THE JOURNAL OF PHYSICAL CHEMISTRY B

ARTICLE

pubs.acs.org/JPCB

Modulation of Ground- and Excited-State Dynamics of [2,2′-Bipyridyl]-3,3′-diol by Micelles

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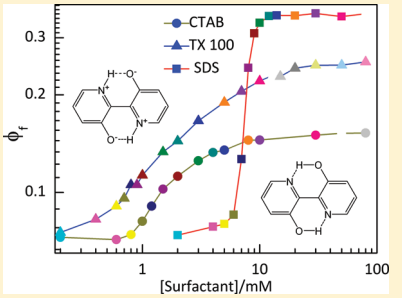
Supporting Information

ABSTRACT: The binding of [2,2′-bipyridyl]-3,3′-diol ($BP(OH)_2$) with ionic and n eutral surfactants like cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and Triton X-100 (TX-100) has been studied by steady-state and time-resolved fluorescence spectroscopy. The absorption as well as emission spectra of $BP(OH)_2$ are highly sensitive toward the variation of surfactant concentration and hydrophobicity of the environment. The fluorescent state of the diketo form gains stability in surfactant assemblies, leading to a red-shifted emission spectra. A sharp increase in the fluorescence quantum yield near critical micellar concentration (CMC) is encountered followed by saturation. This indicates a complete encapsulation of $BP(OH)_2$ in the micelles. The maximum fluorescence quantum yield in anionic SDS is rationalized by the formation of cationic fluorophore at the Stern layer. The increase in quantum yield in neutral TX-100 is attributed to higher microviscosity experienced by the fluorophore in the palisade layer. A direct support in favor of this argument in TX-100 is provided by the viscosity dependence exhibited by the probe in different concentrations of sucrose solutions. CTAB exhibiting only hydrophobic effect shows least increase in qunatum yield of $BP(OH)_2$ among all the surfactants. Time-resolved fluorescence study of $BP(OH)_2$ in micelles is used as a tool to monitor the extent of micellization in the lipophilic cavity. An increase in fluorescence quantum yield as well as lifetime of $BP(OH)_2$ upon micellization indicates an enhanced extent of ESIDPT in hydrophobic medium.



