

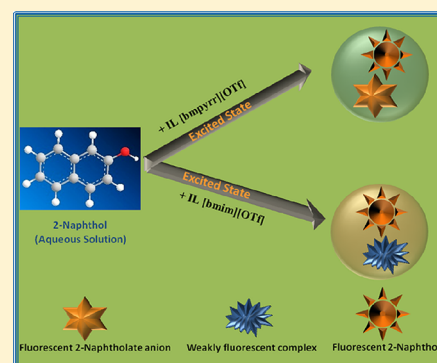
Selective Quenching of 2-Naphtholate Fluorescence by Imidazolium Ionic Liquids

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Supporting Information

ABSTRACT: The effect of addition of water-miscible ionic liquids (ILs), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][OTf]), and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([bmpyr][OTf]), on photophysical properties of 2-naphthol in water at various pHs is reported. Electronic absorbance behavior of 2-naphthol dissolved in aqueous mixtures of ILs is observed to be similar to that found in water at different pHs. The excited-state properties, however, are changed dramatically as the IL is added to the milieu. The presence of imidazolium IL results in significant quenching of the fluorescence emission from 2-naphtholate. On the contrary, pyrrolidinium IL does not quench the fluorescence from the anionic species. The quenching of 2-naphtholate fluorescence by aromatic imidazolium cations in aqueous IL mixtures is found to follow simple Stern–Volmer behavior. The aromatic imidazolium cation acts as an electron/charge acceptor during the quenching process where formation of a weakly fluorescent complex between the imidazolium cation and the excited 2-naphtholate anion possibly involving the acidic C2 proton of imidazolium is proposed. Because of the absence of such an acidic proton, the nonaromatic pyrrolidinium cation is not able to form a complex with the excited 2-naphtholate and cannot act as an electron/charge acceptor. Excited-state emission intensity decay data further corroborate this hypothesis as the intensity decay fits well to a single-exponential decay with no change in recovered lifetimes as [bmpyr][OTf] is added; a double-exponential decay is required to satisfactorily fit the decay data in the presence of [bmim][BF₄], hinting at the presence of a weakly fluorescent complex. The uniqueness of ILs in affecting excited-state properties of the 2-naphthol system is demonstrated through comparison with NaBF₄, NaCl, and polyethylene glycol with an average molecular weight of 200, respectively, as additives.



INTRODUCTION

The proton-transfer reaction is one of the most fundamental reactions in chemistry.¹ Unlike the electron-transfer reaction that involves the exchange of charges between the reactants, the transfer of a proton also results in the transport of mass. Since a proton-transfer reaction is associated with a charge separation along with a mass transfer; the process gets modified remarkably in the excited state as compared to the ground state because of the charge redistribution upon photoexcitation. The innovative works of Weber,² Förster,³ and Weller⁴ have motivated photochemists worldwide to study this phenomenon in great detail. There are a number of excellent reviews covering different aspects of the excited-state proton-transfer (ESPT) process.⁵ ESPT plays a fundamental role in number of photochemical processes and biological functions.⁶ The importance of ESPT is manifested through various applications, such as in developing effective photoprotecting agents as a result of transformation of harmful ultraviolet radiations into thermal energy,⁷ in laser dyes,⁸ in photodynamic therapy,⁹ and in developing fluorescence probes for biological molecules,¹⁰ among others.

The most widely studied ESPT reaction, perhaps, is the ionization of aromatic alcohols.¹¹ A large number of studies

have reflected that ground-state acid dissociation constants (pK_a) are markedly different from the excited-state acid dissociation constants (pK_a^*) for hydroxy aromatic acids.¹² As a result, phenols and naphthols have become representative compounds for investigating proton-transfer reactions in solution. In neutral solution, phenols and naphthols are found to readily lose the phenolic proton in the excited state. Deprotonation occurs more readily in the excited state because electrons on the hydroxyl group are shifted into the aromatic ring, making this hydroxyl group more acidic. The interactions of fluorophores, for example, naphthols, with their surrounding environment in the ground state usually do not involve chemical reactions; however, the fluorophores can undergo chemical reactions while in the excited state. As mentioned, such reactions occur because light absorption frequently changes the electronic distribution within the fluorophore, which, in turn, changes its physical and chemical properties.¹³ Large changes in the acid dissociation constants of organic compounds upon electronic excitation are employed in various fields, especially in biochemistry.¹⁴

