Modulation of the Excited State Intramolecular Electron Transfer Reaction and Dual Fluorescence of Crystal Violet Lactone in Room Temperature Ionic Liquids

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The influence of polarity, viscosity, and hydrogen bond donating ability of the medium on the fluorescence behavior of crystal violet lactone (CVL), which undergoes excited state electron transfer reaction and exhibits dual fluorescence from two different electronic states, termed as CT_A and CT_B, has been studied in six different room temperature ionic liquids (ILs) using steady state and time-resolved emission techniques. It is shown that the excited state $CT_A \rightarrow CT_B$ transformation and dual fluorescence of CVL can be controlled by appropriate choice of the ILs. While dual fluorescence of CVL is clearly observed in pyrrolidinium IL, the molecule exhibits a single fluorescence band in ammonium IL. While the second emission from the CT_B state can barely be seen in 1,3-dialkylimidazolium ILs, dual fluorescence is quite prominent in 1-butyl-2,3-dimethylimidazolium IL, [bmMim][Tf$_2$N]. These contrasting results have been explained taking into account the hydrogen bonding interactions of the 1,3-dialkylimidazolium ions (mediated through the C(2)-hydrogen) with CVL and the viscosity of the ILs. The excited state $CT_A \rightarrow CT_B$ reaction kinetics has been studied in IL by monitoring the time-evolution of the CT_B emission in [bmMim][Tf$_2$N]. The solvation dynamics in this IL has been studied by following the dynamic fluorescence Stokes shift of C153, which is used as a probe molecule. A comparison of the excited state reaction time and solvation time suggests that the rate of the $CT_A \rightarrow CT_B$ reaction in moderately viscous ILs is primarily dictated by the rate of solvation. Very little or negligible excitation wavelength dependence of the emission behavior of CVL can be observed in these ILs.

1. Introduction

Room-temperature ionic liquids (ILs) have now become common names, which no longer require much introduction.[1-5] We have been studying the photophysical behavior of several molecular systems in these media primarily for two reasons.[5-22] The first objective is to obtain an understanding of these complex media from these studies. The second objective is to exploit some of the novel properties of the ILs to regulate the photoresponses of various systems. Our studies and those by many others[23-31] have not only improved our understanding of these substances, but also shown how the viscosity, polarity, and the ionic constituents of the ILs can influence the molecular rotation, electron and proton transfer reaction, molecular diffusion, solvent relaxation dynamics, and so forth. These studies have also indicated that processes, which are seemingly unimportant in conventional less viscous solvents, can become highly important in viscous ILs.[9] That slow solvation in these media and their microheterogeneous nature can give rise to excitation wavelength dependent fluorescence behavior of molecular systems (a phenomenon that is quite uncommon in less viscous conventional media) has also been documented.[6,8,13,24,32-34] Several theoretical and experimental studies have indicated that the bulk viscosity of the ILs can be quite different from the microscopic viscosity experienced by molecules.[8,9,13,18,33,35,36] The studies have also revealed that the dielectric constant of the ILs is low, but the polarity experienced by solute molecules in ILs is comparable to that of liquids having polarity between acetonitrile and methanol.[37]

Crystal violet lactone (CVL, Chart 1), introduced recently by Karpiuk, is an electron donor−acceptor molecule, which

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CHART 1: Chemical Formula of Crystal Violet Lactone (CVL) along with the DMAP and MGL Segments Indicated Separately
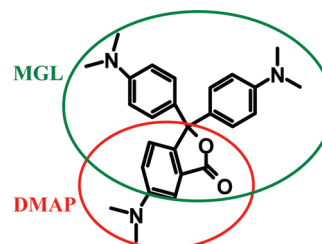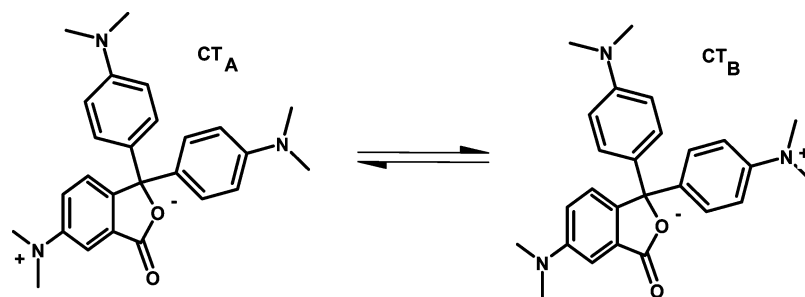

