ESPT of 2-(2′-Pyridyl)benzimidazole at the Micelle−Water Interface: Selective Enhancement and Slow Dynamics with Sodium Dodecyl Sulfate

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The effect of micellar environment on the excited state proton transfer (ESPT) of 2-(2′-pyridyl)benzimidazole (2PBI) has been investigated by steady state and time resolved fluorescence spectroscopy. The ESPT, which occurs to a rather small extent at pH 7, is found to be enhanced remarkably at the interface of sodium dodecyl sulfate (SDS) micelles and water. Such an enhancement is not observed for the cationic cetyl trimethyl ammonium bromide (CTAB) or neutral Triton X-100 micelles. This selective enhancement is explained in the light of a modification of pK_a and a more acidic local pH in the micelle−water interface. A rise time of about 890 ps is observed in the region of tautomer emission. The origin of this rise time is explored, considering three factors, namely, diffusion controlled protonation of the normal form of 2PBI, slow and possibly incomplete solvation of the transition state, leading to a slowing down of the proton transfer process and a similar slow dynamics of the tautomeric excited state.

Introduction

Proton and hydrogen transfer reactions in the excited state have potential applications in lasers, the photostabilization of polymers, and the development of fluorescence sensors and thus have generated a considerable amount of interest.[1−13] Recently, Klymchenko and Demchenko have performed an interesting study on the internal Stark effect on excited state intramolecular proton transfer (ESIPT) processes, where the presence of a positively charged substituent in the fluorophore, as well as its position, affects the extents of ESIPT processes remarkably.[2c] Excited state proton transfer (ESPT) in hydrogen bonded systems such as benzimidazoles, in particular, have been studied extensively.[5−8,9a] In the present study, we focus on a member of this class, namely, 2-(2′-pyridyl)benzimidazole (2PBI). The occurrence of ESPT in 2PBI has been known for quite some time, having been manifested for the first time in the quenching of its fluorescence by small amounts of alcohol in hydrocarbon solvents.[8] In more recent times, Rodríguez-Prieto and co-workers have reported a distinct dual emission in aqueous solutions, at acidic pH. The Stokes shifted emission peak has been ascribed to a solvent-assisted ESPT.[7a] It has been observed that even though the ESPT is predominant only for the cationic form of 2PBI, some emission from the proton transferred tautomer species is also obtained at pH 7.[7a] Interestingly, such ESPT is not observed in 3PBI.[7c] 4PBI, on the other hand, exhibits dual emission even at neutral pH.[7d]

Even though the photophysics of 2PBI and related compounds have been studied extensively in bulk liquids, there has been only one report on its ESPT in a restricted environment by Mukherjee and co-workers,[9a] where the inclusion of 2PBI in cyclodextrins is found to hinder ESPT in this fluorophore to some extent.[9a] This is explained by a shielding of the fluorophore from water, which hinders the solvent-mediated ESPT. This is an example of the changes in excited state processes that occur in restricted environments. Such effects have been reported for other compounds as well and are usually ascribed to the slow and often incomplete solvation in these microenvironments.[3a] It is well-known that the solvation dynamics in bulk water is ultrafast, but over the past decade, there have been several reports of slow solvation dynamics at micelle−water interfaces, studied primarily by time dependent Stokes shift of the emission spectra of fluorescent probes.[3d] This phenomenon has been explained by a dynamic exchange between the bound as well as free water molecules present at the interface.[3e] Such slow solvation has also been observed in other microheterogeneous media.[3f] The remarkable effects of the microenvironment on the extent and dynamics of excited state processes make them excellent tools for probing the local properties of microenvironments.[13] Hence, there has been considerable interest on ESPT and ESIPT in restricted geometries of cyclodextrins,[9] micelles,[10−11] reverse micelles,[12] and lipid bilayers.[13] For example, there was a very recent report by Bhattacharyya and co-workers on the ESPT from 8-hydroxypyrene-1,3,6-trisulfonate (pyranine) to acetate in cationic cetyl trimethyl ammonium bromide micelle.[10c] In this report, the bimolecular quenching constant for the proton transfer has been observed to be affected significantly by the microenvironment of the micelle. The observation has been explained in the light of a change in pK_a and an altered local pH at the micelle−water interface. Another set of studies that are closely related to the present one have been performed by Quina and co-workers, who have investigated the dynamics of ESPT in anionic micelles in detail.[11b,c] In summary, micelles are found to affect the ESPT process remarkably. In some cases, the effect is similar for all kinds of micelles, whereas, in some others, it is greater for some kinds of micelles than for others. Our motivation for the present study is to explore if a prominent ESPT emission of 2PBI can be brought about in the micellar media at neutral pH and, if it can be effected, then whether such a catalytic effect is specific to certain kinds of micelles, as observed for pyranine,[10c] or if it is the same in all kinds of micelles, as observed earlier for fluorophores such as 2-(2′-hydroxyphenyl)benzimidazole.[10a]

