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(2,2′-Bipyridyl)-3-3′-diol in Nafion: Stabilization of Unusual Ground and Excited States

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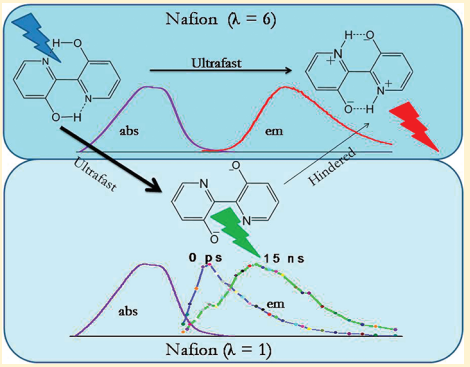
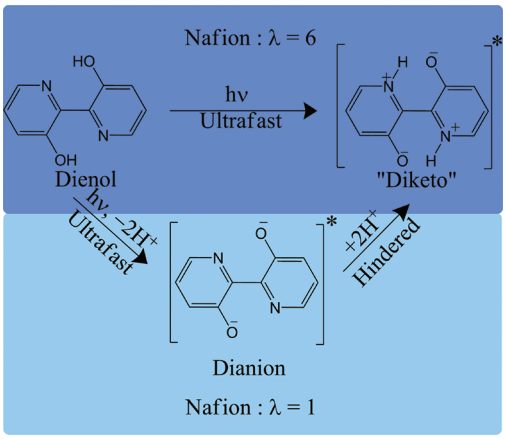
ABSTRACT: (2,2′-Bipyridyl)-3-3′-diol ($BP(OH)_2$) undergoes excited state intramolecular double proton transfer (ESIDPT). The photophysics of this molecule has been investigated, in the highly acidic water channels inside nafion membrane. The dianionic enolate form of the dye, which is formed only in alkaline conditions in neat aqueous solutions, is found to be present in its excited state in native nafion membrane at low water content. This surprising phenomenon has been explained in the light of loss of protons from the fluorophore to the medium, due to increased electrostatic interactions with the pendant sulfonate groups of nafion, at the lower water content. This observation fortifies the model of microscopic interactions that we have proposed in recent past. Further, the ground state of the diketo form, observed only in neat aqueous solutions so far, is found to be present in Na^+-exchanged membranes at lower levels of hydration. The steady-state spectral features of the dye is different in $(CH_3)_4N^+$-exchanged membranes than that of Na^+-exchanged membranes, unlike in our earlier studies with coumarin 102 and 2-(2′-pyridyl)benzimidazole, here we observed formation of an unusual ground state in Na^+-exchanged membranes, while no such feature was observed in $(CH_3)_4N^+$-exchanged membranes.



INTRODUCTION

The excited state dynamics of (2,2′-bipyridyl)-3-3′-diol ($BP(OH)_2$, Scheme 1) is governed by proton transfer.[1−4] It is soluble in various organic solvents[5,6] and exhibits high photostability.[7] The molecule exhibits a strong absorption at 350 nm, attributed to $\pi-\pi^*$ transition in the dienol form of the molecule. In neat aqueous solutions, an additional absorption band occurs at 420 nm. This band has been ascribed to the diketo form.[1,5,8] It has been proposed that this form occurs in its ground state due to formation of hydrogen bonded complexes with water molecules. Such complexes are not observed in other hydrogen bonding solvents like methanol or ethanol.[5] It may be noted here that the term diketo is used here in order to maintain continuity with existing literature. It may also be referred to as a dienolate form. The significantly Stokes shifted emission band occurs at 470 nm, irrespective of the excitation wavelength, implying that the diketo state is singularly responsible for the emission. This state is formed from the dienolic state by excited state intramolecular double proton transfer (ESIDPT), in neat solutions as well as in microheterogeneous media.[1,5,16] In this process, the symmetry between the reactant and the product is retained.[9] There has been a considerable amount of debate regarding the mechanism of ESIDPT in $BP(OH)_2$, on whether the double proton transfer takes place in a single, concerted step or in a stepwise manner.[10−13] It has been proposed to be barrierless in the singlet excited state. However, singlet to triplet transition, during the lifetime of fluorescence of the diketo form, is associated with a large barrier. The process of direct formation of the diketo form by abstraction of protons has been predicted to take place in a time scale of 100 fs. Some authors have proposed a two-step proton transfer mechanism, in which the formation of monoketo isomer from the dienol form takes place in 50 fs, and the second proton abstraction takes place in 10 ps. However, the double proton transfer, being barrierless, takes precedence over the pathway involving the monoketo tautomer. Quantum chemical calculations predict that the

