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Optical properties of irradiated imidazolium based room temperature ionic liquids: New microscopic insights of the radiation induced mutations

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Abstract

Considering the futuristic perspectives of Room temperature ionic liquids (RTILs) in the areas involving high radiation fields (such as nuclear fuel cycle and space applications), it is essential to probe and have a microscopic understanding of the radiation induced perturbations in the molecular structure and the intrinsic bonding interactions existing in the ILs. Herein, a focused investigation concerning the photophysical behavior of the post-irradiated FAP (Fluoro alkyl phosphate) imidazolium ILs revealed considerable rearrangements and bonding realignments of the ionic moieties in the ILs on irradiation, however, their physicochemical properties do not change significantly even at high absorbed doses. Most interestingly, the well-established excitation wavelength dependent fluorescence (FL) behavior of the ILs was considerably perturbed on irradiation and has been attributed to the radiation induced decoupling of pre-existing different associated structures of ions, and subsequent formation of oligomers and other species containing multiple bond order groups. It was further substantiated by the vibrational studies, where peaks appearing in the range 1600-1800 cm^{-1} indicated the formation of double bonded products. Furthermore, in case of hydroxyl functionalized (in the alkyl side chain of the imidazolium cation) IL, a blue shift in the O-H stretching frequency was observed for -OH group H-bonded to FAP anion ($\nu OH\cdots[FAP]^{-}$), while red shift for the same was observed for H-bonded -OH groups in the cationic clusters. The FL lifetime values were found to increase with irradiation, which clearly indicates the enhancement in the rigidity level in the vicinity of the ions, thereby hindering the non-radiative decay processes. Such studies could contribute to the fundamental understanding of the radiation driven perturbations in the structure-property relationships, which eventually affects the radiolytic degradation pathways and the product distribution in RTILs.

Keywords:

Room temperature ionic liquids, Fluoro alkyl phosphate, Microheterogeneity, Photophysical, Oligomers, Vibrational, Molecular organization

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1. Introduction

Photophysical studies of the imidazolium room temperature ionic liquids (RTILs) have been extensively carried out in the recent times, which show unconventional behavior of such solvents.[1a-e] The optical spectroscopic studies of neat imidazolium based RTILs have already been carried out by Samanta *et al.*[1d-g] and other researchers, [2a, b] where an unusual excitation wavelength dependent fluorescence behavior (known as Red Edge Effect or REE or REES) was reported for these media. REES is defined as a shift in the wavelength of maximum fluorescence emission toward higher wavelengths, caused by a shift in the excitation wavelength toward the red edge of the absorption band. REES is generally observed in microheterogeneous media and highly viscous solutions. Essentially, this phenomenon arises from the slow rates of solvent relaxation (reorientation) around an excited state fluorophore, which is a function of the motional restriction imposed on the solvent molecules in the immediate vicinity of the fluorophore. Now, excitation near the peak or on the blue side of an electronic absorption tends to excite a broad distribution of energetically different solute−solvent environments. In contrast, excitation on the red edge of an absorption band preferentially selects a narrowed and red-shifted subset of the overall distribution.[2c] Nevertheless, in ILs, excitation wavelength dependent fluorescence behavior has been attributed to the presence of various associated species and the inefficiency of the excitation energy-transfer between them or an incomplete solvation process.[1d-g , 2] In fact, recently, Ghosh *et al.*[2a] have reported the heterogeneity of the fluorescence lifetime of FAP (Fluoro alkyl phosphate) based imidazolium RTILs, which clearly indicated the absence of any excited state phenomenon (like solvation and energy transfer) in these fluids. Essentially, ILs are microheterogeneous in nature with parallel co-existence of different types of interactions (such as coulombic, dipolar, van der Waals and H-bonding), which makes these fluids unique and complex in comparison to conventional solvents.[3] Keeping this in mind, information regarding the photophysical behavior of irradiated ILs could be useful in gaining better understanding of the radiation driven perturbations in the structure-property relationships, which eventually affects the radiolytic degradation pathways and the product distribution. Moreover, RTILs owing to their unique physicochemical properties have aroused a lot of interest in the recent times for their potential application in areas involving high radiation fields such as nuclear fuel reprocessing, space and other industrial applications.[4]

