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Dario Rodrigues, Gabriela Pabla Sarmiento, Nicolas Ivan Krimer, and Martín Mirenda

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Radioluminescent Ionic Liquids: Designer Materials for Detecting and Quantifying Ionizing Radiation

Dario Rodrigues,[*,†,‡] *Gabriela P. Sarmiento,*[†] *Nicolas I. Krimer,*[†] *and Martin Mirenda*[*,†]

[†]Gerencia Química, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica (CNEA-CONICET), Av. Gral. Paz 1499, B1650KNA San Martín, Buenos Aires, Argentina.

[‡]Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pab. I, C1428EHA, Buenos Aires, Argentina.

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ABSTRACT: A designed radioluminescent ionic liquid (RadIL), composed of a single imidazolium cation and two different fluorescent anions, is presented. The material allows the conversion of the energy released by energetic charged particles into visible

light by radioluminescence. Its capability in detecting and in quantifying alpha and beta particles was proved by its use as a solvent in liquid scintillation counting. A keynote of this performance is that its radioluminescence yield strongly depends on temperature. This feature represents a clear advantage compared with common commercial scintillators composed of organic volatile solvents that cannot be usually heated. The temperature dependence of the radioluminescent material allows the disentangling of the Cherenkov and radioluminescence contributions emerging from samples containing one or more radionuclides. As such, this property can be used for alpha/beta quantification in radionuclide mixtures, following a pre-calibration of the material response to each radionuclide present in the blend. This RadIL represents the first precedent of an innovative family of luminescent ILs to be developed. The rational design of these materials opens interesting possibilities of real-time quantifications of fission products during the reprocessing of spent nuclear fuels.

INTRODUCTION

The last two decades have witnessed a growing interest on the a new class of versatile organic salts normally referred to as ionic liquids (ILs).[1] These designer compounds have been proposed for a manifold of applications in different areas of medicine,[2] electronics,[3] renewable energies,[4,5] lasers[6] and nuclear fuel cycle,[7,8] to cite a few relevant examples. Usually, they are described as *designer compounds*, since their anions and cations can be independently tailored for tuning specific physicochemical properties of interest.[9,10] Due to their low vapor pressures and low flammability, among other peculiar characteristics,[11] they have been proposed as suitable materials for actinide ion extraction[12] and nuclear fuel reprocessing.[13,14] Luminous response to the presence of radioactive material would be a desirable property to quantify the yield of such a reprocessing. As such, the discovery of new scintillation compounds with improved efficiencies represents a continuing challenge.[15]

Six years ago it was reported that pure IL 1-butyl-3-methylimidazolium chloride [$BMIm^+$][Cl^-] IL was able to detect and quantify ionizing radiation by means of Cherenkov counting.[16] More recently, it was showed that the addition of the wavelength-

shifter 1-butyl-3-methylimidazolium 8-hydropyren-trisulfonate [$BMIm^+$][$HPTS^{3-}$] to [$BMIm^+$][Cl^-] enhances the Cherenkov detection efficiency for the most commonly used commercial photomultipliers.[17] In what follows, it is presented here an advanced designed radioluminescent IL (RadIL) that generates luminescence from electronically excited molecular species after being excited by ionizing radiation. This novel material, which combines [$BMIm^+$] as a common cation and [Cl^-], [$HPTS^{3-}$] and tosylate [Tos^-] as anions, represents the first precedent of an innovative family of ILs with interesting applications.

EXPERIMENTAL SECTION

Reagents and synthesis. [$BMIm^+$][Cl^-] was synthesized and purified as described in a previous work.[18] 1-Butyl-3 methylimidazolium 4-toluensulfonate [$BMIm^+$][Tos^-] was obtained from the [$BMIm^+$][Cl^-] and the 4-toluensulfonic acid sodium salt [Na^+][Tos^-] via a metathesis reaction from the exchange between chloride and [Tos^-] anions. [Na^+][Tos^-] was previously obtained from neutralization of an aqueous solution of 4-toluensulfonic acid [H^+][Tos^-] monohydrate (Sigma-Aldrich, purity > 98.5%, used as

received) with an aqueous solution of NaOH (sodium hydroxide, Merk, analytical reagent, used as received) and subsequent evaporation. [Na^+][Tos^-] was added to a solution of [$BMIm^+$][Cl^-] in dichloromethane, in a mole proportion of 1.1:1. The later mixture was left under continuous stirring for seven days at room temperature. The resulting solution was filtered and evaporated under reduced pressure. A metastable colorless viscous liquid was obtained (mp: 63.9 ºC from Differential Scanning Calorimetry, DSC, see Supporting Information). ^{1}H-NMR: (500 MHz, D_2O, δ in ppm) 8.65 (s, 1H), 7.67 (d, 2H, J = 7.4 Hz), 7.42 (d, 1H, J = 1.8 Hz), 7.38 (d, 1H, J = 1.8 Hz), 7.35 (d, 2H, J = 7.4 Hz), 4.14 (t.n.r., 2H), 3.85 (s, 3H), 2.38 (s, 3H), 1.81 (quin, 2H, J = 7.4 Hz), 1.29 (sext, 2H, J = 7.4 Hz), 0.91 (t, 3H, J = 7.4 Hz). (s: singlet; d: doublet, t: triplet, t.n.r.: triplet not resolved, quin: quintuplet, sext: sextuplet). An 1:1 stoichiometric ratio between [$BMIm^+$] and [Tos^-] was estimated from the comparison of the hydrogen's integrated areas of both species. A chloride test using a silver nitrate solution showed negative results.