Scheme 1. Concerted ESIDPT of $BP(OH)_2$ in Hydrated Nafion (λ = 6) and Excited State Double Deprotonation in the Dehydrated Membrane (λ = 6)



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monoketo tautomer emits at 570 nm.[13,14] The dye has been studied under various constrained environments like zeolites,[15] cyclodextrins,[6] serum proteins,[16] surfactants,[1] etc. In all these systems, it has been seen that the ESIDPT is ultrafast.

In the present work, $BP(OH)_2$ has been used as a fluorescent probe of the nanochannels of water in nafion membrane. Nafion has a nonpolar backbone resembling that of teflon, but with pendant sulfonate groups, which define the boundaries of nanochannels containing water. The local acidity of these nanochannels is very high, due to the hydronium ions that are present as counterions of the pendant sulfonate groups. The membrane conducts protons and cations selectively and, so, finds extensive use in fuel cells and chloralkali cells. Nafion is hydrophilic and is known to provide microenvironments of varying rigidity at different levels of hydration. The acidity of nafion membranes decreases upon cation exchange. In recent past, we have used organic fluorophores like coumarin 102[17] and 2,2′(-pyridyl)benzimidazole[18] to explore the microstructure of nafion at different water contents. In highly acidic aqueous solution, coumarin 102 gets protonated at its nitrogen atom. Upon excitation, the nitrogen atom loses the proton, while the oxygen atom takes it up, resulting in an ultrafast excited state proton transfer.[19] In native nafion membranes, a similar protonation and ultrafast excited state proton transfer are found to occur. The proton transfer is slowed down remarkably in nafion membrane that have been dried to $\lambda = 1$.[17] Here, λ is the ratio of number of equivalents of water to that of sulfonate groups.[20] From this observation, we have proposed that electrostatic interactions play an important role in the mobility of cations in nafion. It should be mentioned here that the proton transfer does not take place when coumarin 102 is incorporated in cation exchanged nafion membranes, as these cation exchanged membranes are significantly less acidic than native membranes. Coumarin 102 occurs in its neutral form in these membranes. Upon excitation of the neutral coumarin 102 molecules, a polar excited state is formed. Solvation of this excited state is found to be slower in Na^+-exchanged membranes compared to that in $(CH_3)_4N^+$-exchanged membranes. This has been rationalized by a model involving a greater amount of localization of $(CH_3)_4N^+$-ions near the sulfonate groups and a more uniform distribution of Na^+ ions in the water channels.[21]

In another study, excited state proton transfer (ESPT) in 2,2′(-pyridyl)benzimidazole (2PBI) has been found to be hindered upon cation exchange.[22] This dye can mark the hydration level in native and cation-exchanged nafion membranes and provides further evidence for the proposed role of electrostatic interactions in cation mobility in nafion.[18] Both these studies involve fluorescence from species that have been tentatively assigned to states that are not expected to form. In the case of coumarin 102, the zwitterionic excited state is found to occur because a proton is lost to the medium and is not taken back readily. In the case of 2PBI, a conformational distribution of excited states is proposed to occur. In the two cases described so far, proton transfer involves transport of proton across the molecule via solvent. In the present experiment, (2,2′-bipyridyl)-3-3′-diol ($BP(OH)_2$ has been incorporated in nafion membranes. In this molecule, ESPT involves only a shift of bonds but no physical displacement of protons. This molecule has been studied in order to test the limits of our contention about the role of electrostatic interactions. ESPT in $BP(OH)_2$ can be hindered only if the electrostatic interactions are strong enough to disrupt the strong intramolecular hydrogen bonds. Besides, in $BP(OH)_2$, conformational relaxation is not expected to play a role like it does in 2PBI, as the molecule has a symmetric, planar structure, stabilized by two intramolecular hydrogen bonds. The proton donor and acceptor groups are very close to each other, thus making the loss of a proton to the medium more difficult than in coumarin 102. The emphasis of the present work is thus to investigate if unusual ground and excited states occur for this molecule nevertheless, with a view to test our hypothesis regarding the importance of electrostatic interactions on the mobility of protons in nafion.