Crystal Violet Lactone (CVL)

exhibits dual emission.[38,39] The photophysical behavior of this molecule can be considered as additive response of the two of its subunits, 6-dimethylaminophthalide (DMAP) and malachite green lactone (MGL), both consisting of a dimethylanilino group as electron donor and a 5-membered lactone ring system as electron acceptor (Chart 1). Because of the presence of electron donor and acceptor groups in both the subunits of CVL, the charge transfer in the excited state can be localized in the DMAP or MGL subunit (Chart 1). In nonpolar media, the first excited sate (CT_A, $\mu = 10.7$ D),[38] which is charge transfer in nature and localized in the DMAP moiety, is lower in energy compared to the corresponding charge transfer state (CT_B, $\mu = 25.2$ D)[38] localized in the MGL moiety, and the molecule exhibits fluorescence that is typical of the DMAP subunit (see Scheme 1). However, in polar medium, because of the difference in dipolar character of the two states, there occurs a state reversal (i.e., CT_B level becomes lowers than the CT_A state) and the molecule emits from both the states showing a dual fluorescence

SCHEME 1

behavior. The transformation of the molecule from the CT_A to CT_B state involves the transfer of an electron from the dimethylanilino group to 5-membered lactone ring system and subsequent solvent stabilization of the final state. The effect of solvation dynamics on the kinetics of $CT_A \rightarrow CT_B$ process has also been studied by Karpiuk and co-workers using femtosecond time-resolved pump−probe technique.[39] In conventional less viscous aprotic solvents, the electron transfer process is believed to be extremely fast (occurs within a few femtoseconds) and the overall rate of the $CT_A \rightarrow CT_B$ process is dictated mostly by the solvation dynamics.[39]

Interestingly, even though CVL exhibits dual fluorescence in acetonitrile, it displays a single fluorescence (CT_A) in alcoholic solvents,[38] which are of comparable/more polar than acetonitrile. The lack of CT_B emission in protic solvents is attributed to the H-bonding interaction between CVL and the solvent (with the latter serving as H-bond donor) leading to the quenching of this fluorescence.[38] This property allows CVL to act as a probe of the proticity of the environments.

As the $CT_A \rightarrow CT_B$ transformation of CVL involves both electron transfer and solvation of the charge separated state, the polarity of the medium and dynamics of solvation play important roles in determining the rate and efficiency of the overall process in conventional less viscous solvents. The viscosity of solvent has negligible or no influence provided the medium is not highly viscous (like most of the conventional solvents). However, in highly viscous ILs, where the dynamics of solvation is governed largely by the viscosity of the media,[5] one can as well expect strong influence of the viscosity on the $CT_A \rightarrow CT_B$ transformation of CVL. Recently, the dynamic heterogeneity of the ILs has been investigated by monitoring the dual fluorescence of CVL.[24] The electron transfer reaction and fluorescence behavior of CVL has also been studied theoretically in one of the ILs.[40] As the ILs possess a wide range of polarity and viscosity values and it is also possible to control the proton donating ability of these liquids, we thought it should be possible to modulate the excited-state reaction and hence, the fluorescence response of this molecular system. It is with this intention that we have taken up this study in which we have investigated the photophysical behavior of CVL in six carefully chosen ILs (Chart 2) of different viscosity and hydrogen bond-donating ability. We have been able to establish the formation of the CT_B state from the CT_A state using the time-resolved emission spectra (TRES) and time-resolved area normalized emission spectra (TRANES) studies, follow the time evolution of the CT_B state, demonstrate the influence of hydrogen bond-donating ability of the ILs and investigate the effect of excitation wavelength on the fluorescence response of CVL.

