Electronic Supplementary Information (ESI)

Significance of Weak Interactions in Imidazolium picrate Ionic Liquids: Spectroscopic and Theoretical Studies for molecular level Understanding

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1. Synthesis

XmimI was synthesized and well characterized in our previous work.[1] XmimI (5 mmol, X= me, propyl, butyl, hexyl) was taken in 50 ml round bottom flask, containing 5 ml of triple distilled water. 5.9 mmol of potassium picrate salt (1:1.1 mole ratios) was added. Resulting solution was stirred for 5 hours. The product was extracted using dichloromethane (DCM). After evaporating the solvent, desired product obtained. Further Purification is not required. ^{1}H-NMR, ^{13}C-NMR, and FTIR data confirmed the products.

Characterization of Compounds

Synthesis of mmimpic: Colour: Yellow Solid; Melting Point: 147.5 °C; FTIR (KBr, cm^{-1}): 3159, 3146, 3125, 3058, 2995, 2961, 2927, 2853, 1637, 1569, 1555, 1434, 1362, 1331, 1268, 1159, 1075; ^{1}H-NMR (300 MHz, DMSO-d_6): δ (*ppm*) 10.42 (s, 1H), 8.89 (s, 2H), 7.25 (s, 1H), 7.18 (d, J = 1.2 Hz, 1H), 4.10 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (*ppm*) 160.8, 141.8, 137.0, 125.2, 124.1, 123.4, 35.6.

Synthesis of pmimpic: Colour: Yellow Solid; Melting Point: 68.2 °C; FTIR (KBr, cm^{-1}): 3172,3150, 3066, 3103, 2971, 2957, 2940, 2886, 2815, 1634, 1564, 1483, 1434, 1363, 1331, 1263; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (*ppm*) 10.38 (s, 1H), 8.88 (s, 2H), 7.20 (d, J = 1 Hz, 2H), 4.33 (t, J = 7.2 Hz, 2H); 4.11 (s, 3H), 1.95 (q, J = 7.3 Hz, 2H), 1.00 (t, J = 7.3 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (*ppm*) 163.6, 142.2, 136.7, 129.0, 128.1, 124.4, 123.1, 52.0, 36.5, 23.7, 10.7.

Synthesis of bmimpic: Colour: Yellow Solid; Melting Point: 64.5 °C; FTIR (KBr, cm^{-1}): 3176, 3146, 3133, 3079, 3038, 2960, 2934, 2869, 1630, 1610, 1560, 1516, 1484, 1436, 1365, 1335, 1311, 1270, 1156, 1078, 1014; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (*ppm*) 10.27 (s, 1H), 8.86 (s, 2H), 7.23 (s, 2H), 4.36 (t, J = 7.2 Hz, 2H), 4.11 (s, 3H), 1.88 (q, J = 7.5 Hz, 2H), 1.38, (q, J = 7.4 Hz, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (*ppm*) 162.4, 141.7, 138.6, 49.9, 36.4, 32.2, 19.3, 13.3.

Synthesis of hmimpic: Colour: Yellow Solid; Melting Point: 65.9 °C; FTIR (KBr, cm^{-1}): 3165, 3147, 3095, 3041, 2958, 2930, 2859, 1633, 1557, 1491, 1435, 1364, 1334, 1309, 1265, 1159, 1075; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (*ppm*) 10.29 (s, 1H), 8.86 (s, 2H), 7.22 (s, 2H), 4.34 (t, J = 7.3 Hz, 2H), 4.11 (s, 3H), 1.89 (q, J = 6.9 Hz, 2H), 1.30 (m, 6H), 0.86 (t, J = 6.7

Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (*ppm*) 162.3, 141.7, 138.4, 126.7, 126.1, 123.1, 121.7, 50.1, 36.4, 30.9, 30.2, 25.7, 22.2, 13.7.