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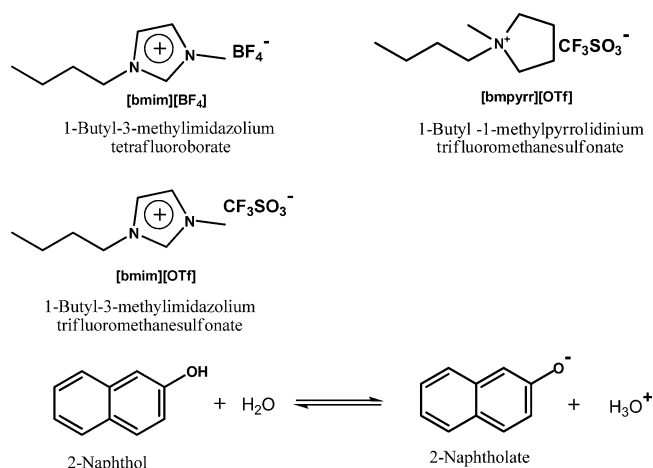
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The process of proton transfer is affected, in general, by the availability of the proton acceptor, ease of solvation of the proton, extent of dissociation of the geminate ion pair, and diffusion of the ion pair. Consequently, the solvation milieu plays a major role in affecting the prototropic equilibria. Unlike the conventional solvents where the constituents are neutral molecules, ionic liquids (ILs) provide an opportunity to study how their ionic constituents can influence the proton-transfer reactions. In this context, we have earlier investigated the effect of addition of ILs on the prototropism of *meso*-tetrakis(4-sulfonatophenyl)porphyrin¹⁵ and fluorescein.¹⁶ The interest of the scientific community to understand how ILs affect ESPT is increasing considerably.¹⁷ Physicochemical properties of ILs vary over a wide range of values upon independent modifications of cations and anions.¹⁸ This makes ILs task-specific substances with adjustable properties.¹⁸ In this paper, we report the effect of the addition of three water-miscible ILs on ESPT of 2-naphthol in aqueous media. We found the fluorescence emission from 2-naphtholate to be significantly reduced in the presence of ILs constituted of imidazolium cations. On the contrary, fluorescence emission from the anionic species is readily observed in the presence of a pyrrolidinium IL. Formation of a weakly fluorescent complex between the excited 2-naphtholate and imidazolium cation is proposed to be the reason for this interesting reduction in fluorescence emission from 2-naphtholate as aromatic imidazolium acts as an electron/charge acceptor during the quenching process. We have demonstrated the uniqueness of imidazolium ILs in affecting the prototropism of 2-naphthol.

EXPERIMENTAL SECTION

Materials. 2-Naphthol was obtained from Sigma-Aldrich in highest purity and was used as received. ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][OTf]), and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([bmpyr][OTf]) (Merck, high purity, halide content < 100 ppm, water content < 100 ppm), were stored in dry conditions and were also used as received (see Scheme 1 for structures). Doubly distilled deionized water was obtained from a Millipore, Milli-Q Academic water purification system having a ≥ 18 M Ω ·cm resistivity. Sodium tetrafluoroborate (NaBF₄)

Scheme 1. Structures of ILs Used and Prototropic Equilibria Investigated in This Study



and polyethylene glycol with an average molecular weight of 200 (PEG200) were purchased from Sigma-Aldrich and were used as received. The highest-purity ethanol purchased from Merck was used to prepare all stock solutions.

Methods. Required amounts of materials were weighed using a Mettler-Toledo AB104-S balance with a precision of ± 0.1 mg. Stock solutions of 2-naphthol were prepared in ethanol and stored in precleaned amber glass vials at ~ 4 °C. The required amount of appropriate stock solution was taken in a cuvette and dried using a gentle stream of pure N₂. The desired pH adjustment was done with the help of dilute aqueous HCl and aqueous NaOH after mixing the appropriate amount of ILs in water. A PerkinElmer Lambda 35 double-beam spectrophotometer with a variable bandwidth was used for acquisition of UV–vis molecular absorbance. Fluorescence emission spectra were acquired on a model FL3-11, Fluorolog-3 modular spectrofluorometer with single Czerny–Turner grating excitation and emission monochromators and a 450 W Xe arc lamp as the excitation source with PMT as the detector. The instrument was purchased from Horiba-Jobin Yvon, Inc. Excited-state fluorescence intensity decay data were acquired in the time domain using a Horiba Jobin Yvon Fluorocube time-correlated single-photon counting (TCSPC) fluorimeter. The samples were excited at 340 nm using a UV-pulsed NanoLED-340 source having a pulse width < 1.0 ns. The emission was collected using a Peltier-cooled red-sensitive TBX-04 PMT detection module. The data were collected with a DAQ-MCA-3 Series (P7882) multichannel analyzer. The excited-state fluorescence intensity decays were analyzed using DAS6 analysis software. All the data were acquired using 1 cm path length quartz cuvettes. Spectral response from appropriate blanks was subtracted before data analysis. All the measurements were taken at least in triplicate starting from the sample preparation and averaged.

RESULTS AND DISCUSSION

Electronic Absorbance and Fluorescence Emission of 2-Naphthol in Aqueous Mixtures of IL [bmim][BF₄]. The pK_a of 2-naphthol in water lies near 9.5.¹⁹ At pH < 8 in water, the neutral form of 2-naphthol is the major absorbing species present in the solution. As the pH is increased, as expected, the ground-state ionization causes a decrease in the characteristic absorption band of neutral 2-naphthol with the appearance of a new absorption band with $\lambda_{\text{max}}^{\text{abs}}$ at ca. 345 nm attributed to the 2-naphtholate anion (Figure 1A). The isosbestic point appears at 320 nm, suggesting the presence of interconverting species with the change in the pH of the media. This is in agreement with what is published in the literature.²⁰ The effect of addition of IL [bmim][BF₄] to the aqueous solution of 2-naphthol is manifested through subtle changes in the electronic absorbance behavior. While Figure 1B presents absorbance spectra of 2-naphthol in a 50 wt % [bmim][BF₄] added aqueous mixture as the pH is changed from 6.9 to 12.3, Figure S1 (Supporting Information), in addition, shows the absorbance behavior in the presence of 1, 2, and 10 wt % [bmim][BF₄]. It appears from the spectra that the absorbance behavior of 2-naphthol in the presence of [bmim][BF₄] is similar to that in water. A close inspection of the absorbance data reveals that, as the weight percent of [bmim][BF₄] is increased to 50 wt %, $\lambda_{\text{max}}^{\text{abs}}$ of the neutral and the anionic forms of 2-naphthol as well as the isosbestic point show bathochromic shifts. The $\lambda_{\text{max}}^{\text{abs}}$ values are observed to red shift by ~ 4 nm for the neutral form and ~ 6 nm for the anionic form, whereas the isosbestic point is found to