In this pretext, numerous radiation stability studies on RTILs (especially imidazolium based) including important reviews are available in the literature.[5] Allen *et al*.[5a] have primarily assessed the effects of α-, β- and γ-radiation on the hydrophilic RTILs such as 1-butyl-3-methyl imidazolium nitrate, ([BMIM] NO_3), 1-ethyl-3-methyl imidazolium chloride ([EMIM] Cl) and 1-hexyl-3-methyl imidazolium chloride ([HMIM] Cl). These authors reported that ~1% of the samples undergo radiolytic degradation up to an exposure dose of 400 kGy. Qi *et al*. and Yuan *et al*. investigated the influence of γ-radiolysis on imidazolium based fluoroanions such as ($[PF_6]^-$) and tetrafluoroborates ($[BF_4]^-$) using spectroscopic methods along with differential scanning calorimetry (DSC).[5b,c,d] Dhiman *et al*.[5e] investigated the radiolytic production of molecular hydrogen in aromatic and aliphatic ILs irradiated with γ-rays, proton and helium ions to determine the functional dependence of the yield (of hydrogen) on particle track structure. It was found by these researchers that the hydrogen gas yield increases considerably on going from low LET (γ-rays) to high LET (protons and helium ions) radiations in case of aromatic ILs, while the same remain essentially constant for aliphatic ILs. Intra-track chemistry of highly excited states has been assigned as the most probable reason for the increase in the hydrogen gas yield in case of aromatic ILs, when irradiated with high LET radiations. However, in case of aliphatic ILs, LET effect was found to be insignificant, [5e] as the H atom abstraction and combination reactions are mainly responsible for the production of H_2. Berthon[5f] and co-workers[5g] examined the radiation stability of the hydrophobic imidazolium based ILs containing anions such as hexafluoro phosphate ($[PF_6]^-$), bis(trifluoromethlsulfonyl) imide ($[NTf_2]^-$) and $[N1444][NTf_2]$ where $[N1444]^+$ is the methyl tributylammonium cation. These authors proposed a possible degradation schemes of the RTILs based on the NMR and mass studies. The effect of commonly used anions i.e. NTf_2^-, Trifluoromethanesulfonate (TfO^-), PF_6^- and BF_4^- on the radiochemical stability of imidazolium based ILs under γ-irradiation was investigated by G. Le Rouzo and co-workers.[5h] Jagadeeswara Rao *et al.*[5i] had reported the influence of radiations on the rheometric and electrochemical properties of some halide and NTf_2 based ILs. Yuan *et al.*[5j] have observed radiation induced darkening of ionic liquid [BMIM] $[NTf_2]$ and subsequent decoloration on adding different oxidants. Majority of these investigations clearly show insignificant variations in the physicochemical properties of ILs (especially imidazolium based) on irradiation to high absorbed doses. Some researchers have also conducted fluorescence and vibrational studies to probe the radiolytic degradation and mechanism of the ILs.[5, 6] For example, Qi *et al.*[5b] reported the fluorescence and the Raman spectra of γ-irradiated IL, $[BMIM][PF_6]$. Radiation induced significant chemical scission of the n-butyl group (e.g. C-H and C-C scission) as well as damage to the $[PF_6]^-$ anion had been observed. FTIR measurements, reported by Yuan *et al.*[5c] showed the signs of slight acceleration of the radiolysis of $[BMIM][PF_6]$ in the presence of nitric acid. The Raman spectral studies by Qi *et al.*[5d] indicated that the radiolysis of $[BMIM][BF_4]$ induces a detectable destruction of alkyl-chain and scission of C-H of ring of imidazolium cation, and relatively small changes in the anion. Recently, Dhiman *et al.*[5e, ℓ] carried out gamma and heavy ion beam irradiation of aromatic and aliphatic ILs. Primarily, H_2 gas yield measurements of the post-irradiated ILs were conducted by these researchers, which were found to be consistent with the findings from the FTIR and UV-Vis analysis. All these studies indicate the necessity of detailed studies focusing the photophysical behavior (such as fluorescence and vibrational studies) of the post-irradiated imidazolium ILs.

Therefore, in this report, an exclusive investigation concerning the photophysical behavior of the FAP based imidazolium ILs before and after irradiation was conducted in conjunction with the elaborate vibrational spectroscopic studies (FTIR and Raman) for the comprehensive understanding of the radiation induced structural changes. Most interestingly, the well established excitation wavelength dependent behavior of imidazolium ILs was considerably perturbed on irradiation. Moreover, the fluorescence lifetime values as measured for neat ILs, were found to increase with irradiation, and the trend was more pronounced in case of hydroxyl group containing IL. From the vibrational studies, interesting aspects were revealed such as significant molecular rearrangements of the ions and realignments of the bonding interactions in the irradiated ILs.

The structures of the ILs studied are shown in Fig.1. It is to be noted that the ILs, 1-Ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([EMIM][FAP]) and 1-(2-hydroxyethyl)-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([EOHMIM][FAP]), has been cited as **FAP1** and **FAP2**, respectively in the current manuscript onwards.

Fig.1

2. Experimental

2.1. Chemicals

FAP1 (1-Ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate, [EMIM][FAP]) and **FAP2** (1-(2-hydroxyethyl)-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate, [EOHMIM][FAP]) were obtained from Merck KGaA, Darmstadt, Germany, with a purity > 99%. Since, these ILs are highly hydrophobic and the water uptake is extremely slight, they were used as such without further processing. Nonetheless, the water content in the as studied FAP ILs i.e. **FAP1** and **FAP2** was also determined and found to be 30 ppm and 55 ppm, respectively by the coulometric Karl-Fischer method using a Metrohm 831 KF Coulometer.

2.2. Irradiation of the ILs

The ILs were irradiated with a 7 MeV electron beam (FWHM ~ 2 μs) obtained from a linear accelerator (LINAC) described elsewhere.[7] The absorbed dose was measured using an air-saturated solution containing 5×10^{-2} mol dm^{-3} KSCN assuming Gε for $(SCN)_2^{\cdot-}$ = 2.6×10^{-4} m^2 J^{-1} at 475 nm.[8] The absorbed dose per pulse was kept at 160 Gy and the samples were irradiated with repeated pulses @ 50 pulses per second accounting for a cumulative dose ranging from 10 to 400 kGy.

2.3. Instrumentation

UV-VIS optical absorption studies were carried out on a JASCO V-650 spectrophotometer at room temperature. It is to be mentioned here that prior to recording the UV-Vis absorption spectra, all the samples were diluted with acetonitrile to avoid the saturation level (observed using both 10 mm and 1 mm path lengths) occurring due to the intense color appeared on irradiating FAP ILs. Acetonitrile was used as a diluent because of its miscibility with FAP ILs and negligible absorption above 200 nm. Photoluminescence (PL) measurements were recorded on a Hitachi F-4500 spectrofluorimeter at room temperature. Emission life time measurements were conducted on a time correlated single photon counting (TCSPC) instrument (model: IBH, UK). The instrument response function (IRF) of the setup was measured by collecting the scattered light from a TiO_2 suspension in water. The samples were excited at 394 nm by a laser source with an IRF of less than 150 ps (full width at half maximum, FWHM) and the decay traces were monitored at an emission wavelength of 500 nm. The optical path length of the cell in all the spectral studies was 10 mm. The FT-IR spectra were recorded using a diamond single reflectance ATR probe in an IR Affinity-1 spectrometer. Raman spectra of the samples were recorded using a STR-300 micro-Raman spectrometer (SEKI Technotron, Japan). The sample solutions were excited at 532 nm sourced from a fibre coupled diode-pumped solid-state laser (DPSS). The scattered light was collected through a fiber-coupled 300 mm spectrograph (Acton series SP 2300i, 1200 gr/mm) and detected by a thermo-electric cooled (−75 °C) charge-coupled device (CCD).