[$BMIm^+$][$HPTS^{3-}$] was synthesized from [$BMIm^+$][Cl^-] and pyranine (8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt, [Na^+][$HPTS^{3-}$], Aldrich, purity > 97%, used as received) via a metathesis reaction from the exchange between the chloride and [$HPTS^{3-}$] anions. Solid pyranine was added to a solution of [$BMIm^+$][Cl^-] in dichloromethane (Merk, purity >99.9%, used as received) in a mole proportion of 1:2.7. The reaction mixture was left under continuous stirring for seven days at room temperature. The solution was filtered and then evaporated under reduced pressure. A yellow/brown solid was obtained (mp: 136.3 ºC from DSC, see Supporting Information). ^1H -NMR: (500 MHz, D_2O, δ in ppm) 9.03 (s, 1H), 8.95 (d, 1H, J = 9.7 Hz), 8.84 (d, 1H, J = 9.6 Hz), 8.77 (d, 1H, J = 9.7 Hz), 8.53 (d, 1H, J = 9.6 Hz), 8.21 (t.n.r., 1H), 8.17 (s, 1H), 6.96 (t, 1H, J = 1.8 Hz), 6.93 (t, 1H, J = 1.8 Hz), 3.63 (t, 2H, J = 7.4 Hz), 3.56 (s, 3H), 1.37 (quin, 2H, J = 7.4 Hz), 0.96 (sext, 2H, J = 7.4 Hz), 0.64 (t, 3H, J = 7.4 Hz). An 1:3.6 stoichiometric ratio between [$HPTS^{3-}$] and [$BMIm^+$] was estimated by comparing the hydrogen's integrated areas of both species. This revealed a remnant of [Cl^-] anions in the final product, indicating that the metathesis was not complete. Chloride test using a silver nitrate solution showed positive results confirming this issue.

[$BMIm^+$][Cl^-] / [$BMIm^+$][Tos^-] / [$BMIm^+$][$HPTS^{3-}$] mixtures were prepared by addition of weighted amounts of the synthesized compounds. The density of all samples was 1.07 g/mL. The samples were heated at 60 ºC in a water bath, and mixed during 24 hours with magnetic stirring to ensure the complete homogenization. Afterward, mixtures were cooled down to room temperature. The RadIL composition was 2.2×10^{-4} M of [$BMIm^+$][$HPTS^{3-}$] in a mixture of 36%, in mass, of [$BMIm^+$][Cl^-] and 64% of [$BMIm^+$][Tos^-].[19] Mixtures obtained without the [$BMIm^+$][$HPTS^{3-}$] component, will be denoted as [$BMIm^+$]$_2$[Cl^-] [Tos^-] because they present a mole ratio between the two ILs of ~1:1. The exposure of the samples to ambient conditions was extremely minimized. However, an undetermined amount of water was inexorably incorporated to the samples due to their high hygroscopicity. Visual observations indicated that RadIL and [$BMIm^+$]$_2$[Cl^-] [Tos^-] exhibited liquid characteristics in the entire temperature range of interest. The results obtained in the thermal experiments were not sufficiently conclusive to determine whether they are supercooled liquids or mixtures with broad melting points affected by the amount of water present (see Supporting Information for details). A more exhaustive physicochemical characterization of ILs, including X-ray and rheology

techniques, could help to discard phase segregations and understand the fluid behavior of the materials.

Aqueous solutions of $[BMIm^+][Cl^-]$ and $[H^+][Tos^-]$ were prepared for the spectroscopic measurements using deionized water (18 MΩ × cm, obtained from a Milli-Q system). Solutions were kept under darkness for 24 hours before use.

Spectroscopic measurements. Absorption measurements were performed in a Cary 50 Conc UV-vis spectrophotometer (Varian), equipped with a thermostated sample-holder. The bandwidth of the excitation slit was 1.5 nm. Depending on the optical densities of the samples, quartz cells of different optical path-lengths were used. A 0.2 cm optical path was used for the following samples: a blend of 2.2×10^{-4} M of $[BMIm^+][HPTS^{3-}]$ in $[BMIm^+][Cl^-]$, RadIL and diluted aqueous solutions of $[BMIm^+][Cl^-]$ and $[H^+][Tos^-]$. On the other hand, a 10 μm optical path was used for $[BMIm^+]_2[Cl^-][Tos^-]$ and the concentrated aqueous solution of $[H^+][Tos^-]$.

Steady-state fluorescence spectra were recorded in a PTI QuantaMaster 4 CW fluorometer, equipped with a xenon short-arc lamp UXL-75XE and a thermostated

sample-holder. Both excitation and emission monochromators have gratings of 1200 line/mm, in which 1 mm corresponds to a bandwidth of 4 nm. The excitation and emission slits were adjusted to a bandwidth of 1.5 nm. Diluted samples were measured in a right-angle configuration using a quartz cell of 1 cm optical path-length. Concentrated highly absorbing samples were measured in transmission geometry using quartz cells of 0.2 cm and 10 μm optical path-lengths and 1 cm width to minimize inner-filter effects. The optical paths used for the different samples were the same as those mentioned above for absorbance measurements. The commercial spectrofluorometer was adapted to a transmission configuration in which the fluorescence was collected at 180° with respect to the excitation beam.[20] An Asahi™ BP260 filter was interposed between the excitation source and the sample in [Tos^-] fluorescence acquisitions, to minimize any spurious excitation light of higher wavelengths from reaching the sample. A Schott UG11 was used to fulfill this requirement in both [$HPTS^{3-}$] and RadIL determinations. For the last two cases, a Schott WG360 filter was also placed between the sample and the detector to avoid the excitation light from reaching the detector. The blank was subtracted in each spectrum, and the experimental data were properly

corrected using the emission corrective function provided by the manufacturer. All measurements were performed at (20.0 ± 0.1) ºC, except those in which the temperature was the variable of interest.