Experimental Results

Table 1: Melting Point and Freezing Point of picrate ILs from DSC experiment[2]

ILs	$^{a}T_m$/°C	$^{b}T_{fr}$/°C
mmimPic	147.5	144.9
pmimPic	74.2	71.3
bmimPic	64.5	62.2
hmimPic	65.9 (1st Cycle) 12.6 (2nd cycle)	- 1.3

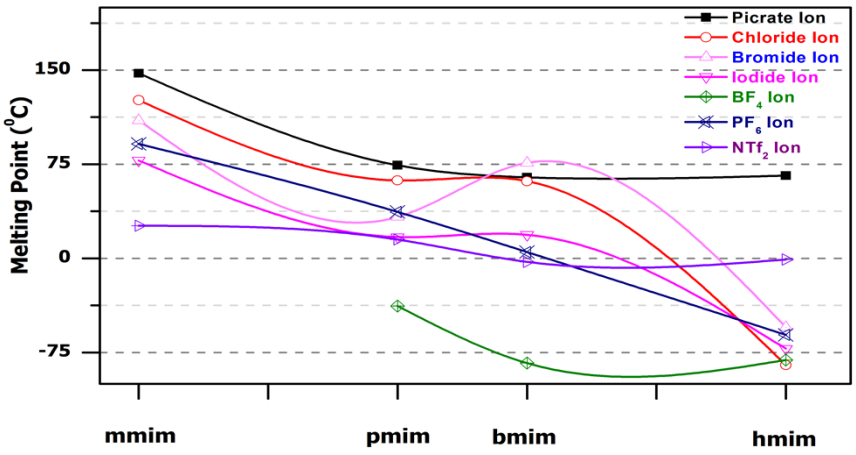


Fig. 1 Melting point of imidazolium based ILs having various anions.

Table 2: Melting point of imidazolium based ILs having various anions.

	Cl	Br	I	BF_4	PF_6	NTf_2
mmim	399.1 ± 4 K[3]	383 ± 1 K[4]	351±2 K[5]	-	364.2 K[6]	299 K[7]
pmim	335.1 ± 2 K[8]	306 K[9]	290 K[10]	235 K[11]	310±2 K[12]	288 K[13]
bmim	334.5 K[14]	349.1 K[15]	291.72 K[16]	189.5 K[17]	278 K[18]	270.2 K[19]
hmmim	188 K[20]	218.1 K[21]	201 K[22]	192 K[22]	212 K[23]	272.1 K[24]

Table 3. Selected bond lengths (Å) and angles (deg) and hydrogen bonding interactions for mmimPic obtained from X-ray diffraction (Geometry parameters)

mimpic IL			
O(1)-C(14)	1.234(3)	O(1)-C(14)-C(19)	125.3(2)
C(19)-N(22)	1.449(3)	O(1)-C(14)-C(15)	123.6(2)
C(17)-N(21)	1.443(3)	O(3)-N(22)-O(2)	121.5(2)
C(15)-N(20)	1.457(3)	O(4)-N(21)-O(5)	123.4(2)
N(22)-O(3)	1.213(3)	O(6)-N(20)-O(7)	122.4(3)
N(22)-O(2)	1.220(3)	C(2)-N(3)-C(4)	108.2(2)
N(21)- O(4)	1.225(3)	C(2)-N(3)-C(6)	125.3(2)
N(21)-O(5)	1.226(3)	C(4)-N(3)-C(6)	126.5(2)

N(20)-O(6)	1.198(4)	C(2)-N(1)-C(5)	108.1(2)
N(20)-O(7)	1.208(3)	C(2)-N(1)-C(7)	125.4(2)
N(3)-C(6)	1.461(4)	C(5)-N(1)-C(7)	126.5(3)
N(1)-C(7)	1.464(4)		

Table 4: Hydrogen bond lengths (Å) and angles (^{O}) in mmimpic IL

mmimPic IL				
D-H…A	d(D-H)	d(H..A)	<DHA	d(D..A)
C2-H2...O1#1	0.930	2.255	142.74	3.048
C2-H2...O2#1	0.930	2.405	146.33	3.221
C4-H4...O5#2	0.930	2.582	125.67	3.215
C5-H5...O4#2	0.930	2.489	149.17	3.322
C6-H6A...O1#1	0.960	2.373	149.66	3.238
C6-H6B...O7#3	0.960	2.574	144.28	3.400
C6-H6C...O3#4	0.960	2.464	150.49	3.333
C7-H7C...O2#1	0.960	2.604	142.48	3.415