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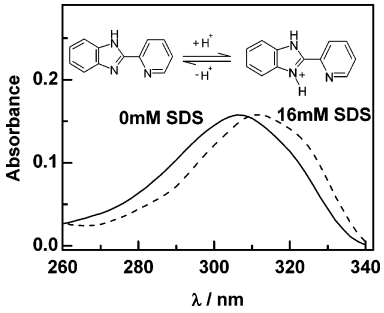


Figure 1. Absorption spectra of 1×10^{-5} M 2PBI in water at pH 7 (solid line) and 16 mM SDS (dashed line). The structures of 2PBI and its cationic forms are shown in the inset.

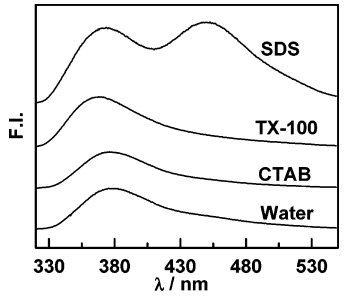


Figure 2. Fluorescence spectra of 2PBI in water and pH 7, 2.5 mM CTAB, 1 mM TX-100, and 16 mM SDS. $\lambda_{ex} = 295$ nm. The spectra are normalized at the peak and are provided with appropriate vertical offsets for the sake of clarity.

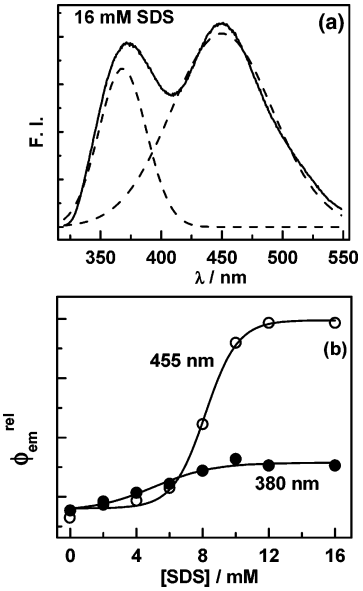


Figure 3. (a) Components of the fluorescence spectrum of 2PBI in the presence of 16 mM SDS, with peaks at 380 and 455 nm. The experimentally obtained spectrum is shown by solid lines, and the components are shown by dashed lines. (b) Variation of the relative fluorescence quantum yields of the components with the concentration of SDS.

Experimental Section

2-(2′-Pyridyl)benzimidazole (AR grade), sodium dodecyl sulfate (SDS), and cetyl trimethyl ammonium bromide (CTAB) (AR grade) from Aldrich have been recrystallized from methanol−water solutions. Triton-X 100 (TX-100) (AR grade) from Aldrich has been used as received. The concentration of 2PBI used is 10 μM. The absorption spectra have been recorded on a JASCO V570 spectrophotometer with a 2 nm band-pass. Steady state fluorescence spectra have been recorded using a Perkin-Elmer LS-55 spectrofluorimeter with $\lambda_{ex} = 305$ nm. Fluorescence decays have been recorded on an Edinburgh TCSPC spectrometer, with $\lambda_{ex} = 295$ nm, obtained from the third harmonic of a mode-locked Ti:sapphire laser from Coherent Inc., Palo Alto, CA.[14a] The fluorescence decays have been collected with the emission polarizer at a magic angle of 54.7° and have been fitted to single or multiexponential functions after deconvolution by the iterative reconvolution method using IBH DAS 6.0 software.[14b] To construct the time resolved emission spectra (TRES), the fluorescence decays of 2PBI across the emission spectrum (350−500 nm) have been recorded at intervals of 10 nm. The fitted fluorescence decays have been scaled with the steady state fluorescence intensities following the usual procedure. The spectra thus generated have been fitted to a sum of two Gaussian functions and are normalized to unit area to generate the time resolved area normalized emission spectra (TRANES).

