Regulation of the Extent and Dynamics of Excited-State Proton Transfer in 2-(2′-Pyridyl)benzimidazole in Nafion Membranes by Cation Exchange

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The effect of the microenvironment of a Nafion membrane 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 mechanism of the ESPT is found to depend remarkably on the water content of the membrane. In the protonated form of the membrane, ESPT is found to involve the dicationic (D) form of the fluorophore, whereas in cation-exchanged membranes, it is found to involve the monocation (C). The change in the mechanism and extent of ESPT in cation-exchanged membranes can be explained by considering dehydration of the membrane as well as the less acidic environment around the 2PBI molecules. The slow dynamics is found to result from two factors, namely, slow and incomplete solvation of the transition state, leading to a slowing down of the proton-transfer process, and a slow solvation of the polar tautomeric excited state.

Introduction

Excited-state proton-transfer (ESPT) reactions have generated a lot of interest due to their interesting dynamic properties and potential applications.[1−13] ESPT in restricted environments is especially important as it can lead to the design of devices and sensors.[10] In this paper, we present our observations on the ESPT of 2-(2′-pyridyl)benzimidazole (2PBI) in Nafion membranes. This is in continuation of a systematic investigation of this fluorophore in restricted environments that we have undertaken recently.[9c,d] The photophysics of this probe in neat solutions is well characterized. In aqueous bulk water at pH 7, a single normal emission maximum is obtained at 380 nm, but at a pH range of 3.5−0.5, there is an additional tautomer peak at 460 nm.[7a] In strongly acidic solutions, the 380 nm emission vanishes and a single fluorescence peak at 435 nm is observed (Scheme 1).[7,8] The inclusion of 2PBI in cyclodextrins hinders the solvent-mediated ESPT to some extent due to a shielding of the fluorophore from water.[9a] Very recently, we have reported that the ESPT of 2PBI is enhanced selectively in the negatively charged sodium dodecyl sulfate (SDS) micelles at pH 7.[9c] This observation has been explained by a lower local pH at the micelle−water interface and a change in the pK_a of the fluorophore.[11] The dynamics of the proton transfer in SDS have been found to be slow, much like in several other excited-state processes where a slowing down occurs in restricted environments, mainly because of the incomplete solvation of the transition state involved, leading to a higher energy barrier to the excited-state process.[11] Slow solvation of the phototautomer also leaves its signature in the temporal evolution of fluorescence of the second band. From our results on the ESPT of 2PBI in the micelle−water interface, we propose that the essential requirements for the observation of this phenomenon at pH 7 consist of water as a proton donor, a nonpolar phase, and a negatively charged interface between them. This has been supported in our more recent experiment in AOT reverse micelles.[9d]

In the present paper, we attempt to verify this hypothesis in a solid membrane of Nafion, a perfluorosulfonate polymer, having hydrophilic sulfonate groups attached to fluorocarbon backbone, giving it a reverse micelle-like structure, which can provide microheterogeneous microenvironments to incorporate organic molecules (Scheme 2).[13−15] FT-IR and NMR studies reveal the presence of free and bound water molecules in Nafion.[12b,15] The water molecules close to the interfacial region exhibit an O−H stretching vibration at 3668 cm^{-1}, whereas the O−H stretching occurs at 3500 cm^{-1} for the free molecules.[12b] The origin of the two stretching modes lies in the different degrees of hydrogen-bonding network in the membrane. Thus, Nafion fulfils the essential requirements for testing our hypothesis regarding the nature of microenvironments required for the promotion of ESPT in 2PBI, except for the fact that the water in it is highly acidic in nature.[12] However, this could be an advantage as it is possible to regulate the water content as well as the acidity quite easily by the incorporation of organic and inorganic cations.[12a,b,13] This makes it possible to control the extent as well as the dynamics of the ESPT process by varying the water content of the membrane. This is what we attempt to do in the present experiment.

Experimental Section

2-(2′-Pyridyl)benzimidazole (AR grade), from Aldrich, has been used as received. Nafion-117 membrane of a thickness of 0.007 in., from Sigma-Aldrich, is carefully cleaned by repeated soaking in boiling HNO_3 (1 M) solution for 1 h and, subsequently, in boiling doubly distilled water. The Na^+-exchanged and Me_4N^+-exchanged membranes are prepared by stirring the acid-washed membrane in concentrated NaOH solution or Me_4-NCl (TMAC) solution, respectively, for 24 h, to reach complete equilibrium. The excess base on the surface of the Na^+-exchanged membrane is removed by repeated washing with doubly distilled water. The 2PBI is incorporated into the swollen Nafion membrane by keeping the membrane for 24 h in 2PBI