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1; #2 -x, -y, -z+2; #3 x, y-1, z; #4 -x+1, -y, -z+1;

Table 5. Selected bond lengths (Å) and angles (deg) and hydrogen bonding interactions for pmimPic obtained from X-ray diffraction (Geometry parameters)

pmimpic IL			
O(1)-C(14)	1.238(3)	O(1)-C(14)-C(19)	125.0(3)
N(20)-C(15)	1.455(3)	O(1)-C(14)-C(15)	124.1(3)
N(21)-C(17)	1.449(3)	O(2)-N(20)-O(3)	121.9(3)
N(22)-C(19)	1.462(3)	O(5)-N(21)-O(4)	123.4(3)
O(2)-N(20)	1.219(3)	O(7)-N(22)-O(6)	122.4(2)
O(3)-N(20)	1.232(3)	C(2)-N(1)-C(5)	108.4(2)
O(4)-N(21)	1.240(3)	C(2)-N(1)-C(7)	125.2(3)
O(5)-N(21)	1.231(3)	C(5)-N(1)-C(7)	126.1(2)
O(6)-N(22)	1.236(3)	C(2)-N(3)-C(4)	108.9(2)
O(7)-N(22)	1.228(3)	C(2)-N(3)-C(6)	125.5(3)
N(1)-C(7)	1.475(4)	C(4)-N(3)-C(6)	125.6(3)
N(3)-C(6)	1.470(4)		

Table 6: Hydrogen bond lengths (Å) and angles (^{O}) in pmimpic IL

pmimpic IL				
D-H…A	d(D-H)	d(H..A)	<DHA	d(D..A)
C4-H4...O6#1	0.930	2.593	141.50	3.371
C2-H2...O7#2	0.930	2.613	139.74	3.376
C2-H2...O1#2	0.930	2.240	143.84	3.040
C5-H5...O3	0.930	2.448	164.20	3.353
C8-H8A...O7#3	0.970	2.646	152.07	3.532
C6-H6A...O2#4	1.032	2.469	152.65	3.418
C6-H6B...O2#2	0.914	2.529	149.39	3.348
C6-H6B...O1#2	0.914	2.513	145.63	3.308
C6-H6C...O1#5	0.959	2.330	170.23	3.279

Symmetry transformations used to generate equivalent atoms: #1 x, y-1, z+1; #2 x, y, z+1; #3 -x, -y+1, -z+2; #4 -x+1, -y+1, -z+2; #5 -x+1, -y+2, -z+1