3. Results and Discussion

On irradiation, colorless and transparent ILs darkened with the increase in absorbed dose. The UV-Vis absorption spectra of pre- and post-irradiated **FAP2** at various absorbed doses have been shown in Fig.2. The picture showing the color evolution in the same IL on irradiation at various doses is provided in the inset of Fig.2. The absorption spectra and the color evolution in **FAP1** have been reported earlier.[9]

Fig.2

It can be seen that the absorption spectra of irradiated ILs showed a peak at ~ 300 nm accompanied by a shoulder at ~ 370 nm. The intensity of the former peak increased, while the later one slightly red shifted with the increase in absorbed dose. The radiolytic products of the imidazolium cation (especially, the oligomeric species of imidazole and its derivatives) were found to be primarily responsible for the color evolution and emergence of peaks in the absorption spectra of the irradiated FAP ILs, as reported in our earlier work.[9] While, the red shift in the shoulder peak (with the increase in absorbed dose) could most plausibly be the indication of the formation of higher order oligomeric species. These trends and observations are in agreement with those reported by various groups on other imidazolium based ILs containing various anions such as $[NTf_2]^-$,[5f, g] $[PF_6]^-$[5b, c, f] and $[BF_4]^-$.[5d]

Most interestingly, the well established excitation wavelength dependent fluorescence behavior of imidazolium ILs was found to be considerably perturbed on irradiation. The emission spectra of pre- and post-irradiated **FAP1** at different levels of absorbed dose have been shown in Fig.3. Fig.S1 represents the emission spectra of **FAP1** irradiated at 400 kGy. As can be seen from Fig.3A, the unirradiated IL shows two emission bands (at ~ 340 nm and a shoulder peak at ~ 450 nm) when excited at lower wavelength region. However, with the increase in the excitation wavelength, the two emission bands merge into single broad peak with simultaneous bathochromic shift.

Fig.3

Surprisingly, there was subsequent quenching of fluorescence at lower excitation wavelengths after irradiation to different degrees of absorbed doses (see Fig.3 & Fig.S2a). At the same time, the maximum emission peaks showed bathochromic shifts for higher excitation wavelengths with gradual increase in the absorbed dose (Fig.S2b). Such corresponding trends can also be envisaged from the plots of $\lambda_{exc.}$ *vs.* λ_{em} shown in the insets of emission spectra of irradiated **FAP1** IL (Fig.3). For better understanding, the maximum fluorescence intensity and λ_{em} values corresponding to the respective excitation wavelengths and absorbed doses for neat

FAP1 (pre- and post-irradiated) have been tabulated in Table S1. It is to be mentioned here that Qi *et al.*[5b] had earlier reported the fluorescence spectra (at only one $\lambda_{exc.}$ = 290nm) of γ-irradiated IL, $[BMIM][PF_6]$ (diluted with dimethylformamide, DMF), which showed the appearance of peaks between 300 to 600 nm, similar to the present case.

Analogous to **FAP1**, the -OH group containing **FAP2** displayed the similar excitation wavelength dependent behavior after irradiation (see Fig.S3). But, in **FAP2**, the decrease in the fluorescence intensity as well as the red shift in the emission peaks were more pronounced for subsequent increase in the excitation wavelengths at higher absorbed doses. These trends can be visualized in Fig.S4 and Table S2. Considering the excitation wavelength of 450 nm and the absorbed dose of 400 kGy, it can be envisaged that the red shift (with respect to the unirradiated IL) in the emission peak was 18 nm for **FAP1**, while it was 60 nm in case of **FAP2** (see Fig.S5). These observations indicate the formation of higher order (in terms of conjugation and introduction of new π-π interactions) radiolytic products in **FAP2**. Nevertheless, as already mentioned, the excitation wavelength dependent fluorescence spectra of imidazolium ILs has been attributed to the existence of various associated structures of cations and anions.[1, 2] In fact, some of the associated forms of cation and anion were observed during the mass spectrometric studies of neat unirradiated **FAP1** and **FAP2**.[9] For instance, ions with m/z values 667.1 ($[(EMIM)_2\ FAP]^+$) and 699.1 ($[(EOHMIM)_2\ FAP]^+$) were noticed in the mass spectra of unirradiated **FAP1** and **FAP2**, respectively. However, these ions were found to be very weak in nature since the collision energy of only 2 eV led to their dissociation into respective parent ions. Therefore, the as described perturbations in the excitation wavelength dependent behavior of irradiated FAP ILs could be attributed to the irradiation induced decoupling or break down of such pre-existing different associated forms of the cations and anions (in the unirradiated IL) and simultaneously driving the formation of oligomers and other species containing multiple bond order groups. Indeed, it was substantiated by the vibrational studies (FTIR and Raman) which are discussed below.

Vibrational studies (FTIR and Raman) of irradiated ILs are very less in literature and that too not in detail. Interestingly, we have noticed a strong correlation between the vibrational changes and fluorescence behavior of irradiated ILs. The FTIR spectra of pre- and post-irradiated **FAP1** are shown in Fig.S6, while Fig.4 represents the spectra of particular wavenumber regions with significant alterations in the amplified scale for better visibility. Some of the discussion regarding the changes in the peak positions and their intensities (on irradiation of **FAP1)** has been provided in the supporting information.