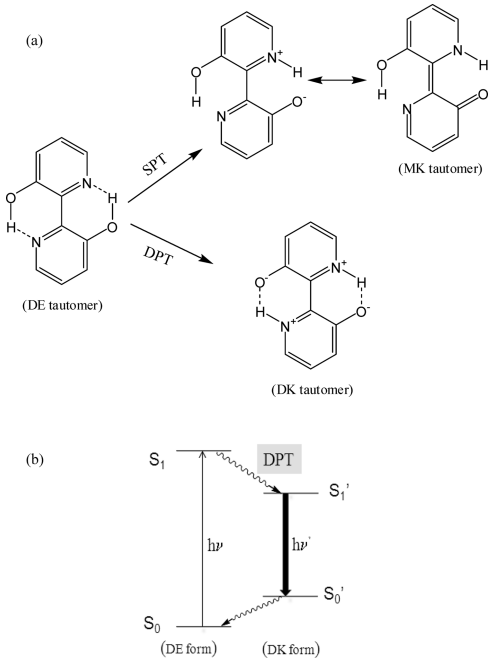
INTRODUCTION

Proton transfer in the excited state has attracted a lot of attention for years.[1−4] Depending upon the molecular structure, the proton transfer can be intermolecular as well as intramolecular. 7- Azaindole dimers,[5,6] 3-hydroxyflavone,[7] hydroxyarenes (ROH) like naphthols,[8−10] phenols,[8] hydroxyquinones,[11,12] pyranine,[13,14] and their derivatives exhibit interesting excited-state proton-transfer dynamics. Such excited-state dynamics are often governed by the properties of the microenvironment of the fluorophore and so these fluorophores can be used as probes in microheterogeneous media.[15,16] [2,2′-Bipyridyl]-3,3′-diol ($BP(OH)_2$) is one such fluorescent molecule which exhibits excited-state intramolecular double proton transfer (ESIDPT)[17] (Scheme 1). This molecule is reported to be planar with two strong intramolecular hydrogen bonds in its dienol tautomeric form (DE) by single-crystal X-ray analysis,[18] and this form exists in all nonaqueous solvents.[19] The three possible tautomers of $BP(OH)_2$ are (i) the dienol tautomer (DE), (ii) the monoketo tautomer (MK) generated via a single proton transfer, and (iii) the diketo tautomer (DK) arising through a double proton transfer (Scheme 1a). The strong green fluorescence observed in $BP(OH)_2$ is attributed to its zwitterionic diketo tautomer[17] generated via ESIDPT from its dienol tautomer (Scheme 1b). Both the dienol and diketo tautomer have negligible singlet excited-state dipole moments while that for monoketo tautomer is 4.0−4.9 D.[20,21] Electrooptical measurements[20] and computational calculations[22−24] reinforced by experimental observation of absence of marked peak shift of fluorescence spectra as a function of solvent polarity confirms a double proton transfer on photoexcitation of $BP(OH)_2$. Moreover, weak temperature dependence of the nonradiative rate and insensitivity toward isotopic substitution further lend credence to a quasibarrierless double proton transfer in $BP(OH)_2$.[19] So far, the monoketo tautomer is reported to form only in the excited state as an intermediate.[25] Several studies to explore the excited-state dynamics of $BP(OH)_2$ using femtosecond fluorescence upconversion[26] and transient absorption measurement[27] suggest both concerted (less than 100 fs) and consecutive reactions for the double proton transfer depending upon nature of solvent, excitation, and emission wavelength.[28−30] In the consecutive reaction the monoketo tautomer is generated in the excited state from dienol tautomer with an ultrafast time of 100 fs followed by relaxation to the emissive diketo tautomer in ∼10 ps. $BP(OH)_2$ and its derivatives show distinct optical properties and, thereby, can be used as dye lasers in inert solvents,[31] solar energy collectors, and photostabilizers of polymers.[32]

The dynamics of ESIDPT in $BP(OH)_2$ has been studied extensively in homogeneous solvents.[33−35] In neat solutions,

Received: October 8, 2010
Revised: December 9, 2010
Published: January 7, 2011

Scheme 1. (a) Different Tautomeric Forms and (b) Double Proton Transfer in $BP(OH)_2$[a]



[a] In aqueous solutions, both the forms (dienol and diketo) exist as intermolecularly hydrogen-bonded water complexes, which are disrupted upon incorporation in micelles.

$BP(OH)_2$ absorbs in 350 nm region and emits in green with quantum yield ranging from 0.2 to 0.4,[19] while, in water, a unique second absorption band in 400−430 nm region due to water solvation appears. This band is due to the intermolecularly hydrogen bonded water complexes of the diketo form of $BP(OH)_2$.[36] Theoretical studies predict that the diketo tautomer is stabilized preferentially by hydrogen bonding with water, compared to the dienol form,[23] and formation of such water complexes is reported in aqueous solution of $BP(OH)_2$.[37] The absorption in the 350 nm region corresponds to the transition to lowest (π, π^*) state of the dienol tautomer.[17,37] Rurack and co-workers reported the effect of variation of pH on the photodynamics of $BP(OH)_2$ in aqueous solutions[36] along with the distribution of lifetimes in different solvents. The fluorescence quantum yield of $BP(OH)_2$ decreases steadily to a value of 0.04 on increasing the pH value with a bimodal decay above pH 5 and finally a complete quenching of fluorescence occurs at very high pH. The four pK_a values of $BP(OH)_2$ are determined to be 0.16, 2.69, 9.2, and 12.4. An application of the pH dependence of photophysics of $BP(OH)_2$ in acetonitrile is as a molecular half-subtractor.[38] However, only a few recent studies have been performed on this molecule in restricted microenvironments of zeolite host,[36] cyclodextrins (CDs),[39,40] human serum albumin (HSA)[39] and in binary mixtures of *p*-dioxane/water.[41] In these studies, an enhancement in the fluorescence quantum yield is observed, due to incorporation of the fluorophore in restricted hydrophobic microenvironments. Surprisingly, the process has not been studied in surfactant assemblies, even though such assemblies are known to affect the dynamics of excited-state proton-transfer process significantly.[42−45] So, in the present investigation, the effect of change of microenvironment around $BP(OH)_2$ on addition of surfactants like cetyltrimethylammonium bromide (CTAB), Triton X-100 (TX-100), and sodium dodecyl sulfate (SDS) has been explored using steady-state and time-resolved fluorescence spectroscopic techniques.