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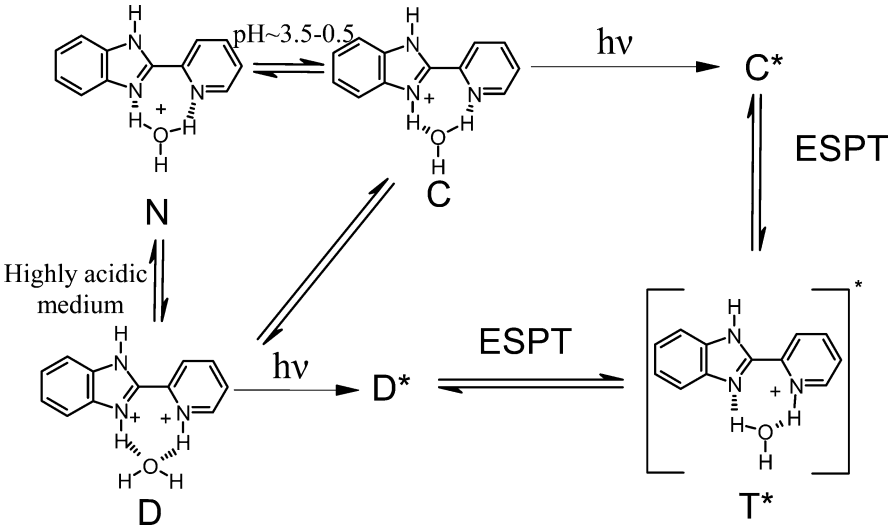
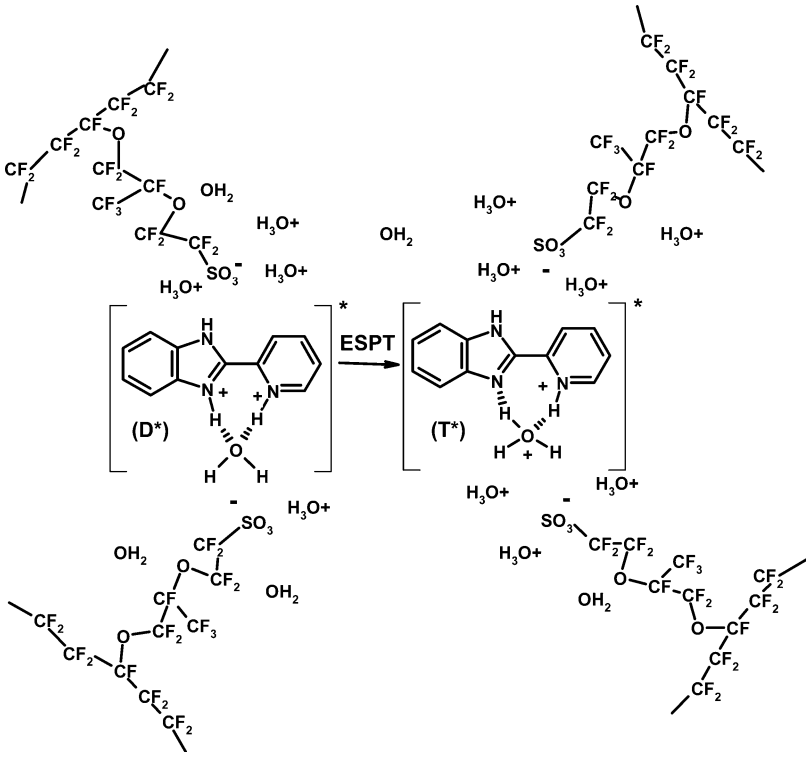
SCHEME 1: Different Channels of ESPT in 2PBI



SCHEME 2: 2PBI in a Nafion Membrane



solution. After loading, and prior to measurements, the membranes are rinsed with doubly distilled water. The amount of 2PBI loaded into the membrane is kept sufficiently low by ensuring that the optical density of the doped membrane is lower than 0.5 at λ_{max}^{abs}.

The absorption spectra have been recorded on JASCO V570 spectrophotometer with 2 nm band-pass. Fluorescence spectra have been recorded on a Perkin-Elmer LS-55 spectrofluorimeter with $\lambda_{ex} = 310$ nm. Time domain fluorescence data have been recorded on a TCSPC spectrometer, with $\lambda_{ex} = 286$ nm, obtained from the third harmonic of a mode-locked Ti:sapphire laser from Spectra Physics, U.S.A.[16a] The fluorescence decays have been collected from the front face of the 2PBI-doped membrane, while ensuring that the specular reflection is guided away from the detection optics. The emission polarizer is kept at the magic angle of 54.7°. The decays have been fitted to multiexponential functions, as well as a distribution of lifetimes, after deconvolution using IBH DAS 6.0 software.[16b,c] To construct the time-resolved emission spectra (TRES), the fluorescence decays of 2PBI across the emission spectrum (330−500 nm) have been recorded at intervals of 10 nm with a band-pass of 2 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).[9c,17]

Results

Absorption and Fluorescence Spectra. It has been reported earlier that 2PBI in aqueous solution at pH 7 has an absorption maximum at 306 nm. In strongly acidic conditions, the absorption maximum is shifted to 329 nm.[7a] On incorporation in the Nafion film, the peak occurs at 330 nm, for acid-washed

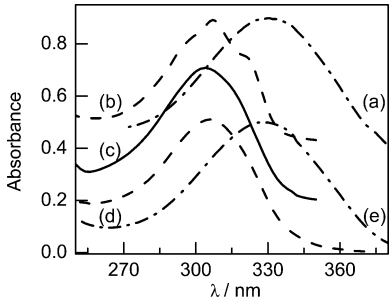


Figure 1. Absorption spectra of 2PBI in (a) Nafion membrane, (b) Na^+-exchanged membrane, (c) Me_4N^+-exchanged membrane, (d) water at pH = 7, and (e) 9 M aqueous H^+. The spectra are peak-normalized and shifted vertically for the sake of comparison and clarity.