Fig.4

Up to a dose of 100 kGy, not many changes could be observed in the FTIR spectra of irradiated ILs, which reflects their radiation stability. However, at high absorbed dose of 400 kGy, some modulations observed are mentioned as follows. The peak at ~ 890 cm^{-1} (see Fig.4a and peak marked as [1] in Fig.S6) has been attributed to the olefinic C-H bending vibrations, which indicates the formation of radiolytic products having vinylidene double bond ($>C=CH_2$).[10] Another absorption band centered at ~ 1736 cm^{-1} (see Fig.4b and peak marked as [2] in Fig.S6) signifies the formation of species with double bonds in the form of C=C, -CF=CF-, $-CF=CF_2$.[11] It has been reported earlier [9] that the amount of the radiolytic products formed on irradiation of FAP ILs was very less (i.e. < 5 % of the parent ion peak) however, we have been able to identify some of the possible radiolytic products possessing double bond units from their mass spectrometric studies. The plausible molecular structures of these products have been shown in

Fig.S7 along with the mass spectra of post-irradiated **FAP2**. Similar types of products were noticed in case of irradiated **FAP1** IL.[9] Moreover, recently, Wang *et al.*[12a] by means of UV-Vis analysis and density functional theory calculations proposed that the color darkening in imidazolium based IL ([BMIm][NTf_2]) upon irradiation originates from the formation of double bonds in the aliphatic chains of pristine organic cations (or radiolytic products of RTILs) and various associated species containing these ‘‘double bond products’’. Therefore, our vibrational analysis provides a direct evidence of the formation of aforesaid radiolytic products containing double bonds, which eventually might be acting as chromophoric units. Besides this, strong evidences are reported by various researchers for the existence of hydrogen bonding interactions in the ILs (especially, imidazolium based ILs) on the basis of spectroscopic (mainly X-ray diffraction, IR and NMR spectroscopy) and computational studies.[12] For example, shorter C–H anion distances, red shifted C–H stretching frequencies and downfield shifted C–H proton chemical shifts are the observed indications of the hydrogen bonding in imidazolium based ILs.[12e] Further, it has been observed in earlier studies, [12d, e] that the hydrogen bonding interactions involving the C(4)–H and C(5)–H groups are weaker as compared to that in case of C(2)–H groups. Reasonably so, a stronger NMR downfield proton chemical shift of about 1 ppm for C(2)–H compared to C(4,5)–H has been reported.[12d] In agreement to this, the quantum-chemical calculations (e.g. for the IL, [BMIM][PF_6] in gas phase) have also suggested stronger hydrogen bonding interactions between the C2 proton and the anion, as compared to that between C(4, 5) protons and the anion.[12f] On the whole, the C-H bond of the imidazolium cation carries important information about the existence and strength of hydrogen bonding network in the RTILs. However, substantial variations in the C-H bond stretching frequencies (in the region 2000-3000 cm^{-1}) of the ethyl and the terminal methyl group attached to the side chain of the imidazolium cation were observed and discussed in the supporting information. Further, peak at ~ 3086 cm^{-1} (for unirradiated **FAP1**) originated due to the (N)CH_3 HCH asymmetric stretching vibrations [13, 14] was red shifted on irradiation of the IL (shown in Fig.4c). Subsequently, the broadening in the peaks signifies the presence of radiolytic products mostly derived from the imidazolium cation with varying C-H bond strengths. Moreover, a red shift observed in the ring NC(H)NCH (or C_2-H) vibrational frequency from 3130 cm^{-1} to 3126 cm^{-1} on irradiation of **FAP1** clearly shows the weakening of the respective bond strength.[5e] Certainly, these variations substantiate the realignment of the intermolecular hydrogen bonding interactions among the ionic moieties in case of post-irradiated **FAP1** IL. Furthermore, it has been reported that the C-2 position of the imidazolium cation is acidic (pK_a=21–22)[15] in nature and prone to deprotonation to form a stabilized carbene. Therefore, the weakening of the bond strength of C_2-H bond on irradiation can be regarded as strong evidence supporting the vulnerability of imidazolium-derived radical species to undergo oligomerization.[5, 9, 16] Consequently, this has been found to be one of the possible contributing factors behind the color evolution in irradiated imidazolium ILs.

The FTIR spectra of post-irradiated **FAP2** at different absorbed doses (same as in case of **FAP1**) have been shown in Fig.S8 & S9. Analogous to **FAP1**, the formation of radiolytic products with multiple bond order functional groups as well as bathochromic shifts in the C-H stretching frequencies were also observed in case of post-irradiated **FAP2** IL (see supporting information). Further, a broad shoulder centered at ~ 3430 cm^{-1} was observed in addition to a peak at ~ 3621 cm^{-1} in case of unirradiated **FAP2** (see Fig.5). These peaks were also observed in the Raman spectra of unirradiated **FAP2**, shown in the inset of Fig.5. Similar type of broad feature at ~ 3425 cm^{-1} and a peak at ~ 3598 cm^{-1} have been reported recently by Katsyuba *et al.*[17] in case of [EOHMIM][PF_6]. The former peak was assigned to the νOH of hydrogen bonded cationic clusters, while the later one was attributed to the OH stretching frequency hydrogen bonded to the F atom of the PF_6 anion ($\nu OH\cdots[PF_6]^-$). More so, the νOH in case of isolated $[EOHMIM]^+$ cation has been reported to be 3690 cm^{-1} by computational analysis.[17] Taking account of these, the peak at ~ 3621 cm^{-1} (observed in the present work) has been attributed to the stretching frequency of -OH hydrogen bonded to the FAP anion ($Im(OH)\cdots[FAP]^-$). While the broad shoulder centered at ~ 3430 cm^{-1} could be assigned to the stretching frequency of -OH hydrogen bonded to the other hydroxyl groups of neighboring cations; the pre-existence of such cationic clusters have been observed and discussed earlier. The as discussed –OH bonding interactions possibly existing in **FAP2** has been pictorially represented in Fig.5.