Results

Steady State Absorption and Emission Spectra. The ground state absorption maximum of 2PBI in aqueous solution at pH 7 is at ∼308 nm, which is close to that reported earlier.[7a,9a] A slight red shift is observed upon addition of SDS (Figure 1), as was observed with α-CD, indicating an incorporation of the fluorophore in the restricted environment.[9a] The excitation spectra of 2PBI are identical to the corresponding absorption spectra. The steady state emission spectrum in water has a maximum around 380 nm (Figure 2). The spectrum is rather broad and can be resolved into two components, with maxima at 380 and 455 nm, similar to the observation of Rodríguez Prieto and co-workers.[7a] The peak position remains practically unchanged upon addition of SDS up to the concentration 6 mM, beyond which a new prominent Stokes shifted peak appears at ∼455 nm (Figure 2). All the spectra can be resolved into the two components mentioned above. The spectrum at a SDS concentration of 16 mM is shown in Figure 3a, along with the components. The relative quantum yields of both of the components increase with SDS concentration, with a sharp jump at ∼8 mM SDS, which is the critical micelle concentration (cmc). The increase in the fluorescence quantum yield of the 455 nm band is substantially more than that of the 380 nm band (Figure 3b). The absorption spectra of 2PBI in CTAB (positively charged) and TX-100 (neutral) remain unchanged and are identical to the excitation spectra. Unlike in SDS, there is no prominent dual fluorescence even beyond the cmc in these surfactants.

Time Resolved Measurements. In aqueous solution at pH ∼ 7, 2PBI exhibits a biexponential decay at 380 nm, with components of 60 ps ($a_1 = 0.9$) and 900 ps ($a_2 = 0.1$) (Table 1, Figure 4a). The decay at 455 nm is also biexponential, with time constants of 60 ps ($a_1 = 0.9$) and 1780 ps ($a_2 = 0.1$). These results are in good agreement with earlier reports.[7a] Upon addition of CTAB and Triton-X 100, there is no significant change in the time constants and amplitudes, except for an increase in the longer time constant at 455 nm from 1.8 to 2.7 ns in Triton-X 100. The fluorescence decays of 2PBI at 380 nm are biexponential for all concentrations of SDS. The shorter time constant increases gradually to 0.09 ns at a SDS concentration of 8 mM. There is a jump in the value at this point (cmc) to 0.25 ns. The amplitude decreases progressively, with a jump at the same concentration (Figure 5a). An exactly opposite trend is obtained for the amplitude of the longer lifetime (Figure 5a), whereas the lifetime itself remains more or less constant for all concentrations of SDS (Table 1). The 60 ps component at λ_{em}

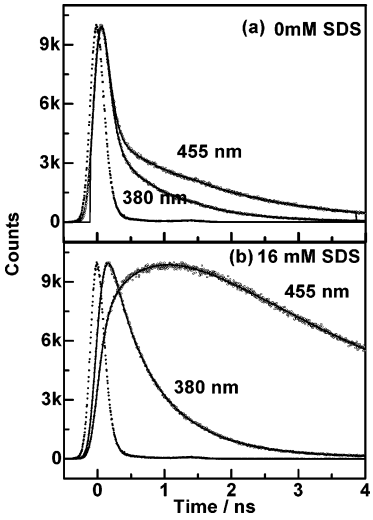


Figure 4. Fluorescence decays of 2PBI at $\lambda_{em} = 380$ and 455 nm in (a) aqueous solution at pH 7 and (b) 16 mM SDS. $\lambda_{ex} = 295$ nm, and the resolution is 4.9 ps per channel. The instrument response functions are shown by dotted lines.

