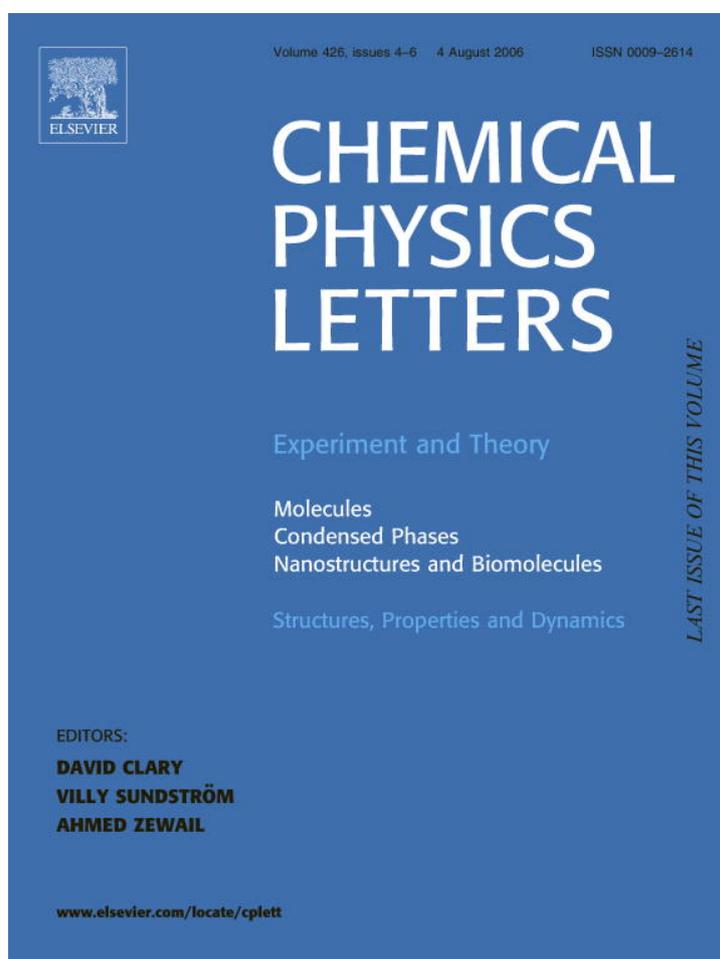


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Fluorescence of dicyanovinyl julolidine in a room-temperature ionic liquid

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Abstract

Steady-state and time-resolved emission of 9-dicyanovinyl julolidine (DCVJ) in 1-butyl 3-methyl imidazolium tetrafluoroborate ([bmim][BF₄]) were studied. The emission spectrum of DCVJ, obtained after properly subtracting the fluorescence of the solvent, peaks at similar wavelength as in acetonitrile, and its total intensity decreases with temperature, as it does in normal liquids. However, the activation energy of the radiationless process is much lower than that of [bmim][BF₄] viscosity, which points to a free volume controlled deactivation for DCVJ excited state.

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1. Introduction

Ionic-liquids (ILs) are low melting-temperature salts (below 373 K) formed by bulky and asymmetric ions that hinder crystallization [1]. Despite the low ionic charge densities, rather strong coulombic forces are responsible for their negligible vapor pressures. For this reason, and due also to their thermal stability, high ionic conductivity, large electrochemical windows, and good solvation power, ILs are envisaged as benign replacement for volatile, toxic, organic solvents in industrial processes. Moreover, ILs are being termed designer solvents, because many properties (*e.g.*, hydrophobicity, viscosity, solubility, acidity or basicity) can be tailored by changing the anion or alkyl chain of the cation [2]. Most studied ILs are imidazolium-based cations, with varying length of the alkyl chain, and fluorinated anions, *e.g.*, 1-butyl 3-methyl imidazolium tetrafluoroborate [bmim][BF₄].