2. Experimental Section

2.1. Materials. CVL was purchased from Sigma Aldrich and recrystallized from acetone. Laser grade C153 was procured

**CHART 2: Structure/Abbreviation of the ILs Used in This Study**
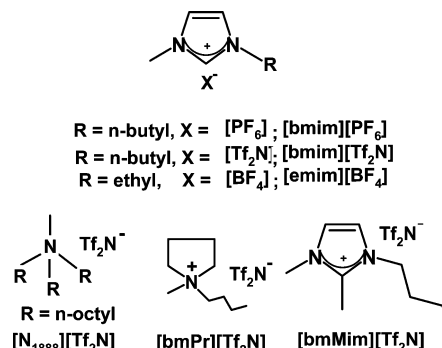
from Eastman Kodak and used as received. The imidazolium ILs used in this work, [bmim][Tf_2N], [bmim][PF_6], and [emim][BF_4] were of "Advanced Materials Research" grade from Kanto Chemicals (Japan) and were used without any purification. The ammonium IL, [N_{1888}][Tf_2N], was purchased from Merck. The pyrrolidinium ionic liquid, [bmPr][Tf_2N], and C(2) methylated imidazolium ionic liquid, [bmMim][Tf_2N], were synthesized following the published procedure.[41] [N_{1888}][Tf_2N], [bmPr][Tf_2N], and [bmMim][Tf_2N] were purified by treating the dichloromethane solution of the ILs with activated charcoal.[42] All the six ionic liquids were dried under vacuum for several hours prior to use.

2.2. Instrumentation and Methods. The viscosities of the ILs were measured by a LVDV-III Ultra Brookfield Cone and Plate Viscometer (accuracy, ± 1%, and repeatability, ± 0.2%). The measured viscosities of the ILs are collected in Table 1. The absorption and steady-state fluorescence spectra were recorded on a UV−visible spectrophotometer (Cary 100, Varian) and a spectrofluorimeter (Fluorolog-3, Horiba Jobin Yvon), respectively. The fluorescence spectra were corrected for the instrument response. Fluorescence quantum yields were measured using 4-aminophthalimide (4-AP) in methanol ($\Phi = 0.1$) as standard.[43] Fluorescence lifetime measurements were carried out using a time correlated single-photon counting (TCSPC) spectrometer (Horiba Jobin Yvon IBH). PicoBrite diode laser source ($\lambda_{exc} = 375$ nm) was used as the excitation source and an MCP photomultiplier (Hamamatsu R3809U-50) as the detector. The pulse repetition rate of the laser source was 10 MHz. The width of the instrument response function, which was limited by the fwhm of the exciting pulse, was around 55 ps. The lamp profile was recorded by placing a scatterer (dilute solution of Ludox in water) in place of the sample. The time-resolved emission decay profiles were collected at 5/10 nm intervals across the steady state emission spectrum. The wavelength selection was made by a monochromator with a band-pass of 1/4 nm. The total number of measurements was 42−46 in each case. Decay curves were analyzed by nonlinear

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TABLE 1: Polarity and Viscosity of the ILs and the Observed Photophysical Parameters of CVL in the Six RTILs[a]

ionic liquid	$E_T^{N\ b}$	$\eta(cP)^d$	$\bar{\nu}_{max}^{em}/10^3\ cm^{-1}$		avg. lifetime/ns		Φ_{fl}	$k_{nr}/10^7\ s^{-1}$
			CT$_A$	CT$_B$	τ_A/(CT$_A$)	τ_B/(CT$_B$)		
[emim][BF$_4$]	0.710	34	22.1		0.460		0.0002	217
[bmim][PF$_6$]	0.676	285	22.3		0.780		0.0050	127
[bmim][Tf$_2$N]	0.645	50	22.4		0.310		0.0046	321
[bmPr][Tf$_2$N]	0.598	73	22.5	17.5	0.750	1.0		
[bmMim][Tf$_2$N]	0.546	90	22.6	17.8	1.2	1.5		
[N$_{1888}$][Tf$_2$N]	-[c]	615	23.6		5.8		0.0580	16

