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Excitation wavelength dependent fluorescence behavior of the room temperature ionic liquids and dissolved dipolar solutes

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Abstract

Room temperature ionic liquids are novel media for a variety of studies and applications. In this article, the excitation wavelength dependent fluorescence behavior of imidazolium ionic liquids and dipolar solutes dissolved in these liquids is highlighted. We discuss the origin of the unconventional fluorescence behavior of the ionic liquids and also of the dipolar systems, most of which show no excitation wavelength dependence in the conventional solvents. The implications of these observations in fluorescence studies involving the ionic liquids are discussed.

Keywords: Room temperature ionic liquids; Imidazolium salts; Excitation wavelength dependent fluorescence; Photophysics; Red-edge excitation effect

1. Introduction

Increasing air and water pollution by the volatile organic chemicals, which are used in large quantities as solvents in research laboratories and industries, has led to the realization of the importance of solvent free synthesis [1], or use of water [2], supercritical carbon dioxide [3] and room temperature ionic liquids (RTILs) [4–11] as alternative reaction media.

RTILs are organic salts composed entirely of ions and unlike the common organic salts, which melt at high temperatures, these are liquid at ambient temperature. The low melting point of these salts is primarily due to the fact that the constituent ions are fairly large with low charge density. Substituted imidazolium ions are the most popular cationic component of the RTILs. Among the anions, $[BF_4]^-$, $[PF_6]^-$ and $[(CF_3SO_2)_2N]^-$ (abbreviated as $[Tf_2N]^-$) are most frequently used. Chart 1 depicts some of the commonly used RTILs. The melting points and viscosities of these liquids are collected in Table 1. Since the properties of the RTILs are very much dependent on the constituent ions, it is possible to obtain an RTIL of desired property by proper choice of the two ionic components. It is therefore not surprising that the RTILs are termed as 'designer's solvent' [4].

Some of the properties that make the RTILs environmentally benign media for various applications are negligible vapor pressure, wide liquid range, high thermal stability, low moisture sensitivity, ability to dissolve both hydrophilic and hydrophobic solutes, non-flammable and recyclable nature [4–11]. Increasing usage of the RTILs as media of organic synthesis [5–7], liquid–liquid extraction [14], electrochemical studies [15], biocatalysis [16], mass spectrometry [17], solar cells [18], synthesis of nanoparticles [19], gas sensors [20] and other applications are evident from the recent literature.

Several spectroscopic measurements have been made on the RTILs with a view to characterizing these liquids and obtaining insight into the nature of various interactions and the structure–property relationships, in solution, solid and liquid phases. These studies have provided conclusive evidences of cation–cation π-stacking interaction among the imidazoliun rings, cation–anion C–H···X and C–H···π interactions [21–23], presence of isomers of the cations [24,25], presence of both contact ion pair and solvent-separated ion pair and acidity of some ionic liquids [26,27].

The steady-state absorption and fluorescence spectral behavior of several solute molecules, whose spectra are sensitive to the polarity of the surrounding environment, has been studied in these media with a view to obtaining information on the polarity of these liquids. These studies generally suggest that RTILs are more polar than acetonitrile, but less polar than methanol [13,28–31]. Time-resolved fluorescence studies on

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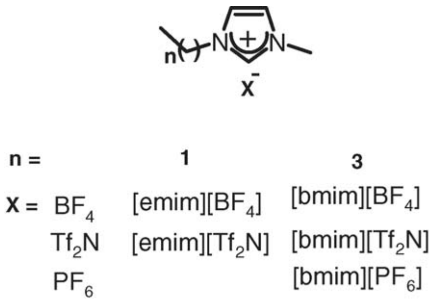

Chart 1. Structures of some common imidazolium ionic liquids, [emim] and [bmim] stand for 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium moieties, respectively.

dipolar solutes, which have revealed wavelength dependence of the fluorescence decay profiles and dynamic fluorescence Stokes shift in the ps–ns time scale [32–46], have thrown insight into the mechanism of solvation dynamics in these media that are conceptually different from the conventional liquids. Among the other photophysical and photochemical processes studied in these media intramolecular excimer formation [47], photoisomerization [48,49] and electron transfer reactions [50–52] are noteworthy.

