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Importance of Electrostatic Interactions in The Mobility of Cations in Nafion

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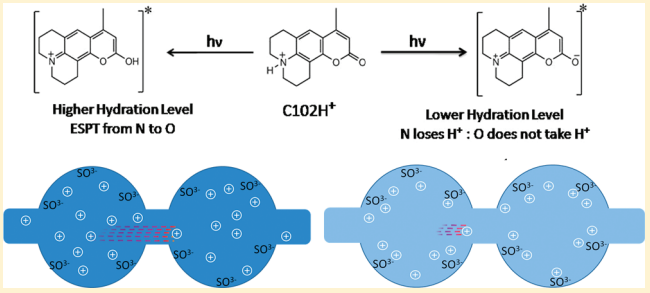
ABSTRACT: A molecular level understanding of the mobility of cations in the Nafion membrane has been attempted, using the excited state proton transfer (ESPT) process in the fluorescent probe Coumarin 102. ESPT is hindered significantly upon decreasing the water content. Using TRANES (time-resolved area normalized emission spectroscopy), the evolution of the ESPT state is clearly observed over hundreds of picoseconds in lower water content, implying that ESPT is hindered even in the nanovolume probed by the dye. Most remarkably, in the partially dried membrane, the predominant fluorescent species is the zwitterionic form, generated by excited state deprotonation of the cationic form. This implies that the molecule loses a proton from its nitrogen center in the excited state, as usual, but cannot recapture it readily at the oxygen center, at low water contents. This phenomenon is rationalized in light of an increased electrostatic attraction that is experienced by cations upon drying.



INTRODUCTION

Polymer electrolyte membranes play a significant role in various physical, chemical, and industrial processes. A major application of such membranes is in fuel cells where the electrode compartments are separated by a diaphragm that conducts either cations or anions selectively. Nafion (Scheme 1), a perfluorosulfonate polymer with pendant sulfonate groups, is the most popular among such membranes because of its significantly high proton conductivity and no anion uptake.[1] The proton conductivity of the membrane is affected by various factors like water content,[2] temperature,[3] and structure of the water channel network.[8] Exploring the structure of the membrane and understanding the transport of H^+ ions have been of primary interest, with a view to design better membranes for fuel cell applications. One of the earliest attempts to understand the morphology of Nafion was by Gierke et al. using small-angle X-ray scattering.[4] This study proposed the occurrence of ionic clusters of sulfonate groups which hold water molecules in pockets. These clusters are believed to join up upon hydration, to form channels that facilitate the movement of water and protons. Quasistatic neutron scattering and NMR experiments have indicated that the water pools are very similar to those of microemulsions.[5,6] At higher hydration levels, the reverse micellar structure is believed to collapse and merge to form a branched network[7] that allows water and protons to diffuse.

This cluster-network model is widely accepted. Yet, it is extensively debated too. Schmidt-Rohr and Chen, for instance, have proposed a parallel cylindrical water channels model[8] which has been briefly described later. Some other models that have been proposed involve polymer bundles in a hydrated matrix,[9−11] hydrated bilayer stacks,[12] network model,[13,14] alternate polymer−water layers,[7] etc. Starkweather proposed the highly crystalline structure characterized from DSC experiments.[15] Gebel et al. have proposed that a modification in swelling process occurs at higher water contents. This is attributed to the inversion of reverse micellar form to form rodlike particles. Later, the same group proposed a fibrillar structure, with water between the fibrils, forming an aqueous continuum. These alternative models contain constrictions of about 0.6 nm, which approximates the thickness of two water molecules. This thickness would be very close to the water around the ionic clusters, with significantly less efficient diffusion.[16] However, the self-diffusion coefficient of water in Nafion is about an order of magnitude larger than that of other persulfonated resins.[17] The parallel water channels in the Schmidt−Rohr model have diameters of ca. 2.4 nm with hydrophilic groups aligned inside resembling cylindrical reverse micelles. These relatively wide channels favor a large hydrodynamic component of water transport. At low water contents a new topology is achieved, resulting from random connectivity of water channels enabling water transport. The model is limited to lengths of a few tens of nanometers. According to Gierke's model, all water, except bound water, should freeze at low temperature, and hence slow diffusion should be observed. This is contrary to the observation.[18] This model involving parallel water channels suggests that water in larger channels freezes, while in narrower channels it continues to diffuse and does not freeze even down to −70 °C. Meanwhile, Kreuer et al. studied diffusion in Nafion membranes and suggested that sulfonate groups hold water molecules tightly, making them unavailable for conduction.[17] In a