[a] Absorption maximum of CVL in these ILs is observed around 362 ± 2 nm. [b] Reference 37. [c] Unavailable in the literature and is assumed to be the lowest among the six ILs based on the absorption and fluorescence properties of CVL in this and other ILs. [d] Measured viscosities at 23 °C.
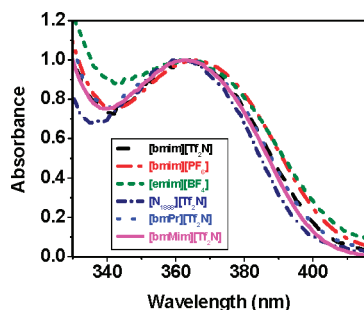
Figure 1. Absorption spectra of CVL (normalized at the low energy maximum) in [bmim][Tf$_2$N] (dash), [bmim][PF$_6$] (dash dot), [emim]-[BF$_4$] (short dash), [N$_{1888}$][Tf$_2$N] (short dash dot), [bmPr][Tf$_2$N] (dot), and [bmMim][Tf$_2$N] (solid line).

least-squares iteration procedure using IBH DAS6 (Version 2.2) decay analysis software. The quality of the fit was assessed by inspection of the χ^2 values and the distribution of the residuals. The time-resolved emission spectra (TRES) were constructed following the standard procedure.[44] The frequencies corresponding to the emission maxima, which were used for the estimation of the solvation time, were obtained by fitting the emission profiles to a log-normal function.[45] The log-normal function can be expressed as

$$F(\bar{\nu}, t) = h \exp\{-\ln(2)[\ln(1 + \alpha)/\gamma]^2\}, \quad \text{for } \alpha > -1$$
$$= 0, \quad \text{for } \alpha \leq -1$$

where, $\alpha \equiv (2\gamma[\bar{\nu} - \bar{\nu}_p])/\Delta$, h is the peak height, $\bar{\nu}_p$ is the peak frequency, γ is the asymmetry parameter, and Δ is the width of the curve. Nonlinear least-squares fitting was used to extract the best-fitted curve until successive iteration gave the identical χ^2 value. All experiments were performed at 23 °C unless stated otherwise.

3. Results and Discussion

3.1. Absorption and Emission Behavior in 1,3-Dialkylimidazolium ILs. To understand the effect of ILs on the excited state intramolecular charge transfer reaction and dual fluorescence of CVL, three 1,3-dialkylimidazolium ILs (Chart 2), [emim][BF$_4$], [bmim][PF$_6$], and [bmim][Tf$_2$N], whose polarities in the E_T^N scale are 0.710, 0.676, and 0.645 (Table 1),[37] respectively and viscosities are 34, 285, and 50 cP, respectively, have been chosen. The long wavelength absorption peak of CVL is found to be insensitive to small difference of the polarity of these ILs and the absorption maximum (λ_{max}^{abs}) is observed around 362 ± 2 nm (Figure 1). On the other hand, significant difference in the emission behavior of CVL is observed with variation of the ILs. In [emim][BF$_4$], the emission spectrum consists of a single fluorescence band ($\bar{\nu} = 22100\ cm^{-1}$), which is typical of

the CT$_A$ emission of CVL. In [bmim][PF$_6$] and [bmim][Tf$_2$N], the fluorescence spectra resembled the CT$_A$ emission of the system, but with an additional shoulder in the long wavelength region, which can perhaps be attributed to the CT$_B$ emission of the molecule. Even though λ_{max}^{abs} of CVL is insensitive to small difference in the polarity of the ILs, presumably due to its small ground state dipole moment (5.5 D)[38] of the molecule, the CT$_A$ emission maximum shows a higher sensitivity and displays a red shift with increase in polarity of the ILs clearly due to the higher excited state dipole moment (10.7 D) of CVL.[38]