Fig.5

Nevertheless, an interesting observation of a blue shift in the peak frequency from ~ 3621 cm^{-1} (for unirradiated **FAP2**) to ~ 3634 cm^{-1} (in post-irradiated **FAP2**) was noticed (Fig.5). This signifies the weakening of the hydrogen bond ($Im(OH)\cdots[FAP]^-$) between the OH and the FAP anion. On the other hand, broad peak at ~ 3430 cm^{-1} was red shifted to ~ 3380 cm^{-1} indicating the reduction in the O-H bond strength. Apparently, it points out towards the possible distribution of the O-H bond strength, which could be due to the involvement of -OH group in multiple non-covalent bonding interactions with the newly formed radiolytic species in its neighborhood. At this stage, it is important to mention that the geometry involving the orientation and the interactions of the cations and the anions in -OH group functionalized ILs is different from non-hydroxyl ILs. Recently, the interaction of $[EOHMIM]^+$ and $[EMIM]^+$ with various anions was investigated using DFT calculations and NMR by Zhang *et al.*[18] According to the optimized geometries obtained by them, the anions were located in front of the imidazolium ring, where the atoms carrying more negative charges were closer to proton at C-2 position in non-hydroxyl ILs. However, the anions are somewhat above the imidazolium ring, moving close to the -OH group in case of hydroxyl containing ILs such as **FAP2**. Considering this, the aforementioned shifts in the vibrational peaks can be regarded as an important evidence for the reorientation or restructuring occurring in **FAP2** on irradiation.

Raman spectra of irradiated FAP ILs further substantiate the FTIR studies. Baseline corrected Raman spectra (Fig.S10 & S11) of neat **FAP1** and **FAP2**, respectively indicates the perturbations and re-organization in the IL lattice on irradiation (see supporting information). A red shift was observed in the symmetric bending modes of $–CF_3$ (at ~ 742 cm^{-1}) for **FAP1** on irradiation (see Fig.6a). Further, a broad peak centered at ~ 985 cm^{-1} appeared in the Raman spectra of both the FAP ILs (see Fig.S12a & Fig.S13b) on irradiation (dose ≥ 50 kGy), which indicates the formation of radiolytic products with vinyl groups.[10] An important observation was the appearance of peaks in the range 1600-1650 cm^{-1} in both the irradiated FAP ILs and have been assigned to the formation of radiolytic products with conjugated C=C groups (alkenyl C=C stretching).[10] It could be regarded as another strong signature of the formation of chromophoric species responsible for the color evolution in imidazolium based ILs on irradiation. Recently, Dhiman *et al*.[5ℓ] also reported the appearance of a peak at 1658 cm^{-1}, which has been attributed to the formation of acyclic di-substituted alkene bonds in the irradiated imidazolium based ILs.

Fig.6

The vibrational studies hitherto categorically reflect the considerable changes in the inherent spatial correlations of the ionic species (in ILs) on irradiation. It is to be mentioned here that NMR (^{1}H and ^{19}F) spectra of both the FAP ILs, before and after the irradiation, were recorded to examine the amount and the mechanism of radiolytic degradation, and have been reported in our earlier work.[9] The ^{1}H NMR of the irradiated ILs (especially, **FAP1**) showed very little changes in the chemical shift values along with the rise of small peaks as compared to the unirradiated one. The interpretation of the slight chemical shifts in the peaks indicated perturbation in the bonding rearrangements of the ionic moieties. For instance, the chemical shift values of C-2 proton in the ^{1}H-NMR spectra of both the FAP ILs decreased on irradiation. Further, the broadening along with the decrease in the chemical shift value of the peak corresponding to the hydroxyl group proton of the irradiated **FAP2** was attributed to the variations in the hydrogen bond between the hydroxyl group of the cation and the fluorine atom of the FAP anion, OH$\cdots$F. The decrease in the chemical shift values of C-2 proton as well as that of the hydroxyl proton were the signature of the alterations in the distribution and the nature of interactions accessible to the aforementioned protons due to the formation of some new species, on radiolysis of the ILs. Similar variations, pointing out towards the radiation induced realignment of the ionic moieties in the ILs have been reported in the earlier work.[9] Indeed, these observations further substantiate the findings (regarding the radiation driven internal molecular restructuring of the ILs) of the present photophysical studies on the post-irradiated FAP ILs.

The influence of irradiation induced decoupling of pre-existing particular arrangements and related perturbations in the bonding interactions (amongst cationic and anionic moieties) were also indicated from the fluorescence lifetime behavior of FAP ILs (shown in Fig.7); especially in case of -OH group containing **FAP2**. On irradiation, the average lifetime of **FAP1** and **FAP2** increases with the rise in the absorbed dose imparted however, the trend was found to be more prominent in the later case (see Table S3). The multi-exponential behavior signifies the heterogeneous nature of these media and indicates the existence of energetically distributed aggregates with different conformations, as has been reported earlier.[1, 2] Nonetheless, the exact reason for the increasing trend in the average lifetime values of FAP ILs with higher absorbed doses is not precisely clear. However, the most probable explanation could be the formation of new intermolecular hydrogen bonds and other non-covalent bonding interactions (i.e. π-π) between radiolytic products and the ionic moieties, as indicated from the vibrational studies.