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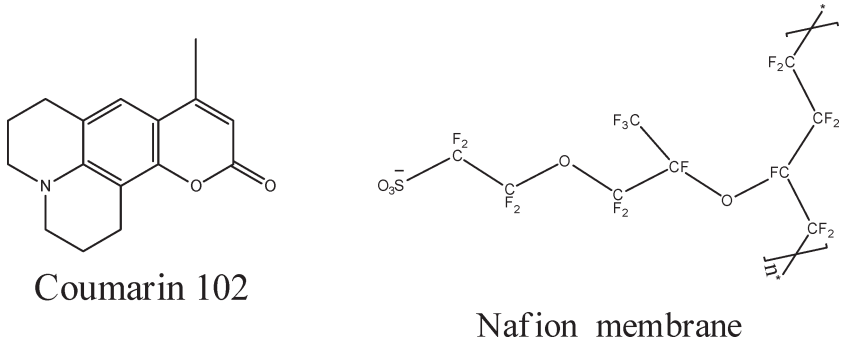
Scheme 1. Structures of Coumarin 102 and Nafion



nutshell, all models eventually converge either to a parallel channel model or to a cluster model, depending on the water content. Molecular dynamics simulations have been used to examine almost all of these model, especially to explain the ionomer peak obtained in scattering studies. Because the debate of the structure of Nafion and the mechanism of proton conduction is not settled by scattering experiments, various other experiments and simulation studies are needed to be carried out to address this issue.

Falk and co-workers have discovered a range of aqueous environments in Nafion, by probing the OH and OD stretching frequencies.[19] Their results predict the presence of a network of interconnected water channels. In more recent times, Fayer and co-workers have explored this issue by sophisticated time-resolved IR (TRIR) and fluorescence spectroscopy.[20] A dramatic decrease in the number of embedded water molecules, which are in close proximity to the fluorocarbon chain, with decreasing hydration level is observed. A distribution of vibrational lifetimes indicative of structural changes in Nafion with varying water content is reported. The time-resolved fluorescence anisotropy experiments have indicated that virtually no reorientation occurs at low water levels, and there is so little water present that it is not possible to find a new hydrogen acceptor for proton transfer to occur.[21,22] It is further observed that orientation dynamics of water are wavelength independent and hence depend on global characteristics of the hydrogen bond rather than local effects.[23] At low water contents, these hydrogen bonds become constrained leading to poor proton mobility. Many experiments have been done using various probes that sense the interface and core;[24,25] e.g., hydroxypyrenetrisulfonate (HPTS) probes the core of the water pool, and Rhodamine 6G being cationic prefers to be at the interface. It is shown that at low water contents the environments experienced by both the molecules are very similar, and both water dynamics and excited state proton transfer (ESPT) are attenuated at low water concentrations.[26,27]

Solvation dynamics of Coumarin 102, a well-known solvation probe,[28] in hydrated Nafion membranes and in cation-exchanged membranes has been studied by our group.[29] In recent times, TDSS is used successfully to understand the dynamics and structure of many interesting microheterogeneous media.[30,31] Our results are in line with the fact that there are at least two regions of water in Nafion. In a separate experiment we have observed that ultrafast ESPT is slowed down by cation exchange in Nafion membranes.[32] We have used the probe C102 to understand the nature of water pools in the Nafion membrane and how they are affected by water content using fluorescence as a tool. In this article, we discuss the effect of lower water content of the Nafion membrane on ESPT in Coumarin 102. The motivation for the present study is to have a molecular level understanding of the role of water molecules in proton transport. Such a study can help in developing membranes by making modifications in the structure or incorporating materials that can affect and enhance the proton transport. It may be mentioned here that a study like this is confined to the microenvironment experienced by the probe molecule. So, the scope is limited to the study of local phenomena.