The fluorescence quantum yield (Φ_F) of $[BMIm^+]_2[Cl^-][Tos^-]$ in water was determined in transmission configuration at 20.0 ± 0.1 ºC relative to a reference, according to the following expression:

$$\Phi_F = \Phi_{F,R} \frac{n^2}{n_R^2} \frac{f_R(\lambda_0)}{f(\lambda_0)} \frac{\int_\lambda L_P(\lambda_0,\lambda)\, d\lambda}{\int_\lambda L_{P,R}(\lambda_0,\lambda)\, d\lambda} \quad (1)$$

where n represents the refraction index, $f(\lambda_0)$ the absorption factor and $L_P(\lambda_0,\lambda)$ the spectral photon irradiance, and the R subscript denotes reference values. A value of 0.059 ± 0.005 was obtained by using a 0.1 M aqueous solution of $[H^+][Tos^-]$ in water as reference (n_D = 1.3323, Φ_F $[H^+][Tos^-]$) = 0.055 ± 0.015). The values of Φ_F at different temperatures were referred to those obtained a 20º. The concentrated reference solution of $[H^+][Tos^-]$ has the same Φ_F as a diluted solution of 1.5 × 10^{-4} M of the same compound, showing no evidence of excimer formation (data not shown). The relative

determination of Φ_F for this diluted sample was obtained by using a solution of 1.6 × 10^{-4} M of toluene (Fluka, puriss. p.a. ACS; > 99.7% CG) in degassed cyclohexane (Merk, Uvasol® for spectroscopy) as reference (nD = 1.4233, Φ_F (toluene/cyclohexane) = 0.14 ± 0.02).[21] In this case, the fluorescence spectra of the diluted samples were acquired in a 90° configuration using a quartz cell of 1 cm optical path.

Refraction indexes measurements. The refractive indexes of samples were measured at 589.3 nm in a thermostated Abbemat 300™ automatic refractometer (Anton Paar).

Thermal analysis. DSC and thermogravimetric analysis (TGA) were carried out with a SDT Q600 V20.9 equipment (TA Instruments). A ramp temperature of 10.00 °C/min was used until reaching 350.00 °C. Endothermic processes were recorded as downward peaks. The samples were dried in a vacuum oven at 100 ° C for about 12 hours and subsequently cooled to -20ºC during a week before use.

Liquid scintillation measurements. Scintillation measurements were performed in a designed home-made system composed of two Burle 8850 photomultiplier tubes arranged at 180 degrees, working in coincidence, at both sides of a thermostated

sample holder. The electronic noise was drastically reduced by only computing events in coincidences within 50 μs temporal windows between the signals generated by both photomultiplier tubes. A few drops (~10-40 μl) of three standardized radioactive aqueous solutions, with a total activity between 5 and 20 kBq, were added into three different standard 5 ml-cylinder glass vials containing 3.2 ml of RadIL (see Supporting Information for details). Two of these sources were prepared using the pure beta emitters ^{14}C and ^{32}P, and the third one with the alpha emitter, ^{241}Am. The maximum energy of the particles emitted by these radionuclides and its Cherenkov threshold energy in ILs are listed in Table 1.

Radionuclide	^{14}C	^{241}Am	^{32}P
Decay	β^-	α	β^-
E_{max}(keV)	~156	~5570	~1711
E_{thr}(keV)	~165	~1.2×10^6	~165
Cherenkov	No	No	Yes

Table 1. Types of decay, maximum energy of the emitted particles and Cherenkov energy threshold in ILs (calculated from n = 1.53) for each radionuclide.

RESULTS AND DISCUSSION

The RadIL components fulfill different functions: a) [Tos^-] anions act as excitation energy harvesters, b) [$BMIm^+$][Cl^-] preclude solidification of the material at the working temperatures and; c) [$HPTS^{3-}$] anions serve as emission wavelength shifters. Figure 1a shows the normalized absorption and fluorescence spectra of the RadIL constitutive ions. The absorption and fluorescence spectra of [$BMIm^+$]$_2$[Cl^-][Tos^-] resembles those of the monomeric species obtained in a diluted aqueous solution of [H^+][Tos^-] (See Supporting Information). Despite the extremely high fluorophore concentration of ~2M in the IL, no aggregates were observed neither in the ground nor in the excited states. The high viscosity combined with the strength of the ionic interactions in the [$BMIm^+$]$_2$[Cl^-][Tos^-] would seem to be sufficient to prevent aggregation. The singular presence of the monomer spectra causes an effective overlap between [Tos^-] emission and [$HPTS^{3-}$] absorption, ensuring a suitable energy transfer in the designed material. The addition of [Tos^-] and [$HPTS^{3-}$] to [$BMIm^+$][Cl^-] causes the blue fluorescence of the

liquid observed in Figure 1b. As such, the composition of RadIL maximizes the emission at 420 nm, which corresponds to the wavelength of maximum cathode sensitivity of many commercial photomultipliers, [22] for standard 5 ml-cylinder scintillation glass vials.

