FULL PAPER

EuIII Luminescence in a Hygroscopic Ionic Liquid: Effect of Water and Evidence for a Complexation Process

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The spectroscopic characteristics (excitation, emission and lifetime) of EuIII dissolved in 1-methyl-3-butylimidazolium bis(trifluoromethanesulfon)imide (BumimTf₂N) are reported. In a first series of experiments, the effect of the presence of water in BumimTf₂N was examined. It appears that non-degassed solutions are most probably inhomogeneous, displaying large water clusters leading to an intense diffusion of the red light of an He:Ne laser. In these samples, the Eu emission spectrum is close to that observed in slightly acidic aqueous solutions. In contrast, when the samples were de-gassed the solution appeared homogeneous and water can be considered as a competitive ligand for the first coordination sphere of Eu. In a subsequent series of experiments, tetrabutylammonium chloride (TBACl) was added to the solution and the resultant species investigated. The ensuing enhancement in the metal-centered luminescence has been interpreted in terms of changes in the inner coordination sphere of the EuIII ion and possible structures are discussed. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Room-temperature ionic liquids (RTIL) appear as "multi-purpose liquids" able to replace usual organic solvents in almost every field of chemistry (e.g. catalysis, synthesis, electrochemistry).[1] Both the cationic and the anionic components of these liquids can be easily varied, and they can therefore be tailored for particular applications or to have specific sets of properties. As a consequence, RTILs represent a green alternative to volatile organic solvents, offering environmentally safe processes.

In particular, in the field of nuclear waste reprocessing, there is still a need for improved routes for the actinide/lanthanide separation/extraction. In addition to promising studies on the use of ionic liquids for liquid/liquid extraction,[2] a recent study has shown that some ionic liquids display reasonable stability under α and γ irradiation,[3] thus reinforcing their potential interest for the nuclear fuel industry. However, despite the increasing number of publications devoted to ionic liquids, the solvation effects, the solute-solvent and solvent-solvent interactions as well as the general structural organization of these solvents are still hardly known. These fundamental aspects are of tremendous importance for understanding the solvating properties of these new solvents, thus limiting their applications for liquid/liquid extraction. In order to gain a better insight into these questions, we have undertaken a spectroscopic investigation on the solvation of EuIII in 1-methyl-3-butyl-imidazolium bis(trifluoromethanesulfon)imide (Bumim-Tf₂N, see Scheme 1). This ionic liquid has been chosen because it can be used, among others, for biphasic separations such as liquid extraction in view of its hydrophobic properties. EuIII has been chosen as a representative lanthanide ion and as a good homologue of AmIII, an actinide of great interest in the nuclear fuel cycle. In this work, we take advantage of the specific properties of EuIII to investigate its solvation in BuminTf₂N by means of luminescence measurements. Specific attention has been paid to the role
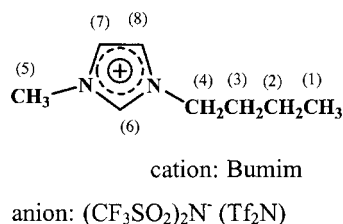
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cation: Bumim

anion: (CF₃SO₂)₂N⁻ (Tf₂N)

Scheme 1

of water (considered as a solute) in the luminescence properties of Eu^{III} and the effect of added tetrabutylammonium chloride has also been investigated.

Results and Discussion

Effect of Water on the Spectroscopic Characteristics of Eu^{III}

Results

Europium triflate (5×10^{-3} M) in BumimTf$_2$N turns to a slight brownish color after degassing (procedure II, see Exp. Sect.) and a very weak absorption band located at 394 nm can be observed corresponding to the transition with the largest oscillator strength in the Eu^{III} spectrum namely the $^5L_6 \leftarrow {}^7F_{0,1}$ transition (Figure 1). The spectrum of a more concentrated and degassed solution (4×10^{-2} M) is displayed in Figure 2, from which a molar absorption coefficient of 0.8 M^{-1}·cm^{-1} (λ = 394 nm) could be estimated. This value is of the same order of magnitude as that reported for Eu^{III}(aq) i.e. 2.4 M^{-1}·cm^{-1}.[4] In two previous studies,[5,6] various lanthanide triflates were dissolved in RTILs, particularly in BumimPF$_6$, at concentrations far below the maximum concentration obtained by us. This may be due in part to the use, in these studies, of anhydrous lanthanide salts.
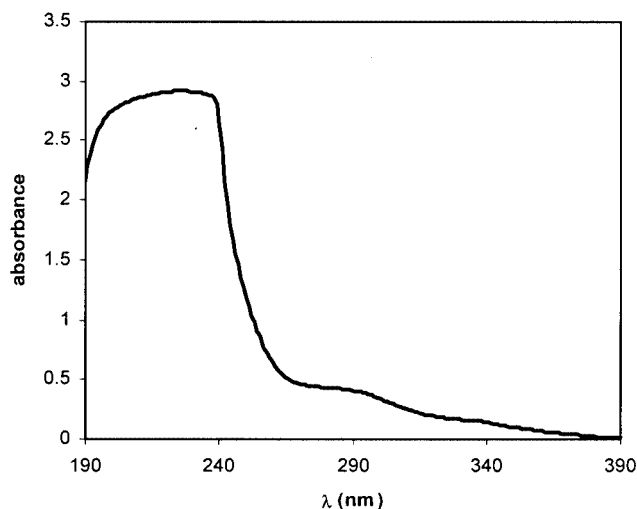