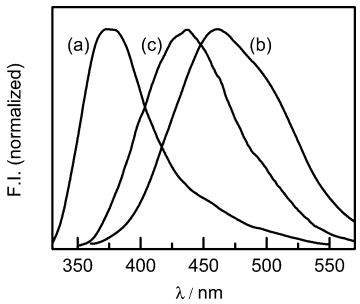


Figure 2. Fluorescence spectra of 2PBI in (a) water at pH = 7, (b) 9 M aqueous H^+, and (c) Nafion film. λ_{ex} = 310 nm. The spectra are peak-normalized for the sake of comparison.

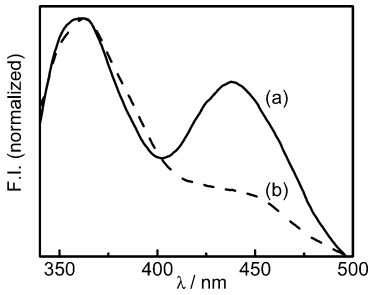


Figure 3. Fluorescence spectra of 2PBI in (a) Na^+-exchanged membrane (solid line) and (b) Me_4N^+-exchanged film (dashed line). λ_{ex} = 310 nm. The spectra are peak-normalized for the sake of comparison.

as well as nonwashed films, irrespective of the loading solvent (Figure 1). On performing cation exchange by Na^+ ion, a distinctly different absorption spectrum is obtained, with a peak at 308 nm and a shoulder at 325 nm, which resembles with that in a nonpolar solvent like *n*-heptane. Similarly, the absorption spectrum of 2PBI in tetramethylammonium chloride (Me_4N^+)-treated Nafion film has a maximum at 305 nm, which is close to that in water at pH 7 (Figure 1). In all the cases, the excitation spectra are superimposable with the absorption spectra. 2PBI in acid-washed Nafion as well as that loaded from water without acid treatment and from acetonitrile solution has λ_{em}^{max} at 440 nm (Figure 2). However, cation exchange by Na^+ ion and Me_4N^+ ion results a drastic change in the emission spectrum of 2PBI. In both cases 2PBI shows a dual emission with peaks at 360 and 440 nm (Figure 3). Here it should be noted that both the bands are blue shifted by 20 nm with respect to that in water. The ratio of normal emission to tautomer emission (I_N/I_T) is higher for the Me_4N^+-exchanged film (I_N/I_T = 4) than that of the Na^+-exchanged film (I_N/I_T = 1.36) by a factor of 3.

Temporal Features of Fluorescence. 2PBI in acid-washed Nafion matrix exhibits biexponential decay at 460 nm (Figure 4a, Table 1). The associated time constants are quite large compared to those in bulk aqueous solution and remain unchanged when 2PBI is loaded from water without acid wash and acetonitrile solution (Figure 4, Table 1). However, cation exchange with Na^+ and Me_4N^+ results in a change in the decay profile of 2PBI. In the Na^+-exchanged films, 2PBI exhibits a triexponential decay at 360 nm (Figure 5a, Table 2). A rise time of 0.48 ns is observed at 460 nm. Similarly, the decay of 2PBI at 360 nm in Me_4N^+-exchanged (TMAC) film is triexponential. A rise time of 0.20 ns is observed at 460 nm, with decay times of 2.05 and 5.33 ns (Figure 5b, Table 2). The fluorescence decays have been recorded at regular intervals with Na^+-exchanged Nafion film, to construct the time-resolved emission spectra (TRES) and time-resolved area-normalized emission spectra (TRANES) (Figure 6), to understand the interstate dynamics in a better way.[17] These spectra exhibit two peaks at 28 149 and 24 000 cm^{-1}, with an isoemissive point at 25 955 cm^{-1}.

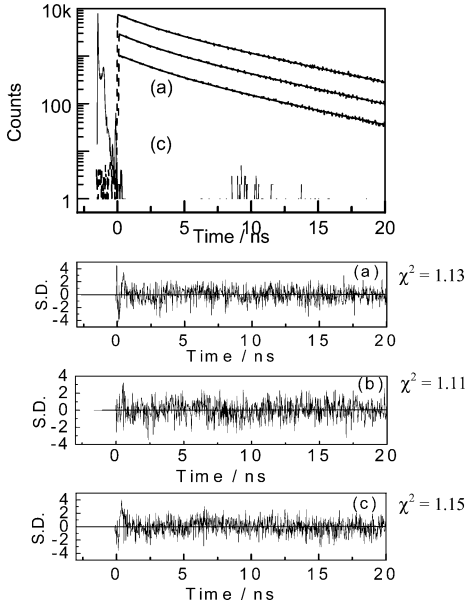


Figure 4. Fluorescence decays of 2PBI at λ_{em} = 460 nm in (a) acid-treated, (b) without acid treatment, and (c) acetonitrile-treated Nafion film. λ_{ex} = 286 nm. The instrument response function is shown in the dashed line and is shifted in time for the sake of clarity. The weighted residuals are shown below the decays.

