Gamma and Heavy ion Radiolysis of Ionic Liquids: A Comparative Study

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Abstract

A variety of imidazolium, quaternary ammonium, and phosphonium cation based ionic liquids were irradiated with γ -rays, 2-15 MeV protons and 5-20 MeV helium ions in order to examine their relative radiation stability and potential hazards for application in advanced nuclear fuel cycles. Molecular hydrogen production can be taken as an overall indicator of radiation stability, and was found to be considerably lower for the γ -irradiated aromatic imidazolium based compounds when compared to the other aliphatic based media. Increasing the length of the aliphatic side chain increases the H₂ yields for all the compounds examined. Little difference is found in the production of H₂ between the quaternary ammonium and phosphonium based ionic liquids with similar length side chains. Yields of H₂ increase substantially from γ -rays to 5 MeV He ions for the imidazolium based ionic liquids, but little variation with radiation type is observed for the quaternary ammonium and phosphonium based ionic liquids. The imidazolium based ionic liquids show a darkening with increasing dose and the UV-visible spectra show an increase in absorption from 240 to 400 nm that is probably due to induced changes in the cation. FTIR spectra show little variation with radiolysis, which is consistent with the low H₂ yields. The formation of a new peak at 1658 cm⁻¹ is attributable to the formation of acyclic disubstituted alkene bonds in the irradiated imidazolium based compounds.

1. Introduction

The only technology deployed on a global scale for reprocessing used nuclear fuel (UNF) is the 60+ year old PUREX process (Plutonium-Uranium Reduction EXtraction). [1, 2] This process and other related technologies are based on the dissolution of UNF into nitric acid solutions, followed by multiple liquid-liquid extraction steps to partition the actinide and various fission product elements. Despite the long history of their use, liquid-liquid extraction processes have some significant shortcomings including the use of organic solvents that can be volatile, toxic, flammable or otherwise unstable towards the radiation and heat generated by self radiolysis. [3-6] Due to these undesirable properties of many conventional organic solvents, ionic liquid-based separation processes are gaining recognition in the nuclear reprocessing industry as possible candidates to replace conventional solvents. [7-13] Ionic liquids (ILs) are attractive alternatives for volatile organic solvents due to the superb tunability of their solvent properties including solute solubility, superior extraction capability and phase separation with other solvents, and their intrinsic wide conductivity range that facilitates electrochemical separations. [14-17] For example, ILs have been shown to protect an extractant (tributylphosphate) from radiolytic damage, whereas the standard kerosene solvent used in the PUREX process (to separate U and Pu) directs damage into the extractant. [18, 19] However, under fuel recycling conditions ILs will be exposed to a wide variety of radioactive fission products that can induce chemical changes to the IL that will hamper the performance of the separation system. [20] Therefore, an understanding of the radiation effects on ILs is essential for their successful use in radiation filled environments. [21-24]

Several research groups have investigated the radiation stability of different hydrophobic ILs using various methodologies. [18, 25-42] An assessment of the radiation effects of α , β and γ

on imidazolium cation based hydrophilic ILs show less than 1 % degradation of the media even when exposed to a dose of 400 kGy, which suggests very high radiation stability for these ILs. [25] Some studies reported changes in the physical properties such as density, viscosity, conductivity, surface tension and refraction index after γ -radiolysis. Pulse electron radiolysis techniques have been used to examine the fast reaction mechanisms and the primary effects of radiation on ILs. [43-47] Shkrob et al. have investigated radical generated species by EPR spectroscopy, showing different degradation pathways for aromatic and aliphatic ILs. [18, 35-42] Degradation pathways have been proposed on the basis of final product identification using spectrometric techniques such as NMR, electrospray ionization mass spectrometry (ESI-MS) and liquid chromatography coupled with ESI-MS. [26, 27] The anion effect on the stability of imidazolium based ILs has been reported using spectrometric techniques. [29] All of these studies suggest that many radiolysis products are formed from ILs, but in small quantities, and that the mechanisms are difficult to quantify. One method to estimate the radiation stability of ILs is by monitoring the production of molecular hydrogen, H_2 , since this species is generally a good indicator of total medium decomposition. Also, from the engineering point of view, the formation of gaseous products such as H_2 is important for the safety and maintenance concerns that might arise with the large scale use of ILs. Basic research will promote improved management of nuclear waste materials and reprocessing technologies employing ILs. A few studies have been reported on the production of H_2 in the γ -radiolysis of ILs. [25, 29, 32, 48] However, no systematic examination of the production of H_2 on the specific type of IL has been performed. Furthermore, used nuclear fuel is primarily composed of uranium along with minor amounts of transuranic fission product elements (e.g. Np, Pu, Am, and Cm), which decay by emitting α particles that have a higher linear energy transfer ($LET = \text{stopping power, } -dE/dx$)