EXPERIMENTAL SECTION

$BP(OH)_2$ purchased from Aldrich is used as received. Nafion 117 membranes, also from Aldrich, are cleaned by heating with 5% H_2O_2 solution for 3 h, followed by rinsing in double distilled water, and then heating in 1 M HNO_3 solution for 3 h. This procedure is repeated until transparent membranes are obtained. The dye is loaded from its aqueous solution until the absorbance is nearly 0.5. The excess of dye on the surface is removed by rinsing with water. Membranes of lower water content are obtained by heating the membrane in vacuum at 70 °C until no further change in weight of membranes is observed. These membranes are kept in sealed cuvettes during the course of the experiment, in order to avoid uptake of water. The hydrated membrane has ∼10% w/w water as this is the weight lost upon drying. This corresponds to $\lambda = 6$ in hydrated membranes and $\lambda = 1$ in less hydrated membranes.[20] The cation exchanged membranes are obtained by dipping the native membranes in 1 M NaOH or 1 M $(CH_3)_4NCl$ solution for 24 h.

The absorption and fluorescence spectra are recorded on JASCO V530 absorption spectrophotometer and Varian Cary Eclipse spectrofluorimeter, respectively. The fluorescence decays are recorded on IBH Horiba-JY Fluorocube. NanoLEDs emitting at 340 nm (fwhm = 750 ps) and 375 nm (fwhm = 300 ps) are the light sources. The detector and excitation source are at 90° to each other. The membrane is kept at 45° to the excitation source such that the reflected light is directed away from the detector and fluorescence is collected from the back surface of the membrane. Fluorescence decays are recorded at regular intervals of wavelength at magic angle polarization with respect to the excitation. The data obtained is fitted by DAS 6.2 software using an iterative reconvolution technique. The fluorescence intensity at time t after excitation, at each emission wavelength, is expressed as

$$I(t) = I_{SS}\frac{\sum_i a_i e^{-t/\tau_i}}{\sum_i a_i \tau_i}$$

where τ_i is the fluorescence lifetime of ith component, and a_i is the amplitude of that component at the wavelength at which decays are recorded.[23] A negative value of a_i denotes a growth in fluorescence intensity with time. I_{ss} is the time integrated intensity at that wavelength, obtained from the steady-state fluorescence spectrum. The emission spectra at different times are obtained by substituting the value of time in this equation and then plotting $I(t)$ against wavelength. These spectra are normalized to unit area in order to generate time-resolved area-normalized spectra (TRANES).[24,25]

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RESULTS AND DISCUSSION

The absorption maximum of $BP(OH)_2$ occurs at 350 nm in native membrane, irrespective of the level of hydration, indicating the existence of the same ground state in both the conditions. The fluorescence spectrum, however, undergoes a blue shift from 465 nm in hydrated membrane (λ = 6) to 400 nm, with an almost equally intense shoulder at 420 nm, in dried membrane (λ = 1) (Figure 1i). The fluorescence excitation

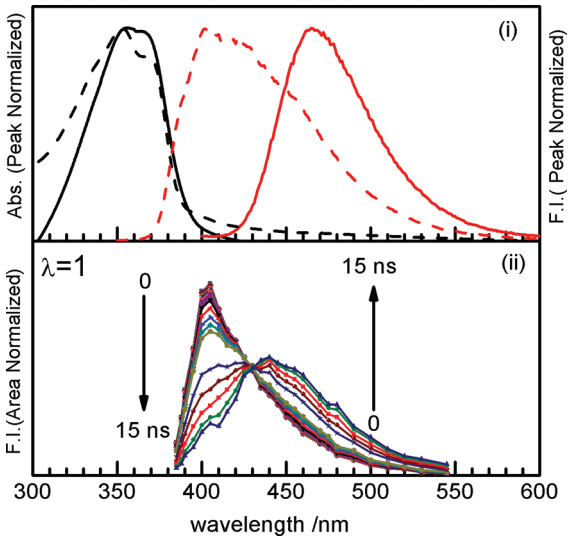

Figure 1. (i) Peak-normalized absorption (black) and fluorescence spectrum (red) of $BP(OH)_2$ in native membrane at λ = 6 (solid lines) and 1 (dashed lines). λ_{ex} = 350 nm for the fluorescence spectra. (ii) Time-resolved area-normalized emission spectra (TRANES) of $BP(OH)_2$. λ_{ex} = 375 nm. The times at which the spectra have been worked out are 0, 0.05, 0.12, 0.15, 0.20, 0.25, 0.40, 0.60, 0.80, 1.0, 3.0, 5.0, 8.0, 12, and 15 ns. The arrows indicate the direction of increase in time.

