Excitation-Wavelength-Dependent Fluorescence Behavior of Some Dipolar Molecules in Room-Temperature Ionic Liquids

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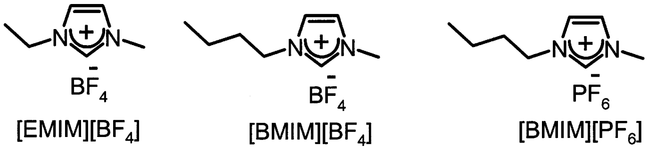
The fluorescence behavior of several dipolar molecules has been studied in three room-temperature ionic liquids, namely, [BMIM][BF$_4$], [EMIM][BF$_4$], and [BMIM][PF$_6$], as a function of the excitation wavelength. Although a large majority of these systems show normal fluorescence behavior with no excitation wavelength dependence, a few systems surprisingly exhibit fairly strong excitation-wavelength-dependent fluorescence behavior in these media. The excitation-wavelength-dependent shift of the fluorescence maximum is measured to be between 10 and 35 nm. The various fluorescence parameters of the systems have been carefully examined to determine the factors that contribute to this kind of behavior, generally not observed in conventional media. It is shown that the existence of a distribution of energetically different molecules in the ground state coupled with a low rate of the excited-state relaxation processes, viz., solvation and energy transfer, are responsible for the excitation-wavelength-dependent fluorescence behavior of some of the systems.

1. Introduction

In recent years, room-temperature ionic liquids (RTILs), particularly the alkylimidazolium salts, have become the focus of extensive investigation.[1−10] These studies are driven by the realization that RTILs can serve as a “green” alternative to the conventional environmentally detrimental volatile solvents. Interestingly, even though the utility of these substances as environmentally benign media has already been documented through a large variety of reactions in these liquids,[1−6,8] little work exploring the potential of these media in photophysical and photochemical studies has yet been undertaken.[11−30] A large majority of the photophysical studies carried out to date have been directed toward quantifying the polarity of these liquids using various solvatochromic absorption and fluorescence probes. These studies have indicated that imidazolium-cation-based ionic liquids are more polar than acetonitrile but less polar than methanol.[11,20,21] On the other hand, recent picosecond time-resolved fluorescence studies on various dipolar systems in these media have revealed a time-dependent Stokes shift of the fluorescence maximum of the molecules in the picosecond to nanosecond time domain, suggesting that solvation is a rather slow process in ionic liquids when compared with that in conventional solvents such as acetonitrile or methanol.[19−24,30] These studies have so far indicated that the interaction between the ionic constituents of RTILs and the solubilized molecules does not give rise to any unusual fluorescence response of the latter and that the RTILs behave very much like conventional solvents.

During the course of our studies on solvation dynamics in RTILs using dipolar fluorescent probe molecules, we observed that 2-amino-7-nitrofluorene (ANF) exhibits an excitation-wavelength-dependent fluorescence spectrum in RTILs. This behavior is considered unusual given that (i) the literature suggests that ANF does not exhibit excitation-wavelength-dependent behavior in conventional molecular solvents,[31] (ii) other dipolar molecules previously examined in RTILs do not exhibit this kind of behavior[19−22] (even though all of them show a time-dependent shift of the fluorescence maximum in the picosecond to nanosecond time domain), and (iii) the observed behavior is contrary to what is prescribed by the well-known Kasha’s rule.[32] To understand the origin of this behavior, we have undertaken the present investigation on several dipolar probes in three different RTILs (Chart 1) of different viscosities. The fluorescence behavior of those systems that show excitation-wavelength-dependent fluorescence spectra in RTILs was also examined in a viscous molecular solvent, glycerol. The molecules studied in this work are shown in Charts 2 and 3. The systems have been organized into two groups: the molecules in the first group, shown in Chart 2, do not exhibit an excitation wavelength dependence whereas those in the second group (Chart 3) show an unusual excitation-wavelength-dependent fluorescence response.