Figure 1. Absorption spectrum of the BumimTf$_2$N batch used in this work (non-degassed)

RTILs are known to be hygroscopic[1,7,8] and previous studies have provided insight into the dependence of the kinetics of water absorption by RTILs upon experimental conditions.[7−9] In order to obtain a deeper understanding of the influence of water on europium luminescence in BumimTf$_2$N, a solution was submitted to cycles combining various degassing procedures and storage durations during which the solution was simply kept in the quartz cuvette with a Teflon cap. Table 1 summarizes these cycles and displays the decay behavior (either mono- or biexponential),
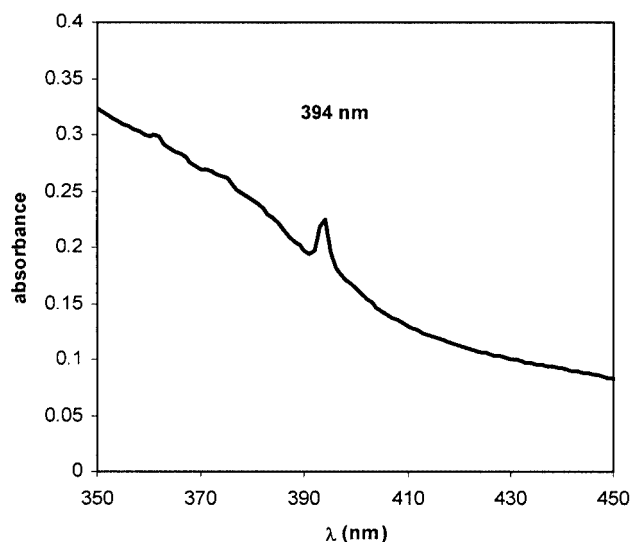

Figure 2. Absorption spectrum of the Eu^{III} triflate salt 4×10^{-2} M in BumimTf$_2$N

the corresponding lifetimes and relative intensities during the cycles. In this table, $t = 0$ corresponds to the end of the first degassing procedure and positive t values indicate the time elapsed since $t = 0$, when the data (decay profile and emission/excitation spectra) were recorded. By definition, the notation $t = -1$ means that the measurement was performed *before* this first degassing procedure when the ionic liquid water content was constant with time (see section "water contents"). Note that a lifetime decay could be obtained for the non-degassed (probably heterogeneous) sample, since no fluctuations of the luminescence intensity were observed. Figure 3 presents the excitation spectra obtained at times equal to −1, 0, and 13 d of the cycle, while emission spectra are displayed in two separate figures (Figure 4, a and b) in view of the large differences in emission intensities. For $t = 25$ d, the excitation and emission spectra are very similar to those for $t = 13$ d and are therefore not shown.

Table 1. Decay behavior, lifetime values (μs), relative intensities (%) and $R_{612/589}$ values for the Eu^{III} triflate salt in BumimTf$_2$N along the degassing/storage cycle (see text)

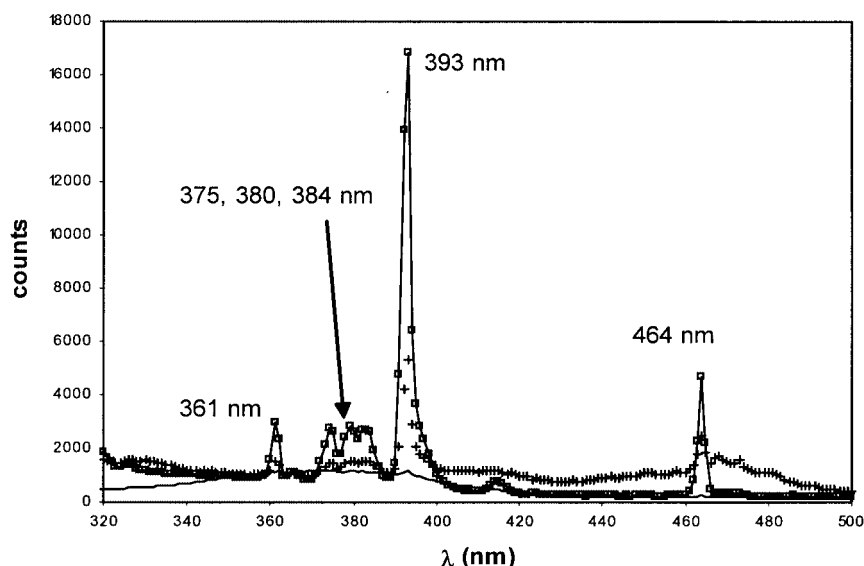| t [d]	Procedure	Decay characteristics	$R_{612/589}$
−1	no degassing	monoexponential $\tau = 159$ μs	< 1
0	degassing (I)	biexponential $\tau_1 = 643$ μs (19%) $\tau_2 = 1596$ μs (81%)	3.4
6	storage	monoexponential $\tau = 350$ μs	n. d.
13	degassing (II)	biexponential $\tau_1 = 689$ μs (85%) $\tau_2 = 2556$ μs (15%)	3.4
20	storage	monoexponential $\tau = 681$ μs	n. d.
25	storage	monoexponential $\tau = 545$ μs	3.4