The fact that a large number of photophysical studies have already been executed in RTILs suggests that these are transparent liquids, which allow absorption and fluorescence studies on the dissolved substances. However, we have recently discovered that all imidazolium ionic liquids have non-negligible absorption in the entire UV and some part of the visible region [53,54]. We have unambiguously established that the absorption has nothing to do with the impurity in the samples, but is due to the imidazolium salts. More interestingly, we have found that excitation at the tail of the absorption band gives rise to an emission that shifts with the change of the excitation wavelength [53,54]. This kind of excitation wavelength dependent fluorescence behavior, which may appear to be in violation of Kasha's rule of excitation wavelength independence of the emission spectrum, has also been observed for some dipolar solutes in ionic liquids. In this review article, we have highlighted the excitation wavelength dependent emission behavior of the imidazolium ionic liquids [53,54] and some dipolar solutes in these media [55]. We have examined the factors that contribute to this observation.

Table 1
Melting point and viscosity (at 25 °C) of most commonly used RTILs

RTIL	mp (°C)	η (cP)
[emim][BF$_4$]	6[a]	66.5[b]
[bmim][BF$_4$]	−81[c]	154[b]
[bmim][PF$_6$]	−61[c]	371[b]
[emim][Tf$_2$N]	−3[d]	34[d]
[bmim][Tf$_2$N]	−4[d]	52[d]

[a] Ref. [8].
[b] Ref. [10].
[c] Ref. [12].
[d] Ref. [13].

2. The experimental findings

The experimental observations have been discussed under two sub-headings. First, the fluorescence behavior of the neat RTIL is described. Next, the excitation wavelength dependent fluorescence behavior of some dipolar solutes dissolved in RTILs is presented.

2.1. *Fluorescence behavior of neat RTILs*

A typical emission behavior of RTIL is illustrated in Fig. 1. The general emission characteristics [53,54] of the other imidazolium ionic liquids are quite similar. All of them exhibit excitation wavelength dependent two-component emission. For short excitation wavelength, the emission band is observed at around 340–360 nm. This band does not shift on variation of the excitation wavelength. However, when excited at longer wavelengths, which correspond to the long tail of the absorption band of the imidazolium ionic liquids (Fig. 2), a second emission band, which appears as a shoulder for short excitation wavelengths, becomes prominent and the maximum corresponding to this band starts shifting towards red when the excitation wavelength is increased. As can be seen from the figure, the magnitude of the shift of the peak is unusually large (>100 nm). In fact, the shift is observable as long as one is able to record a noise-free emission spectrum.

2.2. *Fluorescence behavior of dipolar solutes in RTILs*

The fluorescence peak positions of the dipolar solutes are strongly dependent on the polarity of the surrounding environment because of intramolecular charge transfer nature of the emission. These molecules are routinely employed for the determination of the polarity of various ionic liquids. The excitation wavelength dependent fluorescence behavior of

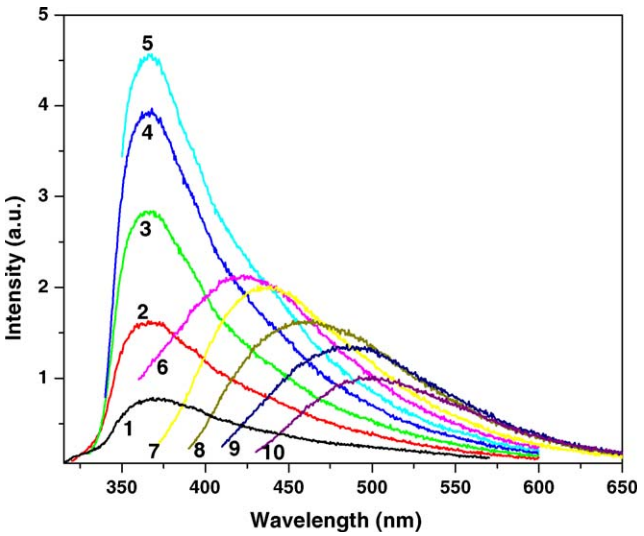

Fig. 1. Excitation wavelength dependent emission behavior of neat [bmim][BF$_4$]. The excitation wavelengths for spectra marked from 1 to 10 are 290, 310, 320, 330, 340, 350, 360, 380, 400 and 420 nm, respectively. Adapted from Fig. 3 of Ref. [54].