EXPERIMENTAL SECTION

Coumarin 102 from Laser Dyes has been used as received. Nafion117 of thickness 0.007 in. and equivalent weight of 1100 g equivalents has been procured from Sigma Aldrich and has been carefully cleaned by repeated soaking in HNO_3 and water alternatively for 3 h each. The process is repeated at least three times or until the membrane is transparent and colorless. The Na^+- and Me_4N^+-exchanged membranes are prepared by soaking the membranes in concentrated aqueous solutions of NaCl and Me_4NCl, respectively, for 24 h. The excess salt on the surface is removed by repeated washing with Millipore water. C102 is incorporated by dipping the membrane in aqueous solution of the dye, containing the same cation as that present in the membrane. The absorbance of C102 in the membrane is kept below 0.5. This ensures that the quantity of dye is sufficiently low so that the inherent properties of the membrane are not affected and there is no possibility of dye−dye interaction either. The dried membranes are prepared by heating the hydrated membranes in a vacuum oven at 70 °C until there is no further loss in weight. They are sealed and kept in a nitrogen environment during the course of the experiment. The hydrated membrane had 10% w/w water in the membrane, as this is the loss in weight upon drying. This corresponds to a value of $\lambda = 6$ in hydrated membranes and $\lambda = 1$ in less hydrated membranes; λ is a measure of water content in Nafion membranes.[33]

The absorption spectra have been recorded in a JASCO V530 spectrophotometer, and fluorescence spectra are measured in a Varian Cary eclipse fluorimeter. The fluorescence decays have been recorded on an IBH Fluorocube TCSPC spectrometer at a resolution of 7 ps/channel and at magic angle polarization with respect to the excitation light. The excitation sources used are 340 nm (fwhm = 700 ps) and 406 nm (fwhm = 200 ps). The fluorescence is collected from the back surface of the Nafion membranes kept at 45° with the incident light beam. That way, the specular reflection is guided to the direction opposite to that of detection. The decays have been fitted to a sum of exponentials by IBH DAS 6.2 software using an iterative reconvolution technique. To construct the time-resolved emission spectra (TRES), the

decays have been recorded at suitable intervals throughout the range of the fluorescence spectrum. The fitted fluorescence decay has been scaled with a steady state spectrum following the usual procedure.[34] The spectra thus generated are normalized to unit area to generate time-resolved area normalized spectra (TRANES).[35,36]

RESULTS AND DISCUSSION

The absorption maximum of C102 in the native Nafion membrane occurs at 277 nm (Figure 1). This corresponds to the absorption of protonated Coumarin 102, with the nitrogen atom bearing the proton. These values are close to the calculated values arising from nearly degenerate HOMO-1 to LUMO and HOMO to LUMO+1 transitions of $C102H^+$.[37] It is not surprising that Coumarin 102 is protonated in Nafion, as the membrane is a superacid.[29,32] No change in the absorption spectrum is observed upon drying the membrane. So, the ground state of the C102 is the same irrespective of hydration levels of the membranes. The small increase in absorbance upon drying can be attributed to the change in concentration that arises due to the decrease in water content. The changes in the fluorescence spectra are more dramatic (Figure 1). In the hydrated membranes, there is a highly Stokes' shifted emission with the spectral maximum at 520 nm. This band is assigned to a state that arises as a result of proton transfer (ESPT) from the nitrogen atom to the oxygen atom of $C102H^+$, post excitation (Scheme 2).[38] Interestingly, a new blue-shifted band at 450 nm appears in the emission spectrum, in addition to the ESPT band at 520 nm, upon decreasing the water content of the membrane (Figure 3a). In the cation-exchanged Nafion membrane[29] the emission band occurs at 480 nm, which is the characteristic emission band of the electroneutral, zwitterionic C102*. Thus, C102 is found to undergo deprotonation in its excited state, upon drying the Nafion membrane. In this context, the ESPT in the native, hydrated membrane can be thought of to consist of a deprotonation at the nitrogen center and a subsequent or concerted uptake of a proton at the oxygen center of $C102H^+$ in its electronically excited state. In the less hydrated membrane, the deprotonation takes place as usual, but the uptake of the proton is obviously hindered. The hindrance to the uptake of proton indicates that the medium has become less prone to donate protons to the probe, upon drying. In other words, the observation is a manifestation, in the molecular level, of the reduced mobility of protons in dried membranes. In the macroscopic scale, that would correspond to the decrease in the all-important proton conductivity in membranes of lower hydration levels. This is intriguing, as the amount of H_3O^+ ions in Nafion remains the same, irrespective of the membrane being hydrated or dried, as the pK_a value of sulfonate groups is -6.[39] The groups remain deprotonated even at extremely high concentrations of proton and are unlikely to combine with protons to form sulfonic acid groups. Moreover, the absorption spectrum of the probe remains unaffected, further bolstering the contention that acidity experienced by the fluorescent probe in the dried membrane is not significantly different from that in the hydrated membrane. It is worthwhile to note that a very small, but observable, signature of locally excited zwitterions is observed in steady state spectra of the hydrated membrane. In the dried membrane, the fluorescence intensities due to the zwiterrion and the ESPT band of the cation are more or less equal. The quantum yield of the probe molecule decreases by more than six times upon drying the membrane. The reason has been explained later.

