

Reactivity Towards Europium(III) of the Radiolysis Products of the Ionic Liquid 1-Methyl-3-butyl-1*H*-imidazolium Bis[(trifluoromethyl)sulfonyl]amide (C₄-mimTf₂N) and Effect of Water: A TRLFS (Time-Resolved Laser-Induced Fluorescence Spectroscopy) Preliminary Study

by **Isabelle Billard*** and **Sylvia Georg**

IPHC, Chimie Nucléaire, CNRS/IN2P3 et UDS, 23 rue du Loess, 67037 Strasbourg Cedex 2, France
(e-mail: isabelle.billard@ires.in2p3.fr)

Dedicated to Professor *Jean-Claude Bünzli* on the occasion of his 65th birthday

The effect of laser irradiation at λ_{exc} 266 nm onto the fluorescence characteristics of Eu^{III} in solution of the ionic liquid 1-methyl-3-butyl-1*H*-imidazolium bis[(trifluoromethyl)sulfonyl]amide (C₄-mimTf₂N) was examined for various amounts of H₂O added. Stable radiolytic products that were generated at very low doses (in the range of 4 kGy) were very reactive with Eu^{III} and led to the appearance of a new europium luminescent species that was characterized by lifetime, relative intensity, and emission spectrum. Although the lifetime and the intensity depended on the H₂O content, the emission spectrum was not influenced by H₂O. It was shown that large amounts of H₂O, although not preventing radiolysis of C₄-mimTf₂N, inhibited the complexation with Eu^{III}.

1. Introduction. – Ionic liquids (ILs) are the subject of an increasing number of studies aiming at demonstrating the huge potential of this new class of solvents for a wide variety of industrial applications, ranging from electrochemistry to catalysis, liquid/liquid extraction, or synthesis [1–3]. The most significant advantages of ILs are, besides nonvolatility and nonflammability, the tunability of their physico-chemical properties by structural modifications of their cationic and anionic constituents. In the fields of radiochemistry and reprocessing of nuclear waste, an additional advantage of ILs, which is often put forward to further justify the great interest of such solvents, is the rather good radiolytic resistance of ILs towards radiation and radiolysis [4–6]. The radiolytic stability of various ILs from the imidazolium or tetraalkylammonium families has been investigated, the counteranions of the ILs being either Cl[−], NO₃[−], PF₆[−], or Tf₂N[−] (= (CF₃SO₂)₂N[−]). Either γ , α , or β irradiations have been conducted, up to very high doses, in the range of 2 MGy at maximum. All these studies agree that ILs are very stable under irradiation, their physical and chemical properties being only slightly affected by irradiation, except for the conductivity and color [5]. Actually, a significant darkening of the ILs under investigation has been reported, which is attributed to the appearance of stable radiolytic products in very low yields but presenting a very high molar absorption [4][5]. Although these radiolytically stable products accumulate in solution linearly as a function of the irradiation dose, their precise chemical determination remains a difficult task, owing to their diversity and very low individual

formation yields [5][6]. Interestingly, it has been shown that the presence of H₂O has no effect on the radiolytic-darkening kinetics [5] and that the degradation products are the same whatever the chemical conditions (presence or absence of air or H₂O) [6]. By comparison with the radiolytic stability of tributyl phosphate (TBP) in kerosene, which is the usual industrial organic solution used to perform the liquid/liquid extraction/partitioning of used nuclear fuels, it is concluded that ILs could be suitable media for the radiochemical treatment of nuclear waste. However, the question remains of the possible reactivity of such stable radiolytic products with the ions of the reprocessing solutions, that may interfere with the reprocessing/partitioning.

In this work, we present a TRLFS (time-resolved laser-induced fluorescence spectroscopy) study of the reactivity of Eu³⁺ (introduced as a hydrated Eu(Tf₂N)₃ salt) with the stable radiolytic products of the ionic liquid 1-butyl-3-methyl-1*H*-imidazolium bis[(trifluoromethyl)sulfonyl]amide (thereafter denoted as C₄-mimTf₂N, with Tf₂N⁻ = (CF₃SO₂)₂N⁻) in the presence of variable amounts of H₂O added to the solution, up to the saturation limit. Radiolysis of the IL solutions was achieved by UV laser light (λ 266 nm), which was also used to excite, through the antenna effect, Eu³⁺ luminescence. The very high sensitivity of Eu³⁺ luminescence parameters to the coordination sphere(s) was used to detect the presence of radiolytic products at very low doses and to evidence their reactivity towards Eu³⁺. The effect of H₂O, acting as a ‘protecting’ agent by competitive complexation was also evidenced.

2. Experimental. – 2.1. *Chemicals.* The 1-methyl-3-butyl-1*H*-imidazolium bis[(trifluoromethyl)sulfonyl]amide (C₄-mimTf₂N) was purchased from *Solvionic* (Toulouse, France). A careful degassing procedure (under reduced pressure $P = 3.5 \cdot 10^{-2}$ mbar, heating at 60° for 2 h, then no heating, still under depression for 1 h to allow the sample to warm to r.t.) allowed for a perfect control of the amount of H₂O remaining in the IL solvent, which was measured by *Karl–Fischer* titration (the final value is the average of the measurement of 5 aliquots, with a global uncertainty of ± 2%) and led to the value $2.4 \cdot 10^{-3}$ M (30 ppm) for the solvent used to prepare all the solns. of this work. Ultra-pure H₂O from *Milli-Q* was used to adjust the total H₂O amount to the desired quantity (from 0 to 8000 ppm). For the H₂O-saturated sample, ultra-pure H₂O (3 ml) was contacted with C₄-mimTf₂N (5 ml) and mechanically shaken for 6 h. Then, the IL phase was separated and used immediately.