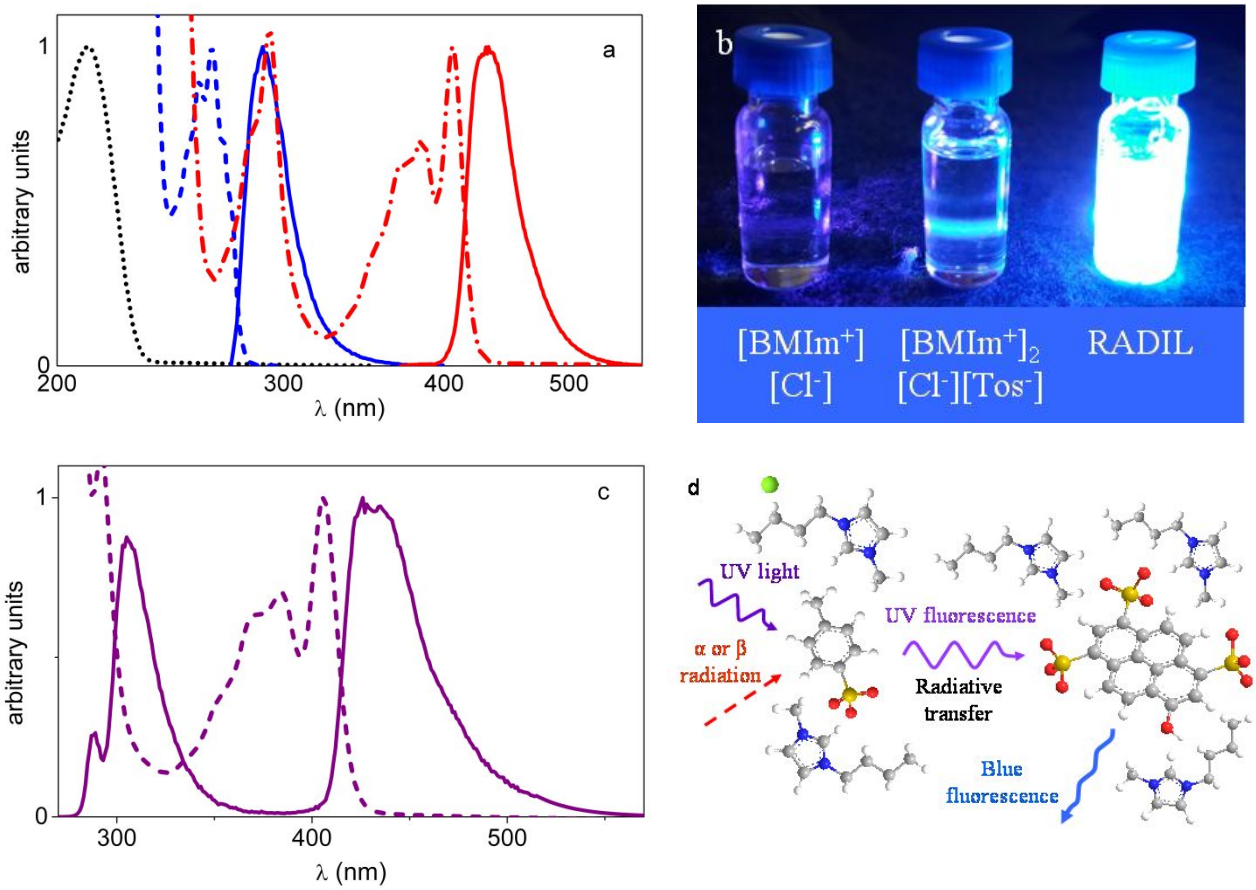

Figure 1. a) Normalized absorption and emission spectra of RadIL constitutive ions: $[BMIm^+][Cl^-]$ in water (dotted black line), $[BMIm^+]_2[Cl^-]$ $[Tos^-]$ (dashed and solid blue lines, by exciting at λ_{exc} = 260 nm) and $[BMIm^+][HPTS^{3-}]$ in $[BMIm^+][Cl^-]$ (dotted-dashed and solid red lines, by exciting at λ_{exc} = 345 nm) ; b) Fluorescence from $[BMIm^+][Cl^-]$, $[BMIm^+]_2[Cl^-]$ $[Tos^-]$ and RadIL, using λ_{exc} = 400 nm. c) Normalized absorption (dashed violet line) and fluorescence (solid violet line) spectra of RadIL, measured in transmission geometry with an optical path-length of 0.2 cm at λ_{exc} = 260 nm. d) Scheme representing the vibronic molecular excitation of $[Tos^-]$ by UV-light or energetic charged particles, followed by radiative energy transfer to the $[HPTS^{3-}]$ and the final emission of blue photons with a maximum around 420 nm.

The absorption and the emission spectra of the RadIL are presented in Figure 1c. Note that both, the fluorescence maximum located at 435nm and the value of 1.9 obtained for the ratio between the maximum absorbance at 406 nm and the first minimum towards the blue at 394 nm, are clear indicators that the polarity of the

surrounding media of [$HPTS^{3-}$] differs from those observed for the same fluorophore in 3M hydrochloric acid aqueous solution.[23]

The scheme presented in Figure 1d depicts the excitation energy transfer mechanisms taking place in the RadIL. Upon vibronic excitation of [Tos^{-}] by the UV-light or by energetic charged particles, the excitation energy is radiatively transferred to [$HPTS^{3-}$] and finally emitted as blue photons, which mostly escape out of the system.