spectrum is superimposable with the absorption spectrum at both levels of hydration. Since there is no change in absorption and excitation spectra upon drying, the blue shift in fluorescence can be ascribed to to an excited state phenomeon. One possibility is that at λ = 1, the fluorescence is predominantly from the monoketo form, which may have been formed as a result of transfer of a single proton. This explanation involves the implicit assumption that ESIDPT in this molecule involves transfer of the two protons one after the other, in two distinct steps, and that only the first step is operative in nafion, at λ = 1. However, this does not seem to be an accurate description of the situation, as the monoketo form is expected to emit at 570 nm, and a red shift would be expected rather than a blue shift if this species would have a significant role to play.[13] Thus, the blue-shifted spectrum cannot be assigned to the monoketo tautomer. An alternative approach to rationalization of the blue shift may be developed, keeping in mind a similar blue shift observed in the fluorescence of coumarin 102 in native nafion membrane at λ = 1, as has been mentioned in the introduction.[17]

With this background, the following sequence of events may be proposed. There have been reports that during ESIDPT in $BP(OH)_2$ in neat solutions, the loss of the two protons from oxygen atoms and their uptake by the nitrogen atoms occur simultaneously.[5] The process is ultrafast. The spectra in nafion, at λ = 6, indicate that the dynamics is ultrafast in the hydrated membrane as well. At λ = 1, however, it is possible that the protons are lost readily by the oxygen atoms but are not taken up by the nitrogen atom as readily. Rather, they are lost to the medium, like the protons lost from the nitrogen atom of coumarin 102, under similar conditions. This would result in the formation of the dianion, BPO_2^{2-} in the excited state. The fluorescence of BPO_2^{2-} has been reported to occur at 420 nm,[8] which is close to the position of the fluorescence maximum of $BP(OH)_2$ in nafion membrane (λ = 1). The small blue shift may be ascribed to the less polar, more restricted micro-environment experienced by the fluorophore within dried nafion. This is an interesting situation, as the dianion is usually observed only at significantly alkaline values of pH = 10, in neat solutions. However, we find that in nafion, the same dianion, in its excited state, can be formed even at very highly acidic conditions inside the membrane.

It is possible that the dianion may not be the only emissive species in nafion membrane at λ = 1. The fluorescence spectrum is quite broad and covers the region of diketo emission as well. In order to gain further insight into the dynamics of the photoprocesses operative in the membrane at lower hydration levels, the time evolution of fluorescence has been studied. The fluorescence decays of $BP(OH)_2$ in native nafion do not vary significantly across the fluorescence spectrum, at λ = 6 (Figure 2). However, there is a marked

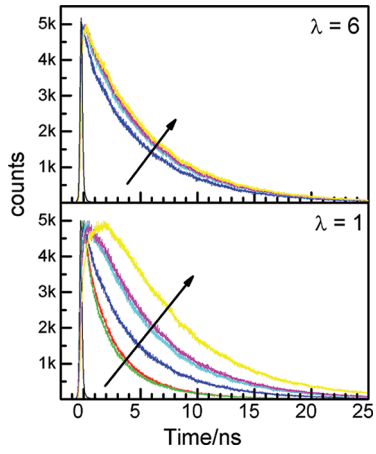

Figure 2. Fluorescence decays of $BP(OH)_2$ in nafion, λ_{ex} = 375 nm. λ = 6 ; λ_{em} = 430 nm, 460 nm, 490 nm, and 545 nm for top panel. λ = 1; λ_{em} = 385 nm, 400 nm, 430 nm, 460 nm, 490 nm, and 545 nm for bottom panel. The arrows indicate the direction of increase in λ_{em}.