CHART 1



2. Experimental Section

2.1. Materials and Methods. ANF was prepared following the method suggested by Sislak and Hamilton.[33] Coumarin derivatives, procured from Eastman Kodak Company, were of laser grade and were used without further purification. 4-Aminophthalimide (AP, Eastman) was recrystallized twice from doubly distilled water. PRODAN [6-propionyl-2-(dimethylamino)naphthalene] was used as received from Molecular Probes. 1-Anilinonaphthalene-8-sulfonate (ANS) was procured from Molecular Probes and was recrystallized from doubly distilled water. The nitrobenzoxadiazole (NBD) derivatives HNBD, 4NBD, 6NBD, and ENBD were synthesized following

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CHART 2

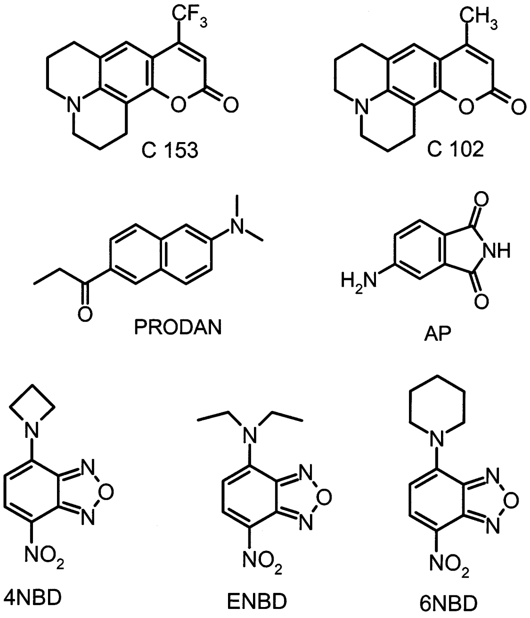
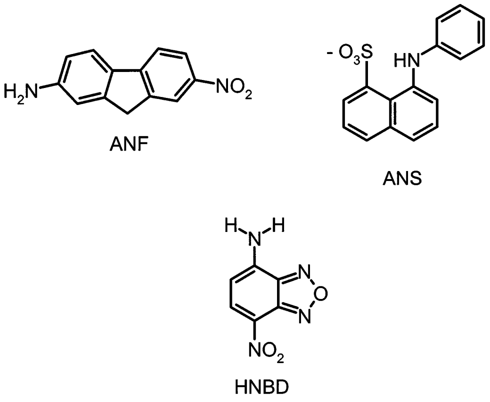


CHART 3



a literature procedure.[34] The RTILs were prepared and purified as follows:[20,21,35] The conventional solvents used for the spectroscopic studies were purified by standard procedures.[36]

2.1.1. Preparation of [BMIM][BF$_4$] and [EMIM][BF$_4$]. [BMIM][BF$_4$] was prepared from its chloride salt, [BMIM]Cl following standard procedure.[37] The latter was first prepared by treating a mixture of 1-methylimidazole and *n*-chlorobutane (1:2 mole ratio) in 1,1,1-trichloroethane at 70 °C for 72 h under N_2. The solution was cooled to room temperature and was washed several times with dry ethyl acetate until the washings were free of unreacted 1-methylimidazole. This was ensured by the absence of the strong absorption peak due to 1-methylimidazole at around 275 nm in the washings. The halide was then recrystallized from an ethyl acetate/acetonitrile mixture before the next reaction step was performed.

A triply distilled acetone solution of a mixture of [BMIM]Cl and NaBF$_4$ (in a 1:1.2 mole ratio) was stirred for 24 h at room temperature. The resulting solution of [BMIM][BF$_4$] was filtered through a plug of Celite, and the volatiles were removed under reduced pressure.

[EMIM][BF$_4$] was prepared from the corresponding bromide salt, [EMIM]Br, following a procedure similar to that employed for the preparation of [BMIM][BF$_4$].