Fluorescence and radioluminescence are not the only phenomena that can be promoted in the RadIL environments. Cherenkov radiation is also generated when charged particles travel faster than the speed of light in that medium. This light can be further re-absorbed by [$HPTS^{3-}$] and finally emitted as blue fluorescence photons as well,[17] contributing to the total signal emerging from the material. Note that the Cherenkov light is actually not included in the current definition of radioluminescence[24] since it originates from neither excited electronic nor vibrational molecular states.[25]

The RadIL capability to convert the energy released by energetic particles into visible light was tested by adding different radionuclide solutions to this material. As such, the

rate of photon bunches emerging from vials containing ^{14}C, ^{241}Am and ^{32}P was determined by liquid scintillation counting (LSC). The main advantage of LSC, in contraposition with other techniques, is its high geometric efficiency since both scintillation and radioactive material are mixed in the same volume. Figure 2 summarizes the results obtained by measuring the counting in temporal coincidence, normalized by the activity, for the three prepared radioactive sources plus a vial with pure RadIL, used as a blank for background determination. All experiments were performed at 20ºC. The figure also includes three results obtained by dissolving ^{14}C, ^{241}Am and ^{32}P in $[BMIm^+][Cl^-]$ plus 2.2×10^{-4} M of $[BMIm^+][HPTS^{3-}]$ as a reference for Cherenkov detection.

Emissions from ^{14}C and ^{241}Am do not yield Cherenkov radiation in the ILs since neither the electrons emitted by ^{14}C nor the alpha particles emitted by ^{241}Am, nor Auger and conversion electrons have enough energy to reach the Cherenkov threshold. In fact, only background signals are obtained for ^{14}C and ^{241}Am in the ILs when $[Tos^-]$ is absent. However, the same radionuclides produce a double coincidence counting

significantly above the background when they are dissolved in the RadIL. Since ^{14}C is a pure beta emitter and there is a negligible probability of photon emission with energies above the threshold energy by ^{241}Am, such an observation can be undoubtedly be attributed to the radioluminescence phenomena. The contribution from direct interaction of X-ray or gamma photons to the photocathode was safely discarded after verifying that the interposing a dark paper in between the vial and the detector reduced the double counting below the background level. On the other hand, the free electrons that could eventually be originated in the RadIL by photoelectric or Compton effects should not exceed the Cherenkov threshold.

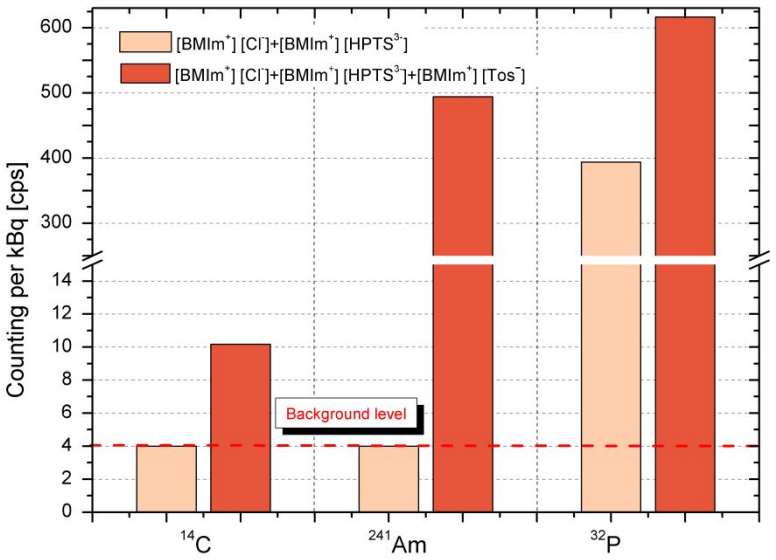

Figure 2. Coincidence counting per kBq of activity obtained in $[BMIm^+][Cl^-]$ + $[BMIm^+][HPTS^{3-}]$ (light yellow bars) and RadIL ($[BMIm^+][Cl^-]$ + $[BMIm^+][HPTS^{3-}]$ + $[BMIm^+][Tos^-]$) (orange bars) for the three radionuclides used in this work. All measurements were performed at 20 Celsius degrees.

Contrasting with the ^{14}C, and the ^{241}Am cases, the electrons emitted by ^{32}P did generate Cherenkov photons in the ILs,[17] since a part of its beta spectrum is above the Cherenkov threshold. Besides, when ^{32}P was dissolved in the RadIL, the double coincidence counting was significantly higher than the one obtained in $[BMIm^+][Cl^-]$ plus 2.2×10^{-4} M of $[BMIm^+][HPTS^{3-}]$. This improvement could be attributed, in principle, to the absorption of Cherenkov light by $[Tos^-]$ ions, followed by a subsequent emission, which enables for $[HPTS^{3-}]$ to shift the luminescence towards the red. However, since

the electrons from ^{14}C do produce radioluminescence, there is no reason why those from ^{32}P – one order of magnitude more energetic on average – would not. Both radionuclides are pure beta emitters, i.e., no other particles except electrons (and the elusive antineutrinos) come out from its nuclei. Hence, as in the former case, this enhancement can also be attributed – at least partially – to the radioluminescence phenomena. As will be shown below, the eventual contribution of the red-shifted Cherenkov emission is not significant compared to radioluminescence.