MATERIALS AND METHODS

The cationic surfactant cetyltrimethylammonium bromide (CTAB), the neutral surfactant Triton X-100 (TX-100), and anionic surfactant sodium dodecyl sulfate (SDS) were purchased from Sigma Aldrich. [2,2′-Bipyridyl]-3,3′-diol ($BP(OH)_2$) was also received from Aldrich, and all the three surfactants along with the probe were used as obtained without any further purification. Throughout all the experiments, micromolar concentrations of the fluorophore were maintained. The aqueous solutions were prepared using deionized double-distilled water. The absorption and the fluorescence spectra of the solutions were recorded on a JASCO V530 spectrophotometer and Varian Cary Eclipse spectrofluorimeter, respectively. The absorbance of the neat aqueous solution of $BP(OH)_2$ was kept below 0.2 to prevent inner filter effect. The concentrations of all the three surfactants were varied from 0 to 80 mM. Sucrose solutions, 0% to 70%, were prepared during the viscosity-dependent study. Quinine sulfate with absolute quantum yield of 0.51 at 25 °C was used as a standard[46] to evaluate the fluorescence quantum yield of aqueous solution of $BP(OH)_2$ in different concentrations of micelles and sucrose. The excitation wavelengths while recording the emission spectra were fixed at 350 and 406 nm. Time-resolved fluorescence data were obtained using a picosecond pulsed diode laser based time-correlated single photon counting (TCSPC) instrument from IBH (United Kingdom) set at magic angle with λ_{ex} = 341 nm. The FWHM of instrument response function at this wavelength is found to be 800 ps with a resolution of 7 ps/channel. The decay traces, thus obtained, were fitted to multiexponential functions using IBH DAS 6.0 data analysis software.[47,48]

RESULTS AND DISCUSSION

Absorption and Emission Spectra in Micelles. Water is known to stabilize the diketo tautomer with a unique absorption in the 400 nm region while the dienol tautomer absorbs at 350 nm.[23,36,39] This band at 400 nm does not occur in any other solvent. Addition of surfactants (CTAB/SDS/TX-100) to a ≈0.03 mM aqueous solution of $BP(OH)_2$ results in an increase of the absorbance at 350 nm with a concomitant decrease of absorbance at 406 nm (Figure 1). The increase in the absorbance at 350 nm is a clear manifestation of a greater hydrophobic environment provided by the micelles, which further stabilizes the ground state of the dienol tautomer of $BP(OH)_2$. The decrease in the absorbance at 406 nm indicates lesser availability of water. The two species in water seem to be hydrogen-bonded water complexes of the two forms of $BP(OH)_2$: the dienol form (high-energy absorption band) and the diketo form (low-energy absorption band). The small changes in absorption in the high-energy band upon incorporation in micelles is likely to be due to the disruption of the hydrogen bonded water complexes of the dienol form and formation of micelle-incorporated dienolic form of $BP(OH)_2$, in which the intermolecular hydrogen bonds with water are replaced by intramolecular hydrogen bonds. The complete suppression of the low-energy band in micelles is

dx.doi.org/10.1021/jp1098359 |*J. Phys. Chem. B* 2011, 115, 1032–1037

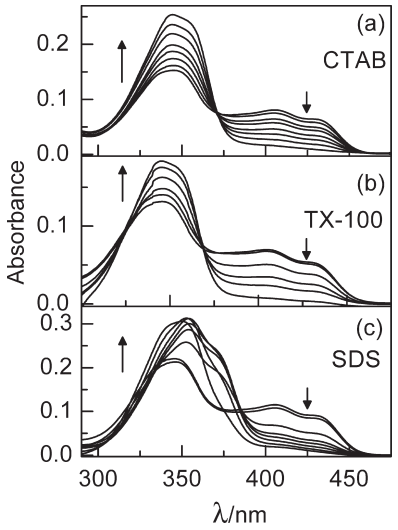


Figure 1. Absorption spectra of $BP(OH)_2$ in aqueous solution with increasing concentration of (a) CTAB, (b) TX-100, and (c) SDS. The arrows indicate the increase in the concentration of surfactants from 0 to 80 mM in all the three cases.