2.1.2. Preparation of [BMIM][PF$_6$]. A dilute aqueous solution of [BMIM]Cl was prepared in a plastic box. To this ice-cold solution was added ice-cooled HPF$_6$ (65% solution in water) (in a 1:1.5 molar proportion) dropwise over 1 h, with constant stirring. This slow addition prevented a significant rise of the temperature and avoided rapid exothermic reaction. The reaction mixture was stirred for 24 h at room temperature. After the upper acidic layer had been decanted, the lower viscous ionic liquid portion was washed with excess water until it was free of acid (checked by pH paper).[35]

2.1.3. Purification of the Ionic Liquids. The BF$_4$ salts were prepared from triply distilled acetone keeping in mind the fact that the solubility of the halides in dry acetone is very low.[38] It is reported[39] that the solubility of NaCl in acetone is 5.5×10^{-6} mol L^{-1}. The PF$_6$ salt, on the other hand, was prepared from and washed several times with conductivity water. The removal of the halide impurities from the ionic liquids was ensured by verifying that the ionic liquids or the washings did not form any precipitate of silver halide when treated with aqueous AgNO$_3$ solution.

All of the ionic liquids were eventually diluted with acetone or acetonitrile, then treated with activated charcoal for at least 48 h, and filtered at least twice by being passed through a Celite column. The liquids thus prepared were then transferred into clean and dry reagent bottles and kept in a vacuum (pressure of $10^{-2}-10^{-3}$ mbar) for 12 h at 60−65 °C for the removal of any organic impurities or water.[7] The purified ionic liquids were characterized by both IR and NMR spectroscopy and stored in a desiccator under dry nitrogen wrapped by aluminum foil.

2.2. Instrumentation. The IR and NMR spectra of the ionic liquids were measured using a Jasco FT/IR 5300 spectrometer and a Bruker AV 400 MHz NMR spectrometer, respectively. The absorption and fluorescence spectra were recorded on a Shimadzu spectrophotometer (UV-3101 PC) and a Spex spectrofluorometer (Fluoromax 3), respectively. The fluorescence spectra were corrected for the instrumental response. The fluorescence lifetimes of the systems (except ANF) were measured using a single photon counting spectrofluorometer (IBH, model 5000). The instrument was operated with thyratron-gated coaxial flash lamp filled with hydrogen gas at 0.5 atm pressure. The lamp frequency was maintained at 40 kHz, and the fwhm of the lamp pulse under the operating condition was ~1.2 ns. The decay curves were analyzed by a nonlinear least-squares iteration procedure using IBH decay analysis software. Because ANF was found to have a subnanosecond fluorescence lifetime, which could not be determined accurately using the setup described above due to poor time resolution, a picosecond-laser-based setup was used for the measurement of this lifetime. The details of the laser system and the complete setup can be found elsewhere.[19]

3. Results

As stated earlier, we first observed the excitation-wavelength-dependent fluorescence behavior in RTILs with ANF, and hence, we describe these results first before proceeding to the other systems.

In conventional solvents, ANF exhibits broad absorption and fluorescence bands characteristics of typical intramolecular charge-transfer (ICT) transitions.[31,40−42] Although both the band positions are dependent on the polarity of the medium, the fluorescence spectrum is much more sensitive to the medium than the absorption spectrum. This is evident from the fact that, when the solvent is changed from nonpolar toluene to polar acetonitrile, the absorption maximum shifts by only 10−11 nm, whereas the emission maximum shifts by more than 150 nm. This behavior is suggestive of an emitting state that is more polar than the ground state. The change in the dipole moment

