvent polarity. In



Scheme 2. Excited-state reaction scheme in hydrocabon solvent.

2BBI, this band is red-shifted to 350 nm [10]. In alcoholic and hydroxylic solvents, 2ABI shows two distinct fluorescence bands, one higher-energy band at ∼334 nm and another large Stokes-shifted lower-energy band at ∼445 nm. Similarly in 2BBI, the two bands occur at 350 and 500 nm [10]. The higher-energy band (340 nm for 2ABI and 350 nm for 2BBI) is considered to originate from ESIPT form of the molecules (III) (Schemes 1 and 2) and the lower-energy band at ∼445 nm is due to formation of anion (IV), which is due to the intermolecular proton transfer between solute and solvent in the excited-state [10]. The positions of fluorescence bands are independent of excitation wavelengths (Fig. 2(a)).

The effect of acid (H_2SO_4) on 2ABI in polar protic and hydroxylic solvents shows some interesting results. The spectral behavior of 2ABI in MeOH with addition of proton donor as acid shows (Fig. 2(b)) a high intense emission peak at ∼375 nm with a simultaneous decrease in intensity of lower-energy anionic emission peak. As the acid concentration is increased in MeOH solution, the intensity of lower-energy band is blue-shifted and the intensities at both of 334 and 455 nm decrease with appearance of a new band at 375 nm. The peak intensity at 375 nm remains fixed up to the acid concentration 0.001N (Fig. 2(b)). Increasing the acid concentration beyond this, an abrupt increase in the emission intensity of 375 nm peak takes place with total disappearance of 455 nm peak. These results indicate the first formation of monocation (V of Schemes 1 and 3) with initial addition of acid and subsequent addition of acid leads to formation of dication (VI of Schemes 1 and 3) of molecule due to protonation in both the sites.

In aqueous solution, 2ABI shows two fluorescence bands, one at 345 nm and another at 470 nm. With increasing acid concentration, the intensity of lower-energy anion band decreases with a blue shift and a new band arises around 385 nm. At the maximum acid concentration, the higher-energy band at 345 nm is totally obliterated (Fig. 3(a)). On the other hand in the case of 2BBI, addition of H_2SO_4 in water changes the fluorescence spectrum a lot. Only one band appears at

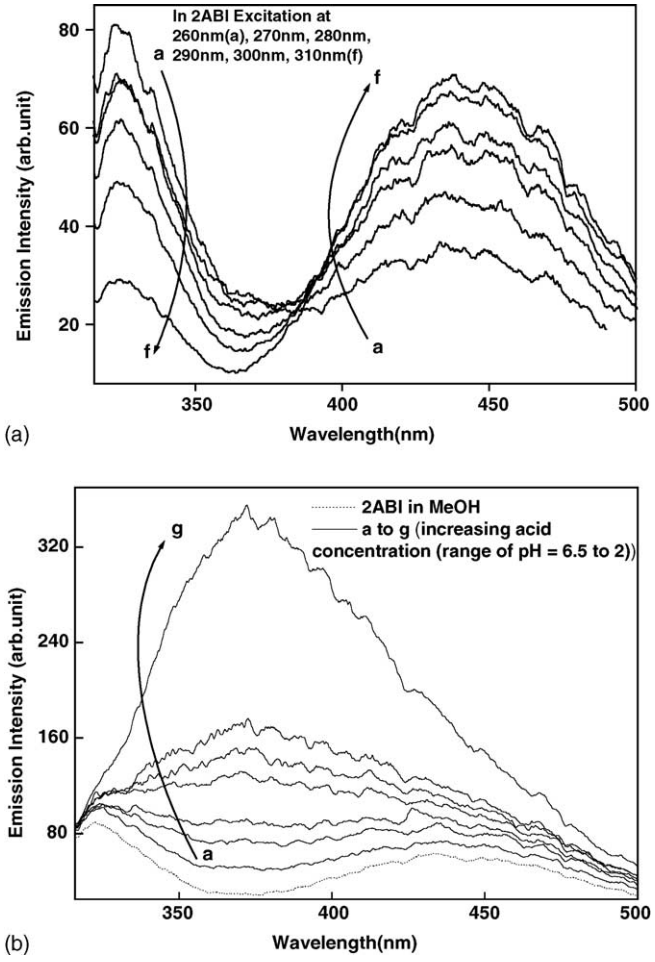
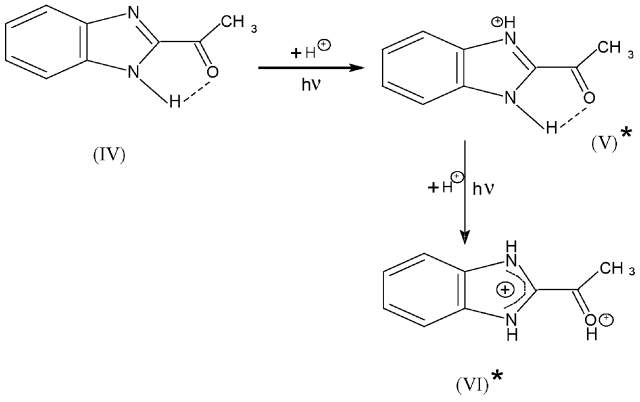
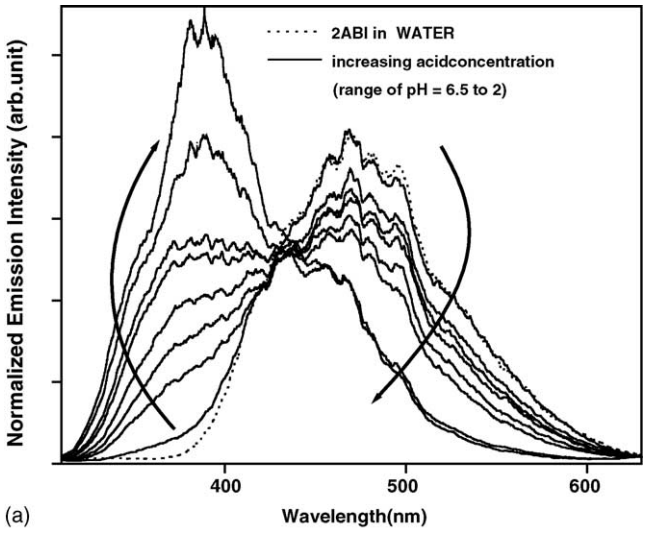