dependence of the dynamics on emission wavelengths at λ = 1. Fast decays are obtained at shorter emission wavelengths, while slower decays, alongwith prominent risetimes, are obtained at longer wavelengths (Figure 2, Table 1). The fluorescence lifetimes in native membranes at λ = 6 are biexponential with lifetimes of 1.4 and 5 ns in the blue end of the spectra, while at the red end, the lifetimes are typically single exponential. The short component can be ascribed to interaction of the $-N^+H$ group with the polar regions in the nafion. Similar interactions have been ascribed to polar aprotic solvents, like dioxane and acetonitrile, and restricted environment, like cyclodextrins.[5] The long 5 ns component can be assigned to hydrogen bonded complexes of $BP(OH)_2$.[5] The contribution from the short component decreases at longer wavelengths. Upon decreasing the water content, i.e., at λ = 1, an additional fast component of 0.5 ns is obtained. This is assigned to the non-hydrogen bonded

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Table 1. Temporal Features of $BP(OH)_2$ in Native Nafion at λ = 1 and 6 Levels of Hydration

water content	λ_{em}	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1	a_2	a_3	χ^2
λ =1	385		1.99	4.15	0.24	0.46	0.29	1.01
	400	0.49	1.84	4.26	0.22	0.50	0.28	1.03
	430		1.47	4.92		0.23	0.77	1.12
	460	0.70		5.49	−0.33		1.33	1.10
	490	0.69		5.72	−0.56		1.56	1.12
	545	1.57		6.34	−1.23		2.23	1.18
λ = 6	430		1.33	5.61		0.12	0.88	1.16
	460		1.46	5.71		0.07	0.93	1.12
	490			5.70			1.00	1.15
	545			5.92			1.00	1.14

diketo form of fluorophore.[5] Thus, the decrease in the amount of water in the membrane is marked by the fluorescence of $BP(OH)_2$. It has been observed earlier that, in restricted microenvironments like micelles and highly viscous medium like sucrose, the decays are slower.[1] It is has been observed by us in the past that the environment inside the nafion membrane, at lower levels of hydration, is highly rigid that even molecular rotations are hindered.[18] Thus, the longest component of 6.3 ns (Table 1) is ascribed to the increased microviscosity experienced by $BP(OH)_2$ molecules in dried membranes. A rise time in fluorescence is observed at λ = 1 but not at λ = 6. This rise time has been ascribed to the evolution of the ESPT state from the dianion. It may be recalled here that lifetime of the dianion is very small.[15] So, it is difficult to observe the lifetime in the presence of other components. Moreover, the rise time in the red end is significantly long. This can be rationalized by considering a slow proton recapture from the solvent and slow hydrogen bond dynamics at lower water contents, especially in view of the knowledge about the importance of hydrogen bonded complexes of $BP(OH)_2$ to its fluorescence.[5] Another factor that is likely to be contributing to the long rise time is the conformational relaxation in the excited state, as it is known that the dianion is nonplanar, while the diketo form is planar.

In complicated situations like the present one, assignment of each and every component to a particular emissive species is usually very difficult. It is best to follow the overall dynamics of process, by following the time evolution of the emission spectra. When these spectra are area-normalized, the time-resolved area-normalized emission spectra (TRANES) is obtained. TRANES analysis provides further insight into the dynamics of the excited state process, as an isoemissive point in such spectra indicates a two-state excited state process. In the native membrane at λ = 1, TRANES consists of a band peaked at 400 nm at shorter times and a distinctly different band with its maximum at 440 nm at longer times (Figure 1ii). A clear isoemissive point is observed in TRANES, indicating that the excited state process involves two distinct emissive states.[24,25] These states are likely to be the dianionic and diketo states, as is indicated by the fluorescence maxima. Hence, the picture that emerges is as follows: the two aromatic OH groups lose the protons at the same instant. In neat solutions, as well as in nafion at λ = 6, these two protons are taken up by pyridyl nitrogen atoms at the same instant as well. The process is ultrafast. At λ = 1, however, the protons are lost simultaneously from the aromatic OH groups but are not taken up by the nitrogen atoms readily. The process is slowed down to the nanosecond time scale. Such a long time for proton transfer can be rationalized only if the protons are lost to the medium before they can be taken up by pyridyl nitrogen atoms. This provides support to the inferences drawn from our previous experiments with coumarin 102 and 2-(2′-pyridyl)-benzimidazole.[17,18] Upon decreasing the water content, the electrostatic attractions between the proton and the sulfonate group increases owing to the decreased electrostatic screening associated with loss of water from the membrane.