TABLE 1: Temporal Features of Fluorescence in the Protonated Form of the Nafion Membrane[a]

	τ_1/ns	τ_2/ns	a_1	a_2	χ^2	$\langle\tau\rangle$/ns
HNO_3-washed membrane	2.32	7.00	0.41	0.59	1.13	4.80
membrane without HNO_3 wash	2.22	6.88	0.49	0.50	1.11	4.70
2PBI loaded from CH_3CN	2.35	6.90	0.49	0.51	1.15	4.83

[a] λ_{em}= 460 nm.

Discussion

In aqueous solution at pH 7, 2PBI mainly remains as a neutral form and exhibits an absorption maximum at 306 nm (Figure 1d).[7a,9a] The large red shift of 24 nm in the absorption spectrum of 2PBI upon incorporation in the Nafion matrix indicates the formation of a protonated form of 2PBI, as the spectrum resembles that of 2PBI in 9 M aqueous H^+ (Figure 1a). The spectral shift cannot be due to a change in polarity, as the position of the major absorption peak in *n*-heptane is not very different from that in water. We have earlier observed a red shift of 6 nm in the presence of SDS micelles, and this has

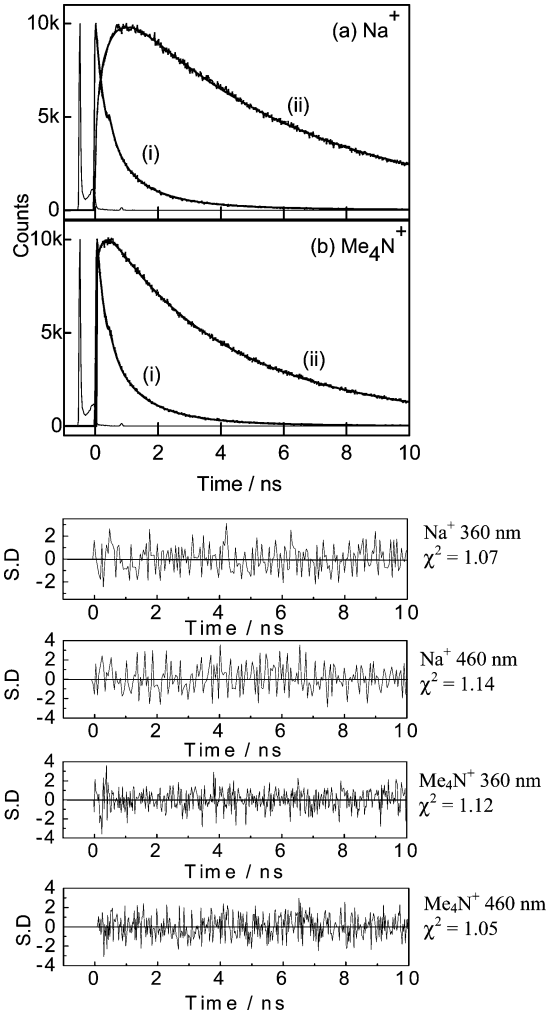


Figure 5. Fluorescence decays of 2PBI in (a) Na^+-exchanged film at (i) 360 nm and (ii) 460 nm; (b) Me_4N^+-exchanged film at (i) 360 nm and (ii) 460 nm. $\lambda_{ex} = 286$ nm. The instrument response functions are shown in the dashed line and are shifted in time for the sake of clarity. The weighted residuals are shown below the decays.

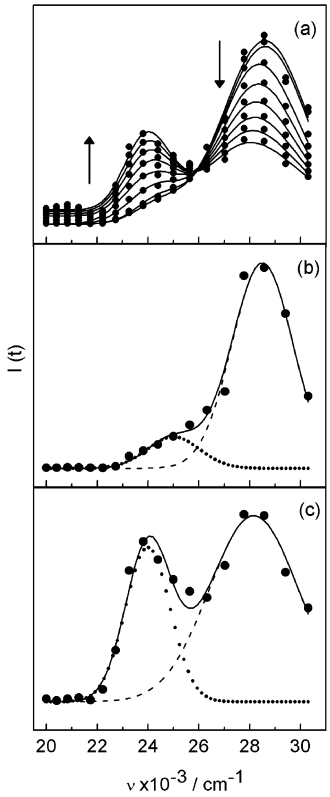


Figure 6. (a) Time-resolved area-normalized emission spectra of 2PBI in Na^+-exchanged film, at times 0, 0.1, 1, 2, 3, 4, 5, and 6.0 ns after excitation. The black circles denote the experimentally obtained time-resolved fluorescence intensities, and the lines denote the best fits to a sum of two Gaussian functions. The arrows indicate the direction of increase in time. The second and the third panels from the top contain the components of TRANES in Na^+-exchanged film at time (b) 0 ns and (c) 6.0 ns after excitation. The fits are shown in solids lines, and the components are shown in the dotted and dashed lines for the C* and T* emissions, respectively.