A keynote of the RadIL radioluminescence is its change in the emission intensity with temperature. The fluorescence of RadIL decreases significantly as the temperature increases, as it is shown in Figure 3a. This behavior can be attributed to the fluorescence quenching of [Tos^-] with temperature. The trend of Φ_F of [$BMIm^+$]$_2$[Cl^-][Tos^-] as a function of temperature depicted in Figure 3b supports this statement. In addition, a similar tendency is observed for the Φ_F of [H^+][Tos^-] in diluted aqueous solution (data not shown). Although the fluorescence intensity of [$HPTS^{3-}$] also changes with temperature, it does in a significantly lesser extent, as it can be seen in

Figure 3c where it is shown the fluorescence spectra of RadIL at different temperatures normalized to 310 nm, the maximum of [Tos^-] emission. Therefore, as mentioned before, all these arguments strongly support that the number of photons radiatively transferred from [Tos^-] to [$HPTS^{3-}$] diminishes with temperature due to the decrease in [Tos^-] fluorescence.

The above-mentioned fluorescence temperature dependence is translated into changes in the detection efficiency (expressed in terms of the experimental double coincidence counts over the activity) when the sources, prepared using RadIL as a solvent, are measured by LCS. We remark that the lower the mean number of radioluminescent photons is, the lower the probability of coincidences. Note that this behavior is incompatible with both Cherenkov radiation and direct interaction of X or gamma photons with the photocathode, reinforcing the argument raised before about the nature of the photons emitted by the RadIL. This feature also constitutes a significant difference compared with all available commercial scintillation cocktails. The organic solvents present in these preparations are volatile and flammable, precluding

the heating of the radioactive sources. On the other hand, the ionic nature of RadIL avoids evaporation losses and flammability risks by warming.

Figure 3d shows the efficiencies of double temporal coincidences in the activity determination of three radioactive sources at different temperatures. As before, the sources were ^{241}Am and ^{32}P, and an extra sample consisting of a mixture of both radionuclides as well. It is observed that the efficiency always decreases as temperature increases, although shows different trends in each particular case.

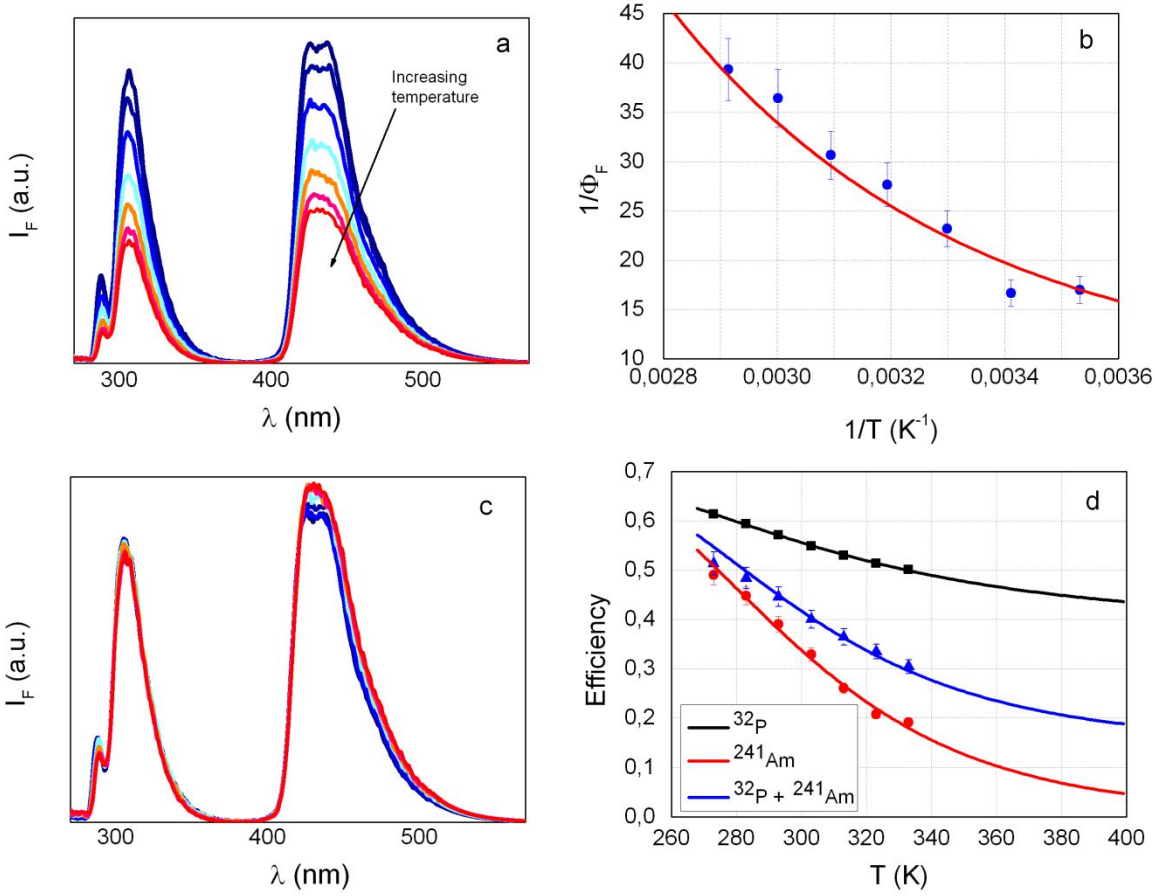
a
Increasing temperature
I_F (a.u.)
300
400
500
λ (nm)
b
$1/\Phi_F$
45
40
35
30
25
20
15
10
0,0028
0,0030
0,0032
0,0034
0,0036
1/T (K^{-1})
c
I_F (a.u.)
300
400
500
λ (nm)
d
Efficiency
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
260
280
300
320
340
360
380
400
T (K)
^{32}P
^{241}Am
^{32}P + ^{241}Am