Fig.7

Consequently, enhancement in the rigidity level in the vicinity of the ions (especially imidazolium cation, which is primarily responsible for the fluorescence behavior of imidazolium based ILs) can be anticipated which eventually might have hindered the non-radiative decay processes leading to the increase in the average lifetime values observed in case of post-irradiated FAP ILs.

4. Conclusions

Although, the physicochemical properties of FAP based imidazolium ILs (especially non-hydroxyl IL) were found to vary insignificantly on irradiation to high absorbed doses[9] however, the photophysical behavior of pre- and post-irradiated FAP ILs categorically points out towards the considerable changes in the orientations and the molecular rearrangements of the ions on irradiation. For instance, (i) bathochromic shifts in the excitation wavelength dependent fluorescence spectra of irradiated FAP ILs (due to irradiation induced break down of pre-existing different associated structures of ions and subsequent formation of various radiolytic products including oligomers), (ii) vulnerability of the C_2-H to undergo deprotonation (indicated form the red shift in the vibrational frequency), (iii) blue shift in the O-H stretching frequency (in case of -OH fictionalized **FAP2** on irradiation) and (iv) the observation of vibrational peaks originated due to multiple bond order groups (which could be a contributor behind color evolution in post irradiated imidazolium ILs) are some of the highlights of this study, which could be useful in having a comprehensive understanding of the radiation driven degradation of ILs and its mechanistic pathways. We believe, the present study would be helpful in gaining the microscopic insight of the radiation induced mutations in the structure-property relationships and the nature of various interactions existing in ILs.

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Supporting information

Plots of fluorescence intensity *vs*. dose (a) and λ_{em} *vs*. dose (b) for **FAP1** and **FAP2** at different excitation wavelengths have been shown. Discussion related to the vibrational analysis of post-irradiated FAP ILs has been provided along with their spectra. Tables showing the corresponding λ_{em} and maximum PL intensity values for neat pre- and post-irradiated FAP **ILs** at $\lambda_{exc.}$ and absorbed dose values. Average lifetime values of neat unirradiated and post-irradiated FAP ILs at various absorbed doses have been provided.

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Caption for Figures

Fig.1. Structures of FAP based imidazolium ILs.

Fig.2. UV-Vis absorption spectra of pre- and post-irradiated **FAP2** at various absorbed doses in kGy. Inset: Picture showing the color change of **FAP2** on irradiation. Doses given in kGy: (a) 0, (b) 100, (c) 200, (d) 300 and (e) 400.

Fig.3. Fluorescence spectra of neat unirradiated (A) and post irradiated **FAP1** at various absorbed doses i.e. 100 kGy (B); 200 kGy (C); 300 kGy (D). Inset: Plot of $\lambda_{exc.}$ *vs*. λ_{em} showing the shifts in the maximum intensity peak positions.

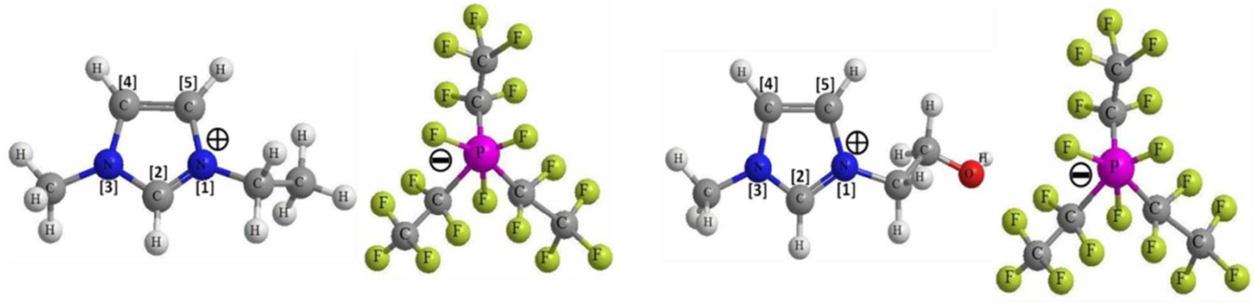
Fig.4. FTIR spectra of neat unirradiated and post irradiated **FAP1** in different wave number regions at various absorbed doses i.e. 0 kGy, 100 kGy and 400 kGy.

Fig.5. FTIR spectra of unirradiated and post-irradiated **FAP2** showing the perturbations in the O-H stretching frequency at various absorbed doses i.e. 0 kGy, 100 kGy and 400 kGy. Inset: Graph showing the Raman spectrum of unirradiated **FAP2** in the same frequency region as that of FTIR. Pictorial representation of –OH bonding interactions possibly existing in **FAP2** has been shown along with the graph.

Fig.6. Raman spectra of neat unirradiated and post-irradiated **FAP1** in different wave number regions at various absorbed doses i.e. 0 kGy, 10 kGy, 50 kGy and 100 kGy.

Fig.7. Lifetime decay profile of neat irradiated **FAP1** (a) and **FAP2** (b) at various absorbed doses.

Figures:



(a) [EMIM][FAP]

(b) [EOHMIM][FAP]

Fig.1

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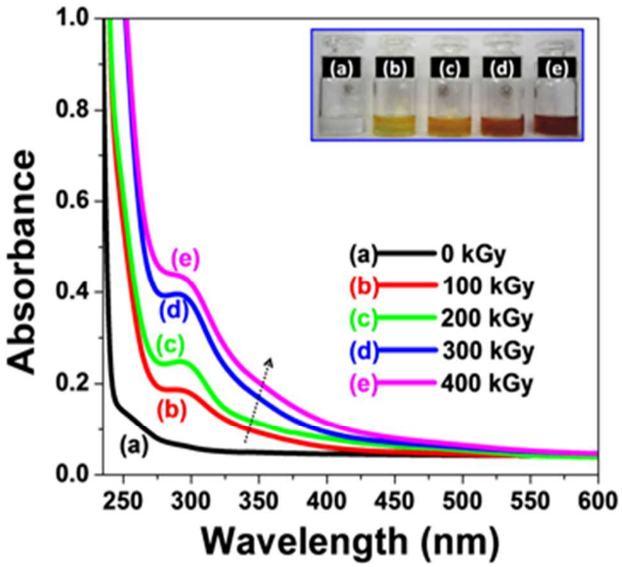