2.2. *Synthesis of the Eu³⁺ Salt.* The synthesis procedure was adapted from the work of *Nockemann* and co-workers [7]. First, HTf₂N was prepared as follows: LiTf₂N (5 g) was dissolved in H₂O (40 ml), and 0.01M H₂SO₄/H₂O (10 ml) was added. Five successive extractions were therefore performed with Et₂O (60 ml), and then the org. phase was washed with H₂O (5 × 10 ml). The remaining phase was then dried under reduced pressure ($P = 3.5 \cdot 10^{-2}$ mbar): HTf₂N, a transparent highly hygroscopic liquid. Subsequently, 1 g of europium oxide (Eu₂O₃) was dissolved in HTf₂N (1.5 ml). The remaining H₂O and HTf₂N were evaporated ($P = 3.5 \cdot 10^{-2}$ mbar) to yield Eu(Tf₂N)₃ · x H₂O as a highly hygroscopic pale brownish-pink solid. The remaining H₂O amount of the salt was measured by *Karl–Fischer* titration, leading to the average formula Eu(Tf₂N)₃ · 2.2 H₂O. As a consequence, a 10⁻² M soln. of the Eu³⁺ salt in C₄-mimTf₂N corresponds to an additional H₂O amount of $2.2 \cdot 10^{-2}$ M (280 ppm).

2.3. *Samples.* Solns. were directly prepared in quartz cuvettes. Approximately 30 mg of the europium salt were added to dry C₄-mimTf₂N (3 ml), and the required amount of H₂O was poured in the cuvette, immediately closed with a *Teflon* cap. Dissolution of the salt, which was achieved by mechanical shaking, could last up to 30 min in dry C₄-mimTf₂N (no added H₂O). Solns. were kept in the cuvettes until the end of all measurements (IR, UV/VIS, and TRLFS). Samples were then sacrificed to check the H₂O amount by *Karl–Fischer* titration. To study the salt itself, it was introduced in a quartz cuvette (1 mm thickness) and capped under dry atmosphere in a glove box. Nevertheless, some hydration of the salt could not be avoided, owing to the time required to fill the cuvette. Some samples were prepared in triplicate, to estimate reproducibility, which appeared to be very good.

2.4. *Measurements and Data Treatment.* IR Spectra (*Bruker*) were recorded for all the samples in the range 4500–8000 cm^{-1} at different irradiation stages. Similarly, UV/VIS absorption and transmission spectra (*Cary 100, Varian*) were recorded in the range 200–800 nm at various irradiation stages. The TRLFS setup consisted of a Nd:YAG laser, (10 Hz, 6 ns pulse duration, quadrupled; *Spectra Physics, GCR-11*) from which the 266 nm wavelength (5 mW) was selected to excite the samples in a thermoregulated sample holder ($T 21 \pm 0.5^\circ$). Luminescence at a given wavelength was collected towards a monochromator (*Jobin Yvon*) through a lense and directed into a photomultiplier (*PM XP 2054B; Philips*) connected to a fast oscilloscope (*Tektronik, TDS 3052*). To improve the signal/noise ratio, the PM signal was averaged over 512 laser pulses (total acquisition duration, including averaging and data storage: 52 s) to give an individual TRLFS plot, as a decay spectrum recorded at a dedicated emission wavelength. Data were not corrected for the light efficiency of the setup. The decay spectra were analyzed by use of a Fortran routine based on least-square minimization (CERN libraries). The quality of the fit was also assessed through the shape of the residuals (experimental minus calculated counts for each channel), allowing for a better determination of the mono- or multi-exponential decay feature of the spectra. In the case of bi-exponential analysis, the luminescence intensities I_1 and I_2 associated to τ_1 and τ_2 were expressed as a percentage of the total spectrum intensity ($I_1 + I_2 = 100\%$). All lifetime and intensity values in this work are the average of five decay spectra, and the uncertainty on lifetime values is $\pm 3\%$, while it is $\pm 7\%$ for intensities. Depending on the emission spectra, decay spectra for lifetime analysis were recorded either at 592 nm or 615 nm. By scanning the Eu^{3+} emission range ($\Delta\lambda = 1 \text{ nm}$), series of decay spectra were collected. By summing all counts at a given wavelength, one had access to the global Eu^{3+} emission spectra, and by decomposition of each decay spectrum into the sum of decaying exponentials with associated lifetimes and relative intensities, one has access to the contributions of the various Eu^{3+} luminescent species to the global emission spectrum. For the range 585–625 nm, the total acquisition time was 36 min. The entire TRLFS setup (monochromator wavelength scan, data acquisition, averages and storage) was controlled by a *Labview* application on a PC. Data were expressed as lifetime values, emission spectra, and R , the ratio of the intensities of the two luminescent bands of Eu^{3+} , calculated at the maximum of emission in the two ranges 610–620 nm and 587–597 nm. For samples prepared in triplicate, the reproducibility on R was better than 10%. By use of this system, the maximum dose rate delivered to the sample was equal to 1.17 Gy s^{-1} so that one lifetime determination (by average of 5 individual decays) corresponded to 304 Gy, while an emission scan amounted to 2.53 kGy, supposing that all the laser energy was absorbed by the sample, which was checked not to be the case for any of the soln. of this study.