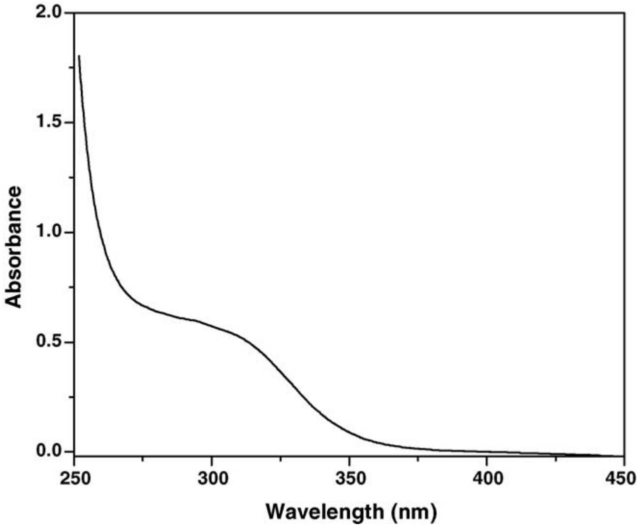

Fig. 2. Absorption spectra of neat [bmim][BF$_4$] as obtained using a 1 cm path length cuvette. Adapted from Fig. 1 of Ref. [54].

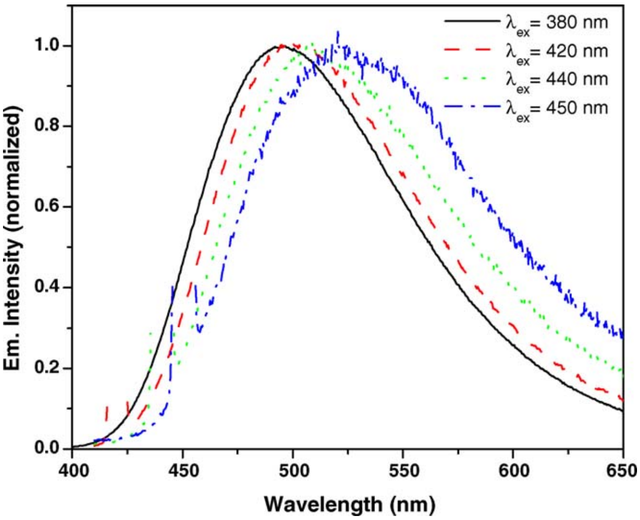

Fig. 3. Excitation wavelength dependent shift of emission spectra of ANS in [emim][BF$_4$]. Scattered excitation wavelengths have been truncated in the figure.

these very well-studied systems was neither expected, nor was such behavior observed until very recently [55]. Among the large number of systems that we have studied in ionic liquids (Chart 2), we could observe excitation wavelength dependent behavior for ANF, HNBD and ANS [55]. A typical excitation wavelength dependent behavior is highlighted in Fig. 3. A plot of the emission peak wavelength versus the excitation wavelength is illustrated in Fig. 4. An important point to note here is that since the fluorescence efficiency of the imidazolium salts is rather small and the dipolar solutes examined here are strongly fluorescent, the fluorescence due to the former species did not interfere with the fluorescence measurements of the latter and it was ensured that the present shift of the fluorescence