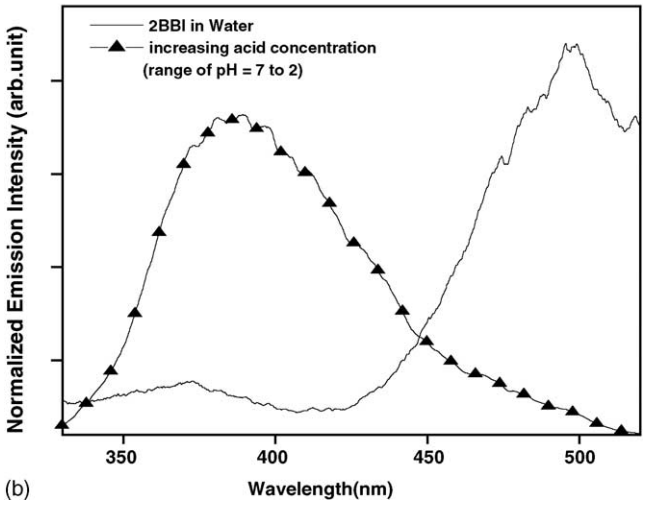
Fig. 2. (a) Fluorescence emission spectra of 2ABI in EtOH (excitation wavelength (λ_{exc}): 260 nm, 270 nm, 280 nm, 290 nm, 300 nm and 310 nm), (b) variation in fluorescence emission spectrum of 2ABI in MeOH by increasing the concentration of acid (H_2SO_4).

395 nm with comparatively higher intensity in acidic medium (Fig. 3(b)). The 2BBI spectrum at high acid concentration shows that appearance of 395 nm band is due to a protonated form. Complete suppression of anion band of 2BBI in acidic medium and formation of a largely blue-shifted



Scheme 3. Excited-state reaction scheme in acidic solution.