Some lifetime determinations were performed through europium excitation ($\lambda_{\text{exc}} 394 \text{ nm}$), on a *PTI Technology* apparatus (pulsed xenon lamp, 200 shots per points, 400 points for the decay, delay from 100 to 1500 μs). In this case, no radiolytic degradation of the sample must be considered.

3. Results and Discussion. – 3.1. *IR and UV Data.* Table 1 summarizes the chemical characteristics of all the samples of this work. The total H_2O amount, $[\text{H}_2\text{O}]_{\text{tot}}$ (calculated), also accounted for the low H_2O amount arising from the incomplete drying procedure of the $\text{C}_4\text{-mimTf}_2\text{N}$ solvent used in this work (see *Sect. 2.1*). For all samples, IR spectra were recorded right after sample preparation, from time to time during the course of this work, and just before *Karl–Fischer* titration. Typical IR spectra are displayed in *Fig. 1*. The general feature of the IR absorbance in the range 5500–6500 cm^{-1} was in agreement with previously published data devoted to various ILs containing the $\text{C}_4\text{-mim}^+$ cation [8][9], while the peak in the range 5000–5500 cm^{-1} was characteristic of the H_2O present in the sample [8]. No significant difference in the IR spectra could be observed as a function of irradiation dose for any of the samples, demonstrating that the samples did not absorb additional H_2O during the course of the work (H_2O -proof quartz cuvettes and cap). The plots of the peak surface (integral from 5356 cm^{-1} to 5385 cm^{-1} or from 5400 cm^{-1} to 4960 cm^{-1}) as a function of the total H_2O

Table 1. Chemical Characteristics of the Samples of this Study

Sample	[Eu] [mM]	[H ₂ O] from the salt [mM/ppm]	[H ₂ O] added [m/ppm]	[H ₂ O] _{tot} [m/ppm]	[Eu]/[H ₂ O] _{tot}
1	9.9	21.8/276	0/0	0.024/306	1: 2.4
2	10.2	22.4/284	0.016/202	0.041/516	1: 4
3	9.4	20.7/262	0.040/504	0.0628/796	1: 6.7
4	9.6	21.1/267	0.080/1009	0.103/1306	1: 11
5	9.6	21.1/267	0.185/2347	0.208/2644	1: 22
6	9.5	20.9/265	0.635/8050	0.658/8345	1: 69
7	9.7	21.3/270	saturation	0.940/11920	1: 97

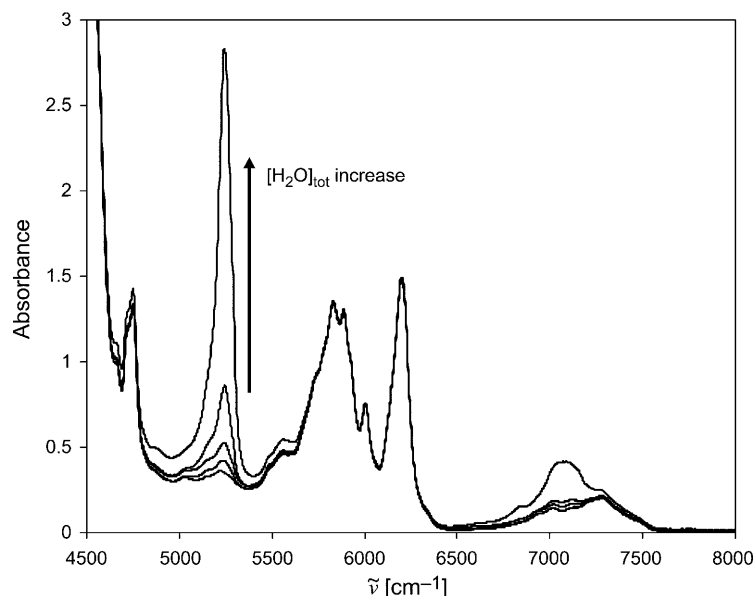


Fig. 1. IR Spectra prior to irradiation for some of the samples of this work (see text)

amount, either calculated or measured by *Karl–Fischer* titration, were linear (linear regression coefficients above 0.996). This demonstrates that the IR data were representative of the *total* amount of H₂O present in the sample, either brought by the Eu³⁺ salt, the solvent itself, or by the human operator, and whatever its solvation state (bulk H₂O or complexed to Eu³⁺). In other words, IR measurements give access to the total H₂O amount (nondestructive experiment), either free in the bulk or complexed to Eu³⁺. Finally, the value of the molar absorbance of the OH transition at 5211 cm⁻¹ (1919 nm) was equal to 1.37 M⁻¹ cm⁻¹, in line with the data provided by *Tran* and co-workers [8][9]. Some of the UV/VIS absorption spectra recorded are plotted in *Fig. 2*. As compared to a H₂O-saturated sample of C₄-mimTf₂N (no Eu added), the effect of laser irradiation was visible, in agreement with a previous publication [5], in the range ca. 320–400 nm, with the rise of a large peak. By the end of laser irradiation, some of the samples had become pale yellow.