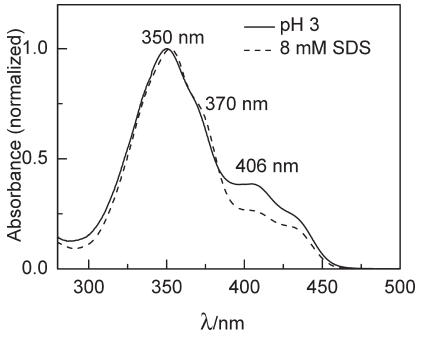


Figure 2. Normalized absorption spectra of $BP(OH)_2$ in an acetate buffer solution of pH 3 and 8 mM SDS.

rationalized by the disruption of the hydrogen-bonded water complexes of the diketo form, which destabilizes the ground state of the diketo form to the extent that the species does not exist when incorporated in micelles. The onset of the change in absorbance around CMC of the respective surfactants marks a transition of location of the fluorophore from bulk water to membrane-like water−micelle interface. The presence of an isosbestic point at 370 nm in the absorption spectra of $BP(OH)_2$ in CTAB and TX-100 indicates the existence of its two distinct tautomeric forms (dienol and diketo forms) in equilibrium with each other (Figure 1, a and b). No such characteristic point is observed in SDS surfactant, indicating that the situation here cannot be described by a simple two-state equilibrium. Moreover, a shoulder is observed at 370 nm in SDS micelle (Figure 1c). These observations are rationalized by the formation of the cationic form of $BP(OH)_2$ at the vicinity of the Stern layer of negatively charged SDS micelle due to a relatively lower local pH (Figure 2 and Figure S1 of the Supporting Information). The pK_a values for the formation of monocation and dication of the fluorophore have been reported to be 0.16 and 2.69.[36] The Stern layer of SDS is found to promote the formation of the cationic form of other fluorophores as well which often enhances the extent of ESPT process.[49] The normalized absorption spectra of

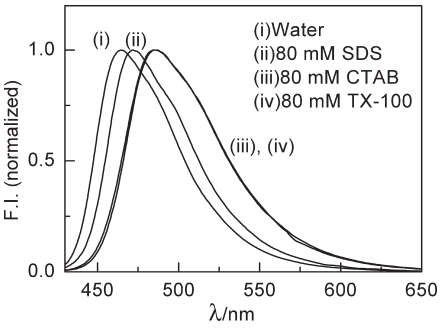


Figure 3. Normalized emission spectra of $BP(OH)_2$ in aqueous solution and 80 mM SDS, CTAB, and TX-100. λ_{ex} = 350 nm.

$BP(OH)_2$ at pH 3 and 8 mM SDS (near CMC) are almost identical except in the 406 nm region due to the destabilization of diketo form in hydrpbhobic environment (Figure 2). This supports the argument that SDS modifies the pK_a value of $BP(OH)_2$ which results in the simultaneous existence of dienol, diketo, and monocationic forms in SDS solution near its CMC. The smaller absorbance at 406 nm in SDS is rationalized in terms of lesser availability of water, as discussed already.