compared to γ -radiation. [20] Final product yields in a given medium can be considerably dependent on the characteristics of the irradiating particle such as its energy, type and LET. All of these parameters can affect the separation processes thru the IL decomposition.

Our earlier studies carried out on 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][Tf₂N] and N-trimethyl-N-butylammonium bis(trifluoromethylsulfonyl)imide [N₁₁₁₄][Tf₂N] showed a strong LET dependence of H₂ in the case of aromatic ILs and little or no effect on aliphatic ILs. [48] The present work extends that effort to include various aromatic and aliphatic quaternary ammonium and phosphonium ILs with different alkyl chain lengths such as [bmim][Tf₂N], [hmim][Tf₂N], [N₂₂₂₆][Tf₂N], [N₂₂₂₈][Tf₂N], [N₁₁₂₍₁₂₎][Tf₂N], [P₂₂₂₆][Tf₂N], [P₂₂₂₈][Tf₂N] and [P₂₂₂₍₁₂₎][Tf₂N] where [bmim], [hmim], [N₂₂₂₆], [N₂₂₂₈], [N₁₁₂₍₁₂₎], [P₂₂₂₆], [P₂₂₂₈] and [P₂₂₂₍₁₂₎] are 1-butyl-3-methylimidazolium, 1-hexyl-3-methylimidazolium, triethylhexylammonium, triethyloctylammonium, dodecyldimethylethylammonium, triethylhexylphosphonium, triethyloctylphosphonium and triethyldodecylphosphonium cation, respectively and [Tf₂N] is the bis(trifluoromethylsulfonyl)imide anion common to all the compounds examined here. A complete list of the compounds examined here is given in Figure 1. Irradiations were performed with γ -rays, 2-15 MeV protons and 5-20 MeV helium ions in order to probe track structure effects. H₂ production was used to determine overall radiation stability. Fourier transform infrared, FTIR, and UV-Visible spectroscopic techniques were used to examine the structural changes of the media occurring in radiolysis.

2. Experimental Section

2.1 Materials

All purified samples of [bmim][Tf₂N], [hmim][Tf₂N], [N₂₂₂₆][Tf₂N], [N₂₂₂₈][Tf₂N], [N₁₁₂₍₁₂₎][Tf₂N], [P₂₂₂₆][Tf₂N], [P₂₂₂₈][Tf₂N] and [P₂₂₂₍₁₂₎][Tf₂N] were obtained from the laboratory of Professor J. F. Brennecke. Water content was determined to be less than 500 ppm in all ILs. Water content was obtained using by the Karl Fischer method using a Metrohm 831 KF Coulometer before irradiation Radiolysis of all compounds was performed under inert atmospheres of ultrahigh purity argon or helium (99.9999%).

2.2 Irradiations

Samples for H₂ analysis and for spectroscopic analysis following radiolysis with γ -rays were placed in Pyrex tubes (diameter $\sim$ 1 cm, length $\sim$ 10 cm), evacuated and flame sealed. Sample weights were typically between 0.5 to 1 g and the γ -radiolysis of the samples was carried out using a self-contained Shepherd 109-68 ⁶⁰Co source at the Radiation Laboratory of the University of Notre Dame. The dose rate was $\sim$ 220 Gy/min as determined using the Fricke dosimeter. [49]