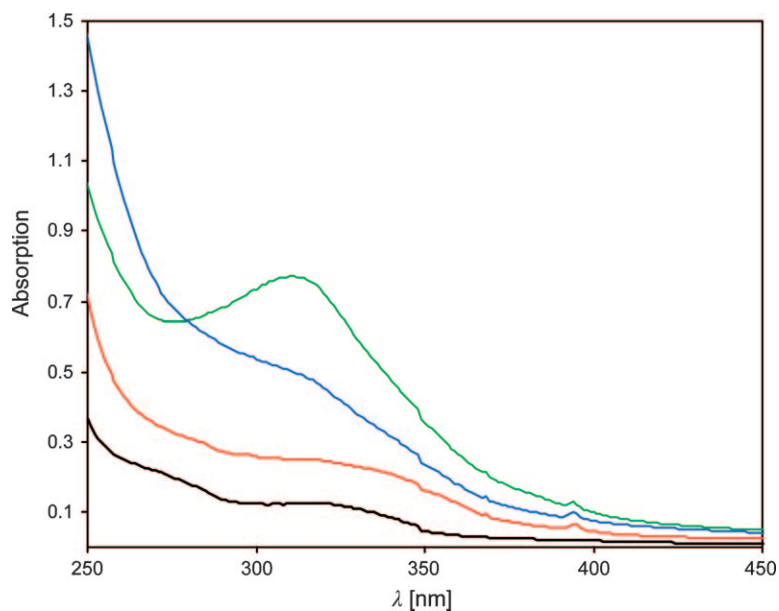


Fig. 2. *Absorption spectra.* Black line: H₂O-saturated C₄-mimTf₂N (no Eu added). Red line: 8000 ppm H₂O, irradiation time 370 min. Blue line: 516 ppm H₂O, irradiation time 254 min. Green line: 1300 ppm H₂O, irradiation time 284 min.

3.2. TRLFS Data. By using Eu(Tf₂N)₃ · 2.2 H₂O as the europium salt, it was possible to restrain the number of spectator species in the solutions to a minimum. No additional anions were introduced in the medium together with the europium cation and Eu^{III} has to be considered as formally dissociated in the solution so that prior to irradiation, besides Tf₂N⁻ anions, the only complexing moieties is H₂O. In a first step, we will focus on the interpretation of the TRLFS data obtained for the very first irradiation sequence (lifetime determination and emission scan) for all samples. Note that *Sample 2* was prepared in duplicate, and the τ and R values were also measured by excitation at λ 394 nm with a pulsed xenon lamp (see *Sect. 2.4*) prior to any laser irradiation, and the values derived with both detection systems agreed perfectly (see *Table 2*).

Fig. 3 presents the first emission spectra recorded for the various samples, together with the emission spectra of the salt, for comparison purposes. For all samples, the intensity of the band ⁷F₁ was normalized at λ 592 nm. In agreement with previous works, the europium emission in C₄-mimTf₂N presented the two strong emissive bands of the transition series ⁵D₀ → ⁷F₁, peaking at λ ca. 592 nm (⁷F₁) and λ 615 nm (⁷F₂, hypersensitive). *Table 2* gathers the values of the ratio R derived from this first emission scan. As is clearly seen, the total amount of H₂O had a tremendous influence onto the intensity of the hypersensitive band ⁷F₂ as R was increasing as [H₂O]_{tot} was decreasing. The value for the salt was almost equal to that obtained in the sample with the lowest H₂O amount. For 8000 ppm of H₂O, R was significant different from 0.3, a value characteristic of free Eu³⁺ in bulk H₂O (denoted as Eu_{3q}³⁺ thereafter) [10][11], although the total amount of H₂O largely exceeded the usual 1:9 ratio of the first Eu

Table 2. *TRLFS Characteristics of the Samples of this Study*

Sample	[H ₂ O] _{tot} [ppm]	τ [μ s]	R	τ_1 [μ s] ^{a)}	τ_2 [μ s] ^{b)}
Salt	–	245.1	2.51	m.e. ^{c)}	m.e. ^{c)}
1	306	245.0	3.04	234.4	582.6
		109.7 ^{d)}		n.a. ^{e)}	n.a. ^{e)}
2	516	182.5	2.28	176.5	529.0
		177.8 ^{f)}	2.14 ^{f)}	172.8 ^{f)}	
3	796	157.4	1.92	144.2	494.7
4	1306	120.6	1.29	114.4	344.3
5	2644	112.2	0.86	m.e. ^{c)}	m.e. ^{c)}
6	8345	102.7	0.48	m.e. ^{c)}	m.e. ^{c)}
7	11920	103.3	0.43	m.e. ^{c)}	m.e. ^{c)}
		99.0 ^{f)}	0.45 ^{f)}	m.e. ^{f)}	m.e. ^{f)}

^{a)} Average of all bi-exponential analysis. ^{b)} Plateau value. ^{c)} m.e.: mono-exponential decay. ^{d)} After addition of H₂O (see text). ^{e)} n.a.: not available. ^{f)} As derived through λ_{exc} 394 nm.