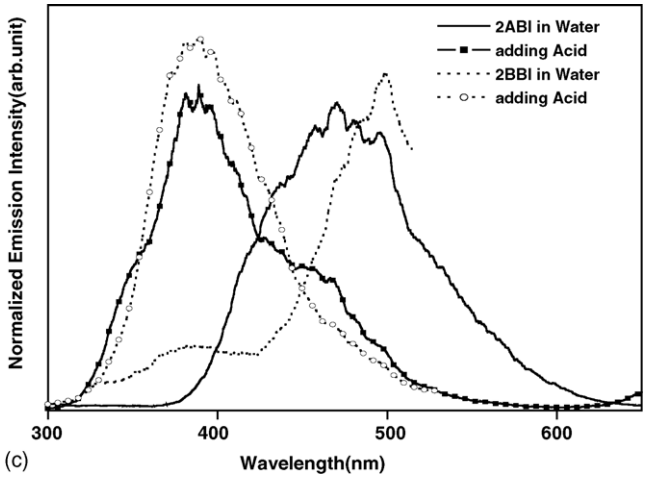


Fig. 3. (a) Fluorescence emission spectra of 2ABI in the presence and absence of acid (H_2SO_4) in aqueous solution, (b) fluorescence emission spectra of 2BBI in the presence and absence of acid (H_2SO_4) in aqueous solution and (c) fluorescence emission spectra of 2ABI and 2BBI in presence and absence of acid (H_2SO_4) in aqueous solution.

band (Fig. 3(b)) vis-a-vis the formation of shorter wavelength band in 2ABI along with a trace of anion band (with a blue shift) in acidic medium (Fig. 3(a)) point to higher rate of protonation in 2BBI than 2ABI. All the experimental data in the absorption and emission spectra for both the molecules show that pyridinium type nitrogen atom in 2ABI and 2BBI is generally less basic, and it becomes more acidic in its first electronically-excited states due to charge density decrement at this nitrogen atom, whereas the charge density increases in pyrrole type nitrogen and thereby rendering it more basic in its first electronically-excited singlet state.

Comparing the emission spectrum of benzimidazole [22,23] with that of 2ABI, the peak at ∼475 nm of 2ABI may be assigned to the fluorescence from the phenolate anion, the 334 nm peak may be assigned to that from zwitterion and the one at ∼385 nm may be assigned to that from cationic 2ABI (Schemes 2 and 3). Analysis of the alteration in peak intensity for both of the species as a function of acid/base variation indicates that the change in intensity solely occurs consequent upon the change in the excited state. We could not observe any spectral change in nonpolar solvents with addition of acid or base. This confirms that the intramolecular hydrogen bond is much stronger in 2ABI in the excited-state as the additives do not affect the molecular configuration in nonpolar medium.

The change in the fluorescence emission spectrum of 2ABI as a function of aqueous β-CD concentration is shown in Fig. 4(a). It is observed that, as the β-CD concentration is increased in the aqueous solution, the intensity of higher-wavelength (475 nm) anion band decreases along with an increase in the intensity of 334 nm zwitterion band. An iso-emissive point is also observed at 393 nm between the higher and lower-energy peaks. In both the bands, all the peak positions remain unchanged (Fig. 4(a)). To explain this phenomenon, we may propose that in aqueous medium the molecule faces a less polar environment inside β-CD cavity which causes the intermolecular proton transfer reaction between solute and solvent to decrease and consequently a change in intensity occurs [17]. Considering the molecular size of encapsulated 2ABI, the proton in the ≥N–H group may not be available for intermolecular hydrogen bonding in the bulk water. The appearance of iso-emissive point indicates the formation of a 1:1 host–guest type inclusion complex between β-CD and 2ABI molecule contrary to the ground state picture. In the event of formation of the 1:1 complex in the excited state, the Benesi–Hildebrand relation must be satisfied [24],

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

where I_0 and I_1 denote fluorescence intensity of the probe molecule in bulk water and in the complex, respectively, I is the fluorescence intensity at a given β-CD 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 $\{1/(I - I_0)\}$ versus $\{1/(\beta\text{-CD})\}$ should yield a straight