Figure 3. Excitation spectra of the Eu^{III} triflate salt 5×10^{-3} M in BumimTf$_2$N during the degassing cycle; emission wavelength: $\lambda = 609$ nm; solid line: $t = -1$ d; open squares: $t = 0$ d (procedure I); $+++$: $t = 13$ d (procedure II)
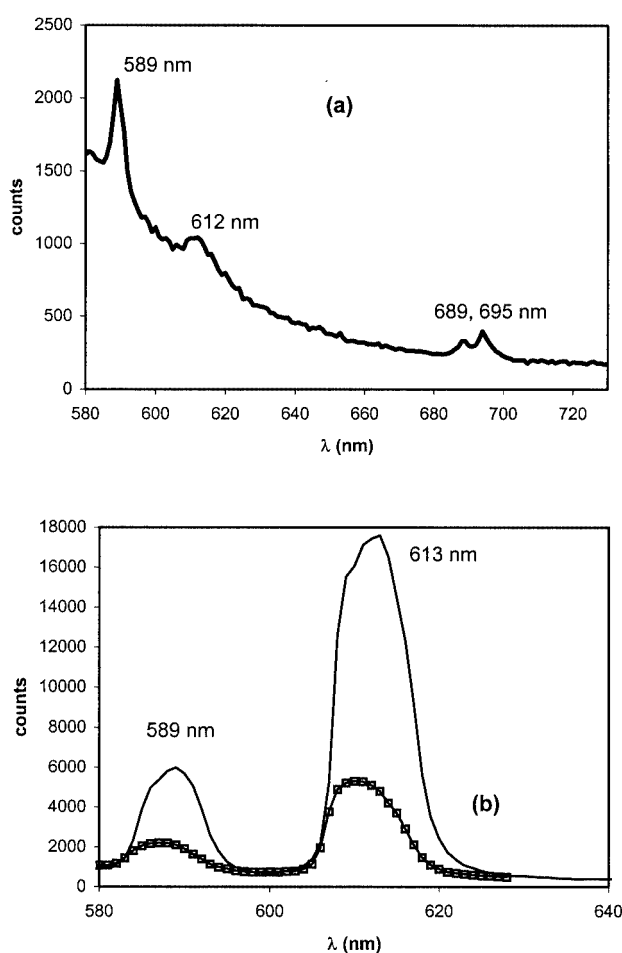

Figure 4. a: Emission of the Eu^{III} triflate salt 5×10^{-3} M in BumimTf$_2$N at $t = -1$ d (see text and Table 1); excitation wavelength: $\lambda = 394$ nm; b: emission of the Eu^{III} triflate salt 5×10^{-3} M in BumimTf$_2$N in function of the degassing procedure (see text and Table 1); excitation wavelength: $\lambda = 393$ nm; solid line: $t = 0$ d (procedure I); open squares: $t = 13$ d (procedure II)

For all samples the excitation spectra essentially display f-f transitions, indicating no antenna effect from the ionic liquid. The energies of these transitions do not vary which is in contrast to their intensities which substantially decrease over time after the first degassing procedure. Similar behavior was observed for the emission spectra and lifetimes. Using excitation at other wavelengths (data not shown), the emission was similar in shape and the intensity change reflects the relative intensities observed in the excitation spectra. The lifetimes exhibit peculiar behavior: a single exponential decay was measured for the non-degassed solution with a short lifetime of 0.159 ms, which became biexponential upon degassing, with much longer lifetimes of 0.64 and 1.6 ms. After 6 d of storage, the decay was again characterized by a single exponential but this again became biexponential after the second degassing. For the air- and water-tight solution, biexponential behavior was still observed more than 12 d after degassing and the lifetime values were perfectly stable.
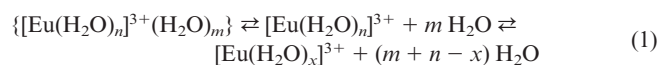
Discussion