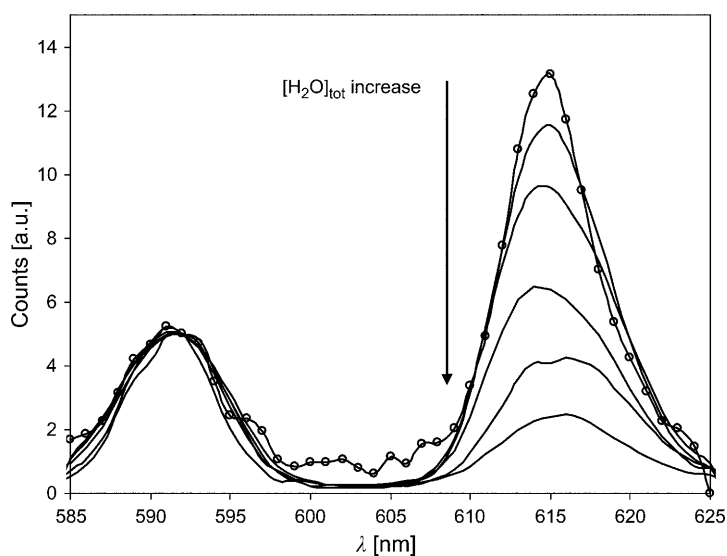


Fig. 3. Emission spectra of some of the samples of this work, first irradiation sequence (solid lines); emission spectra of the Eu³⁺ salt (dots). Normalization was performed at λ 592 nm (see text).

coordination sphere in bulk H₂O [12][13]. For the very first lifetime measurements, all the acquired decay spectra could be satisfactorily fitted with a mono-exponential function, the lifetime values of which are given in Table 2 as τ in μ s. Again, the total H₂O amount appeared to influence the τ values. By contrast to the R variation, from 12000 ppm to 2600 ppm, all samples displayed a somehow constant lifetime, very close to the value τ 110 μ s, representative of Eu_{aq}³⁺ [14][15]. Below 2600 ppm of added H₂O, however, the τ value was significantly larger than 110 μ s, and the lifetime for the salt was in very good agreement with the lifetime of the driest sample. Comparing the R and

τ variations as a function of $[\text{H}_2\text{O}]_{\text{tot}}$, it should be concluded that R is more sensitive than τ to the Eu^{3+} environment. Generally speaking, these results were in agreement with those presented in a recent publication dealing with Eu^{3+} luminescence in various ILs [16] amongst which $\text{C}_4\text{-mimTf}_2\text{N}$, although we investigated a slightly different range of $\text{Eu}^{3+}/\text{H}_2\text{O}$ ratios than in the cited paper (from 2.4 to *ca.* 97 H_2O molecules per Eu^{3+} unit in our case, to be compared to 2.3 to 23 H_2O molecules per Eu^{3+} unit [16]). In particular, our data led to the sigmoid-shaped curves obtained by *Nagaiishi* and co-workers for the $1/\tau$ vs. $[\text{H}_2\text{O}]_{\text{tot}}$ and for the $1/\tau$ vs R variations (data not shown). However, our observed range of R values was slightly different than theirs for the same IL (0.4 to 3.0 in our case and 0.6 to 3.5 [16]). Such small differences can most probably be attributed to a higher maximum H_2O content in our case for the $R = 0.43$ value but can not be related to a change in IL chemical structure for the $R = 3.0$ value. A rough estimation of the coordination environment of Eu^{III} was performed following the empirical method proposed by *Ozaki* and co-workers [17]. Although questionable on a fundamental perspective [18], the empirical formulation used in this approach, when applied to our data, indicated that above 2000 ppm of added H_2O , Eu^{3+} had to be considered as heavily hydrated. However, such a classification and, in particular, the *Horrocks'* law [19] behind this appear somehow restrictive in the case of our data: Samples containing from 12000 ppm to 2600 ppm of total H_2O displayed lifetimes leading to a number of coordinated H_2O molecules ranging from 9.4 to 9.9 (with an error bar on the *Horrocks'* law estimated to be equal to 0.5), while the R value varied from 0.4 to 0.9. Such an R variation is significant and it is well-known [12] that low R values correspond to a very symmetric coordination environment, while high R values are indicative of a highly nonsymmetrical Eu^{3+} environment. Therefore, this would imply that although Eu^{3+} is coordinated to 9 H_2O molecules ($\tau \approx 110 \mu\text{s}$), depending on the total amount of H_2O in the samples, its environment may vary from almost symmetric as in bulk H_2O ($R = 0.43$) to somehow nonsymmetric ($R = 0.9$). In turn, this would indicate that R is sensitive to at least two coordination spheres, while the *Horrocks'* law only gives an insight onto the first coordination sphere.

The mono-exponential behavior of the decays, the lifetime values, and features of the emission spectra obtained in the present work differed from the values previously published by our group [20–22], that were obtained for a rather different experimental procedure. First, in all the three previous publications, we have used the europium triflate salt $\text{Eu}(\text{OTf})_3 \cdot 4 \text{H}_2\text{O}$ [20]. Second, the solutions have been dried *after* introduction of the europium salt so that both the latter and the solvent were dried together, leading to a total amount of remaining H_2O (as measured by *Karl–Fischer* titration and/or IR) of less than 50 ppm. As a consequence of these differences, in our previous publications, the global emission spectrum of Eu^{3+} has been composed of two bands peaking at 588 nm and 610 nm, as compared to the present values of 592 nm and 615 nm and the decays have been bi-exponential, with the values $\tau_1 = 2.5 \text{ ms}$ and $\tau_2 = 1 \text{ ms}$, which were ascribed to Eu^{3+} surrounded by one or zero H_2O molecules and at least one triflate anion [21][22], a situation very different from that of the present study.