Fig.2

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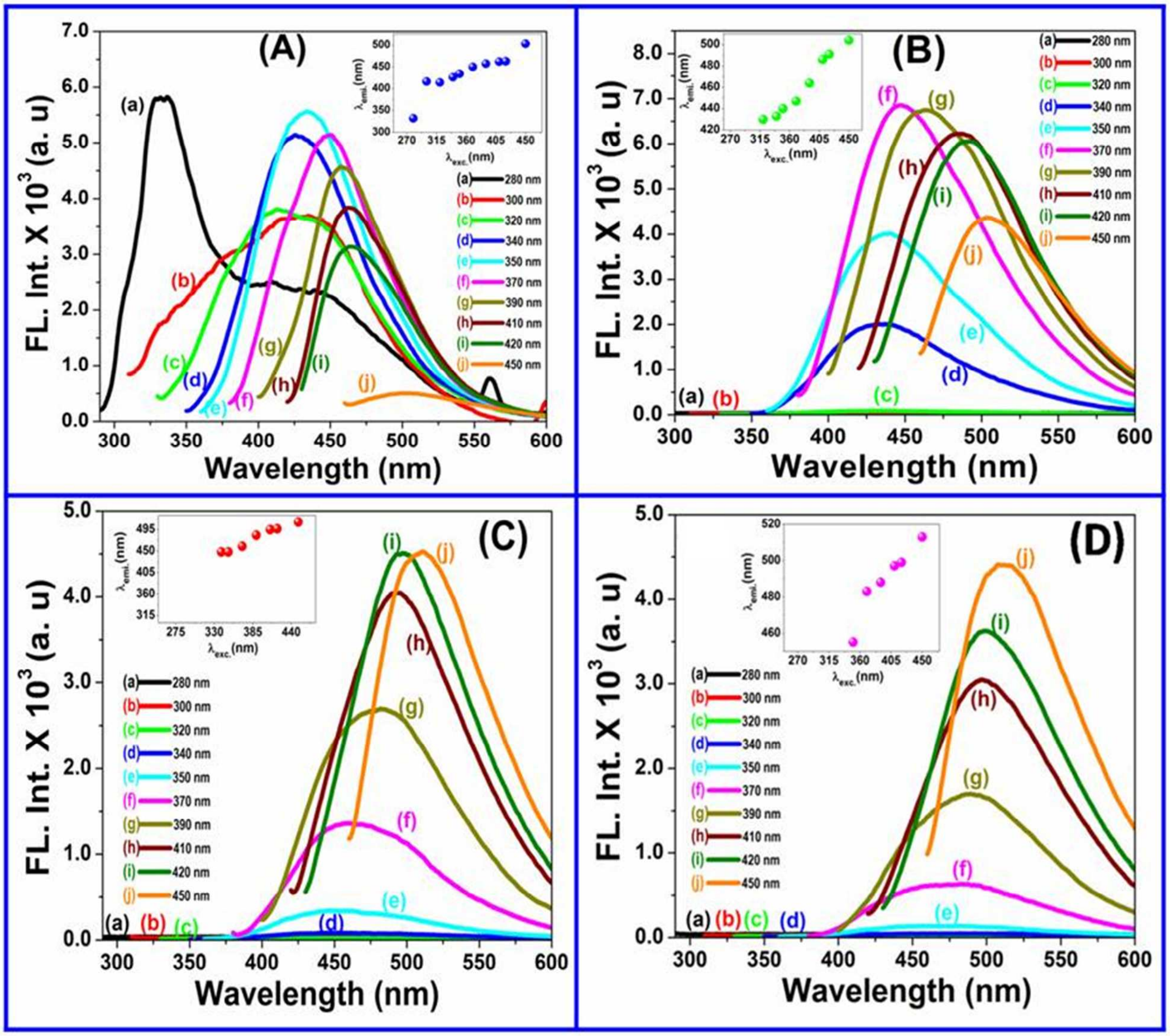

Fig.3

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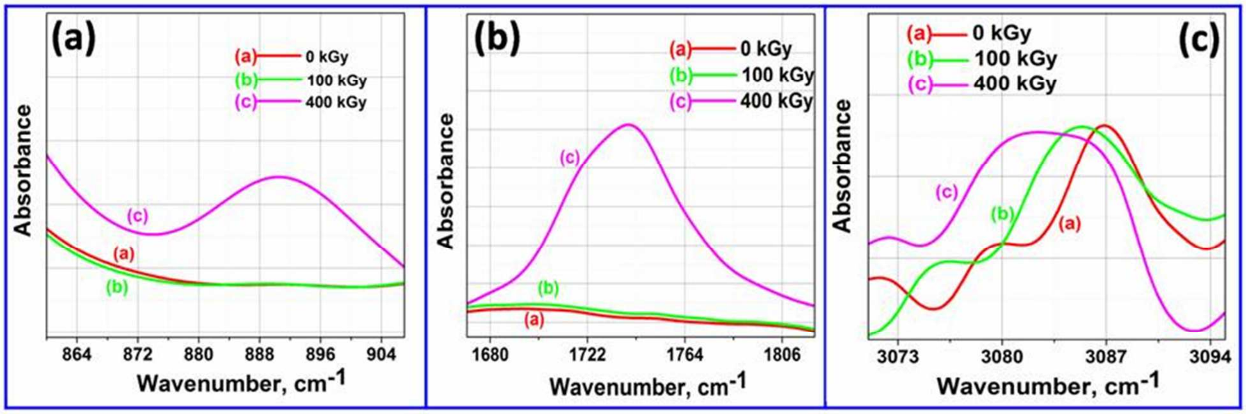