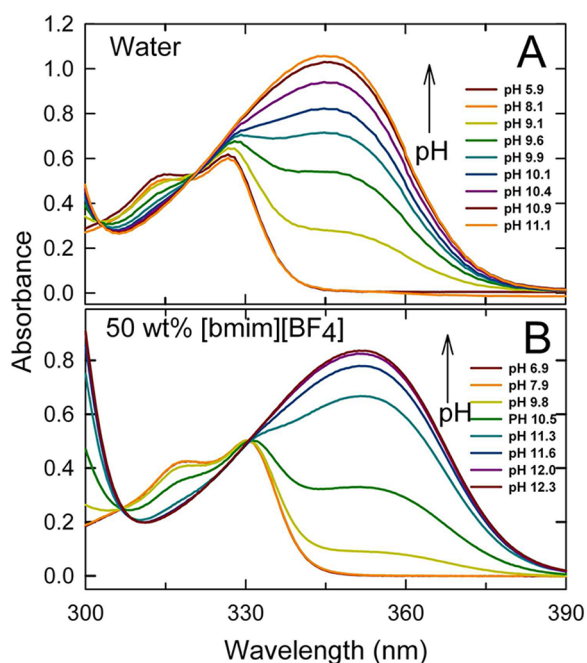


Figure 1. Absorbance spectra of 2-naphthol (300 μM) in water (panel A) and in 50 wt % [bmim][BF₄] added water ($x_{[\text{bmim}][\text{BF}_4]} = 0.0738$ or $[\text{bmim}][\text{BF}_4] = 2.41$ M) (panel B) at ambient conditions.

red shift by ~10 nm. Similar bathochromic shifts are also observed when other additives, such as, [bmim][OTf], [bmpyr][OTf], and PEG200, are added to the system (vide infra).

Several hydroxyphotoacids, such as 2-naphthol, are known to become more acidic in their lowest excited singlet state.²¹ As mentioned earlier, in the case of 2-naphthol, the pK_a decreases from 9.5 in the ground state to 2.8 (pK_a^*) in the excited state.²¹ Their enhanced acidity in the excited state is reasonably well predicted by the Förster equation, $pK_a^* = pK_a - h(\nu_{\text{HA}} - \nu_{\text{A}^-})/2.3RT$, where $h\nu_{\text{HA(A}^-)}$ is the energy of the 0–0 electronic transition for the conjugated acid (base). In addition to a decrease of 6–7 pK_a units upon electronic excitation, such photoacids also transfer very rapidly a proton to a nearby water molecule and, as a result, are capable of transforming a neutral aqueous solution into an acidic one within nanoseconds.²¹ In highly acidic solutions, only the fluorescence emission from neutral 2-naphthol is observed with maxima at ~357 nm, as no excited state ionization takes place at such high acidity. However, near pH ~ 2, excited-state ionization starts, which results in the formation of an electronically excited conjugate base with a fluorescence emission centered ca. 418 nm, as shown in Figure 2A. As the pH is increased, as expected, the fluorescence emission from the anionic species enhances at the expense of the fluorescence emission from the neutral species. In the case of a highly basic aqueous solution, the fluorescence emission from 2-naphtholate dominates. It is reported that, depending on the pH of the solution, the excited-state dissociation of 2-naphthol can be either reversible or irreversible.¹² Hence, the 2-naphthol system illustrates the characteristics of both reversible and irreversible excited-state reactions.

We found surprising fluorescence behavior of the 2-naphthol system in the presence of IL [bmim][BF₄], which is clearly different from the fluorescence behavior of the 2-naphthol system in water. Figure 2B presents the fluorescence emission

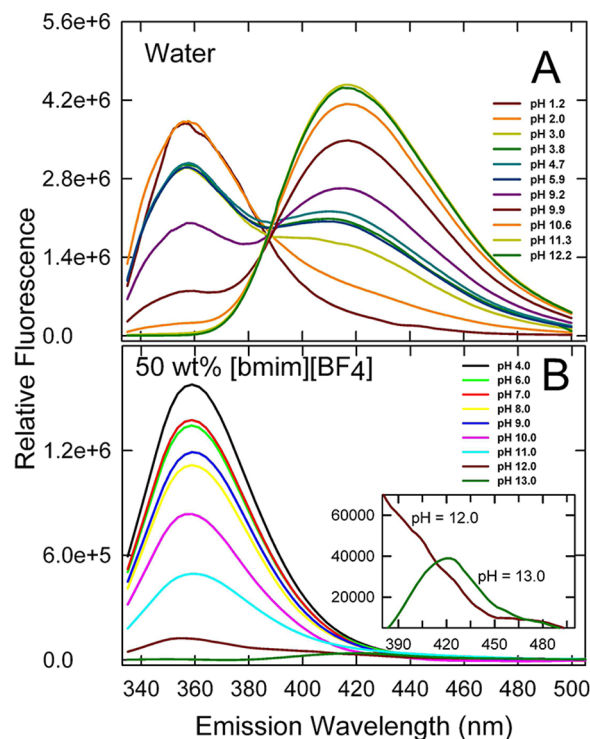


Figure 2. Fluorescence emission spectra of 2-naphthol (20 μM) in water (panel A) and in 50 wt % [bmim][BF₄] added water ($x_{[\text{bmim}][\text{BF}_4]} = 0.0738$ or $[\text{bmim}][\text{BF}_4] = 2.41$ M) (panel B) at ambient conditions ($\lambda_{\text{ex}} = 325$ nm).