A single fluorescence band of CVL in 1,3-dialkylimidazolium ILs was unexpected for two reasons. First, these liquids are more polar than acetonitrile, wherein CVL exhibits dual emission (with the CT$_B$ emission stronger than the CT$_A$ emission)[38] and second, the molecule exhibits dual fluorescence in pyrrolidinium ionic liquid,[24] a solvent whose viscosity (54 cP) and polarity are very similar to the respective quantities of the ILs we have used here. It is thus evident that a weak or no CT$_B$ emission in these imidazolium ILs is not indicative of lack of CT$_A \rightarrow$ CT$_B$ transformation due to the unfavorable viscosity or polarity of these liquids. In fact, that the excited state reaction does take place in these ILs is evident from the short fluorescence lifetimes (τ_f), low fluorescence quantum yields (ϕ_f), and high nonradiative rate constants (k_{nr}) of CVL (Table 1). A close look at this table suggests that the τ_f, ϕ_f, and k_{nr} values and hence, the efficiency of the CT$_A \rightarrow$ CT$_B$ process, are primarily controlled by the solvent reorganization dynamics in these ILs, whose polarities are not very different. In comparatively less viscous ILs, the solvent reorganization is relatively faster and time scale of reorganization is comparable. Hence, the CT$_A \rightarrow$ CT$_B$ rates and k_{nr} values are on the higher side and their magnitudes are not very different in these ILs. However, in highly viscous media such as in [bmim][PF$_6$], the CT$_A \rightarrow$ CT$_B$ reaction is hindered (primarily due to slow solvent reorganization dynamics) thereby making the k_{nr} value the lowest.

The emission behavior of CVL in ILs can be understood by noting that even though the molecule exhibits dual fluorescence in polar aprotic solvents, it displays a single emission (CT$_A$) in conventional protic solvents, which are more polar than acetonitrile or the ILs. It is reported that CT$_B$ emission of the molecule is quenched by the hydrogen bonding interaction with the protic solvent.[38] As the C(2)-hydrogen atom of the imidazolium cation of 1,3-dialkylimidazolium ILs serve as H-bond donor,[46–48] the emission behavior of CVL in these liquids is expected to be similar to that in protic solvents, in which the molecule does not exhibit the CT$_B$ emission.

The two factors that determine the intensity of weak CT$_B$ emission are the quenching interaction of this state with the proton donors and the rate of formation of this state from the CT$_A$ state. As stated already, the polarity of various ILs is not very different and hence, this parameter does not contribute to
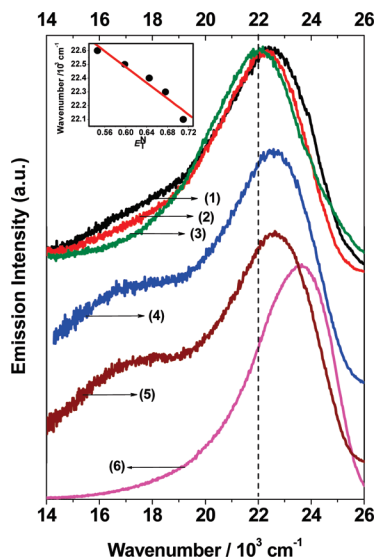
Figure 2. Fluorescence spectra of CVL in [bmim][Tf$_2$N] (1), [bmim][PF$_6$] (2), [emim][BF$_4$] (3), [bmPr][Tf$_2$N] (4), [bmMim][Tf$_2$N] (5), and [N$_{1888}$][Tf$_2$N] (6). Insert shows the linear dependence of the CT$_A$ band maximum on the polarity of the ionic liquid. The vertical dotted line has been used to indicate the shift of the spectral maximum.

Figure 3. Wavelength dependent fluorescence decay profiles of CVL in [bmMim][Tf$_2$N] at 23 °C. The monitoring wavelengths are (a) 405, (b) 440, (c) 505, (d) 585, and (e) 650 nm. Lamp profile is shown as dotted line.

any significant difference in the CT$_A$ → CT$_B$ rate of CVL in these ILs. However, a much higher viscosity of [bmim][PF$_6$] compared to two other ILs can slow down the CT$_A$ → CT$_B$ reaction, thereby making the CT$_B$ emission the weakest. Interestingly, the CT$_B$ emission is found to be the weakest in most polar and less viscous [emim][BF$_4$]. This somewhat surprising behavior can be understood if the hydrophilic nature of [emim][BF$_4$] is taken into consideration.[49] Since the CT$_B$ emission is highly sensitive to moisture, trace quantity of water present in this IL can quench the weak emission. Even though the CT$_A$ → CT$_B$ transformation does not involve any major structural change, the viscosity of the medium can still influence the rate of the process by slowing down the solvent reorganizaion process, as demonstrated later.