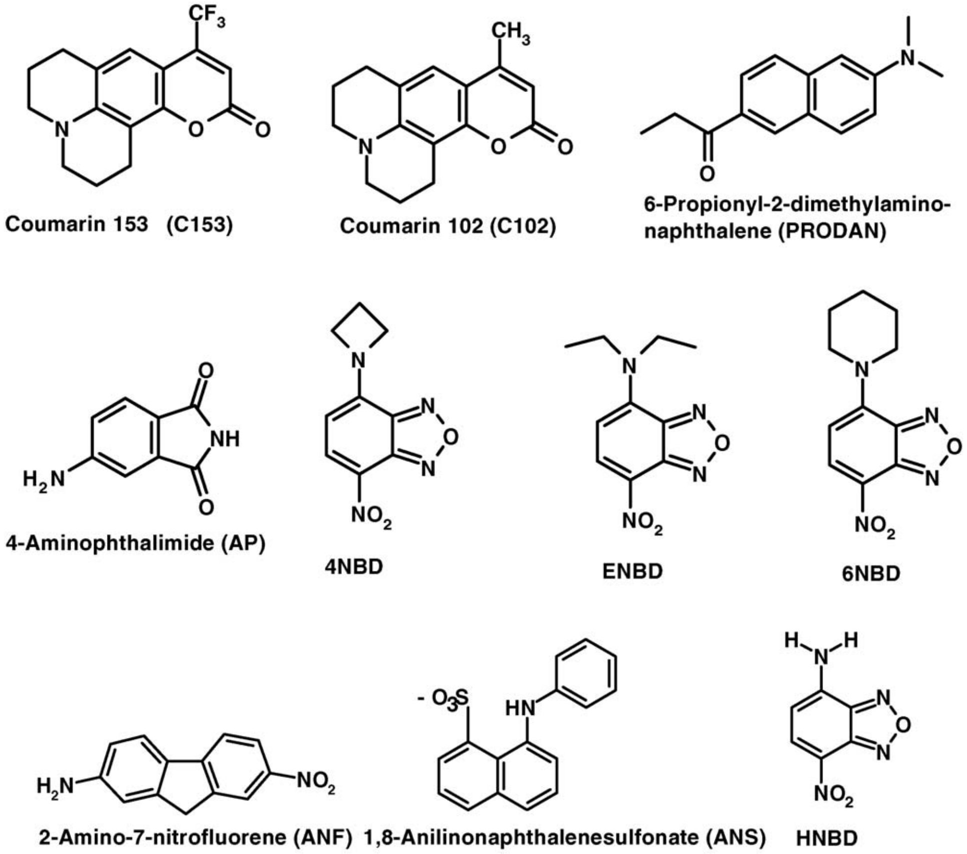

Chart 2. Structures of the dipolar systems investigated for REE. 7-Nitrobenz-2-oxa-1,3-diazole moiety is abbreviated as NBD. The number or letter preceding NBD indicates the nature of the 4-amino substitution in the system.

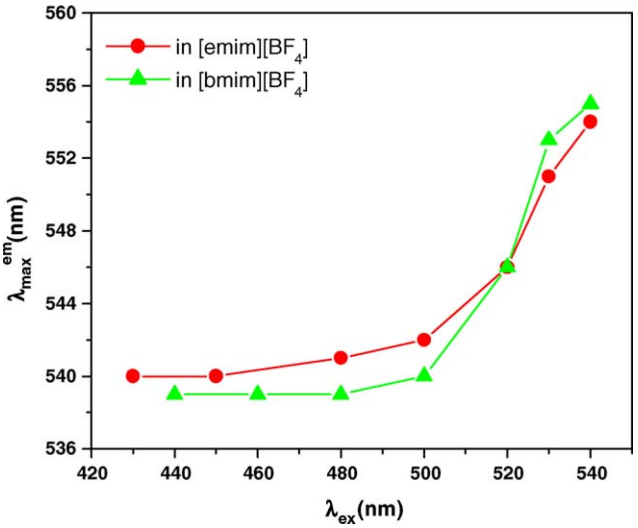

Fig. 4. λ_{em}^{max} vs. λ_{ex} plot of HNBD in neat [emim][BF$_4$] and [bmim][BF$_4$].

Table 2
Maximum shift (in nm)[a] of the fluorescence maximum observed for various systems in different media [55]

	[emim][BF$_4$] (66.5 cP)[b]	[bmim][BF$_4$] (154 cP)[b]	[bmim][PF$_6$] (371 cP)[b]	Glycerol (900 cP)[b]
ANF	10	14	16	30
ANS	30	35	28	2
HNBD	14	16	13	3

[a] ±1 nm.

[b] The bracketed quantities are the viscosities of these media at 25 °C. These values for the RTILs have been obtained from Ref. [10], and for glycerol from Ref. [56].

maximum of the dipolar solutes has nothing to do with that of the ionic liquids. The excitation wavelength dependence of λ_{em}^{max} for ANF, ANS and HNBD is also studied in a highly viscous conventional solvent, glycerol. It is found that ANF exhibits more pronounced excitation wavelength dependence in glycerol, while the other two systems, ANS and HNBD do not show any significant excitation wavelength dependent shift of the fluorescence maximum in this medium. The shift values observed for the systems in RTILs and glycerol are indicated in Table 2.