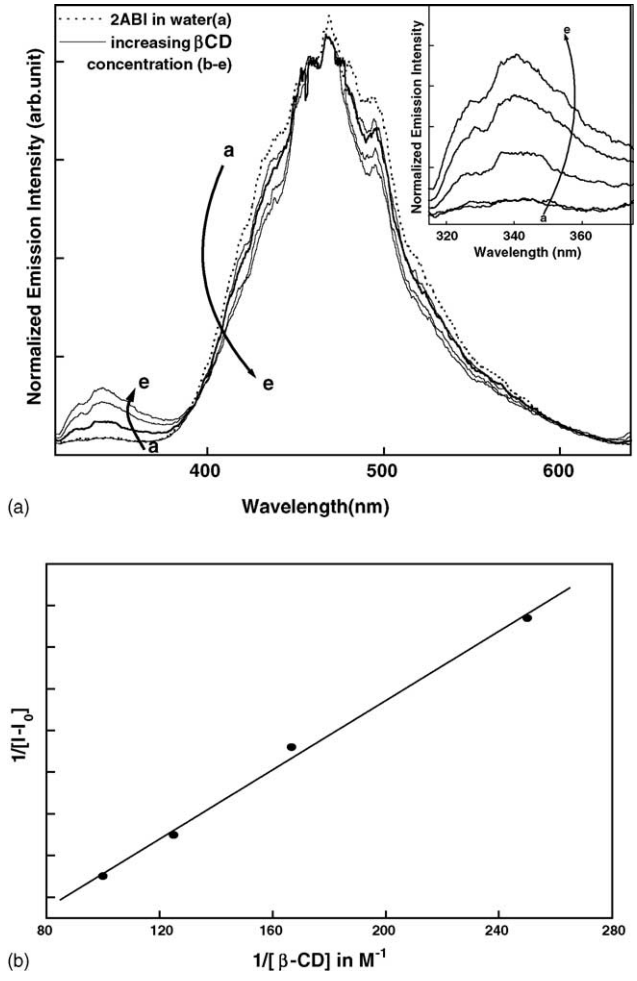


Fig. 4. (a) Fluorescence emission spectra of 2ABI with various concentration of β-CD in aqueous solution: (a) without β-CD (pure water), (b–e) 2.3 mM, 4 mM, 8 mM and 10 mM β-CD. Inset shows the spectral change of 2ABI in lower wavelength region with various concentrations of β-CD in aqueous solution. (b) $\{1/(I - I_0)\}$ vs. $\{1/(\beta\text{-CD})\}$ plot and the solid line corresponds to the fit to Eq. (1).

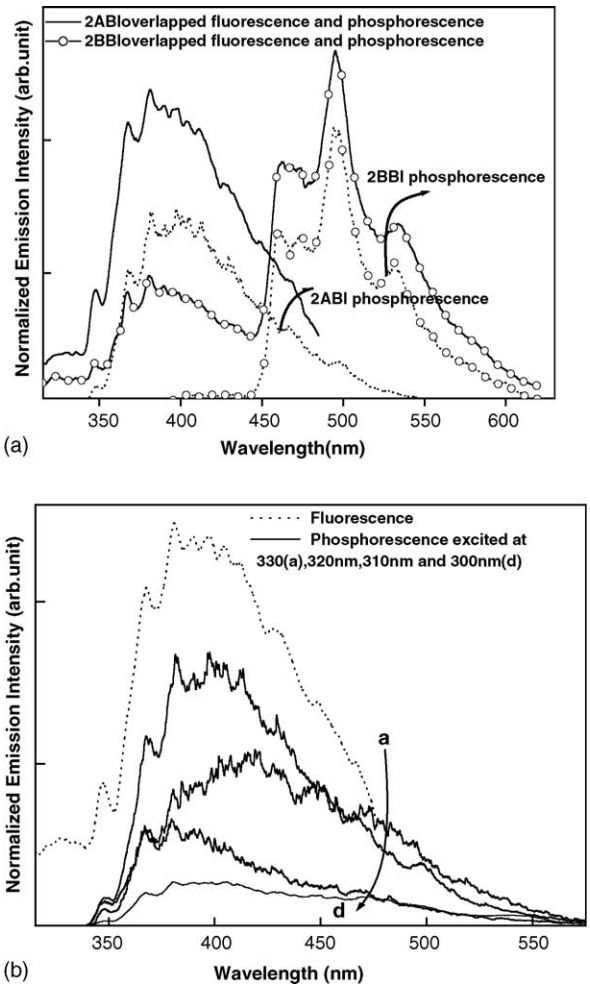


Fig. 5. (a) Emission spectra of 2ABI and 2BBI in MCH glass at 77 K, (b) emission spectra of 2ABI in MCH glass obtained at variation excitation wavelengths (λ_{exc}): 300 nm, 310 nm, 320 nm and 330 nm.

line [24,25]. Fig. 4(b) shows the plot for the complexation of 2ABI with β-CD, which confirms the 1:1 complexation between host and guest molecules in the excited-state and prevention of intermolecular hydrogen bonding [19].

