Chapter 5

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

This chapter depicts the unusual steady state fluorescence behaviour of several dipolar molecules in three imidazolium room temperature ionic liquids, viz., [bmim][BF₄], [emim][BF₄] and [bmim][PF₆]. Various parameters of the fluorescent probes as well as the RTILs have been carefully examined in order to determine the factors that contribute to this kind of behaviour, generally not observed in conventional media.

5.1. Introduction

The utility driven realisation of RTILs as environmentally benign media has already been documented through a large variety of reactions in these liquids.¹⁻⁶ However, a little work exploring the potential of these media in photophysical and photochemical studies has so far been undertaken.⁷⁻²⁴ A vast majority of the photophysical studies carried out till date have been directed towards estimating the polarity of these liquids using various solvatochromic absorption and fluorescence probes.⁸,⁹,₁⁵,₂¹,₂₅ These studies have indicated that the imidazolium cation based RTILs are more polar than acetonitrile but less polar than methanol; to be precise, their polarity is similar to those of the branched chain short alcohols. On the other hand, 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-nanosecond time domain, suggesting that solvation is rather a
slow process in RTILs when compared to that in conventional molecular solvents such as acetonitrile or methanol.\textsuperscript{8,9,11-14,20,24} However, these studies have so far indicated that the interaction between the ionic constituents of the 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 the conventional solvents.

During the course of our photophysical studies in RTILs, on dipolar fluorescent molecules, we observed that 2-amino-7-nitrofluorene (ANF) exhibits an excitation wavelength dependent steady state fluorescence in RTILs, a behaviour that could be termed as unusual for the following reasons. (i) The literature suggests that ANF does not exhibit excitation wavelength dependent behaviour in conventional molecular solvents,\textsuperscript{26} (ii) other dipolar molecules previously examined in RTILs do not exhibit this kind of behaviour,\textsuperscript{8,9,24} and (iii) the observed behaviour is contrary to what is prescribed by the famous Kasha’s rule.\textsuperscript{27} With a view to understanding the origin of this behaviour, we have undertaken the investigation on several electron-donor-acceptor (EDA) molecules in three different RTILs (Chart 5.1.) of different polarity and viscosity. The fluorescence behaviour of those dipolar probes, which show excitation wavelength dependent fluorescence spectra in RTILs, has also been examined in a viscous molecular solvent, glycerol, in order to determine whether it is only viscosity or any other specific effect that governs this unusual behaviour. The molecules studied in this work have been clubbed into two groups; the first group of molecules shown in Chart 5.2. does exhibit unusual excitation wavelength dependent fluorescence response; whereas, the second group of systems, put together in Chart 5.3. does not show this effect.
The shift of fluorescence maximum of some systems towards longer wavelength with an increase in the excitation wavelength is known for some time.\textsuperscript{28-30} Extensive investigations in different media employing a variety of fluorophores, have revealed that this phenomenon could be observed frequently in frozen media such as low temperature glasses, highly viscous media, or in polymer matrices.\textsuperscript{31-33} (See Section 1.4.3. for detail) Although different acronyms have been put forward to describe this phenomenon, we would like to use the acronym REE throughout the thesis. REE has quite well been exploited by several researchers for studies in biological systems and an excellent recent review on this topic is available.\textsuperscript{31} Different excited state reactions can contribute to REE.\textsuperscript{34-38} (See Section 1.4.3. for detail) This phenomenon can also be observed in different media.\textsuperscript{38-45} (See Section 1.4.3. for detail) It is now well understood that that this type of unusual excitation wavelength dependent emission behaviour does not really violate fundamental principles such as the Kasha’s rule. Rather, it arises from the operation in some specific conditions whereby the molecules in the ensemble are distributed in different interaction energy domain with the surrounding molecules. Different reasons that control the REE phenomenon can briefly be stated as follows.

The probe molecules with large change in dipole moment values ($\Delta \mu$), and short fluorescence lifetime are the most suitable candidates to exhibit REE. The larger the polarity and nuclear polarizability of the medium, the stronger is the interaction of the solvent with the probe molecule and hence, greater is the chance to observe REE. The more viscous is the medium, the slower is the intermolecular excited state relaxation process and hence, higher is the possibility to observe REE.
Chart 5.1. Structure of different imidazolium RTILs.

Chart 5.2. Structure of different dipolar molecules, which exhibit REE.

Chart 5.3. Structure of different dipolar molecules, which didn’t exhibit REE.
5.2. Results

Absorption behaviour exhibited by ANF in RTILs, is very much similar to that in conventional solvents. In [bmim][BF₄], when ANF is excited at the blue side (say, at 360 - 380 nm) of the absorption maximum, the fluorescence emission maximum ($\lambda_{em}^{max}$) of ANF in [bmim][BF₄] is observed to be at 643 nm (Fig. 5.1.(a)). Interestingly, it can be seen from this figure, as the excitation wavelength is progressively shifted towards the red side of the absorption maximum, a small but steady shift of the fluorescence maximum is clearly observable. The variation of the emission maximum ($\lambda_{em}^{max}$) of ANF in [bmim][BF₄] on the excitation wavelength ($\lambda_{ex}$) has been shown in Fig. 5.1.(b).