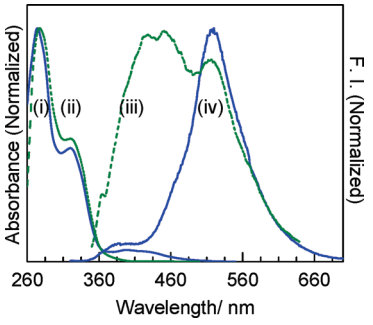
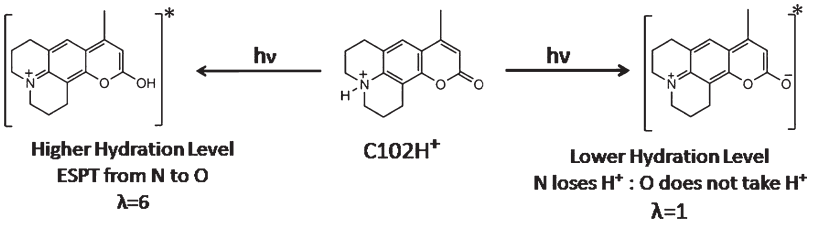


Figure 1. Absorption (i and ii) and fluorescence (iii and iv) spectra of Coumarin 102 in native Nafion membranes that are hydrated to a greater extent (λ = 6, solid blue lines) and to a lesser extent (λ = 1, dashed green lines).

Time-resolved fluorescence experiments have been carried out to probe the proton transfer further. The decays have been recorded at various wavelengths across the emission spectra of C102 in both hydrated and dried membranes. The decays of Coumarin 102 in the hydrated membrane are fitted to multiexponential functions (Table 1). The longest lived state is likely to have arisen due to stronger electrostatic interaction between the cationic excited state and anionic sulfonated groups.[29] The decays do not vary significantly with the emission wavelength (Figure 2). In contrast, the decays of Coumarin 102 in the dried membrane show significant dependence on the emission wavelength. In the blue region, i.e., at 380 nm, there is a fast decay of about 500 ps and another component of average lifetime 5 ns. In the red region, there is a growth of about 500 ps and a slow decay (Figure 2, Table 1). The slow component gets slowed down further, by more than factor of 2, upon drying. This indicates that the probe is in a much more restricted environment in the dried membrane. The rate constants of protonation and deprotonation of Coumarin 102 in the excited state have been determined earlier.[38,40] The deprotonation is known to be dynamic and practically irreversible. The protonation rate is 4.15×10^9 s^{-1}. We observe a fast decay of ~500 ps close to the nonradiative rate determined above. Thus, the component has been assigned to the decay of the neutral species, the locally excited zwitterion. The slow component is associated with the decay of the protonated form of Coumarin 102. The rise time corresponds to evolution of

Scheme 2. Excited-State Processes in Coumarin 102 in Nafion at Different Levels of Hydration