3.3. Emission at 77 K

The emission spectra of 2ABI and 2BBI in hydrocarbon solvents consist of superimposed Stokes-shifted fluorescence and phosphorescence spectra. At 77 K the fluorescence and phosphorescence intensities are found to increase in all the solvents in comparison to those at room temperature. 2ABI shows a single band in 360–430 nm region, whereas 2BBI shows two bands one at 360–430 nm region and another at 460–520 nm region in MCH at 77 K (Fig. 5(a)). Contrary to the room temperature emission, an increase in λ_{exe} results in an increase in emission intensity at low temperature keeping the peak position unchanged (Fig. 5(b)). In 2ABI a phosphorescence band appears at 350–550 nm region. Since 2ABI shows an emission peak at ∼340 nm in MCH at room temperature so there must be an overlap of the fluorescence and phosphorescence bands at low temperature on longer wavelength side. In 2BBI two phosphorescence bands occur at ∼460 and ∼490 nm (Fig. 5(a)). As the two peaks are too close to each other these could be due to some vibronic effect. In polar solvent like EtOH, 2ABI shows superimposed Stokes-shifted fluorescence and phosphorescence but these bands are distinguished from each other (Fig. 6(a)) at ∼392 and ∼472 nm, respectively. In 2BBI at low temperature, only one phosphorescence band occurs in 450–500 nm region and the phosphorescence intensity is stronger than the fluorescence one. In the presence of a strong base, like sodium ethoxide, the intensity of longer wavelength phosphorescence band at ∼490 nm decreases (Fig. 6(b)) a lot than the fluorescence intensity.

The appearance of fluorescence in MCH indicates that the fluorescing species is not anionic in nature (Fig. 5(a)). The fluorescence intensity is decreased while the phosphorescence

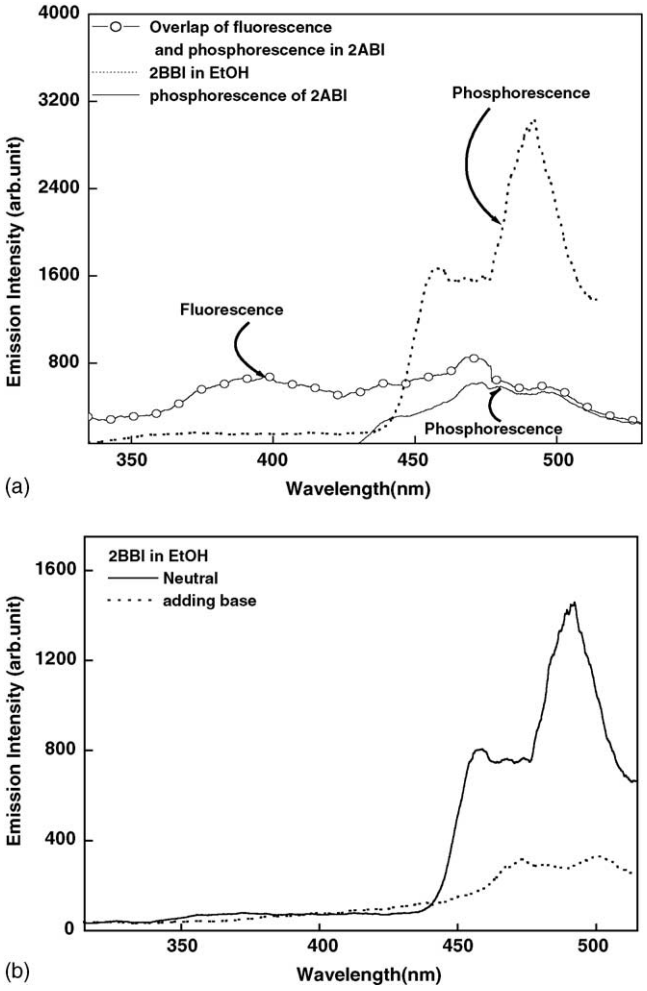


Fig. 6. (a) Emission spectra of 2ABI and 2BBI in EtOH glass at 77 K, (b) emission spectra of 2BBI in the presence and absence of base in EtOH glass at 77 K.

intensity is increased in EtOH (Fig. 6(a)). It seems that the fluorescence is converted to the phosphorescence by lowering the temperature to 77 K only in the case of 2BBI. The conversion of fluorescence into phosphorescence is relatively less efficient in 2ABI compared to that in 2BBI. The presence of the phosphorescence (Figs. 5 and 6) and the relatively long lifetime (τ_p) at low temperature compared to that of room temperature (τ_f) (Table 1) indicate the presence of active intersystem crossing from the excited singlet state to the excited triplet state during the proton transfer process of 2ABI and 2BBI. As was suggested by Nagaoka and co-workers [26,27] the phosphorescence is likely to appear from the intermolecularly hydrogen-bonded open conformer II (Schemes 1 and 2) due to rotation of >C=O group (Scheme 2). The conjugation of the phenyl ring with the benzimidazole ring in 2BBI is less than the conjugation of the $-CH_3$ with the benzimidazole ring in 2ABI, so there would be a propensity of rotation of ketophenyl moiety with respect to the benzomidazole plane in the case of 2BBI. Contrary to this, due to greater congujation in the case of 2ABI the ketomethyl group will be hindered to rotate with respect to the benzimidazole plane so it is obvious that the chance of formation of open conformer in 2BBI is more than 2ABI. So it is interesting to note that rotation of the keto group is involved in the conversion of fluorescence to phosphorescence. The fluorescence bands in 2BBI are considered to originate from the species, which is responsible for the room temperature fluorescence.

