Radiation induced physicochemical changes in FAP (Fluoro alkyl phosphate) based imidazolium ionic liquids and their mechanistic pathways: Influence of hydroxyl group functionalization of the cation

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Supplementary information

^{1}H and ^{19}F NMR spectral features of the FAP ILs:

(a) **[EMIM][FAP]**

^{1}H NMR (DMSO-d$_6$, 200 MHz) δ [ppm]: 1.42 (t, *J* = 7.4 Hz, 3H); 3.84 (s, 3H); 4.20 (q, *J* = 7.4 Hz, 2H); 7.65 (s, 1H); 7.73 (s, 1H); 9.14 (s, 1H)

^{19}F NMR (DMSO-d$_6$, 300 MHz) δ [ppm]: -43.0 (dm, PF); -80.14 (m, CF_3); -81.72 (m, $2CF_3$); -86.0 (dm, PF_2); -115.84 (dm, CF_2); -116.32 (dm, $2CF_2$); $^{1}J_{P,F}$ = 891 Hz; $^{1}J_{P,F}$ = 906 Hz; $^{2}J_{P,F}$ = 106 Hz

(b) **[EOHMIM][FAP]**

^{1}H NMR (DMSO-d$_6$, 200 MHz) δ [ppm]: 3.73 (t, *J* = 4.8 Hz, 2H); 3.85 (s, 3H); 4.20 (t, *J* = 5.4 Hz, 2H); 5.09 (s, -OH); 7.65 (s, 1H); 7.69 (s, 1H); 9.09 (s, 1H)

^{19}F NMR (DMSO-d$_6$, 300 MHz) δ [ppm]: -43.0 (dm, PF); -80.14 (m, CF_3); -81.72 (m, $2CF_3$); -86.35 (dm, PF_2); -115.84 (dm, CF_2); -116.32 (dm, $2CF_2$); $^{1}J_{P,F}$ = 891 Hz; $^{1}J_{P,F}$ = 906 Hz; $^{2}J_{P,F}$ = 106 Hz

TS 1. Bond dissociation energies (kJ/mol).

Bond	Dissociation energy (kJ/mol)
C-P	264
C-C	347
P-F	520
C-F	540

Fig.S1. Shear stress vs. shear rate (A) and viscosity vs. shear rate (B) of [EMIM][FAP] prior to irradiation.

Fig.S2. Shear stress vs. shear rate (A) and viscosity vs. shear rate (B) of irradiated (Dose ≈ 100 kGy) [EMIM][FAP].

Fig.S3. Shear stress vs. shear rate (A) and viscosity vs. shear rate (B) of [EOHMIM][FAP] prior to irradiation.

Fig.S4. Shear stress vs. shear rate (A) and viscosity vs. shear rate (B) of irradiated (Dose ≈ 100 kGy) [EOHMIM][FAP].

Fig.S5. Linear fit plots showing the variation of $\ln \eta_a$ with 1/T for unirradiated and irradiated FAP ILs.

Fig.S6. ^{1}H and ^{19}F NMR spectra of pre- and post-irradiated [EOHMIM][FAP].

Fig.S7. ESI (+) mass spectra of [EOHMIM][FAP] after irradiation to total absorbed dose of 400 kGy.

Fig.S8. MS^2 spectra of ion with m/z = 229.1 in [EMIM][FAP] after irradiation to a total absorbed dose of 400 kGy.

Fig.S9. ESI (-) mass spectra of [EMIM][FAP] after irradiation to a total absorbed dose of 400 kGy.

Fig.S10. ESI (-) mass spectra of [EOHMIM][FAP] after irradiation to a total absorbed dose of 400 kGy.

For a Newtonian liquid, the plot of shear stress versus shear rate follows linearity, while its viscosity must be independent of shear rate. The plots of the shear rates versus shear stress and viscosity versus shear rate of unirradiated and irradiated (dose ≈ 100 kGy) [EMIM][FAP] has been shown in Fig.S1 & Fig.S2, respectively.