The heavy ion irradiations were performed in purged and vigorously stirred cells using the 10 MeV FN Tandem Van de Graaff accelerator of the University of Notre Dame Nuclear Science Laboratory. The ions used in these experiments were: 2, 5, 10 and 15 MeV ¹H⁺; and 5, 10, 15 and 20 MeV ⁴He²⁺ ions. The window assembly and the radiation procedure are the same as reported earlier. [50, 51] Energy loss of the heavy ions in passing through all the windows was determined from a standard stopping power compilation. [52] The samples were irradiated with completely stripped ions at a charge beam current of about 1.5 nA. Total energy deposition was obtained from the product of the integrated beam current and the ion energy incident to the

sample. The sample cell was made of quartz with a thin mica window of about 5 mg/cm² attached to the front for the beam entrance. The cell had inlet and outlet ports designed for purging the sample before and after irradiation.

2.3 Gas analysis

Gas chromatographic analysis of the H₂ was performed using a SRI 8610 apparatus equipped with a thermal conductivity detector. The chromatographic column was 6.4 mm diameter 13X molecular sieve 3 m long maintained at 40 °C. Argon was used as carrier gas. Following γ -irradiation each sample tube was broken in the sampling port of the gas chromatograph and injected directly onto the column using a four-way valve. An inline technique was employed to determine the H₂ production by heavy ion irradiation where the inlet and outlet of the sample cell were connected to the gas chromatograph by a four-way valve. Calibration was performed by injection of pure H₂ gas under normal conditions. The error in gas measurement is estimated to be about 5%, which includes gas measurement and manipulation.

2.4 Spectroscopic analysis

Infrared transmittance spectra of the ILs were recorded using a Bruker Vertex 70 FTIR spectrometer with a resolution 4 cm⁻¹ and 512 scans in the range of 400 - 4000 cm⁻¹. Irradiated samples were mixed with KBr powder, so that the weight fraction of the ILs was about 10 %. These mixtures were used to make pellets of 2 mm thickness and were then analyzed using the FTIR spectrometer. UV-Vis absorption spectra of the irradiated samples were recorded using an Evolution 220 UV-Visible diode array spectrophotometer. Samples were diluted with acetonitrile before measurements unless otherwise stated. A 2 mm quartz cuvette was used and was thoroughly cleaned with acetonitrile between analyses. Baseline corrections were done using acetonitrile prior to collecting UV-Vis spectra.

3. Results and Discussion

H₂ production

The production of H₂ from liquid hydrocarbons varies from a high of about 5.6 molecules/100 eV (1 molecule/100 eV = 0.104 μmol/J) for cyclohexane to about 0.039 molecules/100 eV for the γ-radiolysis of benzene. [53] Radiation-induced decomposition of aliphatic compounds is mainly initiated by ionization, followed by neutralization to produce excited states that result in the breaking of a C – H bond. H atoms produced in this process either combine or abstract another H atom from the parent molecule to form H₂. The latter process is usually the most dominant because of the relatively high concentration of the medium molecules. The parent radical will combine or disproportionate with other siblings or further decompose to give fragment species. Generally, a wide variety of carbon containing products is formed, which makes a quantitative estimation of the total decomposition difficult unless a huge dose is given and loss of the parent compound is measured. Since the initial decomposition is the breaking of the C – H bond, the total production of H₂ is a relatively good measure of the loss of the parent compound and determination of H₂ yield is straightforward.

Aromatic compounds also decompose by the breakage of a C – H bond, but the H atoms produced in this process readily add to the aromatic ring. This process generally initiates a chain process leading to polymer formation. [54] However, even polymer production in aromatic compounds is relatively small and aromatics are generally considered to be radiation inert. [55] The exact mechanism for the decay of aromatic compounds is still uncertain, but excited states formed by the neutralization reaction then decay to the ground state with little molecular decomposition. [56] An interesting situation arises when a molecule contains both an aromatic component and an aliphatic one. For instance, the addition of a methyl group to benzene to give

toluene results in a slightly higher yield of H₂. [56] ILs are expected to be synthesized and used with a wide combination of aromatic and aliphatic components so an understanding of their different contributions to final products is useful for determination of their overall usefulness and stability.