3. Origin of the excitation wavelength dependence

3.1. Literature information

That the fluorescence maxima of some systems can shift towards longer wavelengths with an increase in the excitation wavelength is known for some time [57–59]. The initial reports, which were confirmed later by several workers [60–63], were found to be inconsistent with the Kasha's rule according to which the fluorescence spectrum of a polyatomic molecule in condensed media should always originate from the lowest vibrational level of the first excited singlet state irrespective of the excitation. Extensive studies in different media involving a variety of fluorophores have revealed that the excitation wavelength dependence is a phenomenon that can be observed frequently in frozen media such as low temperature glasses, highly viscous media or in polymer matrices [64]. This phenomenon is known as 'red-edge effect' (REE), edge excitation shift (EES), edge excitation red shift (EERS) or red-edge excitation shift (REES). REE has been exploited quite extensively by several researchers for studies in biological systems and an excellent recent review on this topic is available [64]. REE phenomenon has been observed in different excited state reactions such as photoisomerization [65,66], electron transfer [67,68] and proton transfer [69]. The applications of REE in viscous and glass forming fluids [70,71], binary solvent mixtures of different polarity [72], proteins [73–76], polymers [77,78], micelles [79–82], phospholipid vesicles [83–85] and membranes [86–90] have been demonstrated. It is now understood that the unusual excitation wavelength dependent emission behavior does not really violate fundamental principles such as the Kasha's rule, but is due to non-validity of some of the assumptions on which this rule is based, under certain specific experimental conditions.

3.1.1. Mechanism of red-edge excitation shifts

Some of the earlier interpretations of REE involved emission from multiple states or different conformers of the molecule. However, it is now generally accepted that two conditions must be satisfied to observe REE. First, there must be a distribution of solute–solvent interaction energy leading to inhomogenous broadening of the absorption spectrum. This inhomogeneity, which always exists in the condensed media, is particularly prominent for the dipolar systems in polar media. In organized assemblies, where REE is most common, the inhomogeneity also arises due to the spatial heterogeneity of these assemblies, which consist of hydrophobic and hydrophilic pockets allowing multiple solvation sites. The presence of an ensemble of energetically different molecules in the ground state *alone* does not guarantee excitation wavelength dependent fluorescence behavior since rapid relaxation of the excited state is likely to result in emission from the lowest excited state.

The second condition that must be met to give rise to REE is that the excited state relaxation of the fluorescent species, which can be solvation of the fluorescent state or energy transfer from the fluorescent state to a low-lying energy state of the molecules, must be slower or comparable to the fluorescence lifetime of the species. This condition ensures that it is possible to observe emission from the unrelaxed photoexcited species instead of that from the lowest excited state.

Perhaps it is necessary to discuss why REE is observed only on excitation at the red edge of the absorption spectrum. This is primarily due to the fact that (i) the probe molecules absorbing at the red edge of the absorption band have greater interaction with the solvent molecules than those absorbing in the blue side and (ii) the inhomogenous broadening can only be probed at the red excitation edge where the excitation to the higher vibrational levels does not interfere with this selection.

Some of the criteria to be fulfilled by the probe and solvent for the observation of REES are as follows [64]:

(i) Since inhomogeneous broadening, which dictates photoselection of the energetically different species, is directly proportional to the change of dipole moment ($\Delta\mu$) on electronic excitation, the probe molecules with large $\Delta\mu$ values are the most suitable candidates to exhibit REE. Probe molecules with short fluorescence lifetimes are more likely to exhibit REE than those with long lifetimes.

(ii) The larger the polarity and nuclear polarizability of the medium, the stronger is the interaction of the probe molecule with the solvent and higher is the chance to observe REE. The more viscous is the medium, the slower is the excited state relaxation process (intramolecular) and higher is the possibility to observe REE.

3.2. *Interpretation of REE in RTILs*

It is necessary to find out the origin of the long-wavelength emission band prior to explaining why the emission maximum corresponding to this band shifts continuously. It is found that the long-wavelength emission band is prominently observed when excited at the tail of the absorption band [53,54]. That the long tail of the absorption spectra is due to the presence of various associated species that are energetically different is evident from complete disappearance of the long-wavelength emission band on dilution [53]. Even though it is not possible at this stage to comment on the structures of these associated species, the experimental and computer simulation studies, which have been specifically carried out with a view to obtaining insight into the structures of the imidazolium salts in their liquid state [21–23,91–97], confirm various associated structures in the liquid state.