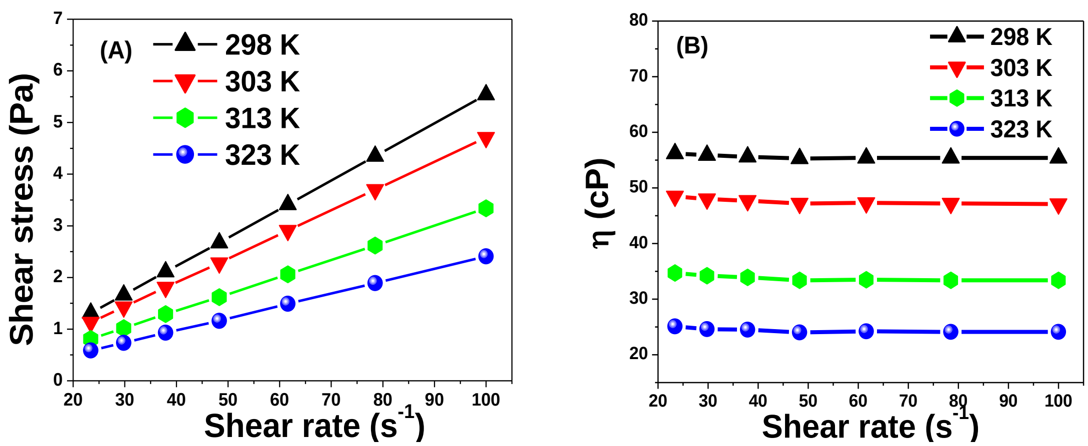

Fig.S1. Shear stress vs. shear rate (A) and viscosity vs. shear rate (B) of [EMIM][FAP] prior to irradiation.

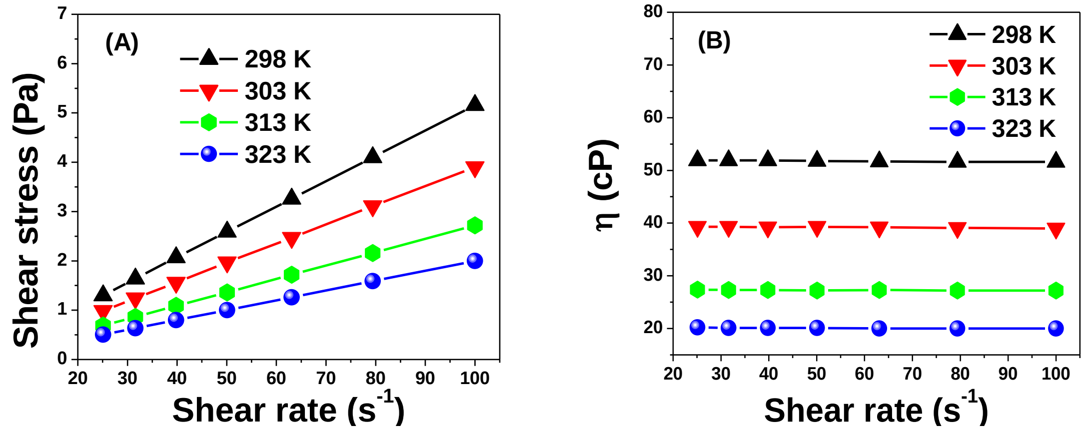

Fig.S2. Shear stress vs. shear rate (A) and viscosity vs. shear rate (B) of irradiated (Dose ≈ 100 kGy) [EMIM][FAP].

Similar plots have been shown for irradiated and unirradiated [EOHMIM][FAP] (Fig.S3 & Fig.S4). It can be observed from these plots that, prior to and after irradiation the shear rate is linearly related to shear stress, while the viscosity remains constant at various shear rates (upto 100 s^{-1}). This indicates that both the ILs exhibit Newtonian behavior before and after irradiation.