Our previous γ -radiolysis studies on the production of H₂ from [emim][Tf₂N] and [N₁₁₁₄][Tf₂N] followed the same general trend found with hydrocarbons. [48] The γ -radiolysis yield of H₂ from the aromatic [emim][Tf₂N] was 0.098 molecules/100 eV, which is much smaller than the value of 0.73 for the aliphatic [N₁₁₁₄][Tf₂N]. Increasing the length of added side chains from n-ethyl to n-butyl to n-hexyl gives yields of H₂ of 0.098 to 0.22 to 0.32 molecule/ 100 eV, respectively, as shown in Table 1. The increase in H₂ yield is not linear with the length of the side chain, but an increase in the aliphatic fraction of the cation definitely increases the H₂ yield. Table 1 also shows the γ -radiolysis results for the quaternary ammonium and phosphonium based ILs. In general, the yield of H₂ increases with the more aliphatic nature of the quaternary ammonium and phosphonium based cations over that observed for the aromatic imidazolium based cations. Very little difference is seen in the H₂ yield with gamma radiolysis on substitution of the nitrogen for a phosphorous suggesting that the side chain length dominates H₂ production. An increase in the length of the aliphatic side chain leads to an increase in H₂ yields for both the quaternary ammonium and phosphonium based ILs.

Differences in H₂ yields can be expected with various types of radiation. Increasing the LET of the radiation results in an increase in the local concentration of reactive species within the track made along the path of the incident particle. An increase in reactive species will enhance second order reactions such as radical – radical reactions. On the other hand, first order reactions like radical abstraction reactions will be independent of LET. Since the radiolysis of

aliphatic compounds are mainly characterized by H atom abstraction reactions one would expect the yield of H_2 to remain relatively constant with LET. Of course, there will always be some competition with radical combination reactions so slight variations with LET can be expected. Previous results with $[N_{1114}][Tf_2N]$ showed little variation of H_2 yields from γ -rays up to 5 MeV He ions. Aromatic compounds behave quite differently than aliphatic ones with increasing LET. Studies suggest that the production of H_2 with aromatic compounds is due to second order reactions of high energy excited states. [56] These states are able to react with each other in the high LET track because of their close proximity as compared to that observed with low LET radiation. The increase in H_2 yields can be dramatic with increasing LET for any compound that has an aromatic entity. [57] Figure 2 shows that the aromatic imidazolium based ILs examined here also show a substantial increase in H_2 yield with increasing LET. The aromatic component dominates the yield of H_2 at high LET as opposed to the dependence on length of the side chain in γ -radiolysis. In fact, almost no difference is observed between $[bmim][Tf_2N]$ and $[hmim][Tf_2N]$ for the 5 MeV He ions where there is almost a 50% increase in γ -radiolysis. These compounds cannot be considered to be radiation inert at high LET.

Gamma radiolysis of the quaternary ammonium and phosphonium based ILs show little dependence on the nature of the heteroatom in the cation, but they exhibit an increase in H_2 with increasing chain length of the aliphatic components. The more complete study with the quaternary ammonium based ILs in Figure 3 shows a slight variation in H_2 yields with LET, especially an initial decrease with protons followed by a slight rise with He ions. This decrease can be due to the competition between H atom combination reactions with H atom abstraction reactions. An increase in LET will increase the second order H atom combination reactions, but this process requires two H atoms to give H_2 as opposed to one H atom in the H atom abstraction

reaction. The result is that H₂ yields initially decrease with increasing contribution of H atom combination reactions from increasing the LET. A similar response is observed in cyclohexane radiolysis. [58] Only γ -rays and 5 MeV He ions were used to examine the phosphonium based ILs, but the results of Table 1 show little variation in H₂ yields between γ -rays and 5 MeV He ions. Aliphatic phosphonium ILs behave similarly to aliphatic hydrocarbons in showing little dependence of H₂ yields with LET and they also show an increase in H₂ yields with increasing length of the aliphatic size chain length for both gamma and 5 MeV He ion radiolysis, Table 1. The results for the ammonium based IL's with 5 MeV He ions is different than the results with the other compounds as given in Table 1 in that the H₂ decreases with increasing length of the aliphatic side chains. A rather substantial difference in H₂ yields is observed between the ammonium and the phosphonium based ILs with long aliphatic side chains. Phosphonium based ILs are much more sensitive to 5 MeV He ion irradiation than the ammonium based ILs. The reason for this difference has not been definitively shown, but it is most likely due to the difference in the competition between H atom combination reactions and H atom abstraction reactions within the He ion track.