Fluorescence spectra in different surfactants are recorded at excitation wavelength of 350 and 406 nm which confirms the excitation-independent optical properties of $BP(OH)_2$. This observation strengthens the contention that the diketo tautomer is the only emitting species as reported.[36,50] On gradual addition of surfactant (CTAB/TX-100/SDS), a red shift is observed which indicates a greater extent of penetration of the fluorophore into the hydrophobic compartment (Figure S2 of the Supporting Information). Unlike SDS, the extent of red shift in CTAB and TX-100 micelles, which involve a simple two-state equilibrium between the dienol and diketo form, is found to be identical (Figure 3). This is reminiscent of the earlier observation of red shift on addition of cyclodextrins (CDs)[39,40] and human serum albumin (HSA).[39] The fluorescence quantum yield (ϕ_f) increases to saturation with surfactant concentration, and a point of inflection is observed at CMC of the surfactants. This result is in line with the observed caging effect of CDs on the fluorescence spectrum of $BP(OH)_2$.[40] The increase in fluorescence quantum yield (ϕ_f) upon excitation at 350 nm in micelles is due to the presence of more ground-state dienol tautomer inside micelles than in water. It may be noted that this state is reported to be very nonpolar[20,21] and so may be expected to be stabilized within the micelles. An alternative explanation can be the probable disruption of the less emissive fluorophore aggregates upon micellization. The increase of quantum yield (ϕ_f) is maximum in presence of SDS followed by TX-100 and least in CTAB micelles (Figure 4). The quantum yield maximizes in SDS due to the lower local pH at the vicinity of the Stern layer which facilitates the formation of monocation with the pK_a value of 2.69[36] of the fluorophore. The monocation is nonemissive.[36] However, upon photoexcitation, it loses its hydroxyl proton to form the corresponding diketo tautomer which emits at 465 nm and so no additional peaks are observed in the emission spectra of $BP(OH)_2$ in SDS (Figure S3 of the Supporting Information). This observation is in line with the reported fluorescence behavior of $BP(OH)_2$ as a function of different pH.[36] In contrast, the increase in neutral TX-100 can be justified in terms of greater microviscosity[51] experienced by the fluorophore when buried deeply inside the palisade layer of TX-100. In order to vindicate

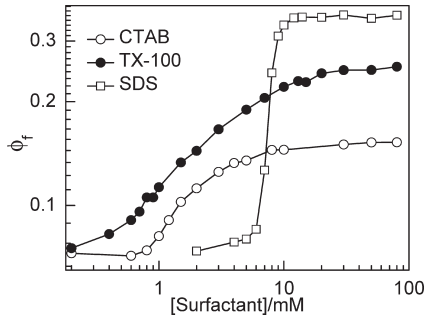


Figure 4. Fluorescence quantum yield plots of $BP(OH)_2$ in aqueous solution with increasing concentration of the surfactants, CTAB, TX-100, and SDS. λ_{ex} = 350 nm.

the contention that the enhanced fluorescence quantum yield in TX-100 on excitation at 350 nm is solely a viscosity effect, a similar study is done with increasing concentration of sucrose in neat aqueous solutions. On addition of sucrose in an aqueous solution of $BP(OH)_2$ the fluorescence quantum yield (ϕ_f) increases as a function of viscosity at both excitation wavelength of 350 and 406 nm. Thus, a plot of quantum yield (ϕ_f) versus viscosity of sucrose solution generates an identical increasing sigmoid curve (Figure 4 and Figure S4 of the Supporting Information) as observed in TX-100 confirming the effect of enhanced microviscosity around the fluorophore in the palisade layer of TX-100. The absence of both local pH effect and viscosity dependence leads to a minimum increment of quantum yield in CTAB. Thus, $BP(OH)_2$ shows an increase in fluorescence quantum yield in all the surfactants as compared to neat aqueous solution with maximum enhancement in SDS and minimum in CTAB. This enhancement is attributed to the stability attained by the nonpolar fluorescent diketo form in the hydrophobic environment created by the organized assemblies. Moreover, the ability of SDS to alter the local pH leading to the formation of monocation further augments the quantum yield of $BP(OH)_2$ while a viscosity-dependent enhancement is achieved in neutral TX-100 micelle. Thus, selective and controlled addition of micelles to the fluorophore can provide micropockets with varying size, local pH, hydrophobicity, and viscosity on the basis of which the dynamics of ground and excited states of different forms of $BP(OH)_2$ can be modulated.