been explained by an increase in the concentration of the cationic form (C) in the Stern layer.[9c] The large red shift of the absorption spectrum suggests that the dication of 2PBI is the principal absorbing species in Nafion, which is known to be a strong acid.[12] The similarity of the absorption spectrum in the Na^+-exchanged film to that in nonpolar solvents, with the absorption maximum at 308 nm and a shoulder at 325 nm (Figure 1b), indicates that the environment around the 2PBI molecules is quite nonpolar. In the Me_4N^+-exchanged membrane, the absorption spectrum resembles that in aqueous solution ($\lambda_{max}^{abs} = 306$ nm), indicating a water-like environment around 2PBI (Figure 1c). This large blue shift of the absorption spectrum of the Na^+- and Me_4N^+-exchanged membranes with respect to that in the H^+-exchanged one indicates that the nature of the absorbing species changes from dication to cation or neutral form, both of which have absorption maxima at 306 nm.[7a,9a,c] The single emission maximum at 440 nm in acidified Nafion film, irrespective of the solution used for loading (Figure 2c), is reminiscent of the observations in solutions of very high acidity where the species involved are the dication (D) and the tautomer (T), and of these D is almost nonfluorescent.[7a] Notably, the 440 nm emission is fairly strong in the Nafion membrane ($\phi_f = 0.56$). This could be due to the lower polarity experienced by the fluorophore in the Nafion membrane. This contention is supported by the observation that the emission is blue shifted by 20 nm as compared to the emission in very highly acidic aqueous solutions. Now, with the understanding that 2PBI experiences a highly acidic, but somewhat apolar, environment in Nafion, we attempt to explore the changes in its photophysics brought about by lowering the acidity of the membrane. This is achieved by exchanging the H^+ ions with Na^+ and Me_4N^+ ions. Such an ion exchange brings about remarkable changes in the water content of the film, as well.[12a,b,13] Cation exchange by Na^+ as well as Me_4N^+ results in dual emission with emission maxima at 360 and 440 nm, which indicates that the neutral (N) as well as the cationic (C) form of 2PBI is present in the matrix (Figure 3).[9c,d] The ratio of normal emission to tautomer emission (I_N/I_T) is higher for the Me_4N^+-exchanged film than that of the Na^+-exchanged film. This is as per our expectation,

TABLE 2: Temporal Features of Fluorescence in the Cation-Exchanged Nafion Membranes

	$\lambda_{em} = 360$ nm							$\lambda_{em} = 460$ nm						
	τ_1 ns	τ_2 ns	τ_3 ns	a_1	a_2	a_3	χ^2	τ_1 ns	τ_2 ns	τ_3 ns	a_1	a_2	a_3	χ^2
Na^+	0.82	0.25	2.30	0.28	0.65	0.07	1.07	3.40	5.60	0.48	0.10	1.80	−0.90	1.14
Me_4N^+	0.84	0.24	2.20	0.13	0.84	0.03	1.12	2.39	5.39	0.22	0.45	0.93	−0.38	1.05

as the bulky Me_4N^+ is known to replace greater amounts of water than Na^+, and hence the number of neutral 2PBI molecules is expected to be higher in the Me_4N^+-exchanged film than that of the Na^+-exchanged film.

In an earlier study, it is reported that the Na^+ or H^+ form of the membrane contains about 40% (wt) water. The microenvironment inside the membrane is not homogeneous, as there are some domains that are quite polar and some that are apolar.[12] From our steady-state absorption and emission spectrum it is clear that despite the high water content of the Na^+-exchanged membrane, 2PBI experiences microenvironments that are quite apolar. In the Na^+-exchanged Nafion, the cationic form of 2PBI remains close to the interface region due to the specific electrostatic interaction with the sulfonate headgroups, where the polarity is quite low compared to that in water. However, in the case of Me_4N^+-form membrane, the situation is quite different, as the cationic form of 2PBI experiences a water-like environment. This could be due to the increased hydrophobic nature of the interface in the membranes that contain the bulky organic cation. The cation, being somewhat hydrophilic, can be expected to move away from the interface toward the water pool in the membrane, in such a situation. 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.

The decay of 2PBI in the acidified Nafion film at 460 nm is biexponential, with time constants of 2.32 ($a_1 = 0.41$) and 7.00 ns ($a_2 = 0.59$) (Figure 4a, Table 1). Similar decay profiles have been observed, when 2PBI is loaded from neutral aqueous (Figure 4b) and acetonitrile solutions (Figure 4c). Earlier studies by Rodriguez-Prieto et al. have shown that, at pH 3.8, the fluorescence profile at 460 nm has a rise time of 0.65 ns and a decay time of 1.8 ns, assigned to the emission from the tautomeric form of 2PBI.[7a] Our previous studies of the ESPT of 2PBI in SDS micelles and Aerosol OT reverse micelles have revealed that the lifetime of the tautomeric form of 2PBI is 3.5−3.9 ns. From the steady-state results it is clear that the only species that emits at 460 nm is the tautomeric form of 2PBI, and hence the biexponential decay at 460 nm is due to the heterogeneity in microenvironments experienced by the tautomeric form in the membrane. The 2.32 ns component is very close to the 1.8 ns component observed in bulk water at pH 3.8 and hence is assigned due to the tautomeric form of 2PBI in the free water pools in the membrane. The 7 ns component is assigned to the tautomeric form of 2PBI located in less polar polymer chains. Here it should be noted that the emission at 460 nm is not associated with a rise time in the time scale investigated, unlike our earlier results in SDS and AOT reverse micelles, where a rise time of 0.8−0.9 ns was observed. This is because the species responsible for the ESPT is not the monocationic form but the dication of 2PBI. The tautomerization of 2PBI can be observed from either the cationic or dicationic form. It is known that in highly acidic media, the large concentration of H^+ ions leads to the formation of the dication, as is evident from the disappearance of the 360 nm band in the steady-state emission spectrum.