Exchange of the hydronium ions in nafion with other cations is known to increase the pH of the membrane. We have proposed earlier that different cations distribute differently inside the membranes.[21] With this background, we have studied the effect of cation exchange on the photophysics of $BP(OH)_2$ in nafion. At the λ = 6 condition, the absorption spectrum corresponds to that of the dienol form. The absorption spectrum in Na^+-exchanged membrane changes upon drying the membrane. At λ = 1, the absorption spectrum resembles that of $BP(OH)_2$ in water with a prominent absorption at 350 nm and a second absorption band at 400 nm (Figure 3). The

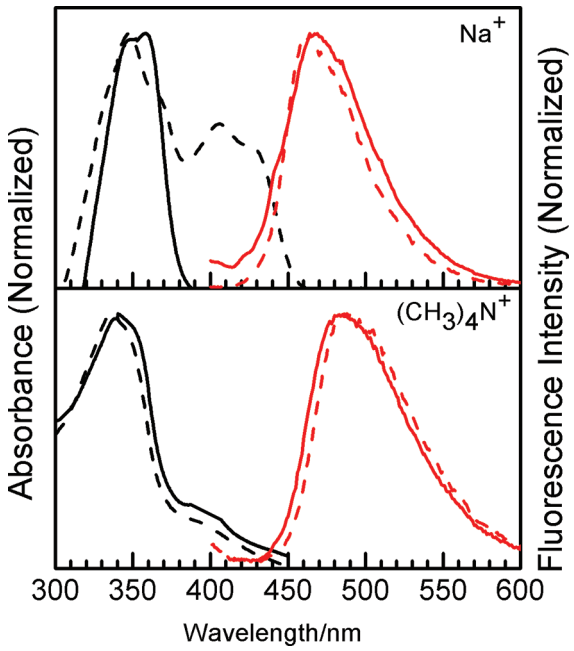

Figure 3. Normalized absorption (black) and fluorescence (red) of $BP(OH)_2$ in Na^+-exchanged (top) and $(CH_3)_4N^+$-exchanged nafion membranes (bottom) at λ = 6 (solid) and λ = 1 (dash). λ_{ex} = 350 nm for the fluorescence spectra.

excitation spectrum is superimposable with the absorption spectrum under both levels of hydrations. The fluorescence spectrum becomes slightly narrower upon reducing the water content, causing a small blue shift in the maximum. The fluorescence at λ = 6 as well as λ = 1 is from the diketo form. In $(CH_3)_4N^+$-exchanged membranes, however, the absorption spectrum does not change upon dehydration. The fluorescence intensity is enhanced by a factor of 1.8, similar to other dehydrated membranes. The appearance of 400 nm absorption band in Na^+-exchanged membrane at λ = 1 indicates that the dizwitterion (diketo) form is stabilized in the ground state in this condition. It may be recalled here that this band has been attributed to hydrogen bonded complexes of $BP(OH)_2$ with water, in neat aqueous solutions.[5] This phenomenon is not

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understood completely at this moment, but it is possible that hydrogen bonding interactions with the sulfonate groups have a role to play here. In $(CH_3)_4N^+$-exchanged membrane, such interactions would not take place, as the $(CH_3)_4N^+$ ions appear to shield the fluorophore from the sulfonate groups.[21] Another possibility would involve the formation of pairs comprising of Na^+ and $BP(OH)_2$, due to electrostatic interaction between the positively charged Na^+ ions and the negatively charged oxygen atoms in the zwitterionic diketo form of the fluorophore, aided by the decreased dielectric constant of the medium at lower levels of hydration. Hydrogen bonded complexes of $BP(OH)_2$ with the water in the solvation shell of Na^+ would likely to be occurring in such a scenario. Such hydrogen bonding would not be possible between $BP(OH)_2$ and $(CH_3)_4N^+$ ions, which lack a hydration layer.

