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Red emitting dye in room temperature ionic liquids: A spectroscopic study

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ABSTRACT

In this article we have reported the photophysics and rotational dynamics of a red emitting dye Nile blue A (NBA) in two room temperature ionic liquids (RTILs). We have chosen two aliphatic RTILs with a common anion. In triethylsulfonium bis(trifluoromethylsulfonyl)imide ($[S_{222}][NTf_2]$) and trihexyl (tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide ($[P(C_6)_3C_{14}][NTf_2]$) absorption maximum of NBA appears at ~635 nm. We have observed a single exponential emission decay of NBA in $[P(C_6)_3C_{14}][NTf_2]$ and $[S_{222}][NTf_2]$. A comparison of activation energy of the non radiative decay (E_{nr}) and activation energy of rotational relaxation (E_{rot}) with activation energy of viscous flow (E_η) was made to check the dependence of the bulk viscosity of the media on the photophysics of NBA in the above RTILs. The rotational relaxation decays are also single exponential in nature. The deviations from the stick and slip hydrodynamics with changing temperature demonstrate complex structural feature of the media and specific solute solvent interaction governing the rotational diffusion.

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1. Introduction

Red emitting dyes are those, which absorb in far red or in near infrared region. These red emitting dyes are of immense biological importance. One of the most prominent members of this arsenal of red emitting dyes is Nile blue A (NBA). As a red emitting dye, its popularity has emerged out due to its high binding capabilities with nucleic acid. Other use include as acid base indicator and as a staining agent for actinomycin in pathological tissues [1]. In contrast to the dyes absorbing in ultraviolet region and in visible region, for red emitting dyes the excitation above 600 nm is entirely non-invasive and curtail the unwanted background signal from cellular auto fluorescence [2]. Beside binding to the DNA, NBA can inflict significant photo damage by acting as a photo sensitizer [3]. Moreover, NBA is also popular because of its low toxicity and retarding power of tumour growth [4,5]. Although environment sensitive, NBA has not been used in different biomimitic medium frequently [6,7]. NBA has also been used as solvatochromic probe molecule [8]. There has been studies on the photophysical properties of NBA where, it has been shown that ground state proton transfer takes place in presence of proton accepting solvent together with the formation of conjugate base [9]. Fluorescence quenching of NBA in electron donating solvent medium was also studied [10]. NBA also shows the capability of resonance energy transfer to the single-wall carbon nanotubes [11]. There are other studies regarding the photophysics of NBA [12,13]. NBA is a red emitting dye with hydrophobic moiety and have the capability to form hydrogen bond with the surrounding solvent molecules. Hence, can be dissolved easily in relatively hydrophobic room temperature ionic liquids (RTILs) having long hydrophobic alkyl chain as well as in short alkyl chain containing RTIL.

In our present study, we have used two different room temperature ionic liquids. Now the question is why we are using the room temperature ionic liquids? Room temperature ionic liquids (RTILs) are advantageous over different neat solvents. One of the most important reasons of increasing popularity of RTILs is the environmental concern throughout the world. The appearance of RTILs as green solvent has opened a new era. The journey of RTILs started more than 100 years ago [14–16]. After the onset of journey, several factors contributed greatly to make this particular type of solvent more attractive and to be termed “green solvents” [17–19]. One of the most important features, which has made RTILs an attractive media for photophysical studies, is microheterogeneous nature of the media. This microheterogeneous nature of the media has inflicted unusual spectral behavior of fluorescent probes compared to that in conventional polar solvents. There are several reports of probing photophysical properties of different fluorophores in RTILs [20–36]. It has been previously reported that the rotational relaxation behaviour in the RTILs are strongly dependent upon solute’s polarity [37,38]. The rotational relaxation dynamics

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in different RTILs using different type of solutes both charged and neutral have been studied by several groups. Those groups have described differing extent of specific solute solvent interaction to affect the rotational diffusion of the probes [39–41]. On the other hand, the study of solvation dynamics in RTILs are found to be independent of nature of solute excepting the cases where specific solute solvent interactions are known to play prominent role [42,43]. In most of the conventional polar solvents, the structure of the solvent molecules are rigid and electric dipole moment is static. On the other hand in RTILs, the distance between the anions and cations vary. Therefore, the solvation sheath formed by the RTILs is significantly different from conventional solvents. This has significant impact on the charge transfer reaction in the excited state probe molecules. RTILs are known to contribute significantly to the emission spectra of many fluorescent dyes [32]. However, in our present study by using the red emitting dye we have expunged the possibility of contribution of the RTILs to the emission spectra. Ghosh et al. reported the monoexponential behavior of two red emitting dyes of RTILs [34]. We have used trihexyl(tetradecyl) phosphonium bis(trifluoromethylsulfonyl) imide ($[P(C_6)_3C_{14}][NTf_2]$) and triethylsulfonium bis(trifluoromethylsulfonyl) imide ($[S_{222}][NTf_2]$) as RTILs. The photophysics and rotational diffusion of NBA in RTILs was studied in this work. Moreover, with variation of the temperature within a range from 278 K to 323 K, we have tried to explore specific interaction and structural heterogeneity of the media, responsible for the interesting photophysics of this red emitting dye in RTILs. By changing both the cationic nature and alkyl chain length, we have tried to demonstrate that structural heterogeneity and specific solute-solvent interaction have profound effect on the different kind of excited state diffusional characteristics of NBA whose ground state and excited state spectral features are not contributed by the emission properties of RTILs.