The intense diffusion of the He:Ne laser light by the non-degassed europium solution compared with almost zero diffusion for pure non-degassed BumimTf$_2$N points to the presence of large aggregates (clusters) in the former. Hence the non-degassed europium solution, which contains approximately 80 H$_2$O molecules per Eu^{III} ion, should be better considered as being an emulsion. The emission spectrum of the non-degassed sample (Figure 4, a) is very similar to the one obtained for Eu^{3+}$_{aq}$ in slightly acidic aqueous solution,[4,10] although the corresponding lifetime is larger (0.159 ms compared with 0.111 ms for Eu^{3+}$_{aq}$, see Table 1). The presence of high-energy O−H oscillators in the inner coordination sphere of Eu^{III} is known to induce a severe quenching of the luminescence.[11] The short lifetime measured for the ionic liquid solution suggests that Eu^{III} is heav-

ily hydrated, possibly to the same extent as in an aqueous solution. Indeed, triflate is only slightly more coordinating than perchlorate[12] and should not bind to the Eu[III] ion in water. In contrast, no data are available on the coordinating strength of Tf_2N^- but since it is present in large excess in the solutions, inner-sphere coordination cannot be excluded. The longer lifetime measured in the RTIL could be due to the limited amount of water in $BumimTf_2N$ leading to a decreased inner-sphere hydration number n and/or a decreased outer sphere hydration number m in the $\{[Eu(A^-)_x(H_2O)_n]^{(3-x)+}(H_2O)_m(A^-)_{(3-x)}\}$ aggregates (A^- stands for an anion). In water, n is fractional (and x is essentially equal to zero), reflecting a fast equilibrium between 8- and 9-coordinate species,[13] while both nona- octa- and hexahydrated Ln^{III} ions have been evidenced in the solid state. The contribution of second-sphere oscillators to the luminescence decay is not well known, but in the case of Eu[III] complexes with cyclen derivatives, it has been estimated to be 0.25 ms^{-1}.[14]

In contrast, the degassed sample at the beginning of the cycle ($t = 0$) exhibited completely different Eu[III] spectroscopic properties, indicating a large loss of inner-sphere water molecules. This is illustrated by the increased intensity of the hypersensitive transition ($^5D_0 \rightarrow {}^7F_2$) at ca. 613 nm by a factor > 3 (see Figure 4, b). The relative broadness of the bands and their lack of crystal-field fine structure may indicate that Eu[III] is imbedded into a medium with properties similar to those of a glass. The degassing procedure drastically decreases the total water amount but some water remains. A water content of 50 ppm still corresponds to one molecule of water per Eu[III] ion.

No information can be gained on which form of water is better extracted in the degassing procedure[9] whether already accommodated in the solvent prior to solution preparation or introduced with the europium salt. As a matter of fact, the absence of laser light diffusion after degassing is evidence for a homogeneous solution and the changes in the emission spectra show that europium is now solvated in the RTIL and no longer in "water clusters". The biexponential behavior of the luminescence decay either in the air- and water-tight cuvette or at the beginning of the storage can be considered to reflect the presence of two different Eu[III] species in solution. One explanation could be the formation of inner-sphere complexes with the counterions [Equations (1) and (2)].

$$\{[Eu(H_2O)_n]^{3+}(H_2O)_m\} \rightleftarrows [Eu(H_2O)_n]^{3+} + m\,H_2O \rightleftarrows \\ [Eu(H_2O)_x]^{3+} + (m+n-x)\,H_2O \quad (1)$$

$$[Eu(H_2O)_x]^{3+} + y\,A^- \rightleftarrows [Eu(A)_y(H_2O)_{x-y}]^{(3-y)+} + y\,H_2O \quad (2)$$

In Equation (2), A^- has been taken as being a monodentate anion, but the triflate could also be bidentate or even act as bridging moiety. The latter assumption is, however, not very probable in view of the relatively high dilution of the solutions. In water, phenomenological calibration curves have been reported which relate the number of inner-

sphere water molecules to the lifetimes measured in water and deuterated water.[11,15] In the absence of structural information on the solvated species in RTILs, and because these phenomenological correlations cannot be easily transposed from one solvent to another, no such relationship is available and therefore an estimate of x is not within reach with the present lifetime data. We note, however, that 1.6 ms is a rather long lifetime [cf. 2.10 ms for $Eu(ClO_4)$ in anhydrous acetonitrile][16] and since the RTIL medium is not dielectrically too different from an organic solvent, the associated species probably contains, on average, less than one water molecule. The subsequent transformation of the decay into a single exponential curve, with a concomitant decrease in lifetime after few days of storage reflects a rehydration of the Eu[III] ion, although not completely, since both the lifetime and the $R_{612/589}$ ratio remain substantially larger than in the non-degassed solution. We have interpreted this in terms of several different hydrated species being in equilibrium. When several water molecules are coordinated in the inner sphere, their lifetimes become comparable. This makes a mathematical resolution of the decays difficult. Moreover, fast water exchange reactions lead to an averaging of the species on the time scale of the luminescence experiment (ms).

After applying degassing procedure II (see Exp. Sect.), the solution again contained two Eu[III] species, one having a relatively short lifetime (which corresponds to the short lifetime measured after procedure I was applied), while the other featured a much longer lifetime than the long lifetime of the previous sample. This clearly demonstrates that further dehydration has occurred. The value of this lifetime, 2.56 ms, probably implies that an anhydrous species has been formed but again, this assessment will need to be confirmed by determining the exact nature of the species in solution. When re-hydration occurred, the decay turned again into a single exponential curve with a lifetime intermediate between the ones obtained after the first and the second degassing procedures.