3.2. Absorption and Emission Behavior in Other ILs. To establish unambiguously that the H-bonding interaction is responsible for single emission of CVL in 1,3-dialkylimidazolium ILs, the photophysics has been studied in two other moderately viscous ILs, which do not possess the H-bond donating ability. The ILs that belong to this category are [bmPr][Tf$_2$N] and [bmMim][Tf$_2$N] (Chart 2). While the former is a pyrrolidinium IL, the later is an imidazolium IL but with its C(2)-H atom methylated. The polarities (E_T^N values) of the two ILs are 0.598 and 0.546[37] and the viscosities are 73 and 90 cP, respectively. The absorption maximum in [bmPr][Tf$_2$N] and [bmMim][Tf$_2$N] appear at around 362 ± 2 nm (Figure 1). As expected, CVL exhibits dual fluorescence (Figure 2) both in [bmPr][Tf$_2$N] and [bmMim][Tf$_2$N] with the CT$_A$ emission maximum at 22 500 cm^{-1} in [bmPr][Tf$_2$N] and 22 670 cm^{-1} in [bmMim][Tf$_2$N]. It is evident from the insert to Figure 2 that the wavenumbers corresponding to the fluorescence maximum follow a linear relationship with the polarity of the different ILs.

The strong influence of the viscosity of the medium is also evident from the fact that even though [bmPr][Tf$_2$N] and [bmMim][Tf$_2$N] are more polar than conventional solvent, acetonitrile (wherein CVL exhibits dual emission with more intense CT$_B$ emission), the CT$_A$ fluorescence is more pronounced in these ILs. To further establish the role of viscosity on the
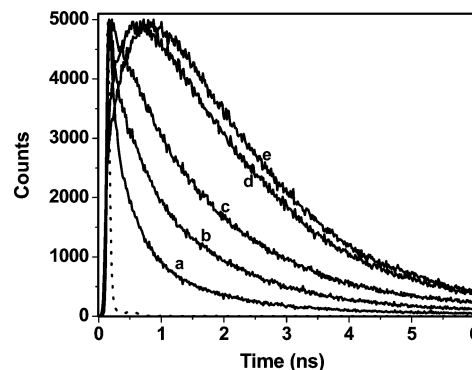
CT$_A$ → CT$_B$ transformation of CVL, we have chosen another IL, an ammonium IL, [N$_{1888}$][Tf$_2$N], which does not possess any H-bond donating center and has a very high viscosity of 615 cP. The idea is that if the viscosity of the medium has no influence on the CT$_A$ → CT$_B$ transformation, the molecule should exhibit dual fluorescence, but if the transformation is viscosity dependent, then one should expect only the CT$_A$ fluorescence of CVL in this IL. The observation of single fluorescence band for the system (Figure 2) is a clear indication of the retardation of the excited state reaction. The long fluorescence lifetime of CVL in this medium (5.8 ns) is also a consequence of the absence of excited-state reaction.
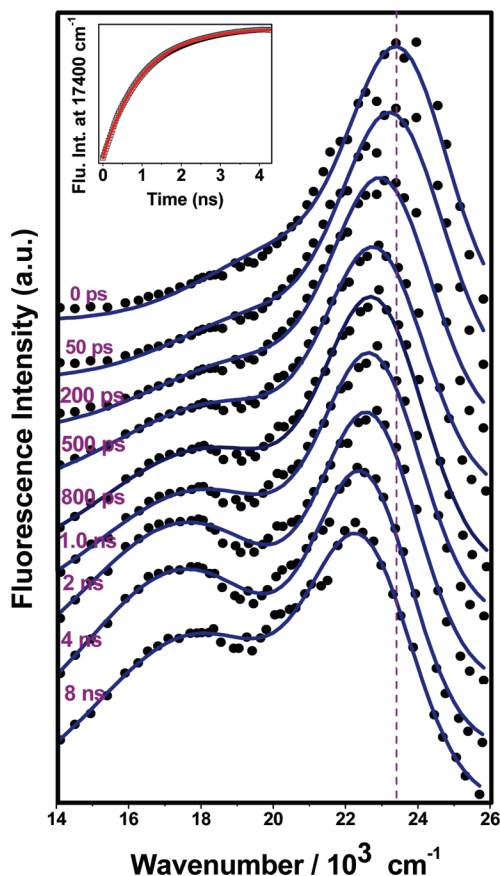
3.3. Time-Resolved Emission Spectra (TRES) and Time-Resolved Area Normalized Emission Spectra (TRANES). TRES of CVL in [bmMim][Tf$_2$N] have been constructed by measuring the fluorescence decay profiles at every 5/10 nm interval across the steady state emission spectrum at 23 °C following a standard procedure.[44] The time profiles in the short wavelength region of the emission spectrum were consisted of only decay; whereas at longer wavelengths the profiles were characterized by a rise followed by the decay (Figure 3). The TRES obtained at different times from the decay profiles are shown in Figure 4. The emission spectrum at time $t = 0$ represents a single emission band with a little hump on the red side. With an increase in time, the hump gradually grows into a new emission band and after $t = 2$ ns, the spectrum clearly consists of two components, as expected from a dual fluorescent system. The emission spectra at different times reveal for the first time the kinetics of the CT$_A$ → CT$_B$ reaction of CVL in IL. It is interesting to note that along with the excited state reaction, a progressive shift of the CT$_A$ emission maximum, which is an indication of slow solvation of the fluorescent state of the molecule in IL, is also observed.