Solute–solvent interactions are of fundamental physico-chemical interest and they play a key role in reactions and

in extraction processes. For this reason, ILs were extensively studied by using fluorescent probes [3–15]. The fluorescent features monitored were spectral distribution and Stokes shift [3,6–9,14], quantum yield [10,15], red-edge excitation shift [3], time-resolved emission spectroscopy [3–9,11–14], and steady-state and time-resolved emission anisotropy [12,14,15].

There are fundamental reasons to consider ILs as special fluids, though in many cases their behavior was found to be similar to normal organic liquids [14,15]. Notwithstanding, solvation dynamics in imidazolium-based ILs has been reported to display a singular, ultrafast response, followed by a slower relaxation with nonexponential behavior [4,5,12,13].

There are many reasons to observe non-exponential solvation dynamics [16]. In particular, in associated liquids, in very viscous media and in fluid media at low temperature, heterogeneity due to incomplete or multimode relaxation contribute to this behavior. ILs, due to their high viscosity and association, and their bicomponent nature, meet these requirements, as confirmed in various studies [4–6,12,13].

9-Dicyanovinyl julolidine, DCVJ (Fig. 1), is a mobility probe [17]. The electronic transition leading to the first

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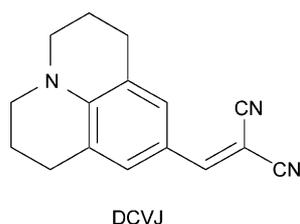


Fig. 1. Structure of 9-Dicyanovinyl julolidine.

excited singlet state has a charge-transfer character, and is accompanied by an increase in the electric dipole moment of the molecule (from 9 to 14 D) [18]. Consequently, it has a moderately large Stokes shift and a positive solvatochromic shift. The dicyanovinyl moiety bonded to the aromatic ring can rotate in the excited state thus providing a nonradiative pathway for electronic energy dissipation, hindered by friction. The emission maximum of DCVJ is sensitive to polarity. This probe was used in various studies of polymers, membranes, and fluids [10,19–22].

Friction-controlled processes at a molecular level often display a fractional exponential dependence with the macroscopic viscosity. The reasons for this are originated either in the spatial or in the temporal domain. Local movements at a molecular level depend on the free volume available and in this way they seem to experience a local friction that is less than bulk viscosity [19,23]. Additionally, very fast processes do not average collisions so that bulk friction is not fully effective in hindering the motion. This fact, normally termed frequency-dependent friction, is observed in fast photoisomerization reactions even in normal liquids [24–26]. DCVJ displays fractional viscosity dependence of nonradiative decay rate constant in glycerol [17,19].

Our interest was friction-controlled processes in [bmim][BF₄]. But during the course of our work we observed the emission of [bmim][BF₄], as reported recently [27,28]. Thus, we examine the emission anisotropy of [bmim][BF₄] and its dependence with temperature. We then study the steady-state emission of DCVJ in [bmim][BF₄] as a function of temperature. We find different activation energy for the steady-state anisotropy of [bmim][BF₄] and for the nonradiative deactivation rate of DCVJ, being the latter appreciably lower. We discuss this difference in the context of the different spatial and time domains in which the two processes take place.

2. Experimental

2.1. Materials

The ionic liquid [bmim][BF₄] was prepared following published procedures [29]. NMR spectroscopy proved the complete conversion of imidazole to imidazolium; the absence of chloride was confirmed by ionic chromatography. The colorless [bmim][BF₄] was vacuum-dried for 4 days at 343 K, and stored in a desiccator with P₂O₅. DCVJ (Molecular Probes) was used as received.

2.2. Spectroscopic and kinetic measurements

Absorption spectra were measured in a Shimadzu 160A or PC3101 spectrophotometer. Corrected steady-state fluorescence spectra were recorded in a PTI Quantmaster spectrofluorometer. For [bmim][BF₄], time-resolved fluorescence was measured in a PTI Time Master apparatus (250 ps per point time resolution, instrument response function, IRF, FWHM of 2 ns); the excitation wavelength was passed through a UG11 Schott filter. For [bmim][BF₄] + DCVJ measurements, a Single Photon Counting IBH5000U System was used (40 ps per point time resolution, IRF FWHM 1.4 ns) with a 370 nm 1 MHz excitation diode laser. In both cases, the emission wavelength was selected with a monochromator. Fluorescence anisotropy measurements were performed using film polarizers (PTI instruments) or prism polarizers (IBH instrument).