We now turn to the sample evolution as evidenced by TRLFS following increasing irradiation times. The samples can be divided in two distinct categories: *i*) high H_2O amounts ($2600 \leq [\text{H}_2\text{O}]_{\text{tot}} \leq 12000 \text{ ppm}$), and *ii*) limited amounts ($[\text{H}_2\text{O}]_{\text{tot}} <$

2600 ppm). For the three samples with the highest H₂O contents, no evolution in τ and R could be observed as the irradiation time increased (up to 4 h), with the R and τ values being constant within uncertainty at the values displayed in *Table 2*. By contrast, the samples with less than 2600 ppm of H₂O displayed a significant evolution of the decay features so that after *ca.* 60 min of laser irradiation, a second europium species was present in the solutions, as the decay spectra could not be reasonably fitted with a mono-exponential function and required a bi-exponential function to be satisfactorily fitted. For some of these spectra, 3-exponential fittings were attempted but did not lead to convincing results (no significant χ^2 improvement, none of the lifetimes in line with that found for the first irradiation sequence) so that this approach was not considered further in this work. *Fig. 4* displays the values of the derived lifetimes based on a mono- or a bi-exponential analysis (either τ or τ_1 and τ_2) as a function of the irradiation time (in min) for some of the samples of this work. Above 300 min of irradiation, the second lifetime τ_2 reached a plateau so that the average of all τ_2 values above 300 min and average of all τ_1 values are listed in *Table 2*. The intensity I_1 associated to τ_1 decreased slightly as the irradiation time increased, to finally reach a plateau value (63% for 800 ppm of H₂O and 71% for 516 ppm). To demonstrate that this second lifetime did not arise from some setup artefact, two samples were also measured (lifetime and emission) by use of a different excitation system for which no radiolysis of the solution was expected (see *Sect. 2.4*). First, *Sample 7* (H₂O-saturated) was examined for an irradiation time of 580 min. Second, a duplicate of *Sample 2* ([H₂O]_{tot} = 516 ppm) was measured prior to any irradiation and after 60 min of laser irradiation. Decay features (mono-exponential for *Sample 7*, bi-exponential for *Sample 2*) and all derived values

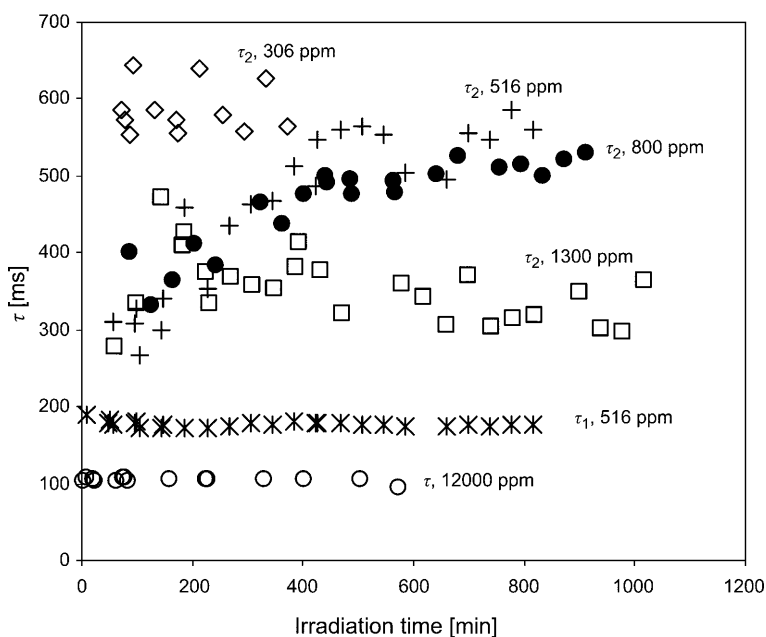


Fig. 4. Lifetime values as a function of irradiation time for some of the samples of this work (see text)

agreed, independent of the setup used (see *Table 2*; for *Sample 2* and an irradiation time of 60 min, $\tau_2 = 312.0 \mu\text{s}$ (Xe lamp) and $\tau_2 = 306.9 \mu\text{s}$ (laser)). It can, therefore, be concluded that the bi-exponential behavior observed was a consequence of laser irradiation and that the H_2O amount of the samples had an effect onto the presence of this new europium species.