Time-Resolved Fluorescence in Micelles. Fluorescence decays of $BP(OH)_2$ in micelles and sucrose solutions are recorded at excitation and emission wavelength of 341 and 465 nm, respectively (Figure 5 and Figure S5 of the Supporting Information). A single component of around 0.60 ns is observed in neat aqueous solutions which is in line with the earlier reported data.[36] Successive addition of surfactant leads to a biexponential decay with another component having a comparatively longer lifetime (τ_2) in the region of 2−4 ns depending upon the type of surfactant (Table 1). Moreover, the contribution from the fast component (τ_1) gradually decreases with a concomitant increase of the slow component and finally at higher concentration of surfactant (more than 10 times of CMC) a monoexponential decay with the longer lifetime (τ_2) is obtained. Successive addition of surfactants has no appreciable effect on the values of either of the lifetimes (τ_1 and τ_2). The shorter lifetime (0.60 ns) is assigned to the hydrogen-bonded water complexes of $BP(OH)_2$ whose contribution decreases significantly with addition of surfactant indicating the lower abundance of the fluorophore in aqueous

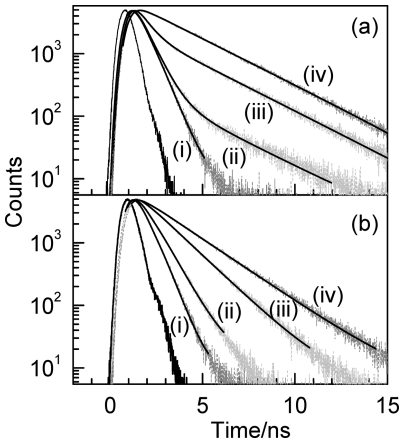


Figure 5. Fluorescence decay traces of aqueous solution of $BP(OH)_2$ at λ_{ex} = 341 nm and λ_{em} = 465 nm in varying concentrations of (a) TX-100 and (b) sucrose. The concentrations of TX-100 are (i) 0 mM, (ii) 0.6 mM, (iii) 3 mM, and (iv) 80 mM, and those of sucrose are (i) 0%, (ii) 10%, (iii) 40%, and (iv) 70% w/v.

Table 1. Time-Resolved Fluorescence Decay Parameters of Aqueous Solution of $BP(OH)_2$ with Varying Concentration of Micelles

surfactant	concn of surfactant (mM)	χ^2	τ_1/ns	a_1	τ_2 /ns	a_2
CTAB	0.0	1.02	0.64			
	0.6	1.02	0.66			
	1.0	1.09	0.63	0.90	1.90	0.06
	2.0	1.02	0.66	0.74	2.09	0.25
	5.0	1.05	0.65	0.45	2.12	0.54
	30.0	1.07			2.16	
	80.0	1.00			2.24	
TX-100	0.0	1.04	0.60			
	0.4	1.13	0.62			
	1.0	1.03	0.56	0.92	2.91	0.07
	5.0	1.01	0.50	0.64	2.92	0.35
	30.0	1.04			2.90	
	80.0	1.03			2.93	
SDS	0.0	1.12	0.63			
	4.0	1.05	0.56	0.76	1.00	0.23
	9.0	1.06	0.61	0.33	3.89	0.66
	12.0	1.05	0.56	0.18	4.00	0.81
	20.0	1.04			3.93	
	80.0	1.05			3.75	

solution upon micellization. The longer lifetime of about 2 ns in CTAB, 3 ns in TX-100, and 4 ns in SDS is attributed to the micellized $BP(OH)_2$ inclusion complex. Their relative amplitude increases as a function of surfactant concentration. The increase in lifetime of the fluorophore upon micellization lends credence to the fact that a net stability is attained by the excited state of diketo form in presence of surfactants. A similar study to explore the viscosity effect on the fluorophore shows an increase in lifetime from around 0.6 to 2 ns with successive addition of sucrose (Table 2). This observation in sucrose is in agreement with the increase in lifetime of $BP(OH)_2$ in TX-100 which also offers a greater microviscosity as compared to other surfactants. A closer inspection to the longer lifetimes (τ_2) in the surfactants

dx.doi.org/10.1021/jp1098359 |J. Phys. Chem. B 2011, 115, 1032–1037

Table 2. Time-Resolved Fluorescence Decay Parameters of Aqueous Solution of $BP(OH)_2$ with Varying Concentration of Sucrose