Table 7: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	X	Y	z	*U*iso*/*U*eq
O1	0.3628 (2)	0.63737 (17)	0.46337 (18)	0.0471 (5)
C14	0.2622 (3)	0.5453 (2)	0.5326 (2)	0.0338 (6)
C19	0.2281 (3)	0.4128 (2)	0.4954 (2)	0.0334 (6)
C18	0.1182 (3)	0.3111 (2)	0.5758 (2)	0.0375 (6)
H18	0.1004	0.2289	0.5463	0.045*
C17	0.0345 (3)	0.3310 (2)	0.7000 (3)	0.0391 (6)
C16	0.0581 (3)	0.4524 (3)	0.7456 (3)	0.0420 (6)
H16	0.0026	0.4641	0.8304	0.050*
C15	0.1638 (3)	0.5551 (2)	0.6649 (3)	0.0384 (6)
N22	0.3104 (3)	0.3828 (2)	0.3662 (2)	0.0426 (6)
O2	0.3860 (3)	0.4756 (2)	0.28127 (19)	0.0649 (6)
O3	0.2991 (4)	0.2650 (2)	0.3447 (2)	0.0805 (8)
N21	−0.0827 (3)	0.2244 (3)	0.7834 (3)	0.0545 (7)
O4	−0.0998 (3)	0.1164 (2)	0.7420 (2)	0.0745 (7)
O5	−0.1611 (3)	0.2472 (2)	0.8917 (2)	0.0793 (8)
N20	0.1769 (4)	0.6833 (3)	0.7165 (3)	0.0618 (7)
O6	0.1646 (5)	0.6756 (3)	0.8347 (3)	0.1220 (12)
C2	0.4444 (4)	0.2159 (2)	0.8072 (3)	0.0401 (6)
H2	0.5141	0.2868	0.7513	0.048*
N3	0.4117 (3)	0.0947 (2)	0.7768 (2)	0.0434 (6)
C4	0.3049 (4)	0.0186 (3)	0.8843 (3)	0.0585 (8)
H4	0.2616	−0.0708	0.8900	0.070*
C5	0.2747 (4)	0.0962 (3)	0.9791 (3)	0.0608 (9)
H5	0.2066	0.0709	1.0635	0.073*
N1	0.3626 (3)	0.2204 (2)	0.9292 (2)	0.0459 (6)
C6	0.4810 (5)	0.0501 (3)	0.6501 (3)	0.0635 (9)
H6A	0.5300	0.1295	0.5858	0.095*
H6B	0.3816	0.0138	0.6182	0.095*
H6C	0.5770	−0.0223	0.6632	0.095*
C7	0.3706 (5)	0.3364 (3))	1.0001 (3)	0.0738 (10)
H7A	0.4662	0.3149	1.0555	0.111*
H7B	0.2536	0.3483	1.0546	0.111*
H7C	0.3971	0.4220	0.9365	0.111*
O7	0.1922 (5)	0.7944 (3)	0.6386 (3)	0.1125 (11)

Atomic displacement parameters (Å2)

	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
O1	0.0518 (11)	0.0405 (10)	0.0454 (11)	−0.0170 (8)	0.0021 (9)	−0.0011 (8)
C14	0.0302 (13)	0.0342 (12)	0.0353 (14)	−0.0041(10)	−0.0053 (11)	−0.0007 (10)
C19	0.0320 (13)	0.0347 (12)	0.0313 (13)	−0.0027 (10)	−0.0028 (10)	−0.0023 (9)
C18	0.0386 (14)	0.0323 (12)	0.0400 (15)	−0.0050 (10)	−0.0075 (12)	−0.0002 (10)
C17	0.0344 (13)	0.0424 (14)	0.0358 (14)	−0.0100 (10)	−0.0038 (11)	0.0060 (10)
C16	0.0380 (14)	0.0565 (15)	0.0303 (14)	−0.0058 (12)	−0.0026 (11)	−0.0060 (11)
C15	0.0383 (14)	0.0425 (14)	0.0366 (14)	−0.0066 (11)	−0.0068 (12)	−0.0104 (10)

N22	0.0470 (13)	0.0408 (12)	0.0382 (13)	−0.0038 (10)	−0.0009 (10)	−0.0071 (9)
O2	0.0879 (16)	0.0607 (12)	0.0394 (12)	−0.0282 (11)	0.0194 (11)	−0.0073 (9)
O3	0.129 (2)	0.0451 (12)	0.0626 (15)	−0.0162 (12)	0.0210 (14)	−0.0222 (10)
N21	0.0502 (15)	0.0619 (16)	0.0440 (15)	−0.0195 (12)	−0.0035 (12)	0.0109 (12)
O4	0.0901 (17)	0.0590 (13)	0.0688 (16)	−0.0388 (12)	−0.0013 (13)	0.0058 (11)
O5	0.0834 (16)	0.0987 (17)	0.0423 (13)	−0.0324 (13)	0.0186 (12)	0.0068 (12)
N20	0.0721 (18)	0.0615 (16)	0.0563 (18)	−0.0158 (13)	0.0028 (14)	−0.0274 (13)
O6	0.206 (4)	0.108 (2)	0.066 (2)	−0.029 (2)	−0.012 (2)	−0.0487 (16)
C2	0.0456 (15)	0.0351 (13)	0.0373 (15)	−0.0115 (11)	−0.0022 (12)	−0.0005 (10)
N3	0.0503 (14)	0.0319 (11)	0.0467 (14)	−0.0095 (9)	−0.0075 (11)	−0.0015 (9)
C4	0.0627 (19)	0.0452 (16)	0.062 (2)	−0.0229 (14)	−0.0069 (16)	0.0083(14)
C5	0.0597 (19)	0.0656 (19)	0.0473 (19)	−0.0222 (15)	0.0008 (15)	0.0131 (15)
N1	0.0512 (14)	0.0490 (12)	0.0342 (13)	−0.0098 (10)	−0.0012 (11)	−0.0014 (9)
C6	0.085 (2)	0.0449 (16)	0.064 (2)	−0.0058 (15)	−0.0049 (18)	−0.0206 (14)
C7	0.100 (3)	0.078 (2)	0.0470 (19)	−0.0159 (19)	0.0009 (19)	−0.0254 (16)
O7	0.177 (3)	0.0594 (15)	0.100 (2)	−0.0424 (17)	0.025 (2)	−0.0343 (14)