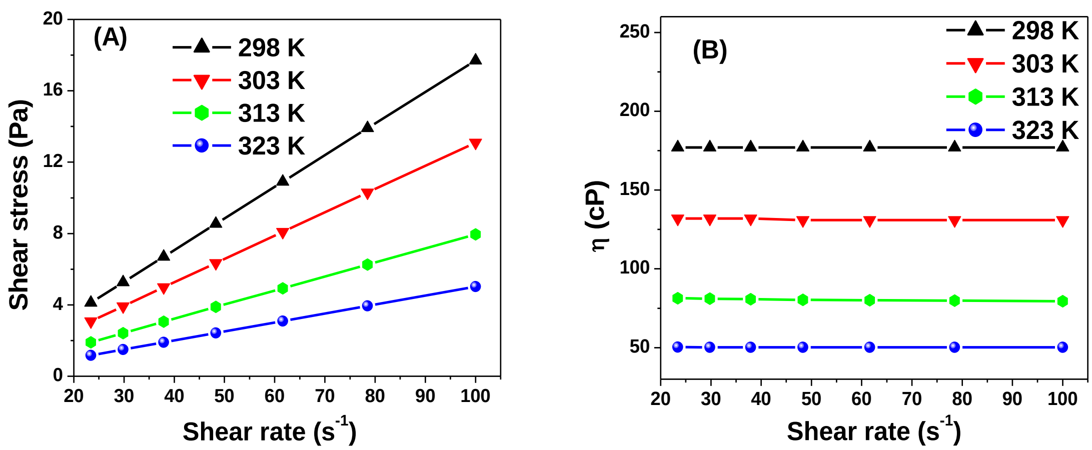

Fig.S3. Shear stress vs. shear rate (A) and viscosity vs. shear rate (B) of [EOHMIM][FAP] prior to irradiation

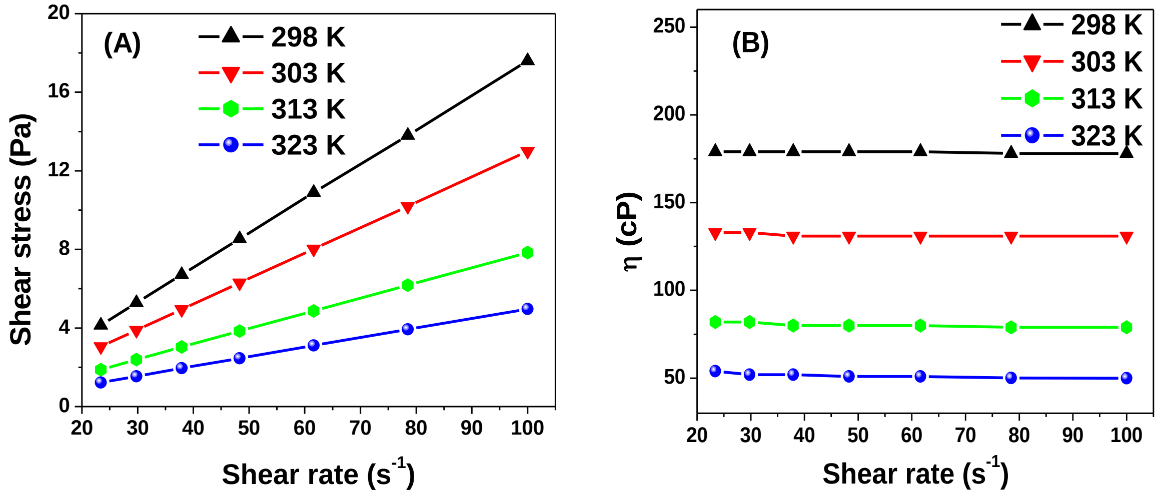

Fig.S4. Shear stress vs. shear rate (A) and viscosity vs. shear rate (B) of irradiated (Dose ≈ 100 kGy) [EOHMIM][FAP]

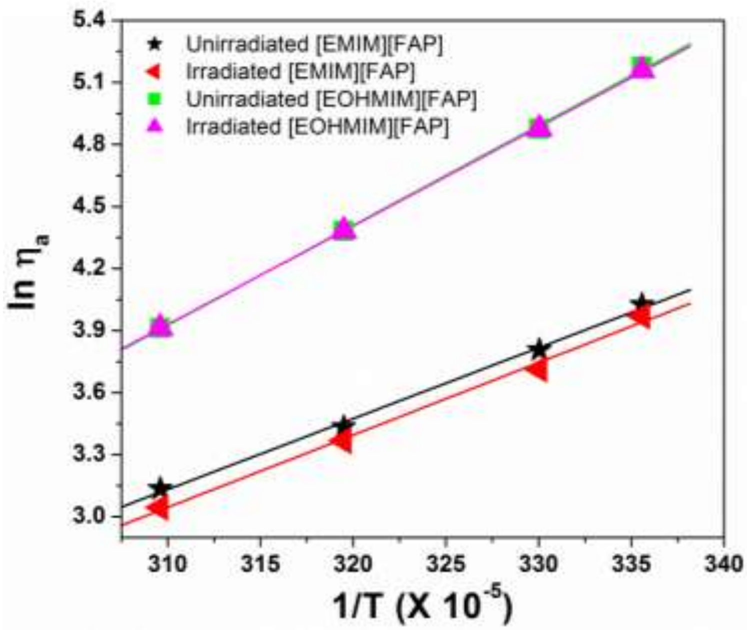

Fig.S5. Linear fit plots showing the variation of ln η_a with 1/T for unirradiated and irradiated FAP ILs.

