APPLICATION NOTE

Solvent Properties of Ionic Liquids Studied by Fluorescence Spectroscopy

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INTRODUCTION

Ionic liquids (ILs) are room-temperature molten salts composed of large organic cations and inorganic anions. They have many potential applications in engineering, environmental sciences and chemical synthesis thanks to their unique physical properties, namely, their chemical stability and low vapour pressure have led to ILs being proposed as 'green', recyclable solvents for the chemical industry.[1]

It is possible to fine-tune the physical properties of an ionic liquid by making small changes to the chemical structure of the ions. Despite this great potential for tunability, their structure-property relationships are not yet fully understood. In particular, for their application as solvents it is important to understand the solvation mechanism and how this changes with IL and solute composition. This can be studied by fluorescence spectroscopy of selected molecules dissolved in the IL.

The fluorescence spectrum, lifetime and quantum yield of a fluorophore depend on the surrounding solvent molecules, so measurements of these properties in different solvents can help understand the factors that influence solvation. In this application note two different fluorescent probes have been studied in two ionic liquids of different polarity. Fluorescence lifetime and anisotropy studies have been carried out to probe the nanostructure of the IL bulk and the solvation dynamics for each molecule.

EXPERIMENTAL SETUP

The ionic liquids studied were [C_2mim][Tf_2N] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) and [C_{12}mim][Tf_2N] (1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). The dyes used were DCM (4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4-H-pyran) and rhodamine 101. The chemical structures of ILs and dyes are presented in Figure 1. The dyes were dissolved in each IL to an optical density of 0.1 and studied in quartz cuvettes.

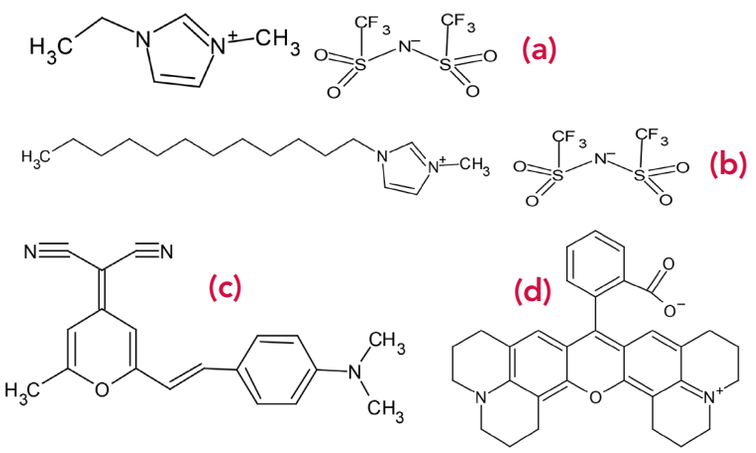

Figure 1: Chemical structures of (a) [C_2mim][Tf_2N], (b) [C_{12}mim][Tf_2N], (c) DCM, (d) rhodamine 101.

Fluorescence lifetime and anisotropy measurements were carried out in an FLS1000 Photoluminescence Spectrometer equipped with an EPL-485 diode laser for pulsed excitation, automatic excitation and emission polarisers, time-correlated single-photon counting (TCSPC) electronics, and a standard photomultiplier tube (PMT-900) as the detector. The instrument featured a double monochromator in the emission path.Fluorescence lifetime decays were acquired with polarisers set at 'magic angle' conditions (54.7°) and the results were analysed with the reconvolution fit available in the standard Fluoracle® software. Time-resolved anisotropy decays were fitted to a spherical rotor model using the advanced lifetime analysis software package, FAST.

RESULTS - DISCUSSION

Figure 2 shows TCSPC decays for DCM (left) and rhodamine 101 (right) acquired in [C_2mim][Tf_2N] and [C_{12}mim][Tf_2N]. It can readily be observed that the fluorescence lifetime of DCM varies significantly with IL solvent, whereas the lifetime of rhodamine 101 does not. This can be explained by the presence of nanodomains in the IL bulk as proposed by other studies[2,3]. It is widely accepted that the alkyl chains in the imidazolium cations aggregate together to form non-polar domains, whilst the imidazolium rings and anions form polar domains.