Spectroscopy

Compared to aliphatic ILs, significant change in the color of the aromatic ILs was observed following γ -irradiation. The dominant color products, based on the structure of the cations, could be mixtures of imidazolium cations containing double bonds, dimers of imidazolium cations, fluorinated imidazolium compounds, etc. Previous work established that the absorption spectrum of irradiated [emim][Tf₂N] shows an increase in absorption in the wavelength region 240 to 400 nm with a shoulder at around 280 nm compared to unirradiated [emim][Tf₂N] [29]. Figures 4 and 5 show the absorption spectra of [bmim][Tf₂N] and

[hmim][Tf₂N] prior to and after γ -irradiation. These spectra were obtained with a dilution factor, DF, of 100 (1 part IL to 100 parts acetonitrile). In both the cases a distinct absorption peak at around 290 nm is observed and a broad shoulder emerges between 350 and 400 nm indicating the formation of new radiolytic products. At a high dilution factor (DF = 2000) unirradiated [bmim][Tf₂N] and [hmim][Tf₂N] both show peaks at 210 nm (Figures 4 and 5, inset). Unirradiated [emim][Tf₂N] has a similar peak at 210 nm. Absorption peaks for neat [bmim][Tf₂N] and [bmim][PF₆] (DF = 0) at 210.5 and 210 nm, respectively, have been reported. [59] The absorption peak at 210 nm can be assigned to a $\pi \rightarrow \pi^*$ transition for the C=C double bond of the imidazolium cation, similar to that observed with imidazole. Little change in the absorption at 210 nm of irradiated aromatic ILs is observed even up to a dose of 1000 kGy. This observation is consistent with that reported by Qi et al., 2008 for γ -irradiated [emim][BF₄]. [30, 31] However, one can see an increase in absorption with dose for the peak around 290 nm with the radiolysis of aromatic ILs indicating that the absorption peak at around 290 nm is due to the imidazolium cations. Also, there is a red shift in the peak with increase in the alkyl chain length from n-butyl to n-hexyl. A similar result was reported by Huang et al., 2011 and Yuan et al., 2009. [34, 60] The absorption spectrum of irradiated [emim][Tf₂N] has a shoulder at around 280 nm, whereas distinct peaks at 284 nm and 288 nm are observed for the irradiated [bmim][Tf₂N] and [hmim][Tf₂N] respectively. [48]

Ammonium and phosphonium based ILs show little change in the color after γ -irradiation to a dose of 1000 kGy. UV-visible spectra of [N₂₂₂₆][Tf₂N], [N₂₂₂₈][Tf₂N], [N₁₁₂₍₁₂₎][Tf₂N] on γ -irradiation with DF = 5 show increases in absorbance in the wavelength region 190 to 400 nm and a shoulder at around 310 nm compared to respective unirradiated ILs. A similar absorption peak at 310 nm has been reported in the case of γ -irradiated [N₁₁₁₄][Tf₂N]. [48] No shift in the

absorption maxima was observed with increasing alkyl chain length from butyl to dodecyl in the case of quaternary ammonium based ILs. UV-visible spectra of phosphonium based $[P_{2226}][Tf_2N]$, $[P_{2228}][Tf_2N]$ show no distinct absorption peak; however, there is an increase in absorption from 190 to 450 nm compared to the unirradiated compounds.