![Fig. 5.1. (a) $\lambda_{em}^{max}$ vs. $\lambda_{ex}$ plots of ANF in [bmim][BF₄] (●) superimposed on the excitation spectrum.](image-url)
The extent of the shift, as measured from $\lambda_{\text{em}}^{\text{max}}$ (Fig. 5.1. (a)), is around 14 nm in \([\text{bmim}][\text{BF}_4]\). This sort of excitation wavelength dependent emission shift has also been observed in two other RTILs, although the extent of the shift is different in different RTILs. In two other RTILs, viz., \([\text{emim}][\text{BF}_4]\) and \([\text{bmim}][\text{PF}_6]\), the observable shift magnitudes are respectively 10 and 16 nm. The $\lambda_{\text{em}}^{\text{max}}$ vs. $\lambda_{\text{ex}}$ plots of ANF in the two RTILs are shown in Fig. 5.2. The shift magnitude of the $\lambda_{\text{em}}^{\text{max}}$ values in three RTILs at room temperature has been collected in Table 5.1. for comparison.
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Fig. 5.2. $\lambda_{\text{em}}^\text{max}$ vs. $\lambda_{\text{ex}}$ plots of ANF in [emim][BF$_4$] (●) and [bmim][PF$_6$] (■).

Table 5.1. Shift magnitude (in nm)$^a$ of the fluorescence maximum observed for dipolar probes in different media$^b$.

<table>
<thead>
<tr>
<th></th>
<th>[emim][BF$_4$] (66.5 cP)$^c$</th>
<th>[bmim][BF$_4$] (154 cP)$^c$</th>
<th>[bmim][PF$_6$] (371 cP)$^c$</th>
<th>Glycerol (900 cP)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANF</td>
<td>10</td>
<td>14</td>
<td>16</td>
<td>30</td>
</tr>
<tr>
<td>ANS</td>
<td>30</td>
<td>35</td>
<td>28</td>
<td>2</td>
</tr>
<tr>
<td>HNBD</td>
<td>14</td>
<td>16</td>
<td>13</td>
<td>3</td>
</tr>
</tbody>
</table>

$^a\pm 1$ nm; $^b$the observed shift values (nm) for ENBD, 4NBD, 6NBD, C102, C153, AP, and PRODAN in [bmim][BF$_4$] are 1.0, 3.5, 2.0, 5.0, 1.5, 2.5, and 4.5 respectively. $^c$The bracketed quantities are the viscosities of these media at 25$^\circ$C. These values for the RTILs have been obtained from ref.5 and that for glycerol from ref.48.
In order to obtain an understanding of the plausible reason(s) for the observation of such a behaviour, we have carefully examined the excitation wavelength dependence (if any) for several other commonly employed dipolar probe molecules (shown in Chart 5.2. and Chart 5.3.). While all the systems shown in Chart 5.3. show normal fluorescence behaviour (with very little or negligible excitation wavelength dependence), we could identify, in addition to ANF, two more systems, HNBD and ANS (Chart 5.2.), which also exhibit appreciable excitation wavelength dependent shift of the fluorescence maximum (Fig. 5.3. (a, b) and Fig. 5.4. (a, b)). The shift magnitude observed for these two systems in the various RTILs has been listed in Table 5.1.

![Chart 5.2](chart5.2.png)

**Fig. 5.3. (a)** $\lambda_{em}^{max}$ vs. $\lambda_{ex}$ plots of HNBD in [bmim][BF$_4$]. The corresponding absorption spectrum is shown as an insert.
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Fig. 5.3. (b) $\lambda_{\text{em}}^\text{max}$ vs. $\lambda_{\text{ex}}$ plots of HNBD in [emim][BF$_4$] (•) and [bmim][PF$_6$] (△).

Fig. 5.4. (a) $\lambda_{\text{em}}^\text{max}$ vs. $\lambda_{\text{ex}}$ plots of ANS in [bmim][BF$_4$]. The corresponding absorption spectrum is shown as an insert.
In order to determine whether specific interaction between the probe molecules and RTILs or the high viscosity controls the REE, we have also examined the excitation wavelength dependence of $\lambda_{\text{em}}^\text{max}$ for ANF, ANS and HNBD in a viscous conventional molecular solvent, glycerol. As can be seen from Fig. 5.5., ANF exhibits a more pronounced excitation wavelength dependence in relatively more viscous solvent glycerol, while the other two probes do not show any significant excitation dependent shift of the fluorescence maximum in this medium.