As DCM is a non-polar probe, it is expected to occupy the non-polar alkyl domains preferentially, which are more prominent in [C_{12}mim][Tf_2N] due to its long chains. However, the excited-state lifetime of DCM becomes shorter in [C_2mim][Tf_2N] because it experiences a more polar solvation environment. Rhodamine 101 in contrast is a polar molecule which occupies the ionic part of the liquid. As the composition of the ionic domains is the same for both ILs, this results in the same fluorescence lifetime.

These differences can be quantified by fitting the decays to a multiexponential lifetime model in Fluoracle. A two-exponential model was found to best fit the data, and the resulting average lifetimes are presented in Table 1.

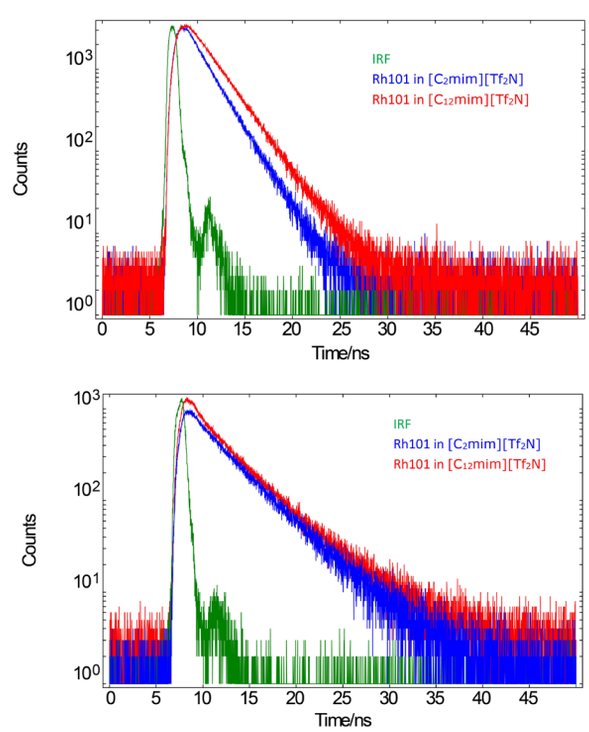

Figure 2: TCSPC decays of DCM (Upper Panel) and rhodamine 101 (Lower Panel) acquired in [C_2mim][Tf_2N] (blue) and [C_{12}mim][Tf_2N] (red). The instrument response function (IRF) is shown in green. Excitation source = EPL485, Repetition rate= 5 MHz, λem = 690 nm, Δλem = 10 nm, Acquisition time = 5 minutes.

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Table 1. Average fluorescence lifetimes obtained from the data in Figure 2.

Dye/IL system	<*t*> (ns)
DCM in [C_2mim][Tf_2N]	2.56
DCM in [C_{12}mim][Tf_2N]	3.10
Rho101 in [C_2mim][Tf_2N]	4.14
Rho101 in [C_{12}mim][Tf_2N]	4.09

Time-resolved emission spectroscopy (TRES) offers further insight into the solvent relaxation dynamics for each dye. Figure 3 shows TRES maps for DCM and rhodamine 101 in [C_2mim][Tf_2N]. In the case of DCM, the emission spectrum shifts to longer wavelength over the course of the decay, indicating that solvent relaxation takes place on the ns timescale. DCM has a long intrinsic relaxation time due to its donor-acceptor character[4], which is further strengthened by the IL solvation environment: the alkyl chains create a more viscous environment resulting in slower rotation and longer relaxation times[5,6]. In contrast, the relaxation of rhodamine 101 is too fast to be observed under the experimental conditions.

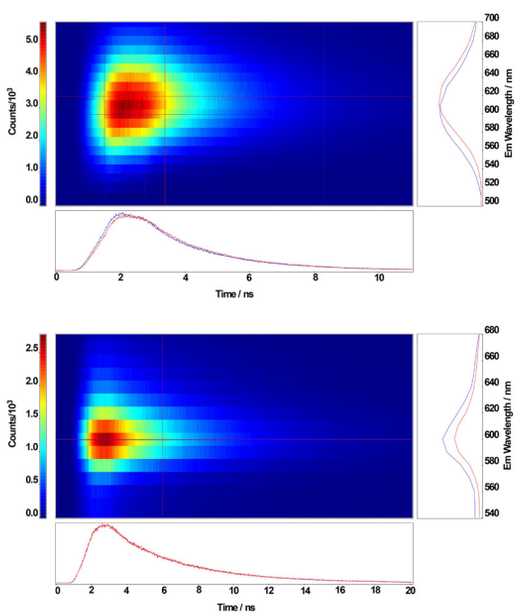

Figure 3: TRES decays of DCM (upper panel) and rhodamine 101 (lower panel) acquired in [C_2mim][Tf_2N]. Cross sections at early (blue) and late (red) delays are indicated in the graphs. Excitation source = EPL485, Repetition rate = 5 MHz, λem step = 10 nm, Δλem = 10 nm, Acquisition time = 120 seconds/decay.