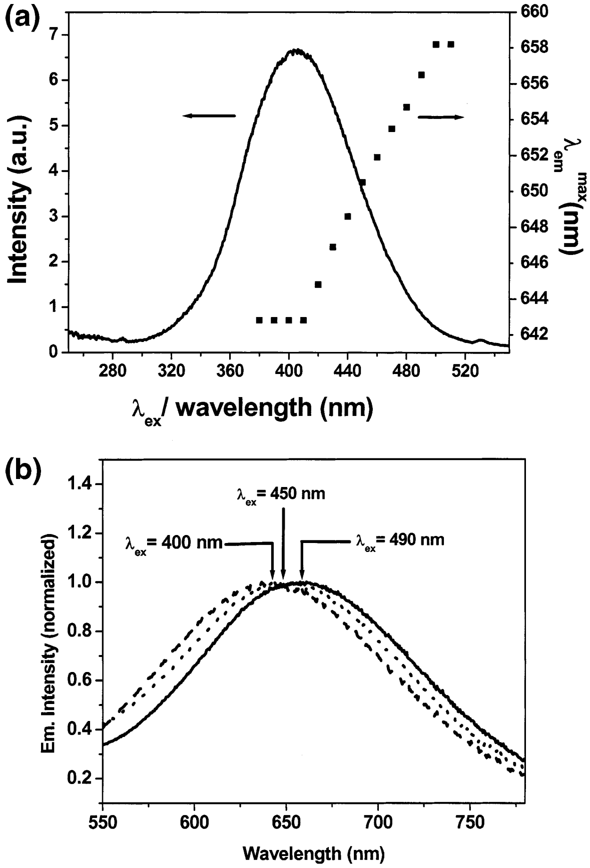


Figure 1. (a) λ_{em}^{max} vs λ_{ex} plots of ANF in [BMIM][BF$_4$] (●) superimposed on the excitation spectrum. (b) Normalized fluorescence spectra of ANF in [BMIM][BF$_4$] at room temperature as a function of excitation wavelength: $\lambda_{ex} = 400$ nm (− − −), $\lambda_{ex} = 450$ nm (• • •), and $\lambda_{ex} = 490$ nm (—). The fluorescence spectra have been corrected for the instrumental response.

of ANF upon electronic excitation is reported to be as high as 25 D.[31,40−42]

In RTILs, ANF exhibits absorption behavior very similar to that shown in conventional solvents. In [BMIM][BF$_4$], when ANF is excited at the blue side (say, at 380−390 nm) of the absorption maximum, the fluorescence maximum (λ_{em}^{max}) of ANF in [BMIM][BF$_4$] is observed at 643 nm (Figure 1). Interestingly, as can be seen from Figure 1, as the excitation wavelength is progressively shifted toward the red side of the maximum, a small but steady shift of the fluorescence maximum is clearly visible. The dependence of λ_{em}^{max} of ANF in [BMIM][BF$_4$] on the excitation wavelength (λ_{ex}) is shown in Figure 1. The extent of the shift, as measured from λ_{em}^{max}, is around 14 nm in [BMIM][BF$_4$]. In two other RTILs, [EMIM][BF$_4$] and [BMIM][PF$_6$], the observable shift values are ∼10 and 16 nm, respectively. The λ_{em}^{max} vs λ_{ex} plots of ANF in the two RTILs are shown in Figure 2. The shifts of the λ_{em}^{max} values in the three RTILs at room temperature are collected in Table 1 for comparison.

We also carefully examined the excitation wavelength dependence (if any) for several other commonly employed dipolar probe molecules (shown in Charts 2 and 3). Whereas all of the systems shown in Chart 2 show normal fluorescence behavior (with very little or negligible excitation wavelength dependence), we could identify two other systems, HNBD and ANS (Chart 3), that also exhibit an appreciable excitation-wavelength-dependent shift of the fluorescence maximum (Figure 3). The shift values observed for these two systems in the various RTILs are listed in Table 1. We also examined the excitation wavelength dependence of λ_{em}^{max} for ANF, ANS, and HNBD in a viscous conventional solvent, glycerol. As can be seen from Figure 4, ANF exhibits a more pronounced excitation wavelength dependence in relatively more viscous solvent glycerol, whereas the other two systems do not show any significant excitation dependent shift of the fluorescence maximum in this medium.