To get a deeper insight into the luminescence characteristics of this second component, the emission spectra of the samples displaying two lifetimes were decomposed into their two contributions. Although such an analysis is difficult to perform in the range 598–610 nm because the overall luminescence was very low, it could nevertheless be achieved successfully. For a given sample, all emission spectra recorded were decomposed independently to give access to the individual emission spectra associated to τ_1 and I_1 and to τ_2 and I_2 . The shape of these individual spectra appeared to be independent of the irradiation time, which is in agreement with the fact that the overall R value did not vary with laser irradiation. Therefore, all individual emission spectra of a given sample were averaged to smooth the values in the range 598–610 nm, and the results are presented in *Fig. 5* (the emission spectra were normalized at λ 592 nm for the sake of comparison). For both samples, the emission spectra associated to τ_1 were peaking at 592 and 615 nm and represented the major part of the total emission spectra displayed in *Fig. 3*. The relative intensity of the band at 615 nm depended on $[\text{H}_2\text{O}]_{\text{tot}}$, in agreement with the data of *Table 2*. By contrast, the emission spectra associated to τ_2 were peaking at 592 and 613 nm and were almost identical for the two samples investigated, speaking in favor of a common chemical structure in both samples.

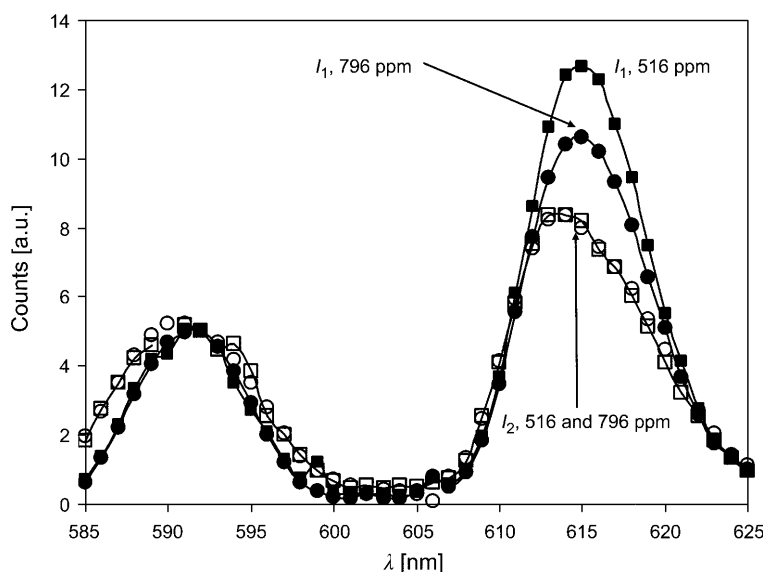


Fig. 5. Individual emission spectra obtained by decomposition for samples at 516 and 796 ppm (see text). All spectra were normalized at λ 592 nm.

Finally, *Sample 1* (no H₂O added) was chosen to better define the role of H₂O onto the presence of the second luminescent component. After an irradiation time of *ca.* 400 min, necessary for the unambiguous appearance of τ_2 and I_2 (see *Fig. 4*), associated to a yellowish color, H₂O was added to the sample to reach $[\text{H}_2\text{O}]_{\text{tot}} = 8000$ ppm. The lifetime decay then measured was a mono-exponential one, with lifetime $\tau = 109.7$ μs and $R = 0.55$, in close agreement with the results for *Sample 6*.

3.3. Discussion. Although very stable to radiolysis, as pointed by previous authors, ILs in general and C₄-mimTf₂N in particular suffer from radiolysis processes, so that various stable radiolytic products are formed upon C₄-mimTf₂N laser irradiation. At least some of these products react with Eu^{III} to form (possibly numerous) additional luminescent species, all together detected as one lifetime (τ_2) of associated intensity I_2 . Actually, although a three-exponential decay analysis was not convincing, this is not the proof that only one single additional Eu³⁺ species was formed upon irradiation. It has been shown [23] that in the case of fast excited-state chemistry, lifetimes merge so that the second component, characterized by τ_2 and I_2 and an individual spectrum as displayed in *Fig. 5* might well be the intricate weighted average of various species in fast equilibrium in the excited state. Previous works devoted to the detection and chemical analysis of the radiolytic products of ILs composed of C₄-mim⁺ and/or Tf₂N⁻ have used γ irradiation (⁶⁰Co source) to deliver increasing irradiation doses [5][6]. To detect and characterize radiolysis products by either NMR or ESI mass spectrometry, requested minimum doses were in the range of 450 kGy [5]. This value has to be compared to the dose that was delivered to the driest samples for the minimum irradiation time needed in our experiments to observe the complexation of Eu³⁺ with some of the radiolytic products: 60 min of laser irradiation corresponds to a maximum dose of 4.2 kGy. However, as noted above, this is just an overestimation of the actual dose absorbed by the samples, as their transmission at 266 nm was in the range of 20–60%, depending on the H₂O amount and on the appearance of the yellowish degradation products. Obviously, samples containing large amounts of H₂O were less sensitive to UV radiation because part of the sample was composed of H₂O (12000 ppm correspond to *ca.* 0.95M of H₂O), which does not absorb significantly the 266 nm excitation light. Nevertheless, our data show that radiolysis products, even formed in such low amounts that they could not be detected by classical analytical means do react with Eu³⁺ and could be easily evidenced by TRLFS. Large amounts of H₂O (*i.e.*, > 2600 ppm in our experiments) do not hamper the formation of radiolytic products, as shown by other works [5] but have a competitive impact onto the Eu³⁺ coordination sphere, as clearly demonstrated by the addition of H₂O in our driest sample. This in turn confirms the explanation about the stability of samples prepared by use of the europium triflate salt: triflate is a more efficient ligand than Tf₂N⁻ so that the europium salt remains nondissociated in ILs solutions, even in the absence of H₂O, therefore preventing reaction with the radiolysis products and their subsequent detection by TRLFS.