% of sucrose solution	χ^2	τ/ns
0	1.10	0.56
10	1.00	0.81
30	1.10	1.32
50	1.05	1.77
70	1.02	2.18

reveals that only for anionic SDS micelle initially a lifetime of 1 ns originates which on further addition of SDS changes to almost invariant 4 ns component (Table 1). The origin of the 1 ns lifetime in SDS is in coherence with the steady state observation of formation of monocation at the Stern layer as $BP(OH)_2$ in acidic medium within pH range 1−3 is also found to exhibit a monoexponential decay with a characteristic lifetime of 0.7−0.9 ns (Figure S6 and Table S1 of the Supporting Information). Thus, $BP(OH)_2$ in presence of SDS exhibits maximum quantum yield and lifetime indicating a remarkable increase in the extent of ESIDPT process.

The complete dynamics of the interaction of $BP(OH)_2$ with organized assemblies formed in presence of surfactant can be monitored using time-resolved spectroscopy which confirms an initial formation of hydrogen-bonded water complexes of $BP(OH)_2$ followed by the coexistence of micellized $BP(OH)_2$ complex post-CMC and finally it is the micellized form which exists predominantly at sufficiently higher surfactant concentration. Depending upon the compactness of the surfactant layers, appreciable amount of water can seep through, leading to the retention of biexponential decay until relatively higher micellar concentration. In summary, steady-state and time-resolved measurements reveal that the increase in fluorescence quantum yield and lifetime of $BP(OH)_2$ with the addition of surfactants is a combined effect of local pH, hydrophobicity and microviscosity of the surfactant assembly.

CONCLUSIONS

The combined effect of polarity and hydrogen-bonding ability of water results in a distinct photophysics and photodynamics of $BP(OH)_2$ in neat aqueous solution as compared to other solvents.[36] The introduction of organized assemblies like micelles in homogeneous aqueous solution of $BP(OH)_2$ further alters the mode of interaction of the fluorophore with different regions within the solution. The heterogeneous microenvironment thereby formed stabilizes the diketo and dienol forms of the fluorophore to different extent leading to the perturbation of their ground- and excited-state energetics. The presence of hydrobhobic environment around the fluorophore stabilizes its nonpolar fluorescent state, resulting in an enhanced fluorescence quantum yield and lifetime in all the surfactants. Though all the three micelles used in this investigation provide similar hydrophobic nanocavities, their binding interactions with the fluorophore are distinctly different as revealed by the steady-state and time-resolved measurements. Among all the surfactants, $BP(OH)_2$ in the presence of SDS micelles exhibits maximum fluorescence quantum yield and lifetime of 4 ns. The presence of negatively charged Stern layer promotes the formation of monocation with a lifetime of 1 ns which like the dienol form generates the diketo form in excited state leading to an increase in the extent of ESIDPT in SDS. On the other hand, interaction of $BP(OH)_2$ with TX-100 is guided entirely by the viscosity effect. Thus, depending upon local pH, hydrophobicity, viscosity, and compactness of the micellar nanaocavity, the fluorescence quantum yield of $BP(OH)_2$ can be enhanced and the extent of ESIDPT can be promoted. Such distinct spectral behavior toward apolar and polar environments marks the dual utility of $BP(OH)_2$ as both biomarker and water sensor. Furthermore, fluorophore entrapped in microvessels provided by micelles highly resembles biomolecules like substrate−enzyme complexes and the ability to modulate their ground- and excited-state photophysics is of great interest for application of the probe in the fields of drug design and drug delivery.

ASSOCIATED CONTENT

Supporting Information. Additional absorption spectra, fluorescence spectra, absolute quantum yield plot, time-resolved decays, and table of decay parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work is supported by the SERC, DST. D.D. thanks the CSIR for a Junior Research Fellowship.

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