The results presented above are of great practical interest and show that, for luminescence measurements, caution should be paid to the degassing procedure and to the water intake by the sample. It should be stressed, however, that luminescence measurements can be performed with reasonable confidence (i.e. results are reproducible) because, as can be seen from Table 1, the absorption of water under our experimental conditions was slow. These slow kinetics compared with those observed by Seddon and co-workers[8] or by Tran and co-workers[9] are mainly due to the absence of vigorous stirring and to the use of a cap for the cuvettes in our case.

Spectroscopy in the Presence of Tetrabutylammonium Chloride (TBACl)

Results

The data presented in Figures 5–8 were recorded immediately after the end of the degassing procedure. Figures 5 and 6 display the excitation and emission spectra for

ratios r = [TBACl]/[Eu] = 4.5, 6 and 9. Compared with Figures 3 and 4, the main difference is the strong band centered around 330 nm seen in the excitation spectra and the well-defined structure in the Eu emission spectra. For comparison, a solution containing only TBACl in BumimTf$_2$N displays a single very broad band of very low intensity centered at 375 nm.

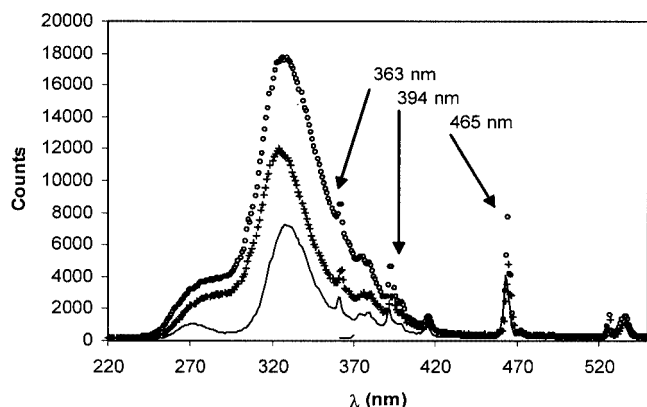Figure 5. Excitation of the Eu^{III} triflate salt 5 × 10^{-3} M in BumimTf$_2$N containing TBACl; emission at λ = 608 nm; solid line: r = 9; +++: r = 6; open circles: r = 4.5
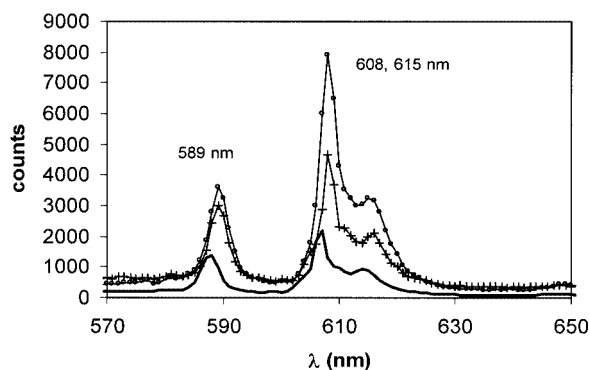
Figure 6. Emission of Eu^{III} triflate salt 5 × 10^{-3} M in BumimTf$_2$N containing TBACl; excitation wavelength: λ = 464 nm; solid line: r = 9; +++: r = 6; open circles: r = 4.5

The total excitation intensity decreases as a function of r, as does the total emission intensity. For all the samples, in contrast to what was obtained without TBACl, the luminescence decays are single exponential curves, even after the degassing procedure. The Eu^{III} lifetime values as a function

Table 2. Lifetime values for the solutions of the Eu^{III} triflate salt containing added TBACl

r = [TBACl]/[Eu]	τ [μs]
3.5	2038
4.5	2060
6	2560
9	2760

of the total TBACl amount are displayed in Table 2. Although incomplete dissolution occurs for r < 4.5, a lifetime value could be obtained.

The excitation and emission spectra of the Eu^{III}/TBA-triflate/BumimTf$_2$N solution (r = 6) are displayed in Figures 7 and 8, together with the data for TBACl for the sake of comparison. Compared with the addition of chloride, the emission intensity was lower when the triflate was added and the bands were much broader.
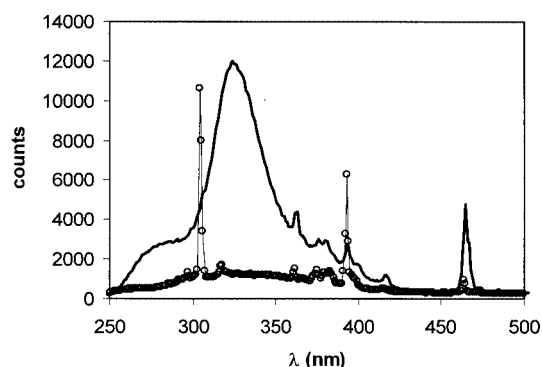