The 0.25 ns component ($a_2 = 0.65$) in the Na^+-exchanged film is assigned to the decay of the normal form, and the 0.82 ns component ($a_1 = 0.28$) is assigned to the decay of the cationic form of 2PBI, as in SDS micelles and Aerosol OT reverse micelles (Figure 5, Table 2).[9c,d] The minor component of 2.30 ns ($a_3 = 0.07$) may be due to the tail of the tautomeric emission. The traces at the red end (460 nm) have a rise time of 0.48 ns, with decay components of 3.40 and 5.60 ns. The decay kinetics at 360 nm in the Me_4N^+-exchanged film are the same as that of the Na^+-exchanged film, but at the red end (460 nm) it exhibits a 0.22 ns rise time (Figure 5, Table 2). Thus, cation exchanged by Na^+ and Me_4N^+ with the film leads to the formation of normal as well as the cationic form of 2PBI. Thus, the time-resolved data are in excellent agreement with the steady-state results. Now, the issue that should to be addressed is the appearance of rise time at 460 nm decay of 2PBI in the Na^+- and Me_4N^+-exchanged films.

Cation exchange is essentially a dehydration or deswelling process.[12a,b,13] With increasing cation concentration, the amount of free water molecules which are capable of forming the H-bonding network is diminished compared to that of the bound water molecules.[12b] In the present study, the ultrafast ESPT of 2PBI in the H^+ form of Nafion can be associated to the presence of the large number of H-bonding networks. In the cation-exchanged film the H-bonding network is disrupted, and the proton tunneling through the available water molecules has to overcome a higher activation energy, and thus the process becomes slow. Moreover, in our recent study we have shown that the dipole moment of the C* is 2.7 D, whereas that of the T* is 7.9 D.[9d] This large change of dipole moment (5.2 D) in the C*−T* tautomerization process results in slow and incomplete solvation of the T* state after it is formed, and hence in the microheterogeneous system, it is likely that both the mechanisms operate simultaneously. In the following paragraph, we present an attempt to address the problem, using the method of time-resolved area-normalized emission spectroscopy (TRANES).[17] However, before we do so it is imperative to explore the issue of possible alternate techniques of analysis of the time-resolved fluorescence data.

Nafion is a complicated microheterogeneous system, which consists of several regions of differing hydrophobicities, each of which might accommodate the fluorophore molecules to different extents. The distribution of fluorophores in these different regions might lead to a distribution of fluorescence lifetimes as well. It is well-known that simple multiexponential decay kinetics might provide apparently good fits in such systems.[18] So such an analysis can be misleading and might lead to erroneous two- or three-state models for systems which should more appropriately be described by a range of closely lying excited states, i.e., by a distribution of lifetimes or a stretched exponential form of the decay law.[19] In fact, the question of the appropriateness of such models of data analysis has recurred in earlier fluorescence studies in Nafion. The emission of $Ru(bpy)_3^{2+}$ in Nafion, for example, was earlier fitted with a distribution of lifetimes.[13a,20a,b] However, in a more recent study, a biexponential decay has been found to be adequate in this system, at low concentrations of the fluorophore.[20c,d] Similarly, the fluorescence decay of the ethidium bromide fluorophore has been found to obey a biexponential rate law.[20e] To ascertain the correct form of the decay law, we have fitted the decays to a distribution of lifetimes. However, such analyses have invariably led to distinct bimodal distributions with very narrow widths in cases where we had earlier obtained biexponential decays. The modal lifetimes have turned out to be the same as the values obtained from multiexponential analyses. The spreads are typically found to be 1−2% of the modal lifetimes, thereby validating the multiexponential analyses that we have performed originally.

Recently Periasamy and co-workers have developed the

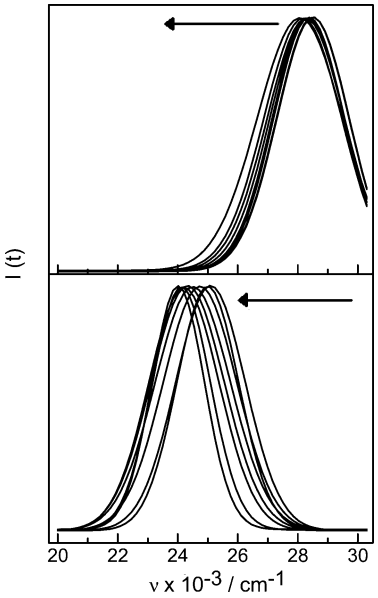


Figure 7. Time evolution of emission spectra at times 0, 0.1, 1, 2, 3, 4, 5, and 6.0 ns after excitation. The upper panel contains the peak-normalized, time-resolved emission spectra of 2PBI in Na^+-exchanged film in the region of normal emission, and the lower panel contains those in the region of tautomer emission. The arrows denote the direction in which time increases.