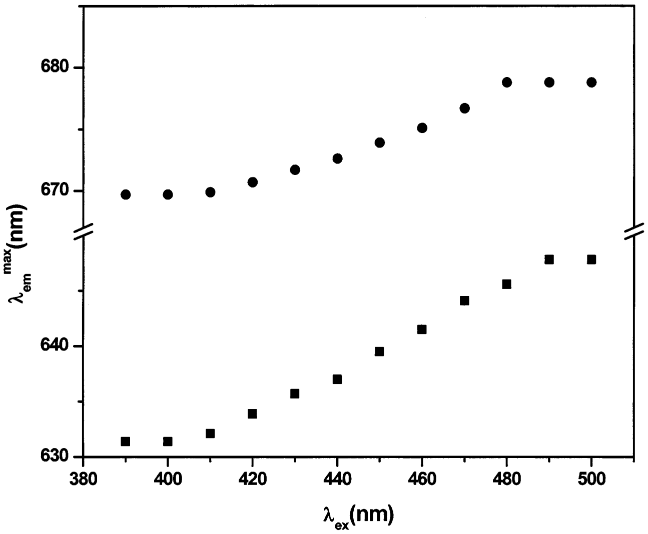


Figure 2. λ_{em}^{max} vs λ_{ex} plots of ANF in [EMIM][BF$_4$] (●) and [BMIM][PF$_6$] (■).

TABLE 1: Maximum Shifts (in nm)[a] of the Fluorescence Maximum Observed for the Various Systems in Different Media[b]

	[EMIM][BF$_4$] (66.5 cP)[c]	[BMIM][BF$_4$] (154 cP)[c]	[BMIM][PF$_6$] (371 cP)[c]	glycerol (900 cP)[c]
ANF	10	14	16	30
ANS	30	35	28	2
HNBD	14	16	13	3

[a] ±1 nm. [b] The observed shift values (nm) for ENBD, 4NBD, 6NBD, C102, C153, AP, and PRODAN in [BMIM][BF4] are 1.0, 3.5, 2.0, 5.0, 1.5, 2.5, and 4.5, respectively. [c] The quantities in parentheses are the viscosities of these media at 25 °C. These values for the RTILs were obtained from ref 7 and that for glycerol from ref 63.

4. Discussion

4.1. Case of ANF. This is the first instance in which an excitation-wavelength-dependent fluorescence behavior of a dipolar molecule has been observed in RTILs. When the homogeneous nature of the RTILs and the literature data on the dipolar molecules already studied in these media are taken into consideration, the present observation appears quite unusual.

However, we note that, when excited at the long-wavelength edge of the first absorption band, a red shift of λ_{em}^{max} of the dipolar molecules is *often* observed in low-temperature glasses; polymer matrixes; and organized assemblies such as micelles, vesicles, proteins, and membranes.[43−45] This phenomenon is termed the “red-edge effect” (REE),[46,47] but is also sometimes called the edge excitation shift (EES),[45] the edge excitation red shift (EERS),[48,49] or the red-edge excitation shift (REES).[50−52] We prefer to use the REE terminology, as this happens to be the first abbreviation for the observed phenomenon.[46,47] REE has been exploited quite extensively by several researchers for studies in biological systems, and an excellent recent review on this topic is available.[43] Although some of the earlier interpretations of REE involve emission from more than one