Figure 7. Excitation spectra of solutions of the Eu^{III} triflate salt 5 × 10^{-3} M in BumimTf$_2$N (λ$_{em}$ = 608 nm); solid line: with TBACl, r = 6; open circles: with TBA-triflate, r = 6; the sharp peak at 304 nm is due to the excitation light (608 nm is the second harmonic)
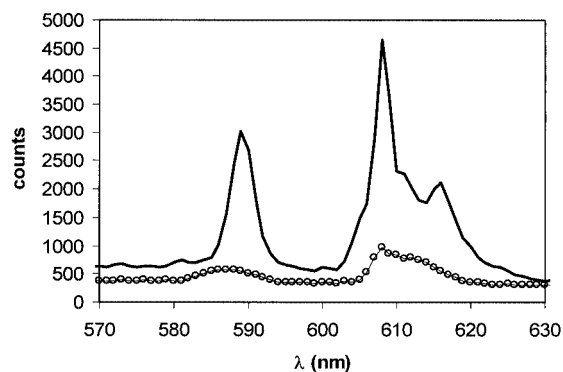

Figure 8. Emission spectra of solutions of the Eu^{III} triflate salt 5 × 10^{-3} M in BumimTf$_2$N (λ$_{ex}$ = 464 nm); solid line: with TBACl, r = 6; open circles: with TBA-triflate, r = 6

The effect of progressive water absorption by BumimTf$_2$N as a function of time has also been studied. In the case of TBACl, and in contrast to the solutions to which no TBA salt was added, the increasing amount of water had no effect at all on the Eu^{III} lifetime and decay behavior for r = 9. Even after 22 d of storage, the lifetime changed by less than 10 μs. On the other hand, the lifetime of the solution to which TBA triflate had been added decreased as a function of time (from τ = 1180 μs after degassing to 492 μs after 3 d of storage).

Discussion

There is no physical evidence for stating that the introduction of TBACl strongly modifies the course of the degassing procedure. Therefore, the single exponential behavior of the decays after the degassing procedure shows that the Eu^{III} coordination sphere is strongly modified compared with the solution without TBACl. This is also illustrated by the changes observed in the excitation and emission spectra as a function of *r*. In comparison with what is known about europium luminescence in other solvents,[16−18] these changes can be ascribed to a complexation process. Slight changes can be observed in the emission spectra at *r* = 3 and 9, especially in the value of R$_{612/589}$. This experimental fact, together with the reduced solubility observed for *r* < 4.5 would indicate that at least two different complexes are present in solution, depending on *r*. TBACl is a 1:1 electrolyte, but it is not clear from our experiments whether it is entirely dissociated in BumimTf$_2$N. Although a detailed symmetry analysis is not possible due to the relative broadness of the emission bands, we note that $^5D_0 \rightarrow {}^7F_1$ generates one symmetrical band while 2−3 components can be seen for the $^5D_0 \rightarrow {}^7F_2$ transition, indicating a relatively high symmetry around the Eu^{III} ion. Trivalent europium is known to form a stable hexachloride with an elpasolite structure and O_h symmetry.[19] In ethanol solution, this species either dissociates or reacts with the solvent to give a species with D_2 symmetry.[20] It is noteworthy that the $^5D_0 \rightarrow {}^7F_2$ spectrum reported for the latter species is very similar to the one reported in Figure 6 for *r* = 6 and so are the spectra for [Cl$^-$]/[Eu] = 26 (in ethanol)[20] and *r* = 9 (Figure 6). Therefore we may safely conclude that upon addition of TBACl, polychloro species are formed in RTIL solution.

The implications of single exponential behavior of the decays of the emission spectra and the lifetime values changing as a function of the ligand concentration (TBACl case) have been discussed long ago[21] and have been revisited recently.[22] Both papers agree that such experimental facts point to a photochemically induced complexation reaction occurring in the solution. It was also agreed that the excitation and emission data collected for *r* = 9 (lifetime plateau value, see Table 2) are those of the higher complex obtained with a lifetime of 2760 μs.

The luminescence enhancement observed could be explained in two ways: (i) the interaction of chloride ions in the inner coordination sphere results in a ligand-to-metal transfer state reflected in the excitation spectrum (Figure 7) and energy transfer takes place between this state and Eu^{III}. Such a state is observed around 33 000 cm^{-1} [23] for [EuCl$_6$]$^{3-}$ in the solid state and excitation in such states may result in metal-centered luminescence when they lie at relatively high energy, which is the case here. Moreover, the spectrum displayed in Figure 8 (top) matches perfectly well the one published earlier for [EuCl$_6$]$^{3-}$ in ethanol.[20] (ii) The inner-sphere chloride ions act as relays between the metal ion and the Bumim$^+$ or TBA$^+$ cations in the second solvation shell, allowing a through-bond energy transfer.