Among the experimental results, the neutron scattering, NMR, X-ray scattering and Raman spectroscopic measurements are particularly important [21–23,91–97]. These studies indicate various structures with both short- and long-range spatial correlations of the cation–anion and cation–cation pairs, which we term as associated species. Even though the large anions are located mostly above and below the plane of the imidazolium ring [93], the existence of multiple structures and the large region of probability of finding an anion in the vicinity of a cation and vice versa are expected to broaden the energy states of the associated species and can contribute to the long tail in absorption spectra.

The excitation wavelength dependence of the long-wavelength emission band can only be accounted for taking into consideration the existence of energetically different associated species [53,54]. As the excitation wavelength is changed, a slightly different associated species is excited and an emission characteristic of this particular species is observed since the energy transfer between these energetically different species is inefficient owing to short fluorescence lifetime and also, due to the low concentration of these species. In essence, we attribute REE-like emission of the imidazolium ionic liquids to heterogeneity of the structure of RTIL, which allows selective photo-excitation of energetically different associated species [53,54]. This fact along with high viscosity and short fluorescence lifetime, which makes the relaxation of the photoexcited species inefficient, contribute to REE-like behavior in neat ionic liquids.

3.2.1. *Case of ANF*

In order to understand why ANF exhibits significant REE in RTILs unlike other dipolar systems such as AP, PRODAN, C153 and C102, it is important to take into consideration the extent of inhomogeneous broadening of the absorption spectrum, which permits initial photoselection of energetically different species. Since the inhomogeneous broadening depends on the change of the dipole moment on electronic excitation ($\Delta\mu$) [64], and this quantity is the largest (25 D) for ANF [98–101] compared to 3–5.4 D for C153, C102, AP and PRODAN [102–104]), it is expected that ANF is a better system to exhibit REE compared to the remaining systems.

The second important factor that contributes to REE of ANF is its short fluorescence lifetime. The measured τ_f value for ANF in 2-propanol is reported to be <50 ps [100]. Our own measurement yielded ∼100 ps lifetime in [bmim][BF$_4$] [55]. On the other hand, recent studies on solvation dynamics suggest that solvation is a much slower process in RTILs [32–46]. The slow component of the solvent relaxation time in [bmim][BF$_4$] is around 3.3–4.0 ns and the average solvation time ranges around 1.4–2.1 ns [35]. Since the average solvent relaxation time ($\langle\tau_{\rm sol}\rangle$) around the photoexcited molecule is an order of magnitude higher than the τ_f value of ANF, it is understandable 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 (in acetonitrile) of AP (14 ns) [103], C153 (5.6 ns) [105], C102 (3.3 ns) [105] and PRODAN (3.2 ns) [106] are higher than the $\langle\tau_{\rm sol}\rangle$ value of the solvent, the fluorescence occurs from a fully solvated (relaxed) state, in these molecules and thus no REE is observed.

That the excitation wavelength dependent emission behavior in [bmim][BF$_4$] is not due to any specific interaction between the ionic liquids and ANF, but is due to incomplete solvation of the fluorescent state in this viscous medium, is evident from the fact that ANF exhibits shift of the $\lambda_{\rm em}^{\rm max}$ in two other ionic liquids, [emim][BF$_4$] and [bmim][PF$_6$] and also, in a viscous conventional solvent, glycerol. Therefore, it can be concluded that it is the incomplete solvation (relaxation) in these viscous media that is primarily responsible for the excitation wavelength dependent spectral shift of ANF.

3.2.2. *Case of ANS and HNBD*

Since it is well known that both ANS and HNBD do exhibit REE in biological systems [86,87,107–109], the excitation wavelength dependent fluorescence behavior of these systems in ionic liquids may not be surprising. However, the case of ANS and HNBD is distinctly different from that of ANF for two reasons [55]: (i) unlike ANF, both ANS and HNBD do not show REE in a much 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 in the RTILs.

In the case of ANS, which is a charged species, the electrostatic interaction is expected to dominate over the non-electrostatic ones and probably plays the most important role in creating a distribution of energetically different molecules in the ground state that allows their selective photoexcitation.