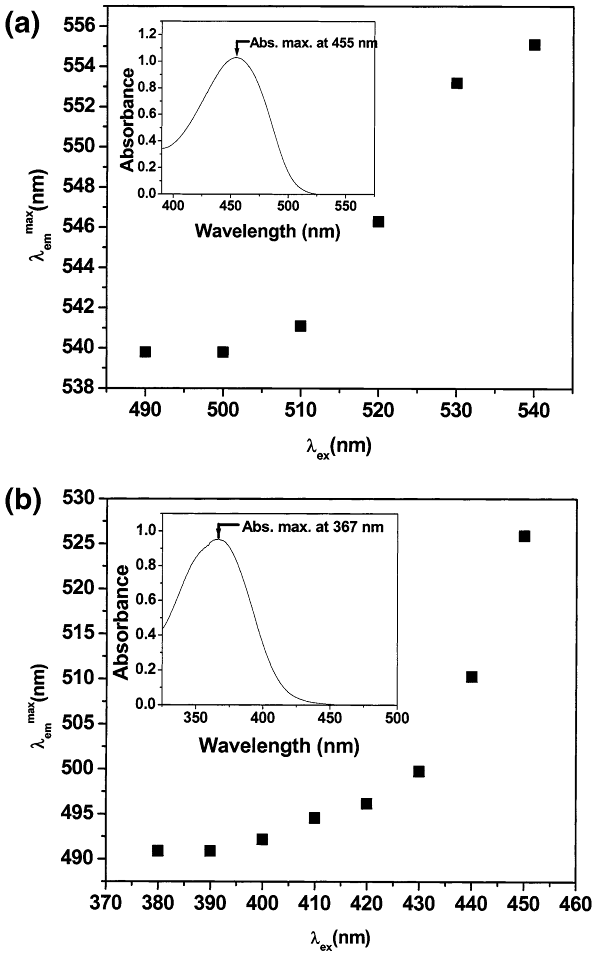


Figure 3. λ_{em}^{max} vs λ_{ex} plots of (a) HNBD and (b) ANS in [BMIM][BF_4]. The corresponding absorption spectra are shown in the insets.

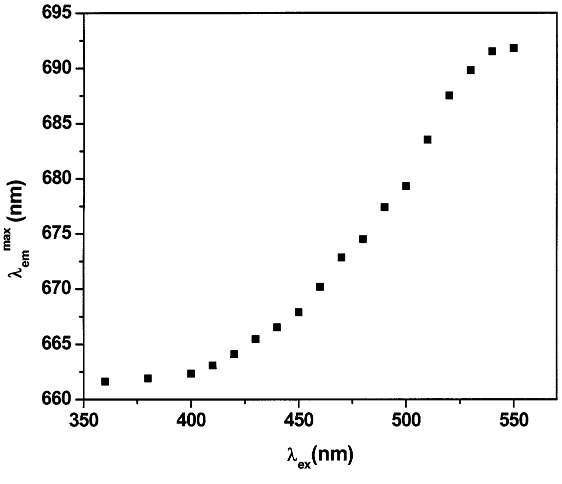


Figure 4. λ_{em}^{max} vs λ_{ex} plots of ANF in glycerol at room temperature.

TABLE 2: Fluorescence Lifetimes of the Different Systems Studied

system	medium	τ_f (ns)	source
ANF	[BMIM][BF_4]	0.1	this work
ANS	[BMIM][BF_4]	8.4	this work
HNBD	[BMIM][BF_4]	9.6	this work
ENBD	acetonitrile	0.27	*a*
4NBD	acetonitrile	9.96	*a*
6NBD	acetonitrile	0.16	*a*
C102	acetonitrile	3.3	*b*
C153	acetonitrile	5.6	*b*
AP	acetonitrile	14	*c*
PRODAN	acetonitrile	3.2	*d*

[a] Reference 34. [b] Reference 56. [c] Reference 54. [d] Reference 57.

electronic state of the molecule or from different conformers of the molecule, it is now established that REE in organized assemblies, where it is most common, arises primarily because of the spatial heterogeneity of these assemblies, which consist of hydrophobic and hydrophilic pockets that allow multiple solvation sites and contribute to inhomogeneous broadening of the absorption spectra.[43]

The excitation wavelength dependence can arise when there exists a distribution of the molecules in the ground state that differ in their solvation sites and, hence, their energies. This inhomogeneity can originate from the difference in the interaction energies between the ionic liquids and the dipolar systems. However, the presence of an ensemble of energetically different molecules in the ground state *alone* does not guarantee an excitation-wavelength-dependent fluorescence behavior because rapid relaxation of the excited state, such as the solvation of the fluorescent state or energy transfer between the energetically different excited states of the molecules, is expected to result in emission from the lowest-energy state irrespective of the excitation. It is only when a system allows selective excitation of the energetically different species and the relaxation of the fluorescent state is slow (hence, incomplete) that REE can be expected.