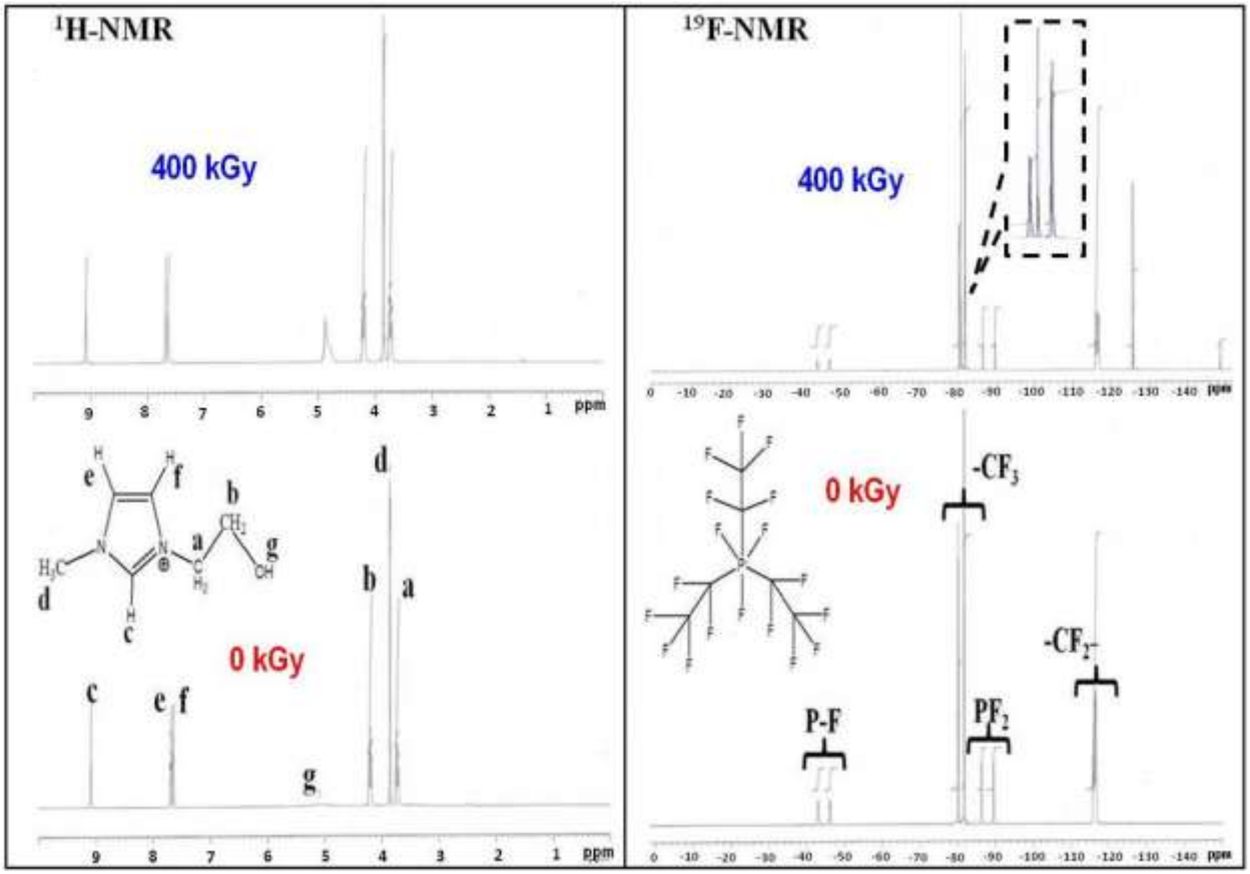

Fig.S6. ^{1}**H and** ^{19}**F NMR spectra of pre- and post-irradiated [EOHMIM][FAP]**