technique of TRANES and have established that an isoemissive point in TRANES indicates the presence of two distinct emissive species.[17a,b] In the present study, the TRANES of 2PBI in Na^+-exchanged Nafion film exhibits two prominent peaks in the region of the normal and tautomer emission. An isoemissive point is obtained at 25 955 cm^{-1} (Figure 6a). The spectra can be resolved into two components, the redder one of which can be assigned to the tautomer emission (Figure 6b,c). With the passage of time, the band at 24 000 cm^{-1} is clearly seen to grow at the expense of the one at 28 149 cm^{-1}. Since the component at the lower energy grows from that at the higher energy, it can be ascribed to the emission from the tautomeric and the cationic excited states, respectively. A small time-dependent Stokes shift (TDSS) is observed for the cationic emission over a period of 6 ns, while the TDSS of the tautomer peak is quite significant (Figure 7). This is clearly a signature of dynamic solvation of the tautomeric form (T*), after it is formed through the ESPT process. So, some amount of the rise time observed at 460 nm must be due to the slow solvation of T*. Moreover, the intensity of the tautomer band at time zero is considerable (Figure 6). Thus, there is a considerable amount of ESPT within the zero time of our experiment. Of course, the mechanism involving the slowing down of the ESPT process itself is also operative, as the TRANES in the time range of 0−6.0 ns shows an isoemissive point, indicating that the ESPT from the cationic 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 the mechanisms discussed above.

Conclusion

Ultrafast ESPT in Nafion films is found to be slowed by cation exchange. This slowing down is accompanied by a changeover in the mechanism of proton transfer. The D*−T* equilibrium makes way for the C*−T* equilibrium as the Na^+ or Me_4N^+ ions displace water and hydronium ions, thereby causing a marked decrease in the water content of the membrane. The free water is mainly displaced, and this is one of the reasons why a growth is observed for the tautomeric emission, as the fractional contribution of the bound water molecules increases upon cation exchange. These observations can indicate a possible application of 2PBI as a ratiometric fluorescent probe of the water content of anionic polymer films.

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References and Notes

(1) (a) Catalan, J.; Perez, P.; Del Valle, J. C.; de Paz, J. L. G.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 419. (b) Agmon, N. *J. Phys. Chem. A* **2005**, *109*, 13.

(2) (a) Schultz, T.; Samoylova, E.; Radloff, W.; Hertel, I. V.; Sobolewski, A. L.; Domcke, W. *Science* **2004**, *306*, 1765. (b) Chou, H.-C.; Ching-Hao, C.; Cheng, Y.-M.; Cheng, C.-C.; Liu, H.-W.; Pu, S.-C.; Chou, P.-T. *J. Am. Chem. Soc.* **2004**, *126*, 1650. (c) Klymchenko, A. S.; Demchenko, A. P. *J. Am. Chem. Soc*. **2002**, *124*, 12372.

(3) (a) Kosower, E. M.; Huppert, D. *Annu. Rev. Phys. Chem.* **1986**, *37*, 127. (b) Petrich, J. W. *Int. Rev. Phys. Chem.* **2000**, *19*, 479. (c) Pal, S.; Balasubramanian, S.; Bagchi, B. *Phys. Rev. Lett.* **2002**, *89*, 115505. (d) Dutta, P.; Sen, P.; Mukherjee, S.; Bhattacharyya, K. *Chem. Phys. Lett.* **2003**, *382*, 426.

(4) (a) Smith, T. P.; Zaklika, K. A.; Thakur, K.; Walker, G. C.; Tominaga, K.; Barbara, P. F. *J. Phys. Chem.* **1991**, *95*, 10465. (b) Pfeiffer, M.; Lau, A.; Lenz, K.; Elsaesser, T. *Chem. Phys. Lett.* **1997**, *268*, 258. (c) Takeuchi, S.; Tahara, T. *Chem. Phys. Lett.* **2001**, *347*, 108.

(5) (a) Rios, M. A.; Rios, M. C. *J. Phys. Chem. A* **1998**, *102*, 1560. (b) Fahrni, C. J.; Henary, M. M.; Van Derveer, D. G. *J. Phys. Chem. A* **2002**, *106*, 7655.

(6) (a) Rodriguez, M. C.; Penedo, J. C.; Willemse, R. J.; Mosquera, M.; Rodriguez-Prieto, F. *J. Phys. Chem. A* **1999**, *103*, 7236. (b) Penedo, J. C.; Mosquera, M.; Rodriguez-Prieto, F. *J. Phys. Chem. A* **2000**, *104*, 7429.

(7) (a) Rodríguez-Prieto, F.; Mosquera, M.; Novo, M. *J. Phys. Chem.* **1990**, *94*, 8536. (b) Novo, M.; Mosquera, M.; Rodríguez-Prieto, F. *Can. J. Chem.* **1992**, *70*, 823. (c) Novo, M.; Mosquera, M.; Rodríguez-Prieto, F. *J. Phys. Chem.* **1995**, *99*, 14726.

(8) (a) Kondo, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3027. (b) Brown, R. G.; Entwistle, N.; Hepworth, J. D.; Hodgson, K. W.; May, B. *J. Phys. Chem.* **1982**, *86*, 2418.