Table 3
Fluorescence lifetime of the different systems studied [55]

Systems	Media	τ_f (ns)	Source
ANF	[bmim][BF_4]	0.1	[55]
ANS	[bmim][BF_4]	8.4	[55]
HNBD	[bmim][BF_4]	9.6	[55]
ENBD	Acetonitrile	0.27	[112]
4NBD	Acetonitrile	9.96	[101]
6NBD	Acetonitrile	0.16	[101]
C102	Acetonitrile	3.3	[105]
C153	Acetonitrile	5.6	[105]
AP	Acetonitrile	14	[102]
PRODAN	Acetonitrile	3.2	[106]

Table 4
FWHM values (in cm^{-1})[a] of the lowest energy absorption band of the NBD derivatives in [bmim][BF_4] [55]

System	FWHM
4NBD	2730
6NBD	2700
ENBD	2990
HNBD	3900

[a] ±100 cm^{-1}.

Previous studies on ANS in micellar media corroborate the important role of electrostatic interactions [110,111]. 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 RTILs and/or an inefficient energy transfer process between the energetically different species. In the absence of literature data on the solvation dynamics in RTILs involving ANS, it is not possible to pinpoint at this stage whether one or both the factors contribute to REE in ANS. Further studies need to be carried out to obtain insight into this aspect.

Among the four structurally similar NBD derivatives studied, only HNBD exhibits the shift of λ_{em}^{max}, even though other two NBD derivatives, ENBD and 6NBD, possess much shorter lifetimes (Table 3). Examination of the absorption characteristics reveals that among the four NBD derivatives, the FWHM value of the first absorption band is the largest for HNBD in RTILs (Table 4). Also, the spectral width of this band in RTILs is relatively larger than that in conventional solvents, which include even the highly viscous solvent, glycerol (Table 5).

What makes HNBD unique among the other NBD derivatives is that it possesses free amino hydrogen atoms, which can enter into hydrogen-bonding interaction with solvents that are hydrogen bond acceptors. Since other NBD derivatives lack this interaction with the solvents, the spectral width of the absorption band for these systems is significantly narrower compared to HNBD. It is thus evident that hydrogen-bonding interaction between the RTIL and HNBD, where the latter plays the role of H-bond donor, provides the ground state inhomogeneity and facilitates the selective photoexcitation. This observation is supported by the fact that among 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] [113,114]. 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. As far as the excited state relaxation is concerned, an inefficient energy transfer between the energetically different molecules, as has been reported earlier [59,115] presumably contributes to the REE in this case.

Table 5
FWHM values (in cm^{-1})[a] of the first absorption band of HNBD in different solvents [55]

Solvent	FWHM
AN	3400
MeOH	3200
Glycerol	3000
[bmim][BF_4]	3900

[a] ±100 cm^{-1}.

4. Concluding remarks

Herein, we have highlighted some of our recent observations on the excitation wavelength dependence of the fluorescence behavior in imidazolium ionic liquids. First, we have shown that the imidazolium ionic liquids display interesting fluorescence behavior. The fluorescence maximum due to the ionic liquid shifts towards red as the excitation wavelength is increased. This observation has been attributed to the presence of energetically different associated forms of the constituent ions of the ionic liquids and slow rate of the excited state relaxation process in these media.

A similar excitation wavelength dependent fluorescence behavior has also been observed for some dipolar solutes in these liquids. This kind of behavior, which is uncommon in conventional solvents, is due to the presence of a distribution of ground state molecules differing in their interaction energies with the RTILs and slow excited state relaxation processes such as solvation and/or energy transfer in these media. Although the ground state heterogeneity, which allows selective photoexcitation of the molecules, exists even in less viscous conventional media, it is due to the slow rate of the excited state processes compared to the fluorescence lifetime, the excitation wavelength dependent emission behavior, which is known in the literature as red-edge effect, is observable in ionic liquids.

The fact that the imidazolium ionic liquids are weakly fluorescent is likely to limit the applicability of these substances as media for fluorescence studies. As such the weak fluorescence may not be a matter of concern when strongly fluorescent samples are studied. However, for weakly emitting species, this could be a serious problem and one needs to be very careful while carrying out such measurements. Since 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 excitation wavelength dependent suggests that utmost care must be taken while selecting the probe molecules for these measurements.

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