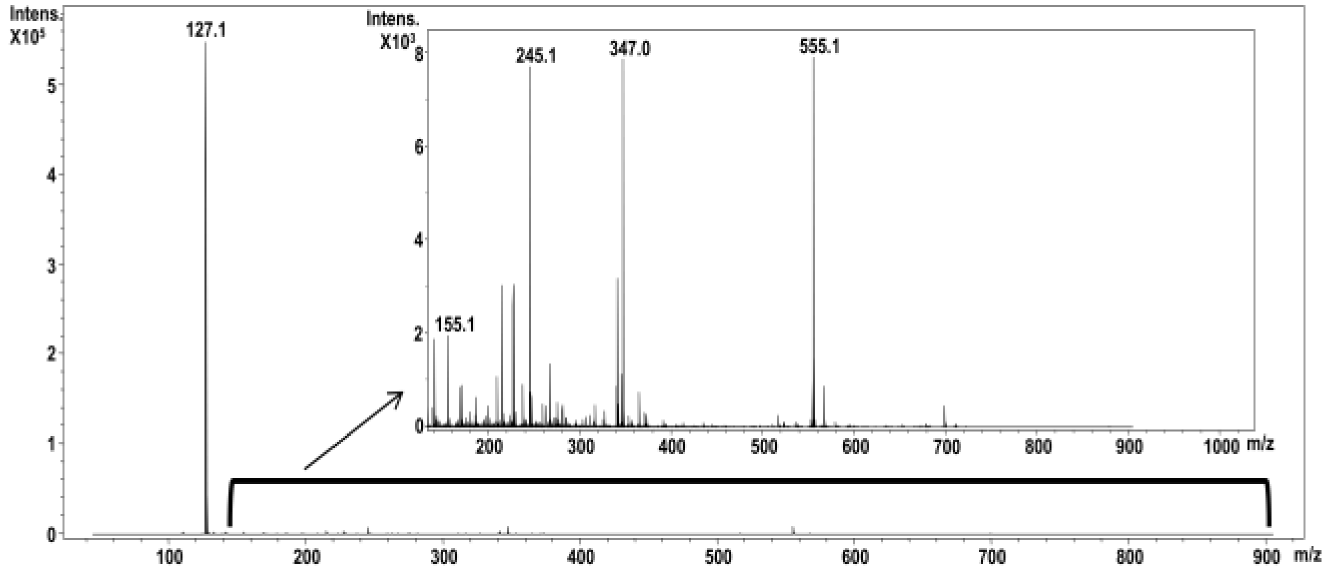

Fig.S7. ESI (+) mass spectra of [EOHMIM][FAP] after irradiation to total absorbed dose of 400 kGy