The excited state transformation, that is, the formation of CT$_B$ state from CT$_A$, is also evident from the presence of an isoemissive point (observed at ∼21 670 cm^{-1}) in the TRANES (Figure 5) constructed following a reported procedure.[50,51] The excitation spectra corresponding to the CT$_A$ and CT$_B$ emission maxima (Figure 6), which resemble the absorption spectrum of CVL, is also an evidence of the excited state formation of CT$_B$ state from CT$_A$.

3.4. Estimation of the CT$_A$ → CT$_B$ Transformation Time. The excited state reaction time is estimated from the rise time of the emission intensity at ∼17400 cm^{-1}. A fit to the emission intensity data according to

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$$I(t) = I_0 - I_1 \exp(-t/\tau_r)$$

where, $I(t)$ is the fluorescence intensity at time "t" and I_0 is the intensity at infinite time, I_1 is the fraction of the excited state reaction observed, and τ_r represents the excited state reaction time, which yielded an excited state reaction time of 985 ps (Figure 4). Considering the fact that the CT_B state of CVL is characterized by a short fluorescence lifetime ($\sim$ 1.5 ns), the measured value should not be considered as very accurate. One should also note that as the $CT_A \rightarrow CT_B$ transformation of CVL involves both electron transfer and solvation of the CT_B state, the measured time obtained from the time evolution of the solvated CT_B state represents the slower of the two processes.


Figure 4. Time-resolved emission spectra (TRES) of CVL in [bmMim][Tf$_2$N] at 23 °C measured at different time delays. The vertical line is used to highlight the time-dependent shift of the CT_A emission maximum due to solvation. Insert shows the fluorescence intensity monitored at 17 400 cm^{-1} as a function of time.
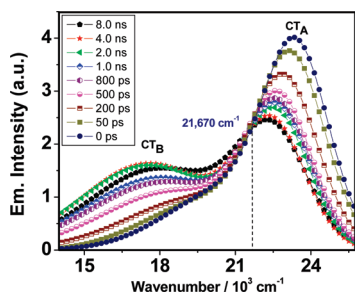
Figure 5. Time-resolved area normalized emission spectra (TRANES) of CVL in [bmMim][Tf$_2$N] at 23 °C measured at different delay times. The data represents the Gaussian fit to the area normalized emission data at different delay times. Isoemissive point observed at 21 670 cm^{-1} confirms the formation of CT_B state from CT_A state.
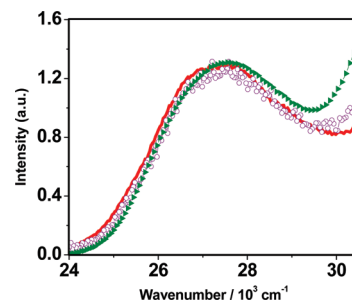
Figure 6. Excitation spectra of CVL in [bmMim][Tf$_2$N]. Solid line represents the excitation spectrum recorded by monitoring emission at 440 nm (corresponding to CT_A band), the spectrum with empty circles represent excitation spectrum recorded by monitoring emission at 575 nm (corresponding to CT_B band). The spectrum with triangles represent absorption spectrum of CVL in [bmMim][Tf$_2$N].
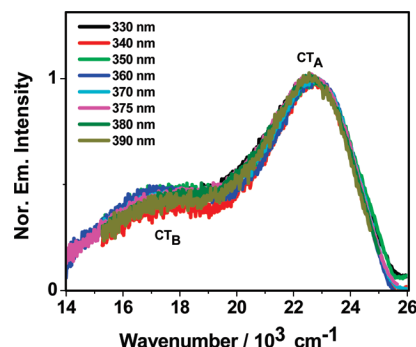
Figure 7. Steady state emission spectra of CVL in [bmMim][Tf$_2$N] at excitation wavelengths of 330, 340, 350, 360, 370, 375, 380, and 390 nm. The emission intensities are normalized to CT_A band to best display the changes in the relative intensities of CT_A and CT_B bands.