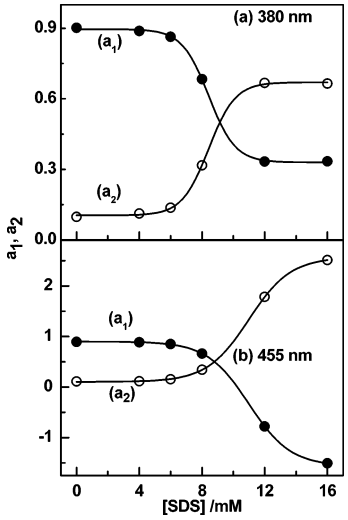


Figure 5. Variation of the amplitudes of the two components of biexponential fits to the fluorescence decays of 2PBI in SDS with the concentration of the surfactant. $\lambda_{em} = 380$ nm in the upper panel and 455 nm in the lower panel.

TABLE 1: Temporal Characteristics of 2PBI in Aqueous Solution at pH 7, in the Absence and Presence of Surfactants

	$\lambda_{em} = 380$ nm					$\lambda_{em} = 455$ nm				
[surfactant] (mM)	τ_1 (ns)	τ_2 (ns)	a_1	a_2	χ^2	τ_1 (ns)	τ_2 (ns)	a_1	a_2	χ^2
Aqueous Solution, pH 7										
0	0.06	0.90	0.90	0.10	1.15	0.06	1.78	0.90	0.10	1.04
CTAB										
0.8	0.06	0.90	0.90	0.10	1.11	0.06	1.80	0.90	0.10	1.07
2.5	0.09	0.90	0.90	0.10	1.20	0.07	1.63	0.90	0.10	1.11
TX-100										
0.2	0.06	0.90	0.90	0.10	1.09	0.06	1.80	0.90	0.10	1.09
1.0	0.07	0.90	0.84	0.16	1.16	0.06	2.72	0.80	0.20	1.20
SDS										
4	0.08	0.88	0.89	0.11	1.04	0.06	1.78	0.89	0.11	1.15
6	0.08	0.86	0.86	0.14	1.15	0.07	1.66	0.85	0.15	1.20
8	0.09	0.87	0.70	0.30	1.20	0.06	3.08	0.66	0.34	1.10
12	0.25	0.82	0.30	0.70	1.13	0.82	3.64	−0.80	1.80	1.15
16	0.36	0.83	0.33	0.66	1.17	0.89	3.49	−1.50	2.50	1.02

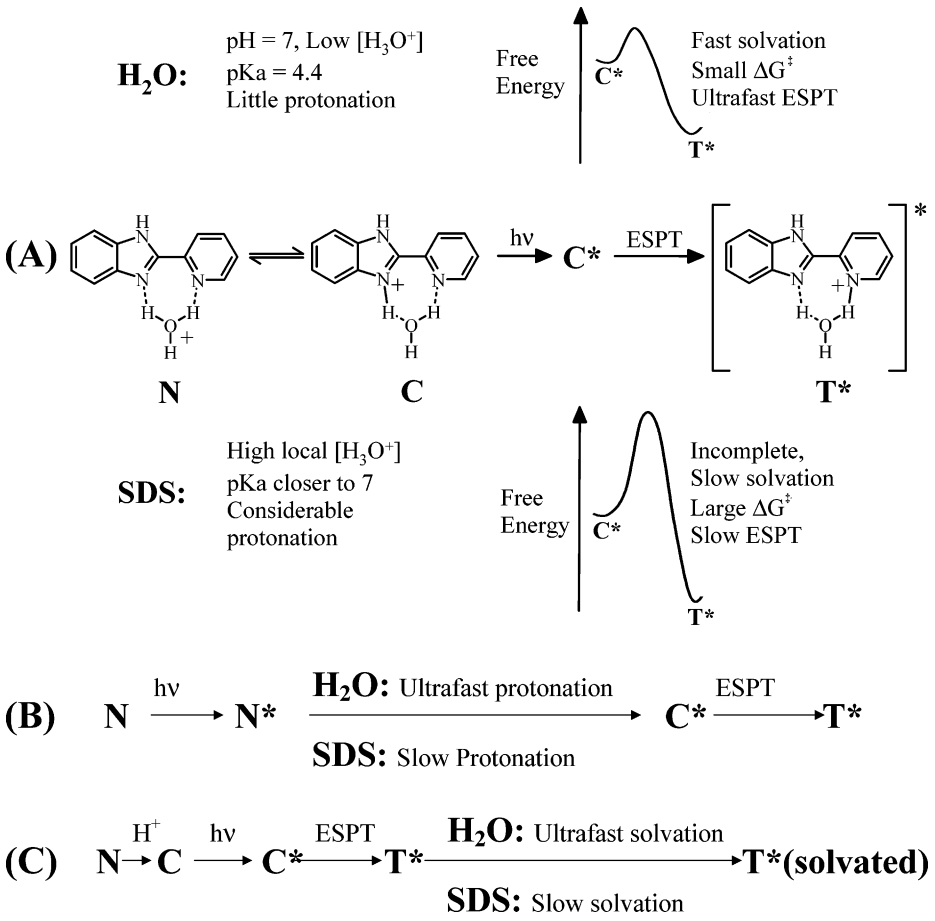
$= 455$ nm remains unaltered until the cmc of SDS. Subsequently, it disappears and a rise time of 800−900 ps sets in (Figure 4b, Table 1). The longer lifetime increases gradually to 3.49 ns. The amplitudes of both of the components exhibit variations similar to those for $\lambda_{em} = 380$ nm (Figure 5b).