In all cases, square 1 × 1 cm septum-stopped quartz cuvettes, previously purged with dried nitrogen, were used. Due care was taken to keep the samples water-free.

The fluorescence emission quantum yield of DCVJ, ϕ_{DCVJ} , at 298 K was calculated using Coumarin 153 in methanol [30] as a reference. For other temperatures, the quantum yield of DCVJ was calculated by comparing the total emission with the emission of the same sample excited at 298 K under identical conditions.

3. Results

3.1. Emission of [bmim][BF₄]

3.1.1. Steady-state emission spectroscopy

Fig. 2 illustrates the strong dependence of the emission spectra of [bmim][BF₄] on the excitation wavelength, λ_{exc} , at 298 K; the spectra are very similar to those reported by Paul et al. [27,28]. At constant λ_{exc} , the emission inten-

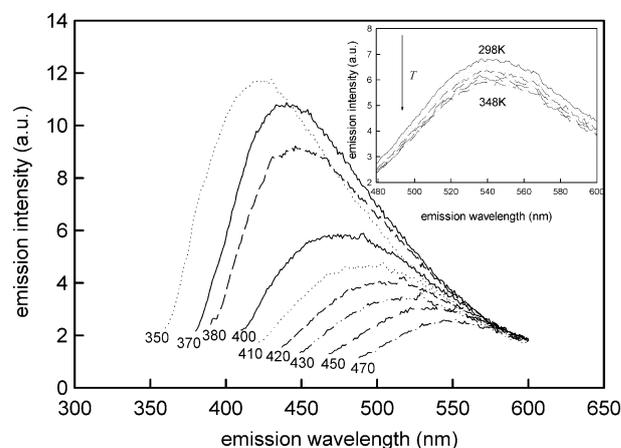


Fig. 2. Emission spectra of [bmim][BF₄] at 298 K for different excitation wavelengths, as indicated in the plot. The inset shows the temperature dependence of the emission spectra for $\lambda_{\text{exc}} = 460$ nm; from top to bottom: 298, 308, 318, 328, 338, and 348 K.

sity decreases slightly with increasing temperature (see inset in Fig. 2).

3.1.2. Time-resolved emission

Fig. 3 shows that the emission decay of [bmim][BF₄] deviates from simple first-order, as already reported [27,28]. The experimental curves are accurately fitted to a biexponential decay function $I = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$ with characteristic times that depend on λ_{em} : at 298 K, $\tau_1 = 7.7$ ns, $\tau_2 = 1.2$ ns, $a_1 = 21\%$, for $\lambda_{\text{em}} = 520$ nm, and $\tau_1 = 5.7$ ns, $\tau_2 = 0.89$ ns, $a_1 = 14\%$, for $\lambda_{\text{em}} = 450$ nm. These fits are also shown in Fig. 3. The respective average lifetimes, $\langle\tau\rangle$, calculated as:

$$\langle\tau\rangle = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \quad (1)$$

are 5.3 ns for 520 nm, and 3.3 ns for 450 nm.