Finally, the quite different spectroscopic properties observed upon addition of TBA triflate, in particular the absence of luminescence enhancement, point to a much weaker interaction between the added anions and the metal ion so that competition with water molecules easily leads to hydrated species with quenched luminescence.

Conclusion

For the first time, a spectroscopic investigation of Eu^{III} dissolved in BumimTf$_2$N has been conducted particularly with respect to the effect of water and added TBA chloride. The results pinpoint the importance of degassing procedures and storage conditions, in view of the highly hygroscopic nature of the solvent. A complexation process between Eu^{III} and the added TBA salts has been evidenced and some insight into the species in equilibrium and the composition of the inner coordination sphere of Eu^{III} has been obtained. A first conclusion is that the behavior of the Eu^{III} ion in degassed BumimTf$_2$N displays trends similar to that exhibited in other organic hygroscopic solvents (e.g. acetonitrile or ethanol), with respect to both its coordination and spectroscopic properties. On the other hand, non-degassed solutions exhibit a highly inhomogeneous nature. In view of the evaluation of RTILs for use in future lanthanide/actinide extraction processes it is essential that basic data on the solvation of metal ions in these liquids be at hand. From this standpoint, the results presented here are very encouraging since they demonstrate that complexation processes analogous to those in common solvents take place in the investigated RTIL, and that they can be monitored by a highly sensitive technique such as time-resolved luminescence. However, some differences have also been unraveled and we are now concentrating our efforts on gathering structural data on these solutions in order to get a much deeper understanding of the nature of the solvated and complexed species in equilibrium.

Experimental Section

Synthesis of BumimTf$_2$N and Experimental Methods: All chemicals were of the highest reagent grade (Aldrich) and were used without further purification. All aqueous solutions were prepared with de-ionized water (Millipore de-ionization system, ω = 18.3 MΩ cm^{-1}). The synthesis of BumimTf$_2$N was derived from the previously reported synthesis of BumimPF$_6$ [23] and was typically performed as described in the following.

First Step. Synthesis of BumimCl: A three-necked round-bottom flask under argon, equipped with a water refrigerant, was loaded with methylimidazole (1 mol, 82.11 g) and *n*-chlorobutane (1 mol, 92.57 g). The mixture was stirred under argon at 70 °C for 48 h until the appearance of a pale yellow viscous mixture. This was then transferred into a flask and stored at 3−5 °C under argon until quantitative precipitation (ca. 12 h). White crystals were obtained which were washed several times with ethyl acetate and filtered each time with a Büchner apparatus. The crystals were transferred to a dry box containing phosphorus pentoxide and placed

under vacuum. A fine white powder of BumimCl was obtained. Yields were typically around 80%.

Second Step. Synthesis of BumimTf$_2$N: A solution of BumimCl (110 g) in water (150 mL) was added to a solution of LiTf$_2$N (200 g) in water (300 mL) and the resultant mixture was stirred at 70 °C for 16 h. Two phases were obtained and the upper layer (aqueous) was decanted. The lower phase (BumimTf$_2$N) was washed several times with de-ionized water (10 × 350 mL). BumimTf$_2$N, as a transparent and slightly viscous liquid, was transferred and stored in a dry box under vacuum containing phosphorus pentoxide. Typical yields: ca. 80%. The water content of the samples was determined by Karl Fischer titration, using standard procedures (Mettler DL18 titrator, hydranal composite 5 (Fluka) and analytical grade methanol). Absorption spectra in the range 190−900 nm were recorded with a Uvikon 930 (Kontron) spectrometer with 1-cm quartz cuvettes. In all cases, the reference was an empty quartz cuvette. No precaution was taken for the storage of the samples which were simply left in the quartz cuvettes (with Teflon cap), so that the water content may have changed with time (see the relevant study in the text). Emission and excitation spectra were recorded with a classical spectrofluorimeter (Photon Technology International) which does not allow for time-resolution but was corrected for gain efficiency of the detector. Data are also presented as $R_{612/589}$, the ratio of the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition (around 612 nm) with that of the $^5D_0 \rightarrow {}^7F_1$ transition (around 589 nm) for an excitation at $\lambda_{exc} = 394$ nm. The uncertainty on the value of $R_{612/589}$ is in the range of ±10%. The time-resolved emission spectroscopy (TRES) apparatus has been described in detail elsewhere.[24,25] Briefly, for decay measurements, the excitation wavelength was set to 266 nm and the decays were recorded at λ = 612 or 589 nm, depending on the transition efficiency. As is usual for time-resolved experiments of this kind, the data analysis was performed by systematically excluding the first 10 μs of each decay, for which the intense short-lived luminescence of the pure BumimTf$_2$N dominates and thus precludes any detection of the long-lived europium species. Therefore, in the following, the discussion of the decay behavior only corresponds to lifetimes ascribable to Eu^{III}. The importance of the decay behavior (either mono- or multiexponential) has been stressed in other papers[22,26] and the quality of the fits was assessed both by the usual χ^2 test and the shape of the residuals (experimental minus calculated values). The error in the lifetime values was of the order of ±3%. Although the measurements of the luminescence spectra and decays are easy to perform under the experimental conditions of this work, they cannot be conducted under optimum conditions for europium assays. For most of the feasible excitation wavelengths, the absorption of the sample was way above the usual 0.05 limit, for which a linear relationship holds between concentration and emission intensity, because of solvent absorption. All experiments were performed at a controlled temperature of 294 K.