2. Materials and methods

Nile blue A perchlorate (NBA) was purchased from Sigma-Aldrich and used as received. Two room temperature ionic liquids trihexyl(tetradecyl) phosphonium bis(trifluoromethylsulfonyl) imide (0.1% moisture content), triethylsulfonium bis(trifluoromethylsulfonyl) imide (0.1% moisture content) were purchased with high purity grade from Sigma-Aldrich. The structures of all chemicals used were shown in Scheme 1. The moisture content in the RTILs was measured using 831 KF Coulometer (Metrohm). The ground state UV–vis absorption spectral studies were executed on a UV/Vis spectrophotometer (Model: UV-2550, Shimadzu). The steady-state emission spectral studies were performed on a Fluoromax-4P spectrofluorometer (Horiba Jobin Yvon). The fluorescence quantum yield values of the NBA in these RTILs were calculated by using the fluorescence quantum yield of NBA in water ($\phi_f = 0.004$) [44] as reference. The quantum yield values were calculated using the following equation:

$$\phi_f = \phi_r \frac{I_s A_r n_s^2}{I_r A_s n_r^2} \tag{1}$$

where subscripts *s* and *r* stand for the sample and reference. *I*,*A*, *n* stand for the total integrated area under the steady state fluorescence spectra under consideration, absorbance at a particular excitation wavelength and refractive index of the solvent medium respectively. The steady state fluorescence emission spectra were fitted using the lognormal line shape function defined by following Eq. (2):

$$I(\nu) = I_0 \exp\left[-\ln 2\left(\frac{\ln\left[1 + 2b(\nu - \nu_p)/\Delta\right]}{b}\right)^2\right] \tag{2}$$

in which ν_p, I_0, Δ and b represent peak frequency, peak height, width parameter and asymmetric parameter, respectively. All fluorescence emission spectra were scaled by a factor of λ^2 before the log-normal fitting of the respective spectra to obtain the peak frequencies. We have used Jeiotech refrigerated bath circulator (Model: RW0525G) to vary the temperature of the experiment from 278 K to 323 K. The concentration of NBA was maintained at 2×10^{-5} (M) in all experiments. The viscosities of the solutions at different temperature were measured by using a Brookfield viscometer (Model: DV-II + Pro). The uncertainties in measurement of the viscosities are ±1%. The absorption and emission spectra of the pure RTILs are subtracted from the absorption and emission spectra of NBA in RTILs. These subtracted spectra are used to determine the fluorescence quantum yield.

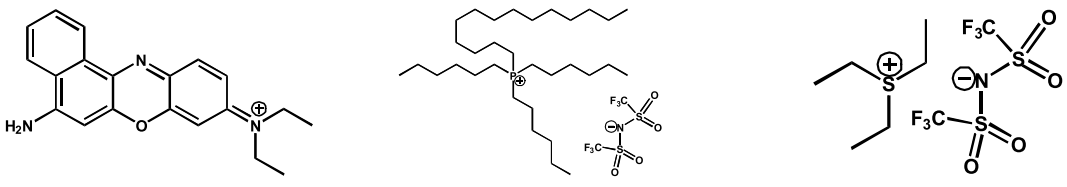
The time-resolved fluorescence emission decays were collected using the picosecond time-correlated single-photon-counting (TCSPC) technique. We used a time-resolved emission spectrophotometer from Edinburgh Instruments (Model: LifeSpec II) and a picosecond diode laser at 635 nm as the excitation source ($\lambda_{ex} = 635nm$). The fluorescence emission decays were collected at the magic angle (54.7°) by using a Hamamatsu MCP PMT (3809U) as the detector. The decays were fitted by using the F-900 software. The fluorescence transients were fitted after deconvoluting IRF by using the following Eq. (3):

$$I(t) = A + \sum_{i=1}^{N} B_i \exp\left(-\frac{t}{\tau_i}\right) \tag{3}$$

where B_i stands for the pre-exponential factor with the characteristic lifetime τ_i and A is the background. The amplitude weighted average lifetime was calculated using the following equation:

$$\left\langle \tau \right\rangle = \sum_{i=1}^{N} C_i \tau_i \tag{4}$$

(4)



Nile Blue A **$[P(C6)_3C_{14}][NTf_2]$** **$[S_{222}][NTf_2]$**

Scheme 1. The structures of Nile blue A and RTILs.

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