3.1.3. Emission anisotropy

Steady-state anisotropy of neat [bmim][BF₄], r_{IL} , measured at constant excitation wavelength ($\lambda_{\text{exc}} = 460$ nm), decreases with increasing temperature (inset Fig. 4), a behavior that is associated to the decrease of the bulk viscosity of the IL. The reciprocal of the anisotropy is plotted as a function of T/η in Fig. 4. In agreement with the Perrin equation (Eq. 2), a straight line is observed. Thus, using the average fluorescence lifetime determined for $\lambda_{\text{em}} = 450$ nm ($\langle\tau\rangle = 3.3$ ns), the hydrodynamic volume of [bmim][BF₄], V_{IL} , is calculated to be $780 \pm 40 \text{ \AA}^3$. This value is about 4 times the calculated van der Waals volume [8,31], $V_{\text{VDW}} = V_{[\text{bmim}]} + V_{[\text{BF}_4]} = (150 + 48) \text{ \AA}^3 = 198 \text{ \AA}^3$, which points to aggregates as being responsible for the observed emission:

$$\frac{1}{r_{\text{IL}}} = \frac{1}{r_0} + \frac{\tau k}{r_0 V_{\text{IL}}} \cdot \frac{T}{\eta} \quad (2)$$

A value of $r_0 = (0.29 \pm 0.01)$ is obtained from the intercept of the plot in Fig. 4.

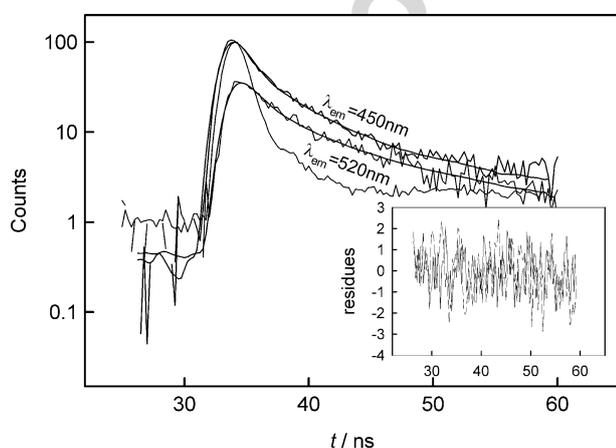


Fig. 3. Emission decay of [bmim][BF₄] for $\lambda_{\text{em}} = 450$ nm and 520 nm. Continuous lines represent the fit of the data to a biexponential decay. Residuals of both fits are shown together in the inset graph.

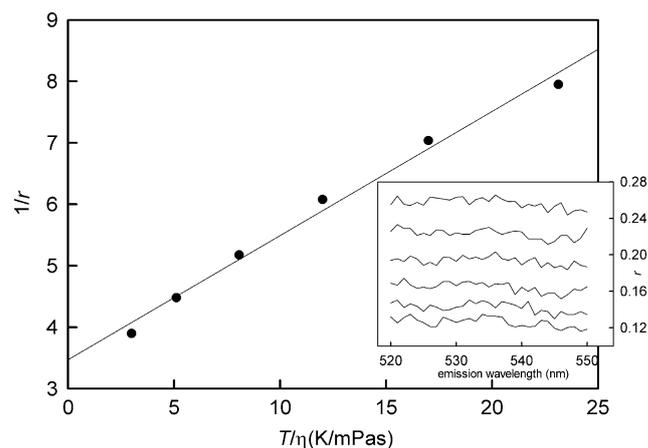


Fig. 4. Perrin plot for the inverse steady-state anisotropy of [bmim][BF₄] as a function of T/η (see Eq. (1)). The inset plots the steady-state emission anisotropy of [bmim][BF₄] for $\lambda_{\text{exc}} = 460$ nm at different temperatures from 298 K (top) to 348 K (bottom) in 10 K increments.

3.2. Emission of DCVJ in [bmim][BF₄]

3.2.1. Emission quantum yield

Emission spectra of DCVJ + [bmim][BF₄] were recorded at different λ_{exc} and temperatures. For each spectrum, the emission of pure [bmim][BF₄], measured under identical conditions, was subtracted to obtain the emission originated in DCVJ. The small absorption at the excitation wavelength ($A < 0.1$) justifies this procedure since absorption and emission of light are additive under this condition. The spectra of the mixture and the subtracted spectrum of the emission originated on DCVJ are shown in the inset of Fig. 5, together with the temperature dependent corrected emission spectra of DCVJ in [bmim][BF₄]. Clearly, the shape of the two spectra differs principally at high λ_{em} , where pure [bmim][BF₄] emits significantly.