Purification and Characterization: The purification procedure previously used for BumimPF$_6$ [27] was also applied to BumimTf$_2$N. However, the absorption band in the range 250−300 nm observed for non-purified BumimPF$_6$,[27] was still present in the absorption spectrum of the purified BumimTf$_2$N (Figure 1). It is probable that some organic impurities still remain. To the best of our knowledge, the absorption spectrum of ultra-pure BumimTf$_2$N is not known, so that comparison with our batch is impossible. On the other hand, repeated measurements of the absorption spectrum showed that the BumimTf$_2$N batch used in this work was stable for more than four months. Due to the synthetic procedure, BumimTf$_2$N contains water even after purification on an alumina column. The

presence of water is a common feature of room-temperature ionic liquids[1,7,28,29] and numerous works have pinpointed the large influence of water on various physico-chemical properties of RTILs.[8,30] This very important point will be addressed in this work.

Water Contents and Dissolution of Salts in BumimTf$_2$N: A previous study[8] focused on the effect of water on the properties of various RTILs, such as BumimBF$_4$ or BumimPF$_6$. In particular, it was shown that above a certain water content (around a molar fraction of 0.5), the viscosities and densities of the resultant mixtures became water-like, so that these samples have to be considered as aqueous solutions of RTILs and not as hydrated RTILs. Another study has shown that water absorption by BumimTf$_2$N may be rapid and important.[9] For the BumimTf$_2$N batch used in this work, the amount of water was equal to 5000 ± 50 ppm (i.e. 0.4 M or 0.5% w/w) after purification. This is a consequence of the numerous water washes at the end of the synthesis and the subsequent purification on the alumina column. This batch is thus not water-saturated when compared with values of up to 14000 ppm reported in the literature for BumimTf$_2$N,[1] but nevertheless contains a substantial amount of water. After several months of storage, the water content did not change much as shown by a new determination of the water content of 5100 ± 500 ppm. In order to control the water content of the samples, we degassed them according to two different methods. In procedure I, batches of 5 mL were pumped at room temperature for 18 h and, additionally, at 50 °C for 10 h (residual pressure: 1.8 mbar); the resultant water content was below 100 ppm (i.e. 8×10^{-3} M or 0.01% w/w). In a few cases (see below), samples were further degassed at 70 °C for 48 h (procedure II). Finally, a solution of europium triflate was degassed (procedure I) directly in a quartz cuvette connected to the degassing setup by a quartz-glass tube. In this case, by use of a tap, the solution in the cuvette was air- and water-tight but, due to the bulkiness of the setup, only lifetime measurements could be performed. Europium(III) triflate (Aldrich), tetrabutylammonium chloride (Aldrich) and triflate (Aldrich), and NaCl (Prolabo) were used as received. Hygroscopic salts were kept in a desiccator with P$_4$O$_{10}$. Unless otherwise specified, the europium concentration was 5×10^{-3} M. Possible changes in density from one sample to another due to different water contents were not considered in the determination of the concentration. A common value $d = 1.43$ for the density (non-degassed BumimTf$_2$N) has been assumed for all the BumimTf$_2$N samples in this work. Even though the europium triflate salt contains 4 water molecules per europium unit, the amount of water introduced with the salt is negligible compared with the water already present in the non-degassed solvent. Upon addition of europium triflate to BumimTf$_2$N, a slightly cloudy solution was obtained which indicates either an incomplete dissolution or, more probably, the formation of inhomogeneous clusters. In fact, these samples strongly diffuse the red light of an He:Ne laser. On the other hand, light diffusion was no more clearly observed even after degassing the samples using procedure I (solutions become clear) or II, so that these samples may be considered as being homogeneous (see also discussion). Various amounts of tetrabutylammonium chloride together with europium triflate ($r = $ [TBACl]/[Eu^{III}] = 3−9) were introduced into BumimTf$_2$N. Due to the very slow rate of dissolution, a small amount of CH$_3$CN (on the order of 0.5 mL), which is totally miscible in BumimTf$_2$N, was also added to the BumimTf$_2$N solutions prior to degassing in order to speed up the process. Considering the vapor pressure, it can be safely assumed that all CH$_3$CN was removed at the end of the degassing procedure. Despite this modified dissolution procedure, not all the salts dissolve for $r < 4.5$, even after degassing (procedure I). No attempts were

made to determine the exact composition of the undissolved residue. For $r > 4.5$, dissolution was fully achieved after degassing. Finally, a single solution of europium triflate with tetrabutylammonium triflate (TBA-triflate, $r = 6$) was prepared and degassed.

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