Discussion

No evidence of the incorporation of 2PBI in CTAB or TX-100 micelles is obtained, as the absorption and emission spectra of 2PBI are unchanged in the presence of these micelles The prominent Stokes shifted emission peak that appears upon addition of SDS can be easily identified with the tautomer emission.[7a] Thus, the inference that one can draw immediately is that SDS micelles promote the ESPT process and lead to the formation of the tautomer in the excited state. Generally, an enhancement in ESPT is observed due to the protection of the fluorophores from water, which can often stabilize conformers that do not undergo ESPT, through the formation of hydrogen bonds.[9b−12] However, in that case, the effect should show up for all micelles and not be specific to any one kind. In the present study, the ESPT is promoted only in the anionic SDS micelle and not in the cationic CTAB or the neutral Triton-X 100. Moreover, ESPT in 2PBI is solvent mediated and requires a protic solvent molecule.[7a] Thus, protection from water is more likely to hinder and not augment the ESPT process, similar to what is observed in cyclodextrins as compared to water at pH $\sim$ 3.8.[9a] At this point, it is useful to recall that ESPT is prominent only in the cationic and not the neutral form of 2PBI.[9a] Since a strong electrostatic attraction exists between the cationic form of the fluorophore and the anionic headgroup of the SDS, this must be a crucial factor that influences the enhancement of ESPT in this surfactant and not in the cationic CTAB or the neutral TX-100. Such specific electrostatic interactions are known to affect the excited state processes rather remarkably.[11b,c,15]

It is well-known that SDS micelles have a local pH that is less than 7, as the hydronium ions of water are attracted toward the negatively charged Stern layer and are distributed to a greater extent in the vicinity of this layer.[16] This effect has earlier been cited to explain the dynamics of proton transfer in micelle−water interfaces.[10c,11b,c] In the system at hand, the increased local acidity can cause the protonation of 2PBI in the Stern layer and the cations thus formed can undergo ESPT to give rise to the tautomer emission. An alternative scheme could involve a change in the pK_a of 2PBI in the presence of SDS (Scheme 1A). It has been reported earlier that some tautomer emission is present even at pH 7.[7a] In the present study, the fluorescence quantum yield of the proton transferred tautomer is found to have a small, but nonzero value even in the absence of surfactants (Figure 3b). This lends some support to the contention about the presence of small amounts of the tautomer at pH 7, as the ESPT can occur only from the excited state of the cationic form.[7a,9a] Upon addition of SDS, it is most likely that these cations distribute themselves preferentially near the Stern layer, much like the hydronium ions of water. This would disturb the equilibrium in the aqueous phase, causing more 2PBI cations to form. These newly formed cations, in turn, would get associated with the Stern layer. A few cycles of this process could lead to a substantial amount of cations to be formed and, consequently, an enhanced ESPT. In summary, the selectivity of the enhancement of the ESPT emission in SDS can be rationalized by either considering the more acidic local pH at the interface of the SDS micelle and water or modifying the pK_a of 2PBI. Both of these phenomena can lead to an increase in the concentration of the cationic form of 2PBI near the