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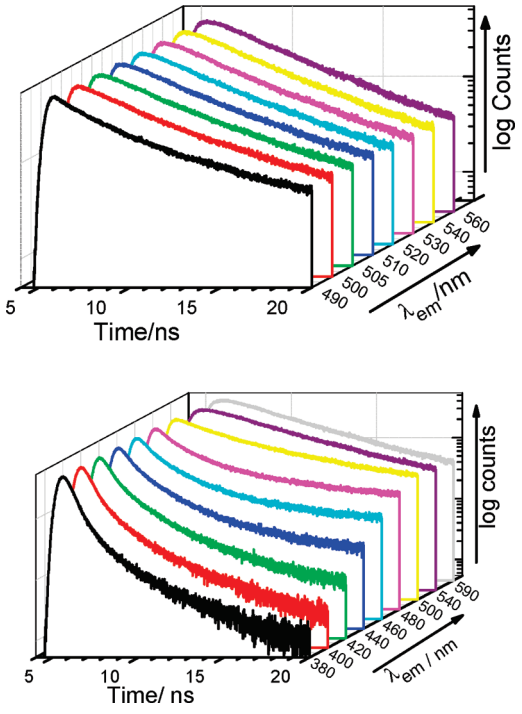

Figure 2. Fluorescence decays of Coumarin 102 in native membranes. Top: λ = 6, λ_{em} = 490 nm (black), 500 nm (red), 505 nm (green), 510 nm (blue), 520 nm (cyan), 530 nm (magenta), 540 nm (yellow), 560 nm (purple). Bottom: λ = 1, λ_{em}= 380 nm (black), 400 nm (red), 420 nm (green), 440 nm (blue), 460 nm (cyan), 480 nm (magenta), 500 nm (yellow), 540 nm (purple), 590 nm (gray).

Table 1. Temporal Features of Fluorescence of Coumarin 102 in Nafion Membranes

	high hydration level (λ = 6)						low hydration level (λ = 1)					
λ_{em}	τ_1 / ns	τ_2/ ns	τ_3/ ns	a_1	a_2	a_3	τ_1/ ps	τ_2/ ns	τ_3/ ns	a_1	a_2	a_3
380	--	--	--	--	--	--	537	2.1	--	0.89	0.10	--
440	--	--	--	--	--	--	587	2.4	--	0.69	0.30	--
490	--	4.8	13.7	--	0.88	0.12	596	3.9	14.6	0.46	0.37	0.15
510	--	4.8	15.3	--	0.91	0.09	420	4.6	14.4	−0.17	0.36	0.81
540	0.41	5.1	--	−1.17	2.17	--	513	4.7	19.3	−1.36	2.19	0.16

the protonated form of Coumarin from locally excited zwitterions. The fast decay observed is responsible for the low quantum yield of dye in the dried membrane, mentioned earlier in this article.

Time-resolved area normalized spectra (TRANES) have been constructed to identify the various components. It has been established by Periasamy and co-workers that the presence of isoemissive points in these spectra indicates the occurrence of multistate equilibria. A single isoemissive point in TRANES is known to indicate a two-state process within the time scale of investigation.[35,36] The TRANES of Coumarin 102 constructed over the first nanosecond in hydrated and dry membranes have been shown in Figure 3b and 3c, respectively. In the hydrated membrane, only the 520 nm emission is observed at all times. In the membrane of the lower hydration level, however, the 520 nm species clearly grows in time, at the cost of the 430 nm component. It may be restated here that the

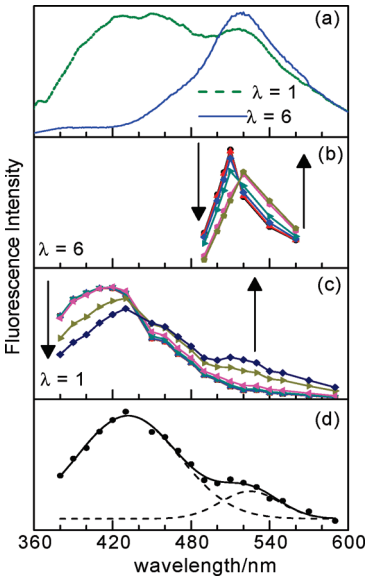

Figure 3. (a) Emission spectra of C102 in Nafion membranes with different hydration levels: λ = 1, dashed green line; λ = 6, solid blue line. (b) TRANES over the first nanosecond in the hydrated membrane. The spectra shown here are at 0, 15, 70, 200, 800, and 1000 ps after excitation. (c) TRANES over the first nanosecond in the dried membrane. The spectra shown here are at 0, 4, 20, 70, 200, 600, and 1000 ps after excitation. The arrows indicate the direction of increase in time, postexcitation, in (b) as well as (c). (d) The fluorescence spectrum at 1 ns. The points denote the experimentally determined time-resolved fluorescence intensities, while the solid line is the fit to a sum of two Gaussians. The component spectra are shown in dashed lines.