Geometric parameters (Å, º) for (shelx)

O1—C14	1.234 (3)	N20—O7	1.208 (3)
C14—C19	1.456 (3)	C2—N1	1.315 (3)
C14—C15	1.458 (3)	C2—N3	1.318 (3)
C19—C18	1.372 (3)	C2—H2	0.9300
C19—N22	1.449 (3)	N3—C4	1.368 (3)
C18—C17	1.374 (3)	N3—C6	1.461 (4)
C18—H18	0.9300	C4—C5	1.329 (4)
C17—C16	1.379 (4)	C4—H4	0.9300
C17—N21	1.443 (3)	C5—N1	1.373 (3)
C16—C15	1.363 (3)	C5—H5	0.9300
C16—H16	0.9300	N1—C7	1.464 (4)
C15—N20	1.457 (3)	C6—H6A	0.9600
N22—O3	1.213 (3)	C6—H6B	0.9600
N22—O2	1.220 (3)	C6—H6C	0.9600
N21—O4	1.225 (3)	C7—H7A	0.9600
N21—O5	1.226 (3)	C7—H7B	0.9600
N20—O6	1.199 (4)	C7—H7C	0.9600
Bonding parameters			
O1—C14—C19	125.3 (2)	N1—C2—N3	109.1 (2)
O1—C14—C15	123.6	(2) N1—C2—H2	125.5
C19—C14—C15	111.12 (19)	N3—C2—H2	125.5
C18—C19—N22	116.0 (2)	C2—N3—C4	108.2 (2)
C18—C19—C14	123.9 (2)	C2—N3—C6	125.3 (2)
N22—C19—C14	120.1 (2)	C4—N3—C6	126.5 (2)
C19—C18—C17	119.9 (2)	C5—C4—N3	107.3 (2)
C19—C18—H18	120.1	C5—C4—H4	126.4
C17—C18—H18	120.1	N3—C4—H4	126.4
C18—C17—C16	121.1(2)	C4—C5—N1	107.3 (3)
C18—C17—N21	119. 6 (2)	C4—C5—H5	126.3
C16—C17—N21	119.3(2)	N1—C5—H5	126.3
C15—C16—C17	119.3 (2)	C2—N1—C5	108.1 (2)
C15—C16—H16	120.4	C2—N1—C7	125.4 (2)

C17—C16—H16	120.4	C5—N1—C7	126.5 (3)
C16—C15—N20	116.6 (2)	N3—C6—H6A	109.5
C16—C15—C14	124.8 (2)	N3—C6—H6B	109.5
N20—C15—C14	118.6 (2)	H6A—C6—H6B	109.5
O3—N22—O2	121.5 (2)	N3—C6—H6C	109.5
O3—N22—C19	118.5 (2)	H6A—C6—H6C	109.5
O2—N22—C19	120.0 (2)	H6B—C6—H6C	109.5
O4—N21—O5	123.4(2)	N1—C7—H7A	109.5
O4—N21—C17	118.3 (2)	N1—C7—H7B	109.5
O5—N21—C17	118.3 (3)	H7A—C7—H7B	109.5
O6—N20—O7	122.4 (3)	N1—C7—H7C	109.5
O6—N20—C15	118.9 (3)	H7A—C7—H7C	109.5
O7—N20—C15	118.6 (3)	H7B—C7—H7C	109.5