from 2-naphthol in the presence of 50 wt % [bmim][BF₄] in water at different pHs (Figure S2, Supporting Information, shows, in addition, the fluorescence emission from 2-naphthol at varying pHs in the presence of 1, 2, 5, and 10 wt % [bmim][BF₄]). It is clear that, whereas the fluorescence emission from the neutral form decreases as the pH is increased, the emission signal from the anionic form, instead of growing, significantly diminishes as the concentration of [bmim][BF₄] is increased in the solution. Even at a mixture pH much higher than the pK_a^* or even the pK_a in water, almost no fluorescence emission from the anionic form is observed in 50 wt % [bmim][BF₄] added water (2.41 M or $x_{[\text{bmim}][\text{BF}_4]} = 0.0738$). As the pH of the mixture containing 50 wt % [bmim][BF₄] is increased up to 13, weak fluorescence emission from the anionic form is observed (inset in Figure 2B). Anionic emission intensity increases with the increase in the pH between pH 12 and 13 (Figure S3, Supporting Information). In aqueous mixtures of IL [bmim][BF₄], the desired pH to have fluorescence emission from the anionic form increases as the concentration of the IL is increased. It is inferred that the presence of a small amount of IL [bmim][BF₄] in the mixture has a great influence on the excited-state properties of 2-naphthol.

Comparison of Additives: NaBF₄, NaCl, and PEG200 versus [bmim][BF₄]. To further assess the specific role of the ions constituting IL [bmim][BF₄] in changing excited-state properties of the 2-naphthol system, fluorescence emission from 2-naphthol was acquired in 3.55 wt % NaBF₄ (0.34 M or $x_{\text{NaBF}_4} = 0.006$) solution in water at different pHs (Figure S4, Supporting Information). It is important to mention that, at concentrations higher than 3.55 wt % NaBF₄, the samples became inadequate for any data collection due to cloudiness.

This highlights the advantage of water-miscible ILs over corresponding salts as additives as ILs, such as [bmim][BF₄], which can be mixed with water at any proportion to obtain the desired property of the medium. It is clear that, in the presence of NaBF₄, depending upon the pH of the solution, fluorescence emission from one or both species is observed. At a lower pH of ~ 0.8 , fluorescence emission from neutral species devoid of the emission from the anion is found, whereas for intermediate pH, fluorescence emission from the neutral species as well as from the anion is observed. In highly basic (pH ~ 13.6) conditions, fluorescence emission from the anionic form devoid of emission from the neutral species is observed. This is similar to the excited-state behavior of the 2-naphthol system in water. Importantly, it is in complete contrast to the behavior observed in IL [bmim][BF₄] added aqueous mixtures. The possible unique role of the IL cation bmim⁺ in affecting the fluorescence emission from the 2-naphthol system is amply established. Further, the effect of addition of NaCl on the excited-state proton dissociation reaction of 2-naphthol was studied by Shizuka et al.²² and Harris et al.²³ They observed a decrease (though not of the same extent as observed in the case of IL [bmim][BF₄] addition) in the fluorescence emission from the anionic form with *enhancement* of the fluorescence emission from neutral 2-naphthol. The enhancement in fluorescence intensity of the neutral form was explained on the basis of the disruption of the water structure by high concentrations of Na⁺ and Cl[−] ions or the increase in the activity coefficient of 2-naphthol. These outcomes are again in stark contrast to those observed for the addition of IL [bmim][BF₄], further highlighting the unique role of this IL in modifying excited-state properties of the 2-naphthol system.

We also compared the role of IL [bmim][BF₄] in altering excited-state properties of the 2-naphthol system with that of another “green” additive, PEG200. IL [bmim][BF₄] may not act as an electrolyte alone at higher concentrations (such as at 50 wt %), and a substantial fraction of [bmim][BF₄] may exist in the undissociated form. The comparison with PEG200 may reveal the contrast in roles of an ionic substance versus a molecular one as additives in affecting the photophysical properties of the 2-naphthol system. Electronic absorbance and fluorescence emission spectra, respectively, of 2-naphthol in the presence of 2, 10, and 50 wt % PEG200 in water at different pHs are presented in Figures S5 and S6 (Supporting Information) (50 wt % PEG200 is equivalent to 2.65 M PEG200). Electronic absorbance and fluorescence emission of 2-naphthol in aqueous mixtures of PEG200 are fairly similar to those found in water. It is worthy to mention that, similar to the observations for IL [bmim][BF₄] added mixtures, bathochromic shifts in absorbance maxima of neutral and anionic forms are observed as the amount of PEG200 is increased; the isosbestic point is also observed to shift to higher wavelengths. Importantly, fluorescence emission from 2-naphtholate is clearly observed even in the presence of 50 wt % PEG200. Contrasting roles of IL [bmim][BF₄] versus PEG200 are highlighted, and the uniqueness of the former in dramatically effecting the fluorescence emission from 2-naphtholate is further confirmed.

Effect of IL Structure: [bmim][OTf] or [bmpyrr][OTf] versus [bmim][BF₄] as Additive. Another water-miscible IL, [bmim][OTf], having a different anion, is examined next to gain insight into the role of the IL anion, if any, in affecting the excited-state properties of the 2-naphthol system. Electronic absorbance and fluorescence emission spectra of 2-naphthol in

50 wt % [bmim][OTf] (1.96 M or $x_{[\text{bmim}][\text{OTf}]} = 0.0588$) added water are presented in Figure 3. Similar to our observations for