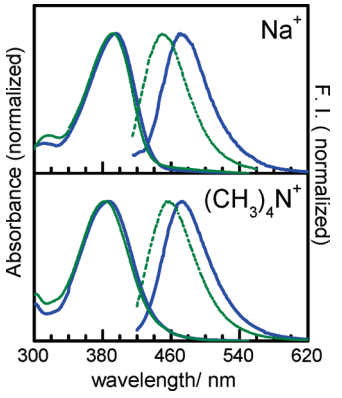

Figure 4. Absorption and fluorescence spectra of C102 in high (λ = 6, solid blue lines) and low hydration levels (λ = 1, dashed green lines) in Na^+ exchanged (top) and $(CH_3)_4N^+$ exchanged (bottom) membranes.

520 nm emission is due to the ESPT state and that the 430 nm emission is due to the electroneutral zwitterionic excited electronic state of Coumarin. The isoemissive point near 440 nm is not very well-defined, as these species get solvated as well. In any case, the two species are distinct and can be identified by comparison with the steady state fluorescence spectrum (Figure 3a). The fluorescence spectrum of C102 in the dried membrane, 1 ns after excitation, has been resolved into its components in Figure 3d, for clarity. Here, the 430 and 540 nm components can be seen clearly. Thus, from the TRANES analysis, it might be said that in the hydrated

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membrane Coumarin 102, which is protonated at the nitrogen atom, loses the proton upon electronic excitation. This proton is taken up by the oxygen atom through ultrafast ESPT, at times not resolvable by the present experiment. In the dried membrane, however, the cationic Coumarin 102 loses a proton upon photoexcitation, but the oxygen atom does not take up the proton as easily as in the native membrane. Even after 1 ns, most of the emission comes from the neutral zwitterionic excited state. Thus, the ESPT is hindered significantly upon decreasing the water content.

This observation leads to a possibly important conclusion regarding the mechanism of proton conduction in membranes like Nafion. As has been stated earlier in this article, it is known that the proton conduction of Nafion is decreased significantly upon drying. The most widely accepted explanation for this is the collapse of water channels upon drying. However, the fluorescent probe used in the present experiment probes only a nanovolume, and we observe that the proton transfer is hindered even in this small volume. The significant decrease in the contribution of the ESPT state may thus be rationalized in light of decreased mobility of protons in dried membranes, irrespective of the collapse of the water channels. With the water content going down, the negatively charged sulfonate groups of the polymer can attract cations more strongly, thus making them less available. At the same time, it should be remembered that the ESPT is not stopped altogether, as the ESPT band is observed in the steady state as well as the longer time TRANES (Figure 3). It is hindered significantly, though.

The experiments have also been performed in Na^+ and Me_4N^+ exchanged membranes, as cations are known to decrease the water content as they displace water from membranes.[32] The cations affect the amounts of free and bound water as well. In these experiments, the absorption and fluorescence spectra are significantly different from those in the native membrane (Figure 4). From the spectra, the absorbing species in the ion-exchanged membranes can be identified as the neutral C102 molecule, while the emitting species can be identified as its electroneutral zwitterionic form. It is explained elsewhere that the pH is higher in cation exchanged membranes.[29,32] Upon drying the cation-exchanged membranes, the steady spectra get blue-shifted by 10 nm, approximately (Figure 4). However, unlike in the native membranes, there is no signature of ESPT. Also, there is no difference in the fluorescence decays monitored at the same wavelength for hydrated and dried cation-exchanged membranes (Figure 5). This shows that drying does not have a significant effect on dynamics of proton transfer in cation-exchanged membranes, presumably because the cations would have already displaced a significant amount of bulk water molecules as the hydrodynamic radii of the hydronium ion and cations vary significantly. The blue shift suggests that the molecule moves to a more restricted environment and that solvation does not play a significant role in this case, as we do not see much change in TRANES in these systems.