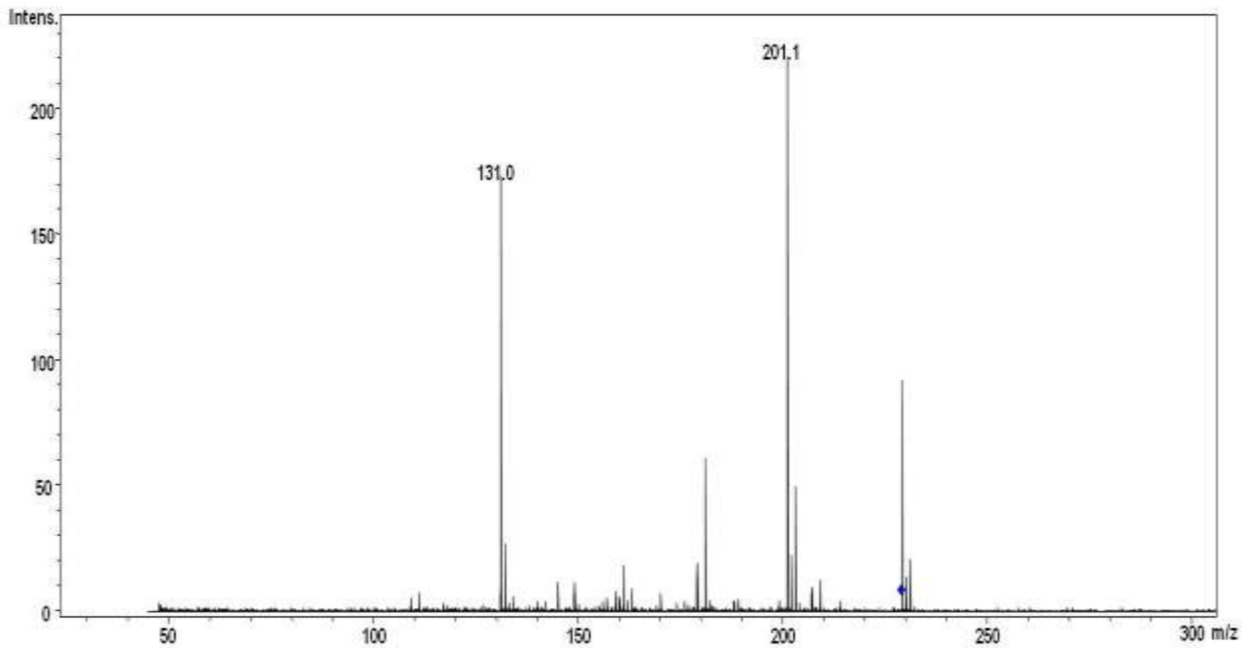

Fig.S8. MS^2 spectra of ion with m/z = 229.1 in [EMIM][FAP] after irradiation to a total absorbed dose of 400 kGy

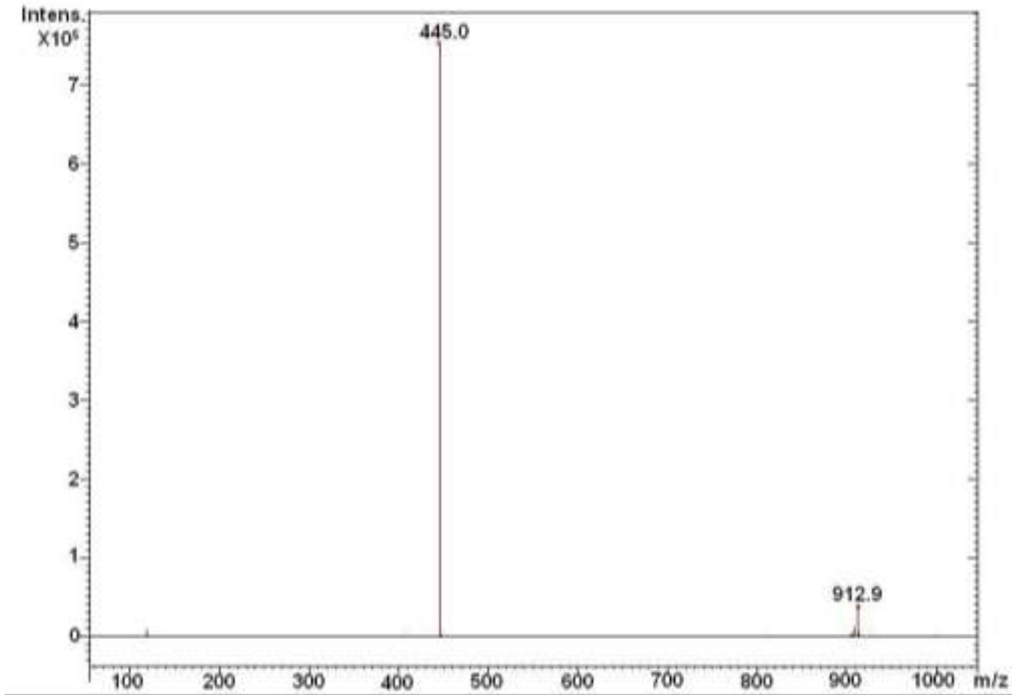

Fig.S9. ESI (-) mass spectra of [EMIM][FAP] after irradiation to a total absorbed dose of 400 kGy