We now attempt to determine why ANF exhibits considerable REE in RTILs whereas the other dipolar systems such as AP, PRODAN, C153, and C102 do not. First, the extent of inhomogeneous broadening of the absorption spectrum, which permits the initial photoselection of energetically different species, depends on the change of the dipole moment on electronic excitation ($\Delta\mu$).[43] As stated earlier, the reported value of $\Delta\mu$ is 25 D for ANF,[31,40−42] whereas for C153, C102, AP, and PRODAN, this quantity is only 4.9−5.4,[53] 3.0−3.8,[53] 3.0−3.7,[54] and 4.4−5.0 D,[55] respectively. From this consideration, ANF is a better system for exhibiting REE than the other systems previously studied in ionic liquids.

The second factor, which is even more important than the first, is that ANF has a rather short fluorescence lifetime (τ_f) compared to the other systems (see Table 2). The τ_f value of ANF in 2-propanol is reported to be <50 ps.[41] Our own measurement yielded a lifetime value of only ~100 ps in [BMIM][BF_4]. On the other hand, recent studies on solvation dynamics suggest that solvation is a rather slow process in RTILs.[19−24] The slow component of the solvent relaxation time in [BMIM][BF_4] is between 3.3 and 3.9 ns, and the average solvation time is around 1.4−2.1 ns. Because the solvent relaxation time ($\langle\tau_{sol}\rangle$) around the photoexcited molecule is an order of magnitude higher than the τ_f value of ANF, it is not difficult to understand why unrelaxed fluorescence, which gives rise to the excitation-wavelength-dependent emission behavior in RTILs, could be observed in the case of ANF. As the τ_f values of AP (14 ns),[54] C153 (5.6 ns),[56] C102 (3.3 ns),[56] and PRODAN (3.2 ns)[57] in acetonitrile are higher than the $\langle\tau_{sol}\rangle$ value of the solvent, the fluorescence occurs from a fully solvated state in these molecules.

That the excitation-wavelength-dependent emission behavior in [BMIM][BF_4] is not due to any specific interaction between the ionic liquid and ANF, but is mainly due to incomplete solvation of the fluorescent state in this viscous medium, is evident from the fact that ANF exhibits a shift of λ_{em}^{max} in two other ionic liquids, [EMIM][BF_4] and [BMIM][PF_6], as well as in a viscous conventional solvent, glycerol. As the plot in

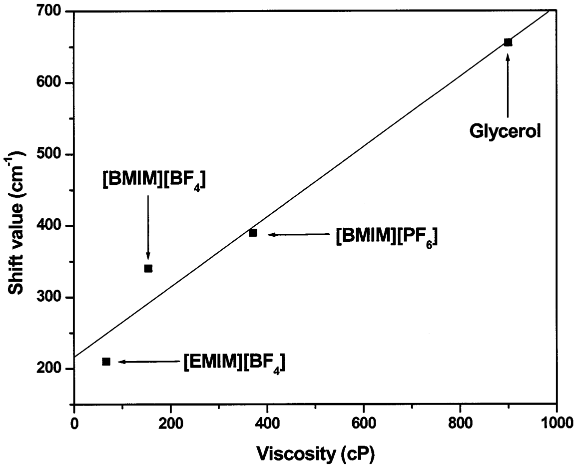


Figure 5. Viscosity dependence of the spectral shift of ANF in three different RTILs and in glycerol.

Figure 5 shows, the spectral shift is linearly related to the viscosity of the medium. In essence, it is the incomplete solvation in the viscous media that is primarily responsible for the excitation-wavelength-dependent spectral shift of ANF.

4.2. Cases of ANS and HNBD. Because both ANS and HNBD are known to exhibit REE in biological systems,[50−52,58,59] the excitation-wavelength-dependent fluorescence behavior of these systems in ionic liquids might not be surprising. However, that the cases of ANS and HNBD are distinctly different from that of ANF is evident from the facts that (i) unlike ANF, neither ANS and HNBD shows much REE in the viscous solvent glycerol and (ii) the τ_f values of ANS and HNBD (8.4 and 9.6 ns, respectively, in [BMIM][BF$_4$]) are significantly larger than the average solvation time of 1.4−2.1 ns. Both of these observations suggest that slow solvation (compared to τ_f) of the fluorescence state, which gives rise to REE in ANF, is not responsible for REE in ANS and HNBD.