SCHEME 1



interface. This, in turn, causes an enhancement of the emission from the tautomeric state. Both of the phenomena can be ruled out for the cationic CTAB and the neutral TX-100, and this explains the absence of dual emission in these micelles. Now, the issue that should be addressed is that of the dynamics of the excited state processes involved. This requires a careful analysis of the time resolved data, a discussion of which is provided in the next couple of paragraphs. This discussion is also found to substantiate the hypothesis about the enhancement of ESPT proposed in the previous paragraph.

As mentioned earlier, our time resolved data in aqueous solution without surfactant match those obtained by Rodríguez Prieto and co-workers.[7a] Thus, the 60 ps component, which is the predominant one in the decays of fluorescence in neat water at 380 as well as 455 nm, is ascribed to the normal emission of 2PBI. The 900 ps component is very close to the 700 ps one obtained earlier and is identified with the emission from the cationic form, which also emits at 380 nm. The 1.78 ns component at 455 nm is identified with the emission from the tautomer. The slight differences from the values obtained by earlier workers is probably because we performed the experiment at a resolution of ~5 ps per channel, with excitation by a femtosecond pulsed titanium:sapphire laser, whereas the earlier studies were performed at a lower resolution, with excitation by nanosecond pulsed flashlamps. Notably, the relative contribution of the shortest component exhibits a sigmoidal decrease with the increase in surfactant. At the same time, the relative contribution of the emission from the cationic form increase sigmoidally. Both of the curves have points of inflection around the cmc of SDS (Figure 5a, Table 1). This indicates a decline in the population of the normal species with respect to that of the cationic one upon binding with micelles. If this is true, then the increase in fluorescence quantum yield with SDS concentration (Figure 3b) must be due to an increase in the radiative lifetime. Indeed, the shortest time constant of the 380 nm emission increases from 60 ps to ~80−90 ps upon addition of surfactants below the cmc and exhibits a sudden jump to 250−360 ps after the cmc. The increase in fluorescence quantum yield as well as the radiative lifetimes of the 380 nm emission can be rationalized in the light of an increase in the population of the cationic species compared to the normal species. As has been reported earlier, the fluorescence quantum yields of the normal and cationic forms, both of which emit around 380 nm, are 0.045 and 0.090, respectively, and the radiative lifetimes are 60 and 800 ps, respectively.[9a] According to our hypothesis, upon addition of SDS, the concentration of the cationic form increases at the expense of that of the normal form. This is expected to be accompanied by an increase in fluorescence quantum yield as well as the radiative lifetimes. A further increase in lifetimes can arise due to the relatively nonpolar environment experienced by the fluorophores in the micelle. Thus, we find that the temporal characteristics of the 380 nm emission support the contention, derived from the steady state data, about the increase in the concentration of the cationic species near the micelle−water interface in the case of SDS.

In the absence of SDS, when the emission at 455 nm is rather weak, the 60 ps component is the major one at this emission wavelength as well. As the fluorescence intensity increases upon addition of SDS, it vanishes and is replaced by a rise time of 0.8−0.9 ns. The 1.78 ns component, that is the minor one in the absence of SDS, becomes the major decay component and is slowed to a saturation value of ~3.5 ns at 16 mM SDS (Table 1). Since this component is due to the emission from the proton transferred tautomeric state, this is in agreement with the

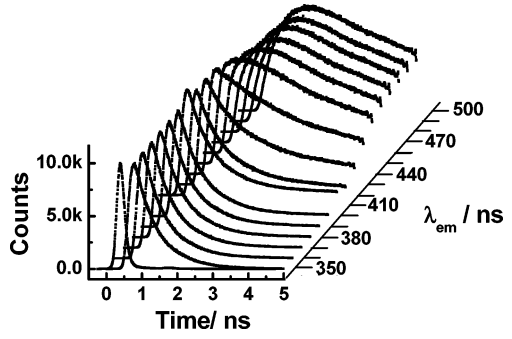


Figure 6. Fluorescence decays of 2-PBI in 16 mM SDS at different wavelengths. The range of wavelengths is 350−500 nm, and the interval is 10 nm.