The FTIR spectra of unirradiated and γ -irradiated $[bmim][Tf_2N]$ and $[hmim][Tf_2N]$ are shown in Figures 6 and 7, respectively. FTIR spectra for the unirradiated ILs show a group of bands appearing between $500\text{--}900\text{ cm}^{-1}$ mainly attributed to the ring bending modes of the imidazolium cations and another group of intense bands in the range of $1000\text{--}1400\text{ cm}^{-1}$ typically dominated by vibrations of the $[Tf_2N]$ anion. [61, 62] These observations are also in agreement with that reported in our previous work on $[emim][Tf_2N]$. [48] Several other bands are observed in the range from $2800\text{--}3300\text{ cm}^{-1}$ corresponding to the in-plane and out-of-plane C4,5-H stretching (3159 cm^{-1}), and C2-H stretching (3123 and 3105 cm^{-1}). For $[bmim][Tf_2N]$ the CH_2HCH asymmetric stretching, CH_2 and CH_3 asymmetric stretching and the terminal CH_3HCH symmetric stretching correspond to FTIR bands at 2968 , 2941 and 2882 cm^{-1} , respectively whereas the same bands are at 2963 , 2937 and 2866 cm^{-1} , respectively, in the case of $[hmim][Tf_2N]$. Very little difference can be observed in the FTIR spectra of unirradiated and γ -irradiated aromatic ILs. However, a new band at 1658 cm^{-1} appears in the γ -irradiated FTIR spectra of both $[bmim][Tf_2N]$ and $[hmim][Tf_2N]$ aromatic ILs. The new band is probably attributable to the formation of acyclic disubstituted alkene bonds in the irradiated imidazolium based ILs. In the case of aliphatic quaternary ammonium and phosphonium based ILs, the changes in the FTIR spectra are even smaller than observed with the imidazolium ILs and no specific product could be identified from the difference of their respective unirradiated and

irradiated FTIR spectra (not shown). No change was observed up to a dose of 1000 kGy suggesting little radiolytic decay, which is consistent with the relative low H₂ yields observed.

Conclusions

This work extends our previous studies on [emim][Tf₂N] and [N₁₁₁₄][Tf₂N] to include various aromatic, aliphatic quaternary ammonium and aliphatic phosphonium ILs with different alkyl chain lengths such as [bmim][Tf₂N], [hmim][Tf₂N], [N₂₂₂₆][Tf₂N], [N₂₂₂₈][Tf₂N], [N₁₁₂₍₁₂₎][Tf₂N], [P₂₂₂₆][Tf₂N], [P₂₂₂₈][Tf₂N] and [P₂₂₂₍₁₂₎][Tf₂N]. Irradiations were performed with γ -rays, 2-15 MeV protons and 5-20 MeV helium ions in order to probe track structure effects and to determine relative radiation stability and potential hazards for the use of ILs in waste separation systems. Molecular hydrogen production can be taken as an overall indicator of radiation stability and was found to be considerably lower for the γ -irradiated aromatic imidazolium based compounds compared to the other aliphatic based media. Increasing the length of the aliphatic side chain increase the H₂ yields for all the compounds examined. Although the production of H₂ is dependent on the aliphatic fraction of the cation, the effect is not linear. Little difference is found in the production of H₂ between the quaternary ammonium and phosphonium based ionic liquids with similar length side chains. Yields of H₂ increase substantially from γ -rays to 5 MeV He ions for the imidazolium based ionic liquids, but little variation with radiation type is observed for the quaternary ammonium and phosphonium based ionic liquids. This type of LET effect is analogous to the radiolysis of hydrocarbons where combination reactions of high energy excited states can occur in the high LET tracks. The imidazolium based ionic liquids show a darkening with increasing dose and the UV-visible spectra show an increase in adsorption from 240 to 400 nm that is probably due to induced

changes in the cation. FTIR spectra show little variation with radiolysis, which is consistent with the low H₂ yields.

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Table 1 Radiation yields of H₂ for in the γ -radiolysis and 5 MeV He ion radiolysis of several ionic liquids.

Compound	G(H ₂)	
	γ -rays	He-ion
[emim][Tf ₂ N] [48]	0.098	0.29
[bmim][Tf ₂ N]	0.22	0.67
[hmim][Tf ₂ N]	0.32	0.57
[N ₁₁₁₄][Tf ₂ N] [48]	0.73	0.85
[N ₂₂₂₆][Tf ₂ N]	1.65	1.92
[N ₂₂₂₈][Tf ₂ N]	2.06	1.36
[N ₁₁₂₍₁₂₎][Tf ₂ N]	2.14	1.19
[P ₂₂₂₆][Tf ₂ N]	1.65	1.44
[P ₂₂₂₈][Tf ₂ N]	1.95	1.67
[P ₂₂₂₍₁₂₎][Tf ₂ N]	2.29	2.05

Figure Legends

Figure 1. Structures of (A) aromatic and (B) aliphatic ionic liquids.