The decays in Na^+-exchanged nafion are slower at $\lambda = 1$ than at $\lambda = 6$ (Figure 4, Table 2). Unlike native membranes, the fluorescence is not dependent on the emission wavelength at which the decays are monitored. At higher hydration levels, we observe two decay components of 1.8 and 4.5 ns. These can be assigned to the non-hydrogen bonded water−fluorophore complex and hydrogen bonded water−fluorphore complex, respectively. The slowing of fluorescence decay upon decreasing the water content can be ascribed to the absence of 1.5 ns component at lower levels of hydration. This may be rationalized in the following manner: at $\lambda = 1$, the diketo isomer is found in the ground state itself. Thus, it has a higher chance to be in a hydrogen bonded complex, and the hydration sphere does not change much upon excitation, and hence, the fluorescence from the non-hydrogen bonded complex of the diketo form is not observed. A rise time is of ∼500 ps is always observed irrespective of the water content or the nature of the cation. This can be ascribed to the formation of the ESPT state from dianion. The process of ESIDPT is probably not as slow as in a dried native membrane to leave its signature in a steady-state fluorescence experiment and not as fast in hydrated native membranes to be missed in the time-resolved experiments. The fluorescence decays in the $(CH_3)_4N^+$-exchanged membrane are faster than those in the Na^+-exchanged membranes and are not affected by the level of hydration (Figure 4, Table 2). The lifetimes indicates that fluorescence is originating from both the hydrogen bonded water−fluorophore complex and the non-hydrogen bonded diketo isomer. The invariance in excited state dynamics can be rationalized on the basis of our proposed model of cation distribution in water channels, and the molecule does not experience very different environments upon reducing the water content.[21] The $(CH_3)_4N^+$-ions being larger in size would have displaced significant amounts of water upon cation exchange. Hence, the excited state dynamics of fluorophore is not different at different levels of hydration.

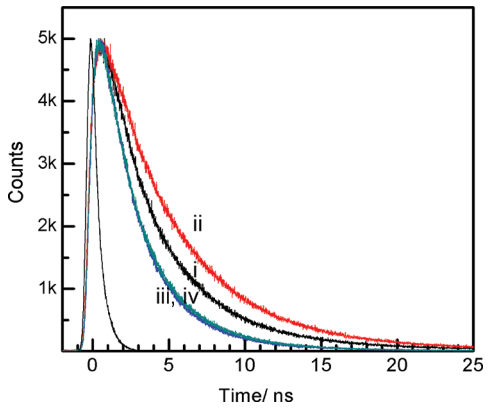

Figure 4. Fluorescence decays of $BP(OH)_2$ in Na^+-exchanged nafion membrane at λ = (i) 6 and (ii) 1 and in $(CH_3)_4N^+$-exchanged nafion membrane at λ = (iii) 6 and (iv) 1. The decays iii and iv are indistinguishable. λ_{ex} = 340 nm. λ_{em} = 375 nm.

CONCLUSIONS

The fluorescent probe $BP(OH)_2$ experiences different environments in native and cation exchanged membranes. The difference in microenvironment because of the presence of the cations in the nafion membranes is manifested in the fluorescence behavior of the dye. In cation exchanged membranes, the emission is observed from the diketo form, as usual. However, the diketo form gets stabilized in the ground state itself in Na^+-exchanged membranes. Thus, the model of differential distribution of the two cations in nafion gains further support. The time integrated and time-resolved spectra of $BP(OH)_2$ in native membranes reveal interesting features. We have observed the slowing down of the proton uptake process by the pyridyl nitrogen after the phenolic oxygen of $BP(OH)_2$ loses protons. This situation is usually ultrafast in homogeneous medium and even in restricted environments like cyclodextrins, surfactant assemblies, and zeolites. It is interesting to note that the phenolate form is usually formed in the alkaline medium. The signature of this phenolate ion is observed in the highly acidic medium of nafion at lower levels of hydration. This is because of the highly restricted environment and an increased electrostatic interaction at lower levels of hydration, which does not allow the protons that are lost to the medium by $BP(OH)_2$ upon excitation to be taken up by the molecule readily. This observation strengthens our earlier inferences on similar lines and indicates that the electrostatic interaction is sufficiently strong so as to be able to disrupt even those proton transfer processes that do not involve a large scale displacement of the proton.

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Notes

The authors declare no competing financial interest.

Table 2. Temporal Features of $BP(OH)_2$ in Cation-Exchanged Nafion Membranes

cation	λ	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1	a_2	a_3	χ^2
Na^+	6	0.59	1.80	4.54	−1.59	1.14	1.44	1.03
	1	0.46		4.90	−1.14		2.14	1.03
$(CH_3)_4N^+$	1, 6	0.52	1.38	4.54	−0.87	0.86	1.01	1.01

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