Table 8: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for pmimPic

	x	*y*	*z*	*U*iso*/*U*eq
N1	0.3501 (4)	0.6949 (2)	1.13596 (19)	0.0275 (6)
N3	0.2909 (4)	0.5499 (2)	1.29372 (19)	0.0229 (6)
C4	0.2579 (5)	0.5031 (3)	1.2017 (3)	0.0311 (8)
H4	0.2176	0.4238	1.2066	0.037*
C2	0.3458 (5)	0.6661 (3)	1.2521 (2)	0.0259 (7)
H2	0.3762	0.7185	1.2968	0.031*
C5	0.2948 (5)	0.5935 (3)	1.1027 (3)	0.0331 (8)
H5	0.2848	0.5884	1.0263	0.040*
C6	0.2625 (6)	0.4849 (3))	1.4182 (3)	0.0295 (8)
C7	0.3878 (6)	0.8209 (3))	1.0564 (3)	0.0419 (10)
H7A	0.4424	0.8686	1.1018	0.050*
H7B	0.2579	0.8790	1.0193	0.050*
C8	0.5384 (5)	0.7937 (3)	0.9622 (2)	0.0347 (8)
H8A	0.5481	0.8797	0.9085	0.042*
H8B	0.4838	0.7448	0.9180	0.042*
C9	0.7537 (5)	0.7128 (4)	1.0093 (3)	0.0422 (9)
H9A	0.8410	0.7017	0.9449	0.063*
H9B	0.7470	0.6253	1.0593	0.063*
H9C	0.8093	0.7601	1.0534	0.063*
O2	0.1630 (4)	0.6064 (2)	0.65085 (18)	0.0468 (7)
O3	0.2124 (4)	0.6412 (2)	0.81543 (17)	0.0458 (7)
O4	0.0796 (4)	1.0959 (2)	0.83076 (18)	0.0440 (7)
O5	0.1374 (4)	1.2549 (2)	0.68049 (19)	0.0432 (7)
O6	0.3062 (3)	1.1675 (2)	0.31791 (17)	0.0358 (6)
O7	0.3269 (3)	0.9733 (2)	0.28796 (17)	0.0374 (6)
O1	0.3317 (3)	0.7613 (2)	0.47132 (16)	0.0315 (6)
N20	0.1972 (4)	0.6790 (2)	0.7074 (2)	0.0259 (6)
N21	0.1270 (4)	1.1372 (3)	0.7272 (2)	0.0318 (7)
N22	0.3014 (4)	1.0469 (3)	0.3532 (2)	0.0236 (6)
C14	0.2731 (4)	0.8473 (3)	0.5251 (2)	0.0203 (7)
C15	0.2125 (4)	0.8163 (3)	0.6479 (2)	0.0186 (6)
C16	0.1683 (4)	0.9072 (3)	0.7119 (2)	0.0216 (7)
H16	0.1353	0.8799	0.7904	0.026*
C17	0.1729 (4)	1.0407 (3)	0.6588 (2)	0.0217 (7)
C18	0.2169 (4)	1.0835 (3)	0.5417 (2)	0.0215 (7)
H18	0.2151	1.1741	0.5065	0.026*
C19	0.2631 (4)	0.9917 (3)	0.4773 (2)	0.0182 (6)
H6A	0.122 (4)	0.459 (3)	1.426 (2)	0.027*