Figure 2. Yields of H_2 in (●) [emim][Tf₂N], (■) [bmim][Tf₂N], and (▲) [hmim][Tf₂N] as a function of track average LET for ¹H and ⁴He ions. The dashed lines show the low LET limiting yields obtained with γ -rays.

Figure 3. Yields of H_2 in (●) [N₁₁₁₄][Tf₂N], (■) [N₂₂₂₆][Tf₂N], (▲) [N₂₂₂₈][Tf₂N] and (◆) [N₁₁₂₍₁₂₎][Tf₂N] as a function of track average LET for ¹H and ⁴He ions. The dashed lines show the low LET limiting yields obtained with γ -rays.

Figure 4. UV-Visible spectra of [bmim][Tf₂N] before and after γ -irradiation (250 and 1000 kGy) diluted by a factor of 100 with acetonitrile. Insert: dilution factor of 2000.

Figure 5. UV-Visible spectra of [hmim][Tf₂N] before and after γ -irradiation (250 and 1000 kGy) diluted by a factor of 100 with acetonitrile. Insert: dilution factor of 2000.

Figure 6. FTIR spectra of unirradiated and γ -irradiated (1000 kGy) [bmim][Tf₂N].

Figure 7. FTIR spectra of unirradiated and γ -irradiated (1000 kGy) [hmim][Tf₂N].

Figure 1. Structure of (A) aromatic and (B) aliphatic ionic liquid.

R	Abbreviation
n-C ₂ H ₅	[emim][Tf ₂ N]
n-C ₄ H ₉	[bmim][Tf ₂ N]
n-C ₆ H ₁₃	[hmim][Tf ₂ N]

R ₁	R	Abbreviation	
		Ammonium	Phosphonium
n-C ₂ H ₅	n-C ₆ H ₁₃	[N ₂₂₂₆][Tf ₂ N]	[P ₂₂₂₆][Tf ₂ N]
n-C ₂ H ₅	n-C ₈ H ₁₇	[N ₂₂₂₈][Tf ₂ N]	[P ₂₂₂₈][Tf ₂ N]
n-CH ₃	n-C ₁₂ H ₂₅	[N ₁₁₂₍₁₂₎][Tf ₂ N]	-
n-C ₂ H ₅	n-C ₁₂ H ₂₅	-	[P ₂₂₂₍₁₂₎][Tf ₂ N]

Figure 2. Yields of H_2 in (●) [emim][Tf₂N], (■) [bmim][Tf₂N], and (▲) [hmim][Tf₂N] as a function of track average LET for 1H and 4He ions. The dashed lines show the low LET limiting yields obtained with γ -rays.

Figure 3. Yields of H_2 in (●) $[N_{1114}][Tf_2N]$, (■) $[N_{2226}][Tf_2N]$, (▲) $[N_{2228}][Tf_2N]$ and (◆) $[N_{112(12)}][Tf_2N]$ as a function of track average LET for 1H and 4He ions. The dashed lines show the low LET limiting yields obtained with γ -rays.

Figure 4. UV-Visible spectra of [bmim][Tf₂N] before and after γ -irradiation (250 and 1000 kGy) diluted by a factor of 100 with acetonitrile. Insert: dilution factor of 2000.

Figure 5. UV-Visible spectra of [hmim][Tf₂N] before and after γ -irradiation (250 and 1000 kGy) diluted by a factor of 100 with acetonitrile. Insert: dilution factor of 2000.

Figure 6. FTIR spectra of unirradiated and γ -irradiated (1000 kGy) [bmim][Tf₂N].

Figure 7. FTIR spectra of unirradiated and γ -irradiated (1000 kGy) [hmim][Tf₂N].