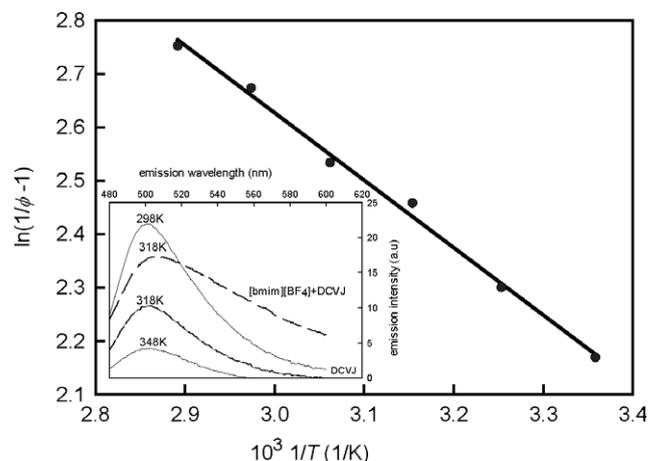


Fig. 5. Arrhenius plot for the ratio of nonradiative to radiative rate constants of DCVJ (see Eq. 3) λ_{exc} was in the range 450–485 nm. The inset plots emission spectra of DCVJ in [bmim][BF₄]. Dashed line: total emission, full lines: emission of DCVJ after subtracting the emission of the IL for three temperatures at $\lambda_{\text{exc}} = 460$ nm.

The corrected spectra of DCVJ were used to calculate its fluorescence emission quantum yield, $\phi_{\text{DCVJ}} = 0.11$ at 298 K. Considering that, in DCVJ, the only process competing with emission is the nonradiative deactivation due to the dicyanovinyl moiety rotation [10,17,19], the ratio of radiative, k_r , to nonradiative, k_{nr} , rate constants can be calculated from ϕ_{DCVJ} :

$$\frac{1}{\phi_{\text{DCVJ}}} - 1 = \frac{k_{\text{nr}}}{k_r} = \frac{A}{k_r} \cdot e^{-\frac{E_{\text{nr}}}{RT}} \quad (3)$$

The last term in Eq. 3 assumes that k_r is temperature independent. Fig. 5 depicts Arrhenius plots of $(\phi_{\text{DCVJ}}^{-1} - 1)$. The activation energy (E_{nr}) of k_{nr} [17,20] was calculated from the slope; the obtained value is $E_{\text{nr}} = 11$ kJ/mol. The activation energy of processes controlled by viscosity was calculated from the literature data [32], $E_{\eta} = R \cdot d(\ln(\eta))/d(1/T) = 33$ kJ/mol. The discrepancy between these two values indicates that the deactivation of the DCVJ is not directly controlled by processes related to bulk viscous flow.

3.2.2. Emission anisotropy

Steady-state emission anisotropy of the mixture combines the anisotropy of IL and DCVJ. The total value depends on the anisotropy of each component, as well as on their proportion of emitted light at λ_{em} and of absorbed light at λ_{exc} . This renders the analysis of the results rather cumbersome. Time-resolved experiments can separate in time the emission of DCVJ from the emission of [bmim][BF₄].

The excited-state lifetime of DCVJ in IL at room temperature falls in the limit of resolution of our equipment. A single exponential decay lifetime, $\tau_{\text{DCVJ}} = 0.15$ ns can be deconvoluted from the excitation pulse. This value is in good agreement with excited-state lifetimes of DCVJ from the literature (340 ps in glycerol [19]).

Time-resolved emission anisotropy showed a constant maximum anisotropy near 0.4 during the first nanosecond of the decay, meaning that DCVJ has no time to rotate during its excited-state lifetime. Steady-state results, after properly subtracting r_{IL} from r_{total} , also rendered the maximum value for r_{DCVJ} .