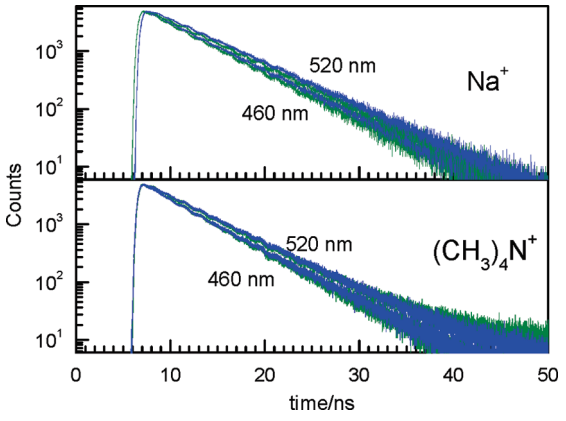
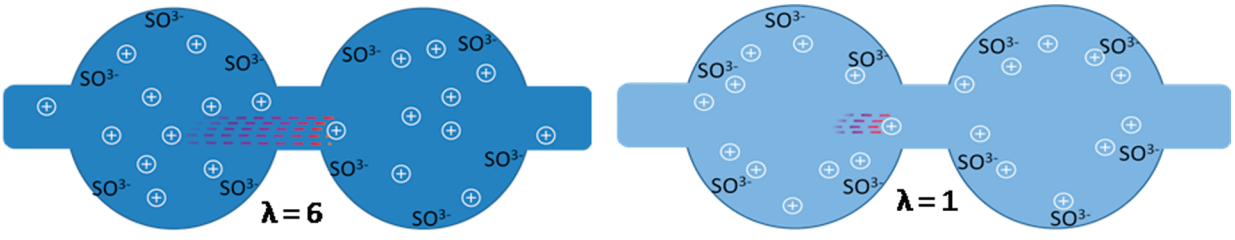


Figure 5. Fluorescence decays of C102 in high hydration (blue) and low hydration (green) of Na^+ exchanged (top) and $(CH_3)_4N^+$ exchanged (bottom) membranes.

CONCLUSIONS

The steady state spectrum of Coumarin 102 changes significantly with the water content of the membrane. Two emitting species, viz., an electroneutral zwitterionic state and an ESPT state, are involved in the emission. The relative contribution of the two species depends on the water content in the membrane. In the hydrated membrane, the emission predominantly occurs from the ESPT state, while in the less hydrated membrane, the predominant emitting species is the electroneutral zwitterionic C102*. The decay of C102* is accompanied by a growth in the red end of the spectrum, marking the evolution of the ESPT state. Further, the time-resolved area normalized emission spectrum (TRANES) analysis shows clearly that the ESPT state grows at the cost of the electroneutral zwitterionic state, over hundreds of picoseconds. This evolution is not observed in the case of hydrated membranes because it is ultrafast in this medium. This shows that in membranes with the lower water content the oxygen atom of the electroneutral zwitterionic excited state does not readily take up the proton that is lost upon excitation. This process of proton transfer from the nitrogen atom to oxygen is more feasible in the hydrated membrane. In other words, the proton transfer is hindered significantly in these less hydrated

Scheme 3. Hindrance of Proton Transfer in Lower Hydration Levels of Nafion Membranes[a]



[a] The + sign represents the protons. The intensity of the blue color corresponds to water content. The hydration levels used in the present experiment are mentioned.

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Nafion membranes. It is beyond any doubt that the dye molecules probe a very small volume as compared to the dimensions of the channels. The hindrance of proton transfer in such a small length scale is most likely due to the more efficient attraction of cationic species by the negatively charged sulfonate groups of Nafion, upon drying. In the presence of a considerably less amount of water, the shielding of the oppositely charged ions from each other is significantly less, and that is what retards the movement of the cations. This observation does not exclude the possibility of the water channels collapsing upon drying, but the local electrostatic interactions are found to be of the utmost importance in the hindrance of the mobility of cations in the water channels of Nafion, when the membrane loses water (Scheme 3).

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