(9) (a) Rath, M. C.; Palit, D. K.; Mukherjee, T. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1189. (b) Douhal, A.; Fiebig, T.; Chachisvilis, M.; Zewail, A. H. *J. Phys. Chem. A* **1998**, *102*, 1657. (c) Mukherjee, T. K.; Ahuja, P.; Koner, A. L.; Datta, A. *J. Phys. Chem. B* **2005**, *109*, 12567. (d) Mukherjee, T. K.; Panda, D.; Datta, A. *J. Phys. Chem. B* **2005**, *109*, 18895.

(10) (a) Kim, S.; Chang, D. W.; Park, S. Y.; Kim, K.; Jin, J.-I. *Bull. Korean Chem. Soc*. **2001**, *22*, 1407. (b) McAnaney, T. B.; Park, E. S.; Hanson, G. T.; Remington, S. J.; Boxer S. G. *Biochemistry* **2002**, *41*, 15489.

(11) (a) Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. *Acc. Chem. Res.* **1991**, *24*, 357. (b) Dutta, P.; Halder, A.; Mukherjee, S.; Sen, P.; Sen, S.; Bhattacharyya, K. *Langmuir* **2002**, *18*, 7867. (c) Giestas, L.; Yihwa, C.; Lima, J. C.; Vautier-Giongo, C.; Lopes, A.; Macanita, A. L.; Quina, F. H. *J. Phys. Chem. A* **2003**, *107*, 3263. (d) Roy, D.; Karmakar, R.; Mondal, S. K.; Sahu, K.; Bhattacharyya, K. *Chem. Phys. Lett.* **2004**, *399*, 147.

(12) (a) Szentirmay, M. N.; Prieto, N. E.; Martin, C. R. *J. Phys. Chem.* **1985**, *89*, 3017. (b) Mauritz, K. A.; Gray, C. L. *Macromolecules* **1983**, *16*, 1279. (c) Zhao, F.; Zhang, J.; Kaneko, M. *J. Photochem. Photobiol., A* **1998**, *119*, 53. (d) Mehata, M. S.; Joshi, H. C.; Tripathi, H. B. *Spectrochim. Acta, Part A* **2003**, *59*, 559.

(13) (a) Lee, P. C.; Meisel, D. *J. Am. Chem. Soc.* **1980**, *102*, 5477. (b) Szentirmay, M. N.; Martin, C. R. *Anal. Chem.* **1984**, *56*, 1898. (c) Yeager, H. L.; Steck, A. *Anal. Chem.* **1979**, *51*, 862. (d) Moore, R. B., III; Wilkerson, J. E.; Martin, C. R. *Anal. Chem.* **1984**, *56*, 2572.

(14) (a) Lee, P. C.; Meisel, D. *Photochem. Photobiol.* **1985**, *41*, 21. (b) Robertson, M. A. F.; Yeager, H. L. *Macromolecules* **1996**, *29*, 5166. (c) Tachikawa, T.; Ramaraj, R.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. B* **2005**, *109*, 3381.

(15) Komoroski, R. A.; Mauritz, K. A. *J. Am. Chem. Soc.* **1978**, *100*, 7487.

(16) (a) Thiagrajan, V.; Selvaraju, C.; Padma Malhar, E. J.; Ramamurthy, P. *ChemPhysChem* **2004**, *5*, 1200. (b) Mishra, P. P.; Koner, A. L.; Datta, A. *Chem. Phys. Lett.* **2004**, *400*, 128. (c) Mukherjee, T. K.; Mishra, P. P.; Datta, A. *Chem. Phys. Lett.* **2005**, *407*, 119.

(17) (a) Koti, A. S. R.; Krishna, M. M. G.; Periasamy, N. *J. Phys. Chem. A* **2001**, *105*, 1767. (b) Koti, A. S. R.; Periasamy, N. *J. Chem. Phys.* **2001**, *115*, 7094. (c) Maciejewski, A.; Kubicki, J.; Dobek, K. *J. Phys. Chem. B* **2003**, *107*, 13986.

(18) (a) James, D. R.; Ware, W. R. *Chem. Phys. Lett.* **1985**, *120*, 455. (b) James, D. R.; Liu, Y. S.; De Mayo, P.; Ware, W. R. *Chem. Phys. Lett.* **1985**, *120*, 460.

(19) (a) Flomenbom, O.; Velonia, K.; Loos, D.; Masuo, S.; Cotlet, M.; Engelborghs, Y.; Hofkens, J.; Rowan, A. E.; Nolte, R. J. M.; der Auweraer, M. V.; de Schryver, F. C.; Klafter, J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 2368. (b) Pevenage, D.; Van der Auweraer, M.; De Schryver, F. C. *Langmuir* **1999**, *15*, 4641.

(20) (a) Colon, J. L.; Martin, C. R. *Langmuir* **1993**, *9*, 1066. (b) Ishiji, T.; Kudo, K.; Kaneko, M. *Sens. Actuators, B* **1994**, *22*, 205. (c) Demas, J. N.; De Graff, B. A. *Sens. Actuators, B* **1993**, *11*, 35. (d) Mazzetto, S. E.; de Carvalho, I. M. M.; Gehlen, M. H. *J. Lumin.* **1998**, *79*, 47. (e) Bunker, C. E.; Rollins, H. W.; Ma, B.; Simmons, K. J.; Liu, J.-T.; Ma, J.-J.; Martin, C. W.; DesMarteau, D. D.; Sun, Y.-P. *J. Photochem. Photobiol., A* **1999**, *126*, 71.