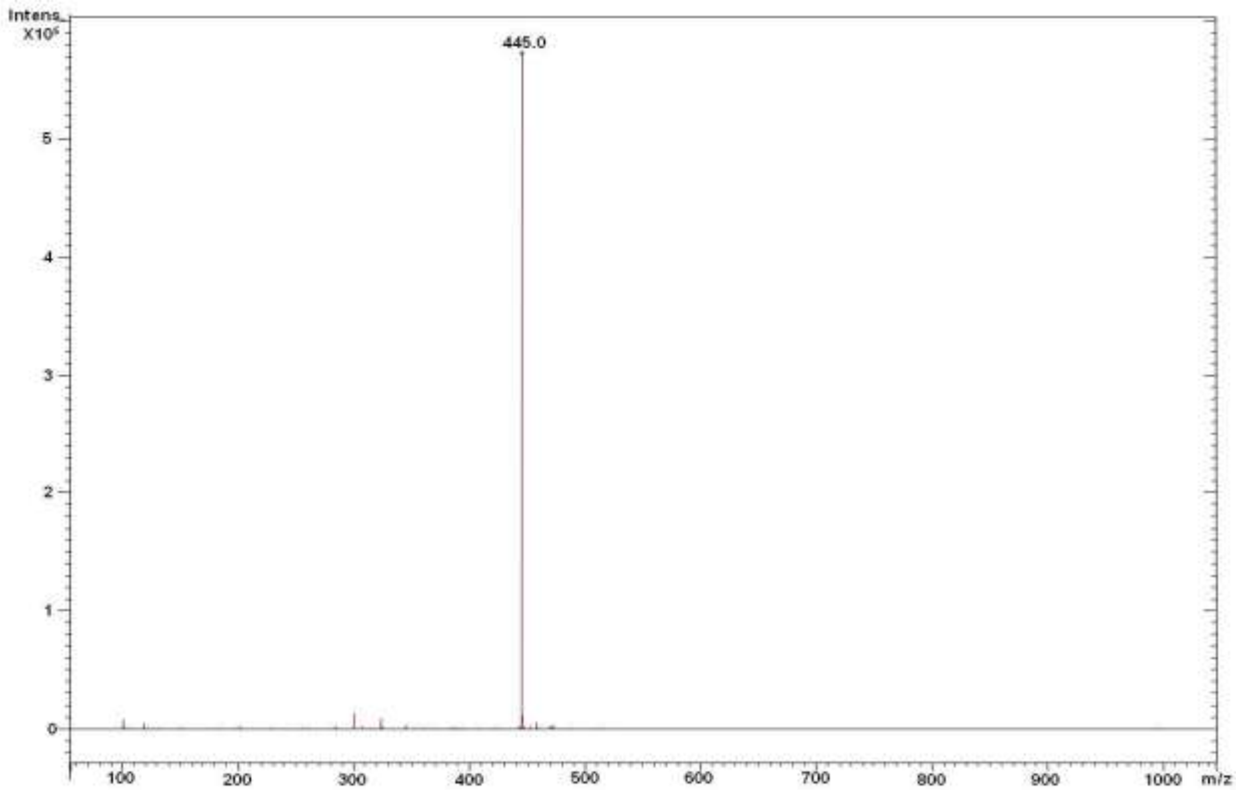

Fig.S10. ESI (-) mass spectra of [EOHMIM][FAP] after irradiation to a total absorbed dose of 400 kGy

Note, (Fig 9): The ion with m/z = 193.1 might be attributed due to the combination of parent cation ($[EMIM]^+$) and the radical species, $CH_3^{\bullet}$ and $CF_3^{\bullet}$, generated from the fragmentation of cationic and anionic moieties, respectively. The peak with m/z = 257.1 has been assigned to the ion formed from the adjoining of radicals, $C_2H_5^{\bullet}$ and $C_2F_5^{\bullet}$ with the parent cation ($[EMIM]^+$). The ions with m/z values 311.1, 329.1 and 347.0 are having the same basic structural composition with the subsequent addition of F atom. The ion peak with m/z = 347.0 was also observed in the ESI (+) mass spectra of irradiated [EOHMIM][FAP] as shown in Fig.S7. This peak with m/z = 347.0 has been identified to the cation, [(EMIM)-Y], where Y = 2 ($C_2F_5^{\bullet}$). The composition of ion peak with m/z = 347.0 was observed as $(C_{10}H_9N_2F_{10})^+$. Similarly, the composition of ion peaks with m/z values 311.1 and 329.1 has been assigned to $(C_{10}H_{11}N_2F_8)^+$ and $(C_{10}H_{10}N_2F_9)^+$, respectively. Further, there is also an evidence of the disintegration of the imidazolium cation as the ion with m/z = 139.1 have been identified as the recombination of the $[EMIM]^+$ cation with the C_2H_5 unit, fragmented from another parent cation.