Table 1
Lifetime data for 2ABI and 2BBI at various solvents at room temperature and at 77 K

Solvent	Room temperature fluorescence lifetime (τ_f) [ns]		Low temperature phosphorescence lifetime (τ_p) [ms]	
	2ABI	2BBI	2ABI	2BBI
MCH	3.0	3.1	1800	224
EtOH	3.4	3.3	350	175

EtOH is a strong hydrogen bonding solvent to rupture the intramolecular hydrogen bond of the closed conformer of the excited-state and the formation of open conformer and anion [10] would follow it. We observe that with addition of base the phosphorescence intensity decreases, so we may conclude that in EtOH the large dielectric relaxation time does not allow the molecule to reorient and this induces the formation of deprotonated anion. So the conversion of anion as a result of proton dissociation is not possible and the presence of emission is due to the open conformer (II of Schemes 1 and 2).

The foregoing observation indicates that strength of intramolecular hydrogen bonds depends mainly upon the substitution on the >C=O group. This intramolecular hydrogen bond may be ruptured by the strong interaction with solvent. Once this bond is ruptured, the formyl group can rotate easily to form the open conformer and the phosphorescence may be observed. Experimental evidence explains the phenomenon of 2BBI by suggesting that the phosphorescence should be obtained from the open conformer [17], which may be formed due to rotation of carbonyl group (Schemes 1 and 2). This rotation is slower in 2ABI than in 2BBI, so the intensity of phosphorescence emission in 2BBI is more than that of 2ABI. In polar solvents, the phosphorescence intensity increases because the formation of the open conformer is favourable after irradiation [17]. In nonpolar solvents, the phosphorescence is weak but in polar solvents the phosphorescence is strong. This indicates that the intramolecular hydrogen bond of 2BBI is stronger in nonpolar solvents.

4. Conclusion

In summary, the change in pK_a values in the ground state indicates the existence of different species. For both the molecules, red-shifted fluorescence bands were observed in hydrocarbon (small red shift) and hydroxylic (large red shift) solvents. Besides the vibrational relaxation in the upper state, the excited Franck-Condon state is further stabilized to the equilibrium excited-state due to solvent relaxation. This is

more for the solvents of increased polarity as shown from the red shift in fluorescence band maximum. In acidic medium, 334 and 445 nm bands decrease and simultaneously a new band at ~375 nm gets pronounced due to monocation formation. Increasing further acid concentration, one band arises at 385 nm, possibly due to dication. These results reflect the existence of monocation and subsequent formation of dication due to protonation in the two sites. For 2BBI almost the same type of results were obtained in the excited-state at room temperature. The disappearance of anion band of 2BBI in water with addition of acid and appearance of new band at higher-energy side suggest at higher protonation in 2BBI than in 2ABI. For 2BBI, the rate of intermolecular proton transfer is very much higher compared to 2ABI. The effect of β-CD, while forms 1:1 complexation with both the molecules occurs only in the first excited state. The nonpolar cavity prevents the intermolecular hydrogen bonding due to the inclusion inside the cavity and consequently the anion band intensity decreases along with an increase in zwitterion band intensity. All the forms were depicted in different schemes.

In MCH rigid glass, 2ABI and 2BBI show Stokes-shifted fluorescence and phosphorescence at 77 K. In EtOH at low temperature, 2ABI shows both fluorescence and phosphorescence but 2BBI shows a high intense phosphorescence band alone. These results show that, in the case of 2BBI due to less conjugation of phenyl ring with benzimidazole ring, the benzoyl group rotates easily to form the open conformer. So the appearance of phosphorescence in MCH and EtOH glass was attributed to the formation of open conformer due to rotation of the acetyl and benzoyl groups. The phosphorescence intensity is increased in EtOH due to formation of intermolecularly hydrogen bonding.

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