![Fig. 5.4. (b) $\lambda_{\text{em}}^\text{max}$ vs. $\lambda_{\text{ex}}$ plots of ANS in [emim][BF$_4$](●) and [bmim][PF$_6$](▼).](image-url)
5.3. Discussion

5.3.1. Case of ANF

We would like to find out why ANF exhibits considerable REE in RTILs whereas the other dipolar systems such as AP, PRODAN, C153, and C102 do not. First, it is known that 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 ($\Delta \mu$).\textsuperscript{31} As reported earlier, the estimated $\Delta \mu$ is 25 D for ANF,\textsuperscript{26,46,47} whereas, for C153, C102, AP and PRODAN, the values are 4.9 - 5.4,\textsuperscript{49} 3.0 - 3.8,\textsuperscript{49} 3.0 - 3.7,\textsuperscript{50} and 4.4 - 5.0 D,\textsuperscript{51} respectively. From this consideration, ANF
clearly appears to be better suited to exhibit REE compared to the other EDA systems previously employed in the study in RTILs.

The second factor, which is even more important than the first one, is that ANF has a very short fluorescence lifetime (\(\tau_f\)) compared to the other systems (vide Table 5.2.). The \(\tau_f\) value of ANF in 2-propanol is reported to be <50 ps.\(^{46}\) Our own measurement yielded a lifetime value of only \(~100\) ps in [bmim][BF\(_4\)]. As we have discussed in the earlier chapter, recent studies on solvation dynamics suggest that solvation in imidazolium based RTILs is rather a slow process. 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.\(^8\) Since the solvent relaxation time (\(<\tau_{\text{sol}}\)) around the photoexcited molecule is an order of magnitude higher than the \(\tau_f\) value of ANF, it is quite understandable why unrelaxed fluorescence, which gives rise to the excitation wavelength dependent emission behaviour in RTILs, could be observed in the case of ANF, even in the steady state. As the \(\tau_f\) values of AP (14 ns),\(^{50}\) C153 (5.6 ns),\(^{52}\) C102 (3.3 ns),\(^{52}\) and PRODAN (3.2 ns)\(^{53}\) in acetonitrile are higher than the \(<\tau_{\text{sol}}\) value of the solvent, the fluorescence occurs from a fully solvated state in these molecules and thus there is no chance of unrelaxed emission and hence no REE.

That the excitation wavelength dependent emission behaviour in [bmim][BF\(_4\)], or in other two RTILs, is not due to any specific interaction between the RTILs and ANF, but is mainly due to incomplete solvation of the fluorescent state in these viscous medium, is evident from the fact that ANF does exhibit an excitation wavelength dependent shift of \(\lambda_{\text{em}}^{\text{max}}\) in a highly viscous conventional molecular solvent, glycerol also (Fig. 5.5.). As the plot in Fig. 5.6. shows, the magnitude of spectral shift is linearly related to the viscosity of the media and thus specific interaction with the RTILs is not responsible for REE. In essence, it
is the incomplete solvation in the viscous media that is primarily responsible for the observed excitation wavelength dependent spectral shift of ANF.

**Fig. 5.6.** Viscosity dependence of the spectral shift of ANF in three different RTILs and in glycerol.

### 5.3.2. Case of ANS and HNBD

Both ANS and HNBD are known to exhibit REE in biological systems. Thus, the excitation wavelength dependent fluorescence behaviour of these two probes in RTILs may not be surprising. However, that the case of ANS and HNBD is distinctly different from that of ANF is evident from the fact that (i) unlike ANF, both ANS and HNBD do not show much REE in a higher viscous solvent, glycerol and (ii) the $\tau_f$ values of ANS and HNBD (8.4 and 9.6 ns respectively in $[\text{bmim}][\text{BF}_4]$) are significantly larger than the average solvation
time of 1.4 – 2.1 ns in RTILs. Both these observations establish that the slow solvation (compared to $\tau_1$) of the fluorescence state, which gives rise to REE in ANF, is not responsible for REE in ANS and HNBD. Obviously other factors contribute to REE for ANS and HNBD.

In case of negatively charged ANS, it is the electrostatic interaction which is expected to dominate the other interactions and probably plays the most significant role in creating a distribution of energetically different molecules in the ground state, which allows their photoselection. Previous reports on ANS in micellar media\textsuperscript{57,58} corroborate this view of ours. 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 process between the energetically different species.