4. Discussion

Fluorescence emission is a minor deactivation process of the IL. The change in the emission spectrum with excitation wavelength (Fig. 2) indicates heterogeneity of emitting species. This also explains the nonexponential decay of the emission, the change in the representative lifetimes of the biexponential decay used to fit the data and the variation in the relative amplitude of each component with the emission wavelength. The large hydrodynamic volume obtained from the Perrin plot of the IL anisotropy (Fig. 4), compared to the volume of the ionic pair, suggests that aggregates are responsible for the emission. The linearity of the Perrin plot shows that the rotation of the IL is governed by bulk viscosity. The emission quantum efficiency slightly

decreases with temperature (Fig. 2), possibly due to an increase of radiationless deactivation favored by temperature.

Fluorescence emission of DCVJ renders information on solvent through its quantum yield (viscosity) and emission maximum (polarity). DCVJ, with a molecular volume of 239 Å³ [33], is expected to rotate with a rotational correlation time of 6 ns in the IL at 298 K ($\eta = 99$ MPa s). This time is much higher than the excited-state lifetime of 0.15 ns, explaining why the anisotropy of DCVJ does not provide any information.

From the emission maximum of DCVJ (502 nm) [bmim][BF₄] shows a polarity similar to acetonitrile [18,21] in coincidence with results of other fluorescent probes in this [4] and other IL [5,6]. This is remarkable because the static dielectric constant of acetonitrile (37.5) is much larger than the value reported for [bmim][BF₄] (11.4) [34].

The radiationless deactivation of DCVJ yields interesting information because its activation energy is appreciably lower than the activation energy of viscosity for the IL, being these values $E_{\text{nr}} = 11$ kJ/mol and $E_{\eta} = 33$ kJ/mol, respectively. In contrast, in most liquids, k_{nr} of DCVJ has a similar activation energy as the bulk viscosity [17,19]. A lower activation energy for this appointed process was observed in ethanol glasses and interpreted in terms of availability of free volume [19]. The behavior in IL can be similarly explained by the existence of voids large enough to allow a more free rotation or at least wagging of the dicyanovinyl moiety with a smaller sweeping volume requirement than the one associated to the reorientation of the solvent molecules.

From $\phi_{\text{DCVJ}} = 0.11$ at 298 K and $\tau_{\text{DCVJ}} = 0.15$ ns, $k_r = 7.3 \times 10^8$ s⁻¹ (to be compared with ca 2.6×10^8 s⁻¹ in a series of *n*-primary alcohols and 1.1×10^8 s⁻¹ in glycerol [19]). From Eq. 3, $k_{\text{nr}} = 5.9 \times 10^9$ s⁻¹ is calculated at 298 K. Considering $E_{\text{nr}} = 11$ kJ/mol, $A_{\text{nr}} = 5.0 \times 10^{11}$ s⁻¹ is obtained. This means that the movement of the dicyanovinyl moiety takes place with a characteristic time of 2 ps, 1000 times shorter than the calculated molecular rotational correlation time.

The isomerization of the carbocyanine DODCI takes place with an activation energy of 44 kJ/mol in [bmim][PF₆] [15]. This value coincides with the sum of the activation energy of the IL viscosity (33 kJ/mol) [32], and the intrinsic barrier for isomerization (11 kJ/mol) [24]. The frequency factor for the barrier crossing process in the excited state of DODCI is 6×10^{12} s⁻¹ [24] suggesting that processes involving motions of 300 Å³ moieties in the picosecond time range are also totally controlled by viscosity. Therefore, the low involvement of viscosity control in the nonradiative deactivation of DCVJ does not seem to be a consequence of a very fast process but a result of the spatial requirement of the movement.

In view of our results and discussion we can arrive to the conclusion that in [bmim][BF₄], due to packing mismatch of cation and anion, there is enough free space to allow

rotation of small moieties (of the order of 70 \AA^3 , the volume of the dicyanovinyl group) experiencing less friction than that provided by bulk viscosity but movement of greater species are viscosity-controlled.

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