increase in the ESPT emission. The rise time of ∼0.8−0.9 ns now needs to be accounted for. The magnitude of the rise time practically matches that of the decay time of the cationic form of 2PBI. As the ESPT takes place from this form, it is tempting to assign the time constant to that of the ESPT process. This is not unreasonable, as, even though ESPT is generally ultrafast and is associated with time constants of a few picoseconds in most cases, it can occur at longer time scales if the process involves some long range motion of the solute.[3−5,10c,17] For example, in perylene quinones such as hypocrellins A and B and calphostin C, a viscosity dependent time constant of the order of 100 ps is observed for the ESIPT process and is associated with the change in conformation of a seven-membered ring or the long range motion of a long side chain.[17] Besides, the time constant may be slowed due to an incomplete solvation of the highly polar transition state involved in the process, as is manifested in the long rise time in the emission of the deprotonated form of pyranine in CTAB.[10c] The long rise time of the tautomer emission in the present study can also be explained by a similar argument, that involves a slowing down of the ESPT process due to an increase in the reaction barrier due to slow and incomplete solvation (Scheme 1A). However, there are other possibilities that cannot be ruled out. For example, if protonation of the excited state of the normal form is involved, then the process can become diffusion controlled. In that case, formation of the cationic excited state can get slowed (Scheme 1B). As the ESPT takes place from the cationic excited state, it would also get slowed and a slow rise time in the ESPT emission would show up. This situation would be somewhat similar to the slow dynamics of deprotonation of a photoacid, studied by Quina and co-workers.[11c] It is also possible that the ESPT process is ultrafast even in SDS and it is the tautomer that undergoes slow solvation at the micellar interface (Scheme 1C). There have been reports where the emission from the proton transferred state has been enhanced, but no long rise time has been obtained.[10a] The mechanism involving the excited state protonation of the normal form can be eliminated right away, as it would involve a rise time in the emission of the cationic form and no such rise time is observed in the wavelength range 350−440 nm (Figure 6). However, it is not easy to choose between the mechanisms involving a slowing down of the ESPT process and that of slow solvation of the tautomeric excited state. In reality, both of the mechanisms can operate simultaneously. One needs to perform femtosecond experiments to settle this issue conclusively, but in the following paragraph, we present an attempt to address it with the data that we have, using the method of time resolved area normalized emission spectroscopy (TRANES).[18]

The phenomenon of the evolution of emission spectra with time can indicate two distinct kinds of dynamics of the emissive

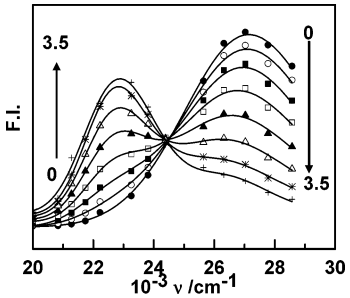


Figure 7. Time resolved area normalized emission spectra of 2PBI in 16 mM SDS solution, between time zero and 3.5 ns at intervals of 0.5 ns. The arrows indicate the direction of increase in time.

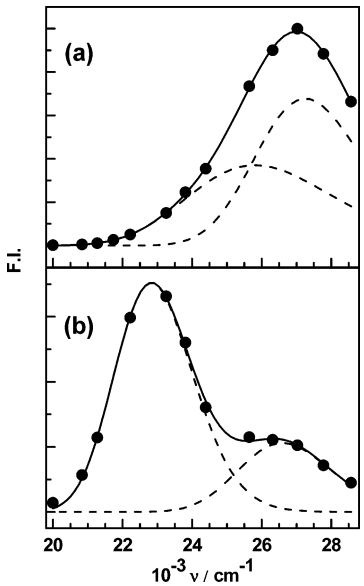


Figure 8. Components of TRANES of 2PBI in 16 mM SDS solution at time (a) zero and (b) 3.5 ns after excitation. The fits are shown by solid lines, and the components, by dashed lines.