Table 5.2. Fluorescence lifetime of the different systems studied.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Media</th>
<th>$\tau_1$ (ns)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANF</td>
<td>[bmim][BF$_4$]</td>
<td>0.1</td>
<td>This work</td>
</tr>
<tr>
<td>ANS</td>
<td>[bmim][BF$_4$]</td>
<td>8.4</td>
<td>This work</td>
</tr>
<tr>
<td>HNBD</td>
<td>[bmim][BF$_4$]</td>
<td>9.6</td>
<td>This work</td>
</tr>
<tr>
<td>ENBD</td>
<td>Acetonitrile</td>
<td>0.27</td>
<td>59</td>
</tr>
<tr>
<td>4NBD</td>
<td>Acetonitrile</td>
<td>9.96</td>
<td>59</td>
</tr>
<tr>
<td>6NBD</td>
<td>Acetonitrile</td>
<td>0.16</td>
<td>59</td>
</tr>
<tr>
<td>C102</td>
<td>Acetonitrile</td>
<td>3.3</td>
<td>52</td>
</tr>
<tr>
<td>C153</td>
<td>Acetonitrile</td>
<td>5.6</td>
<td>52</td>
</tr>
<tr>
<td>AP</td>
<td>Acetonitrile</td>
<td>14</td>
<td>50</td>
</tr>
<tr>
<td>PRODAN</td>
<td>Acetonitrile</td>
<td>3.2</td>
<td>53</td>
</tr>
</tbody>
</table>
Among the four structurally similar NBD derivatives we have studied, since only HNBD exhibits the shift of $\lambda_{em}^{\text{max}}$ (not ENBD or 6NBD, which possess subnanosecond fluorescence lifetime (vide Table 5.2.), the origin of the excitation wavelength dependent spectral shift in HNBD has to be something different from slow solvation. Examination of the absorption characteristics of these four NBD derivatives reveals that, the full width at half maximum (FWHM) value of the first intramolecular charge transfer (ICT) band is the largest for HNBD in [bmim][BF₄] (Table 5.3.). Also, the spectral width of this band of HNBD in RTILs is relatively larger than that in other solvents including glycerol (Table 5.4.).

Table 5.3. FWHM values (in cm$^{-1}$)$^a$ of the lowest energy absorption band of the NBD derivatives in [bmim][BF₄].

<table>
<thead>
<tr>
<th>System</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 NBD</td>
<td>2730</td>
</tr>
<tr>
<td>6 NBD</td>
<td>2700</td>
</tr>
<tr>
<td>ENBD</td>
<td>2990</td>
</tr>
<tr>
<td>HNBD</td>
<td>3900</td>
</tr>
</tbody>
</table>

$^a$ ± 100 cm$^{-1}$

Table 5.4. FWHM values (in cm$^{-1}$)$^a$ of the first absorption band of HNBD in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>3400</td>
</tr>
<tr>
<td>MeOH</td>
<td>3200</td>
</tr>
<tr>
<td>Glycerol</td>
<td>3000</td>
</tr>
<tr>
<td>[bmim][BF₄]</td>
<td>3900</td>
</tr>
</tbody>
</table>

$^a$ ± 100 cm$^{-1}$
From the structural viewpoint, what makes HNBD unique among the rest of the systems of this group is that it possesses free amino hydrogen atoms and hence, this probe can enter into hydrogen bonding interaction utilising the hydrogen atoms. Since all the other NBD derivatives lack this type of interaction with the solvents, the spectral width of the ICT 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 hence facilitates the initial photoselection. Since the amino group of HNBD can form hydrogen bonding with the anionic part of the RTILs, it provides the ground state inhomogeneity. In fact, in addition to the electrostatic effects, hydrogen-bonding interaction of ANS, which contains –NH moiety, with the RTILs may also contribute to inhomogeneous broadening and slow excited state dynamics. This observation is supported by the fact that, between the two [bmim] salts used in this study, the hydrogen bond accepting ability, judged from the reported hydrogen bond basicity parameter ($\beta$), is higher for [bmim][BF$_4$] than [bmim][PF$_6$].\textsuperscript{60,61} Perhaps this is why the magnitude of the excitation wavelength dependent shift of the emission maximum is larger in [bmim][BF$_4$] although [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 stated earlier, presumably contributes to the excitation wavelength dependent fluorescence behaviour in these cases.

5.4. Conclusion

An excitation wavelength dependent shift of the fluorescence emission spectra of some dipolar molecules has been observed in RTILs. This observation not only suggests that there exists a distribution of ground state molecules
differing in their interaction energies with the RTILs, but also implies that the excited state relaxation processes such as solvation and energy transfer are significantly slower in these media. While the ground state heterogeneity, which allows photoselection of the molecules is always present for these systems, even in conventional fluid media, it is the slow rate of the excited state processes, which governs the excitation wavelength dependent fluorescence behaviour in RTILs. Since the measured $\lambda_{\text{em}}^{\text{max}}$ 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 proper care is extremely necessary, while choosing the probe molecules for these measurements.

5.5. References

(44) Chattopadhyay, A.; Mukherjee, S. Biochemistry 1993, 32, 3804.
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