As can be seen from the next section, the time measured here is a reflection of slow solvation dynamics in the IL.

3.5. Estimation of the Solvent Relaxation Time. Even though the signature of slow solvation of the excited state of CVL is clearly evident from the time-dependent shift of the spectral maxima, the solvation time in [bmMim][Tf$_2$N] cannot be precisely estimated from these data owing to the short fluorescence lifetime of the system and parallel excited state reaction. This is why we have obtained an estimate of the solvation time in this medium by measuring the time-dependent fluorescence Stokes shift of C153 as a probe molecule. These measurements yielded an average solvation time of 690 ps, a value consistent with the viscosity of the IL. Therefore, it is evident that the excited state reaction time and solvation time in [bmMim][Tf$_2$N] are of the same order of magnitude and comparable. The results therefore confirm that the rate of $CT_A \rightarrow CT_B$ transformation, which consists of electron transfer and solvation of the charge separated state, is essentially controlled by the dynamics of solvent reorganization.

3.6. Excitation Wavelength Dependence. As ILs are considered to be microheterogeneous media comprising hydrophobic and hydrophilic domains, it is likely that at any given instant the CVL molecules will experience different molecular environments and may exhibit an excitation wavelength dependent emission behavior.[6,8,13,24,32−34] In fact, the dynamic heterogeneity of some ILs has been demonstrated by exploiting the fluorescence response of this system. The emission spectra recorded for different excitation wavelengths are shown in Figure 7. Interestingly, we could hardly observe any variation of the spectral position or the relative intensities of the CT_A and CT_B bands on variation of the excitation wavelength in these ILs.

This behavior is, however, not completely unexpected as a large majority of the fluorescent systems do not display any excitation wavelength dependent behavior and whether a system would display excitation wavelength dependence depends on factors such as inhomogeneous broadening of the absorption spectrum due to solute−solvent interaction, and fluorescence lifetime of the solute.[13]

4. Conclusion

The fluorescence response of CVL has been investigated in several ILs. It is shown that the polarity, hydrogen bond-donating ability, and viscosity of the ILs can be conveniently exploited for the modulation of the excited state reaction and fluorescence response in these media. The slow solvation dynamics, which is a consequence of the viscous nature of the ILs, retards the $CT_A \rightarrow CT_B$ transformation significantly making this process viscosity dependent in these viscous media. In fact, it is shown that in highly viscous IL such as $[N_{1888}][Tf_2N]$, the $CT_A \rightarrow CT_B$ transformation is completely prevented. The strong influence of the viscosity of the medium is also evident from the fact that even though $[bmPr][Tf_2N]$ and $[bmMim][Tf_2N]$ are more polar than conventional solvent, acetonitrile (wherein CVL exhibits dual emission with more intense CT_B emission), the CT_A fluorescence is more pronounced in these ILs. The high viscosity coupled with the hydrogen bond donating ability of most 1,3-dialkylimidazolium ILs makes the CT_B fluorescence quite weak in these media. A comparison of the measured solvation time and excited state reaction time suggests that the $CT_A \rightarrow CT_B$ reaction rate in moderately viscous ILs is primarily dictated by the dynamics of solvation.

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