The molecular rotation of the dyes can be studied in detail by means of time-resolved fluorescence anisotropy measurements in the FLS1000. Polarisation-dependent TCSPC decays were fitted to a spherical rotor model using the FAST software package. The model accounts for rotational diffusion and fluorescence decay independently, and provides a rotational diffusion time, Φ, as well as the fluorescence lifetime, τ.

$$I_{VV}^{m}(t) = \frac{I_0}{G}\left[e^{-\frac{1}{\tau}} + 2r_0 e^{-\left(\frac{1}{\tau}+\frac{t}{\emptyset}\right)}\right]$$

$$I_{VH}^{m}(t) = \frac{I_0}{G}\left[e^{-\frac{1}{\tau}} - r_0 e^{-\left(\frac{1}{\tau}+\frac{t}{\emptyset}\right)}\right]$$

In the above equations, I_{VV} is the fluorescence intensityrecorded with vertical polarisation on the excitation and emission paths, I_{VH} is the intensity with vertical excitation and horizontal emission polarisation, r_0 is the fundamental anisotropy of the dye defined as $r_0=\frac{2}{5}\left(\frac{3cos^2\beta-1}{2}\right)$(where β is the angle between absorption and emission transition dipole moments), and G is the G-factor of the instrument defined as $\frac{I_{HH}}{I_{HV}}$ (H indicates horizontal polarisation of the excitation light).

The results of the fit are presented in Table 2. There is much better agreement with the average lifetime values in Table 1 for rhodamine 101, which can be explained by the fact that it is a more spherical molecule than DCM.

Table 2: Fit results of the time-resolved anisotropy data to the spherical rotor model in FAST. Measurement conditions: Excitation source = EPL485, Repetition rate = 5 MHz, λem = 690 nm, Δλem = 10 nm, Acquisition time = 5 minutes.

FIT RESULTS	r_0	Φ / ns	τ / ns	expected Φ / ns
DCM in [C_2mim][Tf_2N]	0.241	4.6	2.26	10
DCM in [C_{12}mim][Tf_2N]	0.241	14.5	2.69	54
Rh101 in [C_2mim][Tf_2N]	0.261	5.3	4.14	21
Rh101 in [C_{12}mim][Tf_2N]	0.22	11.5	4.04	108

The rotational relaxation times can be compared to the theoretical values estimated from viscosity measurements, $\Phi = 3\theta = 3\eta V / RT$. In this equation, η is the viscosity of the liquid, V is the molecular volume of the probe, R is the gas constant and T is the absolute temperature (θ is the rotational correlation time). The results obtained from the fitting process are much lower than expected, but are consistent with [C_2mim][Tf_2N] presenting a less viscous solvation environment to the rotating fluorophores.

It is also worth noting that the theoretical values predict a greater change in Φ with IL for the case of rhodamine 101, but the experimental results show the opposite trend. The difference in viscosity between [C_2mim][Tf_2N] and [C_{12}mim][Tf_2N] arises from the alkyl domains. Since rhodamine 101 resides preferentially in the polar domains, it experiences a microviscosity that is different from the bulk value and this results in more similar rotational behaviour between the [C_2mim][Tf_2N] and [C_{12}mim][Tf_2N] cases.

CONCLUSION

The FLS1000 Photoluminescence Spectrometer has been employed for a complete characterisation of the lifetime and anisotropy of fluorescent probes in ionic liquids. The measurements were performed in one instrument incorporating all the necessary accessories and data acquisition software. Advanced analysis of anisotropy decays was carried out with the FAST software package.

Fluorescent probes of different polarity were used to probe the different nanodomains of each IL. The results show clear differences in the solvation properties of [C_2mim][Tf_2N] and [C_{12}mim][Tf_2N] and provide further evidence of nano-segregation into polar and nonpolar domains.

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