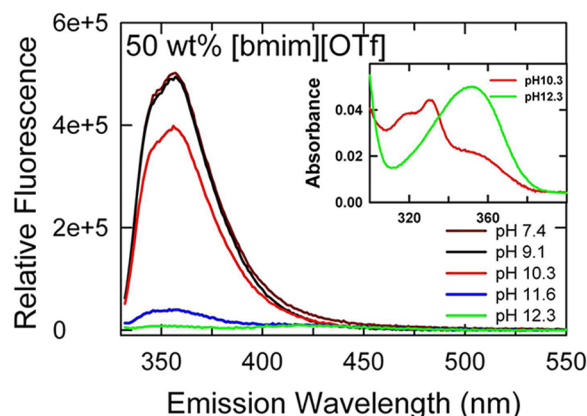


Figure 3. Fluorescence emission spectra of 2-naphthol (20 μM) in 50 wt % [bmim][OTf] added water ($x_{[\text{bmim}][\text{OTf}]} = 0.0588$ or $[\text{bmim}][\text{OTf}] = 1.96 \text{ M}$) at ambient conditions ($\lambda_{\text{ex}} = 325 \text{ nm}$). Inset shows absorbance spectra for pH 10.3 and pH 12.3 mixtures.

[bmim][BF₄] added mixtures, it is found that absorbance spectra of 2-naphthol at two extreme pHs within the 50 wt % [bmim][OTf] added mixture are similar to those obtained in the presence of [bmim][BF₄] (inset in Figure 3). Most importantly, almost no fluorescence emission from the ionized form of 2-naphthol is observed even at a mixture pH of 7.4. As before, it appears that the neutral 2-naphthol is converting into its anionic form in the excited state as the fluorescence emission from the neutral form decreases in the presence of [bmim][OTf] as the pH is increased. However, similar to the observations for [bmim][BF₄], negligible fluorescence emission from the anionic form even at a high pH of 12.3 is still the most surprising outcome.

To our surprise, a significantly different 2-naphthol excited-state behavior is observed when IL [bmpyrr][OTf] is used as the additive. Unlike bmim⁺, the cation bmpyrr⁺ is not aromatic in nature. Electronic absorbance and fluorescence emission spectra of the 2-naphthol system in the presence of 50 wt % [bmpyrr][OTf] (1.91 M or $x_{[\text{bmpyrr}][\text{OTf}]} = 0.0582$) in water at different pHs are shown in Figure 4. The absorbance spectra of 2-naphthol (inset in Figure 4) at pH 6.4 and 13.0 are similar to those obtained in water or in either of the 50 wt % aqueous mixtures of IL [bmim][BF₄] or [bmim][OTf]. A careful examination of the fluorescence emission spectra in Figure 4, however, reveals the surprising outcome: significant fluorescence emission from the 2-naphtholate anion is observed in the presence of 50 wt % [bmpyrr][OTf]. This is in sharp contrast to what was observed when ILs constituted of the bmim⁺ cation are used as additives (vide supra).

Role of Imidazolium ILs in Changing Excited-State Properties of 2-Naphtholate. To assess the effect of change in the medium due to IL addition to water on acid dissociation constants in ground as well as excited states of 2-naphthol, we estimated ground-state and first excited-state ionization constants (i.e., $\text{p}K_{\text{a}}$ and $\text{p}K_{\text{a}}^*$) using the Förster cycle within different weight percent [bmim][BF₄] in water mixtures. The values are reported in Table 1. It is important to mention that our $\text{p}K_{\text{a}}$ and $\text{p}K_{\text{a}}^*$ in the absence of an IL are in good agreement with what is reported in the literature.¹⁹ It is interesting to note the similarities in $\text{p}K_{\text{a}}$ and $\text{p}K_{\text{a}}^*$, respectively,

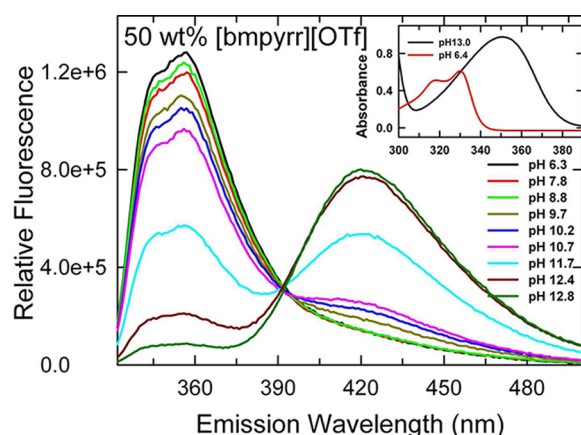


Figure 4. Fluorescence emission spectra of 2-naphthol (20 μM) in 50 wt % [bmpyrr][OTf] added water ($x_{[\text{bmpyrr}][\text{OTf}]} = 0.0582$ or $[\text{bmpyrr}][\text{OTf}] = 1.91 \text{ M}$) at ambient conditions ($\lambda_{\text{ex}} = 325 \text{ nm}$). Inset shows absorbance spectra ($[2\text{-naphthol}] = 300 \mu\text{M}$).

Table 1. Ground-State ($\text{p}K_{\text{a}}$) and First Excited-State ($\text{p}K_{\text{a}}^*$) Acid Dissociation Constants of 2-Naphthol in Aqueous Mixtures of IL [bmim][BF₄] at Ambient Conditions

concn of [bmim][BF ₄]				
wt %	M	x	$\text{p}K_{\text{a}}$	$\text{p}K_{\text{a}}^*$
0	0	0	9.5 (± 0.2)	2.9 (± 0.1)
1	0.04	0.0008	9.3 (± 0.2)	2.7 (± 0.1)
2	0.09	0.0016	9.4 (± 0.3)	2.8 (± 0.2)
10	0.45	0.0088	9.5 (± 0.2)	3.2 (± 0.3)

in the absence and presence of 1, 2, and 10 wt % [bmim][BF₄] in water: the acid dissociation constants, especially the $\text{p}K_{\text{a}}^*$, do not change significantly as the medium is modified by adding IL [bmim][BF₄] to water. Calculation of $\text{p}K_{\text{a}}^*$ was not possible for 50 wt % [bmim][BF₄] added water due to the absence of meaningful fluorescence emission. It can be proposed that the extent of dissociation in both ground and excited states does not alter significantly in the presence of ILs.