Figure 3. a) Temperature fluorescence dependence of RadIL, measured at λ_{exc} = 260 nm in transmission geometry with an optical path-length of 0.2 cm; b) temperature dependence of $[BMIm^+]_2[Cl^-][Tos^-]$ fluorescence quantum yield at λ_{exc} = 260 nm; c) Normalized spectra of Item a at 310 nm, the maximum of $[Tos^-]$ emission; and d) Experimental efficiencies of double coincidences for ^{241}Am (red circles), ^{32}P (black squares) and a mixture of both radionuclides (blue triangles) as a function of temperature. The solid lines represent the simulated efficiencies.

A simplified description for the probability of double coincidences produced by an alpha emitter, $\varepsilon_\alpha(\mathrm{T})$, can be achieved by expressing it as a function of the mean number of emitted photons, *m*:

$$\varepsilon_\alpha(\mathrm{T}) = \left[1 - e^{-\nu_\alpha \cdot \mathrm{m}}\right]^2 \quad (2)$$

where ν_α is a parameter that depends on the quantum efficiency of photomultipliers, among many other characteristics of the detection system.[26] The charge, energy and

mass of ionizing particles determine the density of individual molecular excitations and ionizations. The local density of excited and ionized ions created by electrons is lower than those created by alpha particles of the same energy. The scintillation response is then practically proportional to the particle's energy when it is produced by electrons, while being roughly constant when it is produced by alpha particles.[22] Therefore, Equation 2 remains valid – to a good approximation – for alpha particles without adding more information about the decay.

A temperature dependence of the expression in Equation 2 can be obtained if m is written as a function of the same parameters describing the above-mentioned fluorescence temperature behavior of the RadIL (see Supporting Information). The results shown in Fig. 3d reveal that the model reproduces the observed trend for ^{241}Am. In particular, the efficiency diminishes as the temperature is raised and is controlled by the radiative rate-constant (k_{F}) and the temperature independent non-radiative rate-constant (k'^{0}_{nr}) of [Tos$^-$].

On the other hand, compared to the ^{241}Am results, the temperature dependence of the efficiency for ^{32}P looks milder. Although the radioluminescent photons are strongly quenched at such conditions, the Cherenkov radiation still remains present. The refraction index of ILs only suffers very small changes with temperature (See Supporting Information), while the Cherenkov intensity remains fairly constant. As such, the efficiency of double temporal coincidence produced by both radioluminescent and Cherenkov photons after a beta decay, $\varepsilon_{\beta+Ch}(\mathrm{T})$, can be described according to the following expression:

$$\varepsilon_{\beta+Ch}(\mathrm{T}) = \int_0^{\mathrm{E}} \mathrm{N}(\mathrm{E}') \cdot \left(1 - \mathrm{e}^{-\left[\nu_\beta \cdot \mathrm{m}(\mathrm{E}') + \nu_{\mathrm{Ch}} \cdot \mathrm{k}(\mathrm{E}')\right]}\right)^2 \mathrm{dE}' \qquad (3)$$

where E is the energy, $\mathrm{N}(\mathrm{E}')$ is the spectrum of the beta particles, $\mathrm{k}(\mathrm{E}')$ is the number of Cherenkov photons, and ν_β and ν_{Ch} are two fitting adjustable parameters.[27] Note that $\mathrm{m}(\mathrm{E}')$ here is explicitly considered as a function of the energy.

Equation 3 describes satisfactory the observed trend for ^{32}P shown in Figure 3d, when $\mathrm{m}(\mathrm{E}')$ is written as a function of the temperature by using the same parameters

describing the fluorescence temperature behavior of the RadIL (see Supporting Information).

The efficiency of the ^{241}Am and ^{32}P mixture, $\varepsilon_M(\mathrm{T})$, remains intermediate between the efficiency values of the individual radionuclides. Figure 3d shows $\varepsilon_M(\mathrm{T})$ as a function of temperature, obtained by a linear fitting of a combination of the efficiencies of each radionuclide weighted by their activities. As a result, a good agreement between the activities used to adjust the efficiency of the mixture and the activity of each radionuclide separately was found. This example clearly illustrates the use of the RadIL for α/β quantification after pre-calibration of the material response to each radionuclide present in the mixture.

CONCLUSIONS

A radioluminescent IL was successfully synthesized, aiming at representing the starting point in the research of new non-volatile liquids materials for detecting and quantifying ionizing radiation. The RadIL obtained in this work was specially designed to gather different anions to adequately modulate the radiative energy transfer

phenomenon to ensure an effective conversion of the excitation energy into visible emission. The efficiency of the present material is not yet comparable with those from commercial cocktails, but further research in the area is carried out to improve this aspect. The keynote of this material is the temperature dependence of the radioluminescence. This feature was proved to be used for alpha/beta quantification in radionuclide mixtures, following a pre-calibration of the material.