Fig.4

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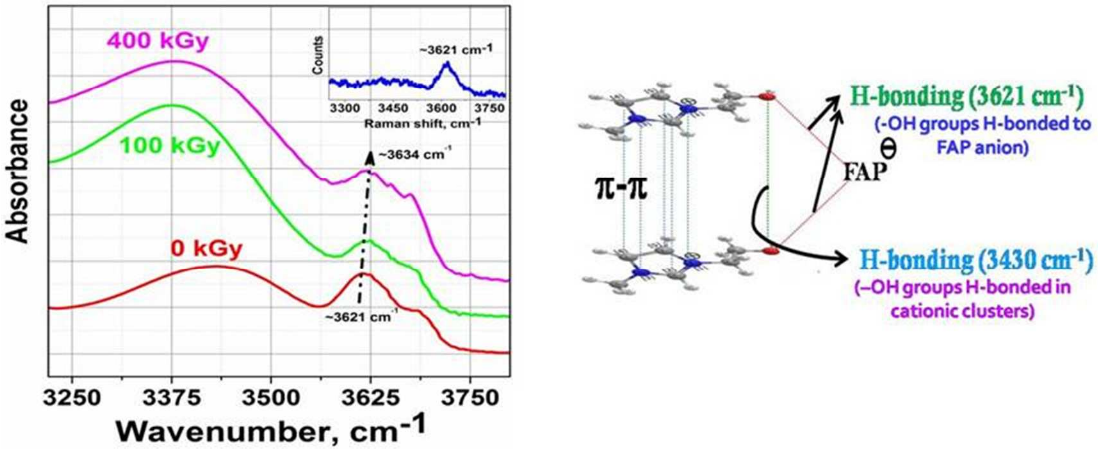

Fig.5

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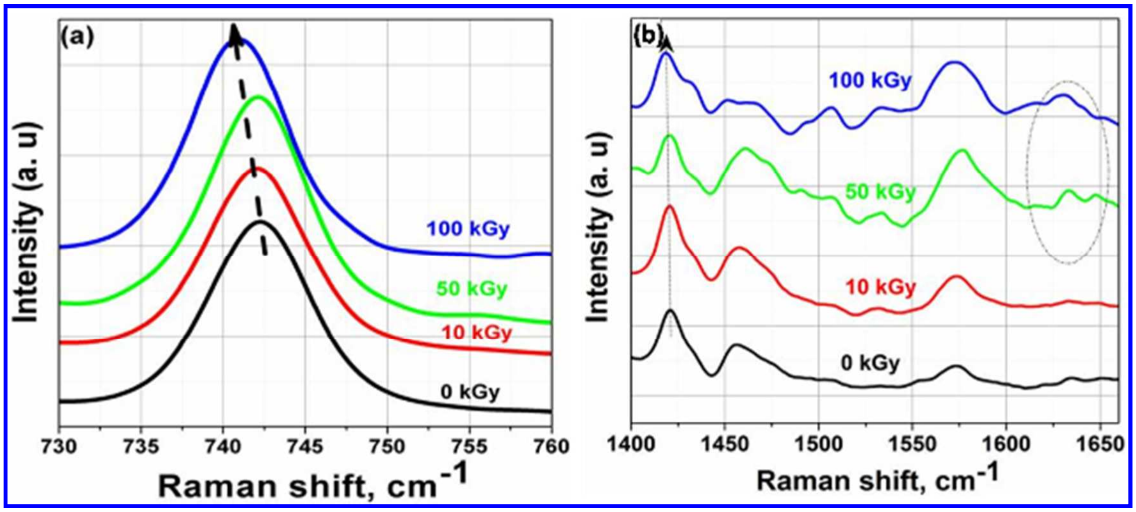

Fig.6

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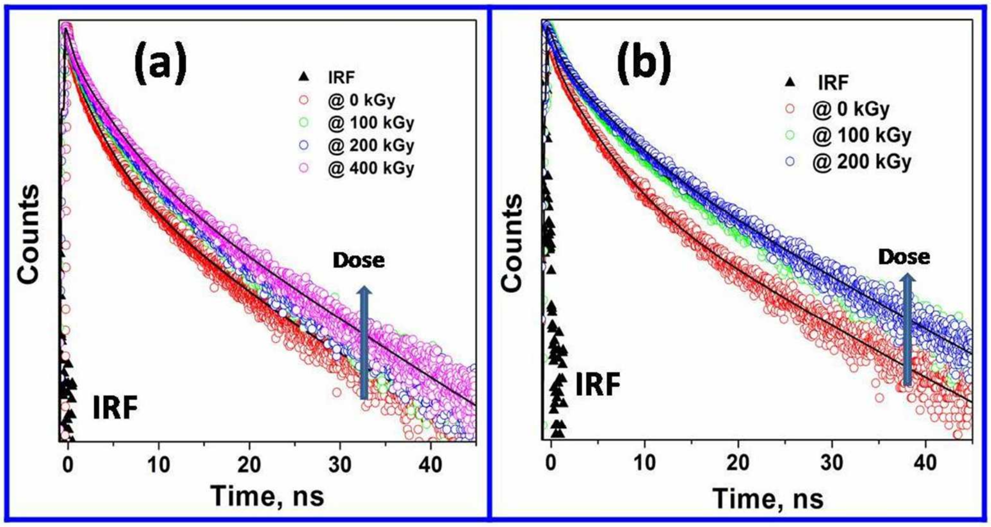

Fig.7

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