4. Conclusions. – The reactivity of stable degradation products of C₄-mimTf₂N with Eu^{III} were evidenced for very low doses for which no analytical technique is available. The luminescent species they formed with Eu³⁺ were characterized by TRLFS (overall lifetime, relative intensity, and emission spectrum). These results point to the very high

reactivity of such species, which are nevertheless less complexing than H₂O and usually ‘noncomplexing’ anions such as triflate, provided these are present in sufficient quantities to successfully compete with radiolytic moieties. The question remains of the possible reactivity of such radiolytically stable products with other species, such as neutral extracting moieties used for nuclear reprocessing.

The help of Dr. L. Charbonnière for the measurements by use of a Xe lamp is greatly acknowledged. This work has been performed with the financial support of the Groupement national de recherche ‘PARIS’.

REFERENCES

- [1] T. Welton, *Chem. Rev.* **1999**, *99*, 2071.
- [2] P. Wasserscheid, T. Welton, ‘Ionic Liquids in Synthesis’, Wiley-VCH, Weinheim, 2003.
- [3] H. Ohno, ‘Electrochemical Aspects of Ionic Liquids’, John Wiley & Sons, Inc., Hoboken, NJ, 2005.
- [4] D. Allen, G. Baston, A. E. Bradley, T. Gorman, A. Haile, I. Hamblett, J. E. Hatter, M. J. F. Healey, B. Hodgson, R. Lewin, K. V. Lovell, B. Newton, W. R. Pitner, D. W. Rooney, D. Sanders, K. R. Seddon, H. E. Sims, R. C. Thied, *Green Chem.* **2002**, 152.
- [5] L. Berthon, S. I. Nikitenko, I. Bisel, C. Berthon, M. Faucon, B. Saucerotte, N. Zorz, P. Moisy, *Dalton Trans.* **2006**, 2526.
- [6] É. Bossé, L. Berthon, N. Zorz, J. Monget, C. Berthon, I. Bisel, S. Legand, P. Moisy, *Dalton Trans.* **2008**, 924.
- [7] P. Nockemann, K. Servaes, R. Van Deun, K. Van Hecke, L. Van Meervelt, K. Binnemans, C. Görrler-Walrand, *Inorg. Chem.* **2007**, *46*, 11335.
- [8] C. D. Tran, S. H. De Paoli Lacerda, D. Oliveira, *Appl. Spectrosc.* **2003**, *57*, 152.
- [9] C. D. Tran, S. H. De Paoli Lacerda, *Anal. Chem.* **2002**, *74*, 5337.
- [10] S. Lis, S. But, *J. Alloys Comp.* **2000**, *300–301*, 370.
- [11] T. Vercouter, B. Amekraz, C. Moulin, E. Giffaut, P. Vitorge, *Inorg. Chem.* **2005**, *44*, 7570.
- [12] J.-C. G. Bünzli, R. G. Choppin, ‘Lanthanide Probes in Life, Chemical and Earth Sciences: Theory and Practice’, Elsevier, Amsterdam, 1989.
- [13] Y. Takahashi, T. Kimura, Y. Kato, Y. Minai, Y. Makide, T. Tominaga, *J. Radioanal. Nucl. Chem.* **1999**, *239*, 335.
- [14] S. Lis, T. Kimura, Z. Yoshida, *J. Alloys Comp.* **2001**, *323–324*, 125.
- [15] C. Moulin, J. Wei, P. Van Iseghem, I. Laszak, G. Plancque, V. Moulin, *Anal. Chim. Acta* **1999**, *296*, 253.
- [16] R. Nagaishi, M. Arisaka, T. Kimura, Y. Kitatsuji, *J. Alloys Compd.* **2007**, *431*, 221.
- [17] T. Ozaki, M. Arisaka, T. Kimura, J. A. Francis, Z. Yoshida, *Anal. Bioanal. Chem.* **2002**, *431*, 1101.
- [18] I. Billard, ‘Lanthanide and Actinide Solution Chemistry as Studied by Time-Resolved Emission Spectroscopy’, in ‘Handbook on the Physics and Chemistry of Rare Earths’, Eds. A. K. Gschneider, J.-C. G. Bünzli, and V. K. Pecharsky, Elsevier, 2003, Vol. 33, p. 465.
- [19] W. De Horrocks Jr., D. R. Sudnick, *J. Am. Chem. Soc.* **1979**, *101*, 334.
- [20] I. Billard, S. Mekki, C. Gaillard, P. Hesemann, G. Moutiers, C. Mariet, A. Labet, J.-C. G. Bünzli, *Eur. J. Inorg. Chem.* **2004**, 1190.
- [21] S. Stumpf, I. Billard, P. J. Panak, S. Mekki, *Dalton Trans.* **2007**, 240.
- [22] S. Stumpf, I. Billard, C. Gaillard, P. J. Panak, K. Dardenne, *Radiochim. Acta* **2008**, *98*, 1.
- [23] I. Billard, K. Lützenkirchen, *Radiochim. Acta* **2003**, *91*, 285.

Received April 24, 2009