state: a two-state process or a continuous time evolution like dynamic solvation. It is often difficult to distinguish between the two situations, and it is here that TRANES are more useful than the more conventional peak normalized time resolved emission spectra (TRES). Periasamy and co-workers have developed this technique and have established that an isoemissive point in TRANES indicates the presence of two distinct emissive species.[18a−c] In the present study, the TRANES of 2PBI in a SDS micelle exhibit two prominent peaks in the region of the normal and tautomer emission. A clear isoemissive point is obtained at 24 440 cm^{-1} (Figure 7). The spectra can be resolved into two components, the redder one of which can be assigned to the tautomer emission. (Parts a and b of Figure 8, for example, respectively show the spectra at time zero and 3.5 ns after excitation, along with the components.) With the passage of time, the band at 22 800 cm^{-1} is clearly seen to grow at the expense of the one at 27 100 cm^{-1}. Since the component at the lower energy grows from that at the higher energy, they can be ascribed to the emissions from the tautomeric and cationic excited states, respectively. A small time dependent Stokes shift (TDSS) is observed for the cationic emission over a period of 2 ns, while the TDSS of the tautomer peak is quite significant (Figure 9). This is clearly a signature of dynamic solvation of the tautomeric form, T*, after it is formed by the ESPT process. Thus, some amount of the rise time observed at 455 nm must be due to the slow solvation of T*. Moreover, the intensity of the tautomer band at time zero is considerable (Figure 8). This cannot arise from tautomer emission from free 2PBI molecules

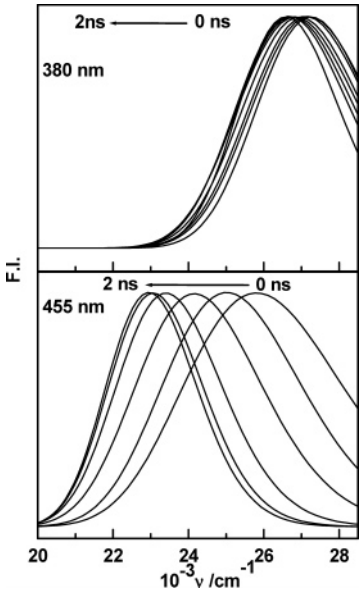


Figure 9. Time evolution of emission spectra. The upper panel contains the peak normalized, time resolved emission spectra of 2PBI in 16 mM SDS in the region of normal emission, and the lower panel contains those in the region of tautomer emission. The times are 0, 0.1, 0.5, 1, 1.5, and 2.0 ns in all cases. The arrows denote the direction in which time increases.

for two reasons. First, all the emission parameters saturate at a concentration of 16 mM SDS, indicating a total binding of 2PBI at this surfactant concentration (Figures 3b and 5). Besides, the 60−80 ps component that characterizes the normal emission of free 2PBI at 455 nm is absent at this surfactant concentration (Table 1). Thus, there is a considerable amount of ESPT within the zero time of our experiment or, in other words, the ultrafast component of ESPT is present even in micellar solutions. Of course, the mechanism involving the slowing down of the ESPT process itself is also operative, as the TRANES in the time range 0−3.5 ns show an isoemissive point, indicating that the ESPT from the cationic species to the tautomeric species is in progress in this time range as well. Thus, we find that the TRANES analysis of the data indicates that the rise time of the tautomer emission is most likely to be a convolution of both of the mechanisms discussed above.

Conclusion

The extent of ESPT of 2PBI at neutral pH is found to be enhanced in the presence of SDS micelles. This phenomenon is absent in CTAB and Triton-X 100. The enhancement in tautomer emission can be explained in two ways, either by considering a decreased local pH at the SDS micelle−water interface or by considering a mechanism by which SDS alters the pK_a of 2PBI. It is most likely that both of the effects contribute to the enhancement of ESPT. The origin of the 890 ps rise time, in the tautomer emission, has been explored by time resolved area normalized spectroscopy. It has been ascribed to a convolution of two factors. The first of these is the slow and incomplete stabilization of the transition state involved in the ESPT process, causing an increase in the reaction barrier, and the second one is the dynamic solvation of the tautomeric species formed by ESPT. A summary of the possible contributions to the slow rise time in the tautomer emission is provided in Scheme 1.

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