To pinpoint the reason for the decreased fluorescence emission from 2-naphtholate, fluorescence spectra are acquired as the concentration of [bmim][BF₄] in water is gradually increased at fixed pH 12.0 (inset in Figure 5A). In the absence of [bmim][BF₄], only one fluorescence emission band corresponding to the 2-naphtholate anion is observed. Furthermore, at such a high pH, no back reaction can be expected as the pH is much more than the reported $\text{p}K_{\text{a}}^*$ in water (vide infra). As the concentration of [bmim][BF₄] is increased, a monotonic decrease in the fluorescence emission from the anionic form is clearly observed. This decrease is attributed to the quenching of the fluorescence from 2-naphtholate by the IL cation bmim⁺. A simplified Stern–Volmer treatment was carried out on the fluorescence quenching data where F_0/F versus [bmim⁺] in M (F_0 and F are the fluorescence intensities in the absence and the presence of the quencher bmim⁺, respectively) is plotted (Figure 5A).¹³ Linear regression analysis of the data shows an $R^2 = 0.9856$ (standard error of estimate = 0.7001), and the recovered intercept is found to be close to 1. The slope provides the Stern–Volmer quenching constant (K_{sv}), which is equal to $43.5(\pm 3.2) \text{ M}^{-1}$. A bimolecular quenching rate constant $k_{\text{q}} = K_{\text{sv}}/\tau_0$, where τ_0 is the fluorescence lifetime in the absence of quencher [bmim][BF₄], is thus calculated to be equal to

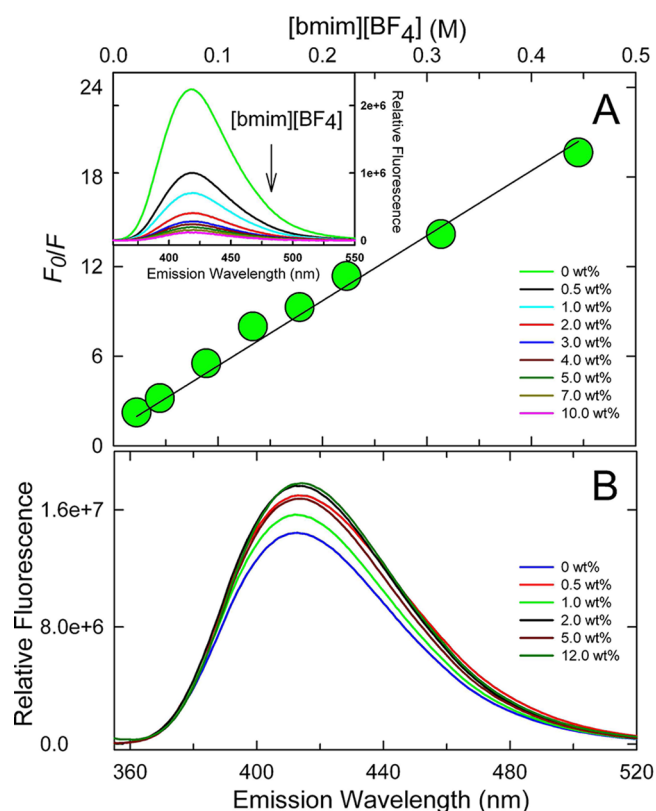
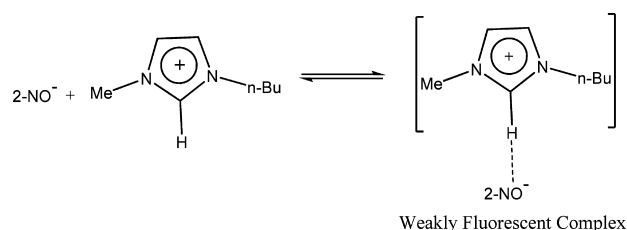


Figure 5. Stern–Volmer plot (panel A) for fluorescence quenching of the 2-naphtholate anion by [bmim][BF₄] (inset shows fluorescence emission spectra as the concentration of [bmim][BF₄] is increased). Panel B shows fluorescence emission spectra from different weight percent [bmpyrr][OTf] added water. All data are for pH 12.0 mixtures at ambient conditions ($\lambda_{\text{ex}} = 325 \text{ nm}$).

$4.8(\pm 0.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (fluorescence lifetime data are presented later). This K_{sv} and k_{q} indicate that this quenching process is fairly strong. Surprisingly, when [bmpyrr][OTf] instead of [bmim][BF₄] or [bmim][OTf] is gradually added to the system at fixed pH 12.0, fluorescence emission from 2-naphtholate does not get quenched at all (Figure 5B). It appears that only bmim⁺ ILs reduce the fluorescence emission from 2-naphtholate.