In general, the use of radioluminescent ionic liquids provide several improvements with respect to the commercial cocktails; without begin exhaustive, the following list includes some relevant examples:

a) They provide customized solubilities for radioactive compounds, especially considering that they can be designed with tailored properties. Regarding solubility, they also hold up higher amounts of water compared to many commercial cocktails, which generally form emulsions that hinder scintillation measurements upon the incorporation of minimum contents of aqueous solutions.

b) Secondly, an interesting advantage is the possibility of repeatedly performing heating-cooling cycles without evidencing of evaporation losses or flammability risks. This makes possible to implement a safe temperature control when they are used as solvent for radioactive sources. This property also offers an alternative method for efficiency determination in very accurate and absolute LSC techniques as CIEMAT-NIST[28] and Triple to Double Coincidences Ratio (TDCR), by using the temperature as a quenching parameter.

c) They can also be re-used after removing aqueous solutions residues by simple evaporation in a vacuum oven when short-lived radionuclides are measured. Of course, the great stability of the ILs opens the possibility to implement several techniques based on solvent extraction to separate the radioactive analytes and followed by the recovery and reuse of the material. Their special properties also make this novel material suitable for real-time quantification of the yielding achieved by solvent extraction of lanthanides, actinides, and fission products into IL solutions during nuclear fuel reprocessing. The

research on these interesting and complex areas, with several potential applications, represents a present challenge worth pursuing.

d) They usually have high refractive indexes and therefore lower Cherenkov thresholds compared to water. For instance, for the ^{18}F radionuclide, its implementation yields a 100% enhancement in the detection efficiency.[16]

e) The ionic interactions prevailing in the ILs along with the high viscosity seem to prevent the aggregation of species both in the fundamental and excited states, even at extremely high local chromophore concentrations. In this sense, the proper management of the size of the alkyl substituents could be a suitable tool to modulate the appearance of these species, similarly to what has already been reported for molecular liquids.[29,30] Besides, the adequate selection of the constitutive ions and the tuning of their emission spectra allow the quest for an efficient energy transfer between donors and acceptors to achieve a highlighted fluorescence in the spectral region of interest.

f) Fluorophores incorporated into ILs are generally exposed to lower extents of oxygen quenching compared with organic solvents. This fact improves the quantum efficiency and the optical stability of these liquid materials.[31]

The previous considerations provide clear evidence of a paramount of applications of radioluminescent ionic liquids beyond the detection and quantification of ionizing radiation, especially in those applications in which excitation energy, regardless of its nature, must be efficiently manageable.

ASSOCIATED CONTENT

Supporting Information. A theoretical approach describing the temperature dependence of efficiencies is presented. The refraction index data of RadIL as a function of temperature, the characteristics of the standardized sources, DCS and TGA results, and absorption and fluorescence spectra of $[BMIm^+]_2[Cl^-][Tos^-]$ and $[H^+][Tos^-]$ aqueous solutions are also included. The following file is available free of charge.

RADIL_SI.pdf

AUTHOR INFORMATION

Corresponding Authors

*E-mail: dariorodrigues@cnea.gov.ar; mirenda@cnea.gov.ar

ORCID

Dario Rodrígues: 0000-0002-7952-7168

Gabriela P. Sarmiento: 0000-0001-5945-9359

Nicolás I. Krimer: 0000-0003-0261-827X

Martín Mirenda: 0000-0003-0478-5178

Author Contributions

G.P.S. and N.I.K. synthesized, purified and characterized the ILs. N.I.K. and D.R. performed the fluorescence measurements. D.R. built the home-made scintillation system and carried out the scintillation experiments. D.R. and M.M. performed the analysis of experimental data. M.M. proposed the original idea of ILs as scintillation solvents. D.R. discovered the radioluminescence temperature dependence of RadIL. All

authors contributed to the discussion of the results and writing of the manuscript. D.R. and M.M. are the corresponding authors.

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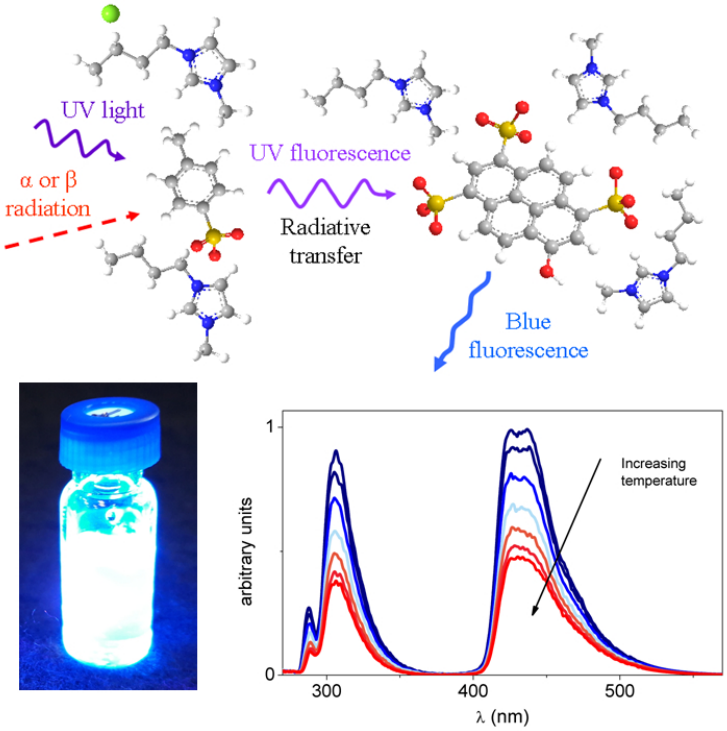

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