In the case of ANS, the electrostatic interaction is expected to dominate the other interactions and probably plays the most important role in creating a distribution of energetically different molecules in the ground state that allows their photoselection. Previous studies on ANS in micellar media corroborate this view.[60,61] Two factors could be responsible for the slow relaxation of the excited state: retardation of solvation due to the electrostatic forces induced by charged ANS and/or an inefficient energy transfer between the energetically different species. In the absence of any literature data on solvation dynamics in RTILs involving ANS, we are unable to pinpoint at this stage which of the two is the slow process. We are planning to carry out experiments to throw light on this issue.

Among the four structurally similar NBD derivatives we have studied, because only HNBD exhibits a shift of λ_{em}^{max} [not ENBD or 6NBD, which exhibit subnanosecond fluorescence lifetimes (see Table 2)], the origin of the excitation-wavelength-dependent spectral shift in HNBD is something other than slow solvation.

Examination of the absorption characteristics reveals that, among the four NBD derivatives, the fwhm value of the first ICT band is the largest for HNBD in [BMIM][BF$_4$] (Table 3). Also, the spectral width of this band of HNBD in RTILs is relatively larger that than that in other solvents, including glycerol (Table 4).

TABLE 3: fwhm Values (in cm^{-1})[a] of the Lowest-Energy Absorption Band of the NBD Derivatives in [BMIM][BF$_4$]

system	fwhm
4NBD	2730
6NBD	2700
ENBD	2990
HNBD	3900

[a] ±100 cm^{-1}.

TABLE 4: fwhm Values (in cm^{-1})[a] of the First Absorption Band of HNBD in Different Solvents

solvent	fwhm
acetonitrile	3400
MeOH	3200
glycerol	3000
[BMIM][BF$_4$]	3900

[a] ±100 cm^{-1}.

From the structural viewpoint, what makes HNBD unique among the systems in this group is that it contains free amino hydrogen atoms and, hence, can enter into hydrogen-bonding interactions by donating the hydrogen atoms. Because all of the other NBD derivatives lack this mode of interaction with the solvents, the spectral width of the ICT bands for these systems is significantly narrower compared to that for HNBD. It is thus evident that hydrogen-bonding interactions between the RTIL and HNBD, where the latter plays the role of the H-bond donor, provide ground-state inhomogeneity and facilitates initial photoselection. This observation is supported by the fact that, of the two BMIM salts used in this study, the hydrogen-bond-accepting ability, judged from the reported hydrogen-bond basicity parameter (β), is higher for [BMIM][BF$_4$].[14,62] Perhaps this is why the magnitude of the excitation-wavelength-dependent shift of the emission maximum is larger in [BMIM][BF$_4$] even though [BMIM][PF$_6$] is a more viscous solvent. Regarding excited-state relaxation, an inefficient energy transfer between the energetically different molecules, as has been demonstrated earlier,[46,47] presumably contributes to the excitation-wavelength-dependent fluorescence behavior in this case.

5. Conclusion

We have observed for the first time the occurrence of an excitation-wavelength-dependent shift of the fluorescence spectra of some dipolar molecules in room-temperature ionic liquids. This not only suggests the existence of a distribution of ground-state molecules differing in their interaction energies with the room-temperature ionic liquids, but also implies that the excited-state relaxation processes such as solvation and/or energy transfer are significantly slower in these media. Although the ground-state heterogeneity that allows photoselection of the molecules is always present for these systems even in conventional fluid media, it is because of the low rate of the excited-state processes that the excitation wavelength dependence can be observed in ionic liquids. Given that the measured λ_{em}^{max} values of the dipolar systems are routinely used for the estimation of the polarity of the RTILs, the observation that these values can be dependent on the excitation wavelength suggests that utmost care is needed while selecting the probe molecules for these measurements.

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picosecond time-resolved fluorescence decay behavior of ANF was measured at the National Centre for Ultrafast Processes, Chennai, India.

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