It is clear that bmim⁺ acts as the quencher of the fluorescence emission from 2-naphtholate in aqueous media at high pH. It appears that the aromatic imidazolium cation acts as an electron/charge acceptor during the quenching process. The quenching of 2-naphtholate fluorescence may occur as a result of the formation of a weakly fluorescent complex between the 2-naphtholate anion in the excited state and the aromatic bmim⁺ cation as a result of excited-state electron/charge transfer. Apart from the energetics between the two species that facilitates the complex formation between excited 2-naphtholate and bmim⁺, it is possible that the acidic C2 proton of bmim⁺ may play a role in the complex formation as well. The 2-naphtholate anion may get involved in complex formation with the bmim⁺ through the C2–H site (Scheme 2). Formation of such a complex between the C2–H proton of bmim⁺ and oxygen-containing anions has been demonstrated earlier by Ross and Xiao.²⁴ This proposition is supported by a clear lack of quenching of 2-naphtholate fluorescence by IL [bmpyrr][OTf] as, in contrast, bmpyrr⁺ does not possess an acidic proton similar to C2–H of bmim⁺. The absence of aromaticity

Scheme 2. Proposed Formation of the Complex between the 2-Naphtholate Anion (2-NO^-) and the IL Cation bmim^+



associated with bmpyrr^+ contributes to it not acting as a fluorescence quencher toward 2-naphtholate emission as some aromatic species are known to quench the fluorescence from certain fluorophores.²⁵ The presence of the mere Coulombic attractive interaction is deemed not sufficient to facilitate complex formation between the IL cation and the 2-naphtholate anion.

The measurement of the fluorescence lifetime in the absence and presence of the quencher is an excellent method to provide further insight into the mode and the mechanism of the quenching process in general. We have collected the excited-state intensity decay of 2-naphthol dissolved in different weight percent $[\text{bmpyrr}][\text{OTf}]$ and $[\text{bmim}][\text{BF}_4]$ added water, respectively, at a fixed pH of 12.0 using a 340 nm NanoLED for excitation (Figure 6). Results of the fit of the excited-state intensity decay data are presented in Table 2. It is interesting to note that, irrespective of the concentration of $[\text{bmpyrr}][\text{OTf}]$ in the aqueous mixture, excited-state intensity decays are satisfactorily fit to a single-exponential decay model and the

Table 2. Recovered Excited-State Intensity Decay Parameters along with the Goodness-of-the-Fit (χ^2) for 2-Naphthol ($20\ \mu\text{M}$) Dissolved in Aqueous Mixtures of ILs $[\text{bmpyrr}][\text{OTf}]$ and $[\text{bmim}][\text{BF}_4]$, Respectively, at pH = 12.0 at Ambient Conditions^a

wt % IL (x_{IL})	τ_1 (ns)	τ_2 (ns)	χ^2
$[\text{bmpyrr}][\text{OTf}]$			
0 wt %	9.11		0.99
0.5 wt % (0.0003)	9.02		1.08
1.0 wt % (0.0007)	9.19		1.07
2.0 wt % (0.0015)	9.17		1.05
5.0 wt % (0.0032)	9.29		1.02
12 wt % (0.0083)	9.31		1.12
$[\text{bmim}][\text{BF}_4]$			
0 wt %	9.11		0.99
	7.79 ($-\alpha_1 = 0.42$)	8.18 ($\alpha_2 = 0.58$)	1.03
1 wt % (0.0008)	3.62		1.01
	2.67 ($\alpha_1 = 0.84$)	6.06 ($\alpha_2 = 0.16$)	1.00
5 wt % (0.0042)	7.36		2.63
	1.09 ($\alpha_1 = 0.80$)	10.05 ($\alpha_2 = 0.20$)	1.01
10 wt % (0.0088)	9.77		2.97
	0.87 ($\alpha_1 = 0.73$)	11.20 ($\alpha_2 = 0.27$)	1.01

^aExcitation at 340 nm using NanoLED, and emission is collected at 420 nm. Error in recovered decay times is $\leq 5\%$.

recovered lifetimes are found to not change with increasing concentration of $[\text{bmpyrr}][\text{OTf}]$. This is in nice agreement with the observation that the steady-state fluorescence emission from 2-naphtholate is not quenched by $[\text{bmpyrr}][\text{OTf}]$. In

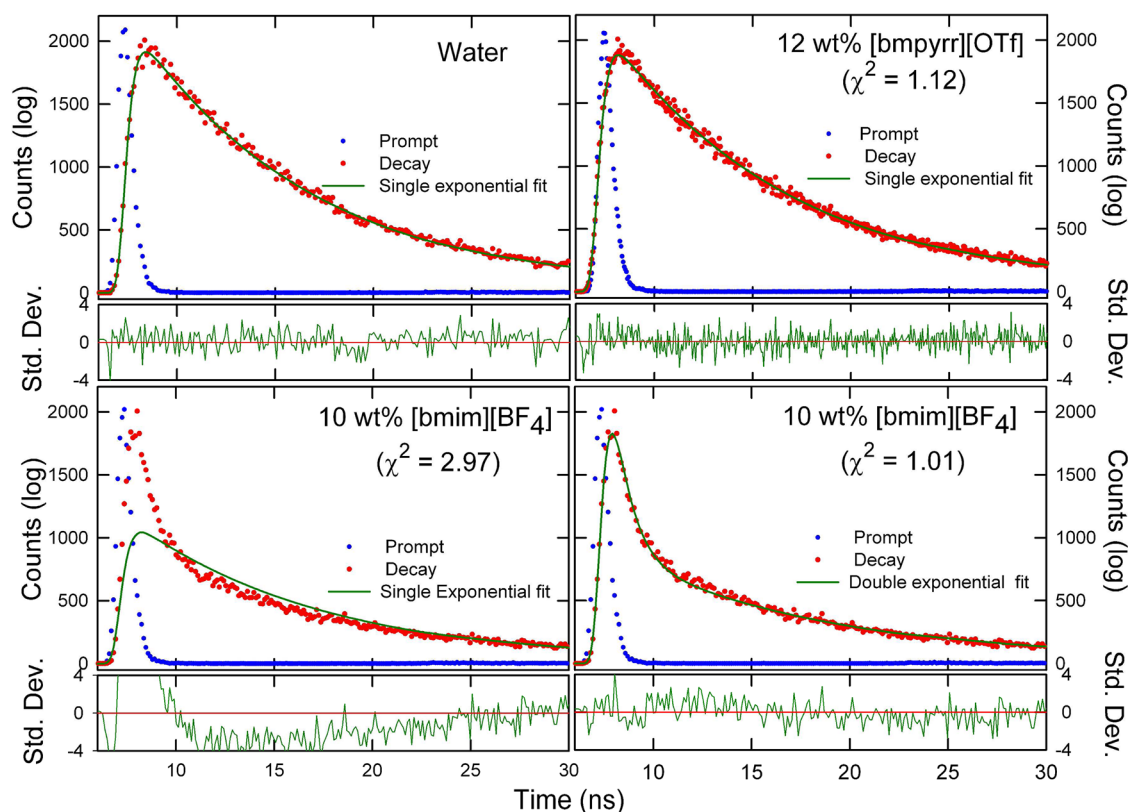


Figure 6. Excited-state intensity decay data of 2-naphthol ($20\ \mu\text{M}$) for pH 12.0 IL added water mixtures at ambient conditions. Excitation is carried out using a 340 nm NanoLED, and emission is collected at 420 nm. The bottom curves (blue) denote the instrumental response function (IRF) measured using a dilute glycogen suspension, and the lower panels show weighted residuals for the corresponding fits.

stark contrast, in the presence of IL [bmim][BF₄], the excited-state intensity decays do not fit satisfactorily to the single-exponential decay model; a second decay time is necessary to obtain a satisfactory fit: the double-exponential decay model affords vastly improved fitting parameters (Table 2 and Figure 6). A careful examination of the two recovered decay times hint at two populations of fluorescing species in the milieu: possibly 2-naphtholate along with a weakly fluorescent complex. It is noteworthy that the lifetime recovered by us in the absence of any IL is in good agreement with that reported for 2-naphtholate in the literature.²⁶ Formation of a weakly fluorescent complex between bmim⁺ and 2-naphtholate is corroborated nonetheless.

Within 20 wt % [bmim][BF₄] added water at pH 12.0, the fluorescence emission corresponding to the anion diminishes significantly. Surprisingly, the appearance of a new band corresponding to neutral 2-naphthol near 355–360 nm is observed (Figure S7A, Supporting Information). Almost no unionized 2-naphthol is expected to be present at such a high pH, yet the appearance of the emission band centered ca. 355 nm corresponding to neutral species hinted at the fact that the presence of bmim⁺ IL in water might have resulted in the back reaction in which the 2-naphtholate anion abstracts H⁺ from C2–H so as to form the neutral species. The extent of this back reaction in such unfavorable conditions (i.e., high pH) is considered not too significant. Subsequently, fluorescence emission spectra were acquired at different weight percent [bmim][BF₄] aqueous mixtures at pH 10.5 (Figure S7B, Supporting Information). It is clear that, with addition of IL [bmim][BF₄], as observed earlier, a decrease in the fluorescence emission from the anionic species was observed; however, the fluorescence emission intensity increases for the band centered at ca. 355 nm for 1, 5, and 10 wt % [bmim][BF₄] added water relative to those for pH 12.0 mixtures showing the facilitated extent of back reaction. The phenomenon of geminate recombination was also observed in the case of excited-state fluorescence emission for the 2-naphthol system within increasing weight percent of ethanol added water at pH 12.0 (Figure S8, Supporting Information). This could be attributed to the decreased static dielectric constant of the medium, which favors ion recombination and hence the presence of neutral 2-naphthol in the mixture. The diminished fluorescence emission from 2-naphtholate as IL is added appears to be specific to ILs and may be due in major part to the fluorescence quenching as a result of formation of a weakly fluorescent complex between the 2-naphtholate anion and bmim⁺, where bmim⁺ acts as an electron/charge acceptor, and in minor part to the back reaction (geminate recombination, i.e., the combination of ejected proton and the parent anion).

CONCLUSIONS

Fluorescence emission from 2-naphtholate is severely diminished in the presence of ILs having imidazolium cations. In contrast, the fluorescence emission from 2-naphtholate is not affected within aqueous mixtures of an IL having pyrrolidinium cations. The effect of the imidazolium IL as additive, in this respect, is very different from that of IL [bmpyr][OTf] or NaBF₄/NaCl salts or the small-chain polymer PEG200 as additive. Quenching of the 2-naphtholate fluorescence by an aromatic imidazolium cation is proposed to be the major reason for this observation. It is hypothesized that a weakly fluorescent complex forms between the imidazolium cation and the excited 2-naphtholate anion, which results in severe fluorescence

quenching. Apart from the inherent aromaticity of the imidazolium cation that may help it act as an electron/charge acceptor in the process, the role of the interaction between C2–H of the imidazolium cation and the O[−] of 2-naphtholate in the formation of a weakly fluorescent complex is suggested. A minor contribution from the back reaction where geminate recombination between the ejected proton and the parent anion takes place may also contribute to the reduced fluorescence. The selective nature of imidazolium ILs in quenching 2-naphtholate fluorescence is demonstrated as fluorescence from neutral 2-naphthol is not quenched by the imidazolium cation. This hints at the potential application of such a system as an effective photoprotecting media by transforming harmful ultraviolet radiation into thermal energy as the radiation is absorbed, but not emitted, under basic conditions.

ASSOCIATED CONTENT

Supporting Information

Figures S1–S8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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