H6B	0.251 (4)	0.546 (3)	1.461 (2)	0.027*
H6C	0.372 (4)	0.406 (3)	1.449 (2)	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0419 (18)	0.0239 (15)	0.0164 (13)	−0.0075(13)	0.0068 (12)	−0.0063 (12)
N3	0.0271 (15)	0.0245 (15)	0.0176 (13)	−0.0074 (12)	0.0024 (11)	−0.0060 (11)
C4	0.037 (2)	0.035 (2)	0.0280 (17)	−0.0175 (16)	0.0045 (15)	−0.0139 (16)
C2	0.036 (2)	0.0215 (17)	0.0210 (16)	−0.0060 (15)	0.0034 (15)	−0.0086 (14)
C5	0.044 (2)	0.040 (2)	0.0230 (17)	−0.0141 (17)	0.0018 (15)	−0.0182 (16)
C6	0.040 (2)	0.028 (2)	0.0200 (17)	−0.0091 (16)	0.0020 (16)	−0.0047 (15)
C7	0.068 (3)	0.027 (2)	0.0276 (18)	−0.0118 (18)	0.0136 (18)	−0.0037 (16)
C8	0.055 (2)	0.0302 (19)	0.0200 (16)	−0.0157 (17)	0.0100 (16)	−0.0063 (15)
C9	0.047 (2)	0.056 (2)	0.0323 (19)	−0.025 (2)	0.0022 (18)	−0.0156 (18)
O2	0.089 (2)	0.0393 (15)	0.0283 (13)	−0.0385 (14)	0.0141 (13)	−0.0164 (12)
O3	0.0803 (19)	0.0377 (15)	0.0184 (12)	−0.0237 (13)	−0.0054(12)	0.0026 (11)
O4	0.0671 (18)	0.0422 (15)	0.0268 (13)	−0.0106 (13)	0.0079 (12)	−0.0196 (11)
O5	0.0617 (18)	0.0270 (14)	0.0466 (15)	−0.0132 (12)	0.0041 (13)	−0.0178 (12)
O6	0.0484 (15)	0.0283 (13)	0.0295 (12)	−0.0162 (11)	0.0091 (11)	−0.0013 (11)
O7	0.0578 (16)	0.0384 (14)	0.0216 (12)	−0.0183 (12)	0.0125 (11)	−0.0133 (11)
O1	0.0475 (15)	0.0258 (13)	0.0220 (11)	−0.0057 (11)	0.0079 (10)	−0.0113(10)
N20	0.0314 (16)	0.0284 (16)	0.0188 (13)	−0.0086 (12)	0.0000 (12)	−0.0069 (12)
N21	0.0341 (17)	0.0349 (18)	0.0311 (16)	−0.0060 (13)	0.0002 (13)	−0.0185(14)
N22	0.0168 (14)	0.0281 (15)	0.0249 (14)	−0.0074 (11)	0.0010 (11)	−0.0046 (13)
C14	0.0167 (16)	0.0231 (17)	0.0220 (15)	−0.0044 (13)	−0.0005 (13)	−0.0078 (14)
C15	0.0207 (16)	0.0176 (16)	0.0171 (14)	−0.0052 (13)	−0.0022 (13)	−0.0033 (13)
C16	0.0197 (17)	0.0299 (18)	0.0154 (14)	−0.0067 (14)	−0.0007 (13)	−0.0060 (14)
C17	0.0228 (17)	0.0228 (17)	0.0206 (15)	−0.0032 (13)	−0.0041 (13)	−0.0094 (14)
C18	0.0211 (17)	0.0184 (16)	0.0239 (16)	−0.0048 (13)	−0.0015 (13)	−0.0041 (13)
C19	0.0157 (16)	0.0258 (17)	0.0133 (14)	−0.0082 (13)	0.0011 (12)	−0.0032 (13)

Geometric parameters (Å, º) for (shelx)

N1—C2	1.327 (3)	C9—H9B	0.9600
N1—C5 0	1.377 (4)	C9—H9C	0.960
N1—C7	1.475 (4)	O2—N20	1.219 (3)
N3—C2	1.326 (3)	O3—N20	1.232 (3)
N3—C4	1.368 (3)	O4—N21	1.240 (3)
N3—C6	1.470 (4)	O5—N21	1.231 (3)
C4—C5	1.349 (4)	O6—N22	1.236 (3)
C4—H4	0.9300	O7—N22	1.228 (3)
C2—H2	0.9300	O1—C14	1.238 (3)
C5—H5	0.9300	N20—C15	1.455 (3)
C6—H6A	1.03 (3)	N21—C17	1.449 (3)
C6—H6B	0.91 (3)	N22—C19	1.462 (3)
C6—H6C	0.96 (3)	C14—C19	1.460 (4)
C7—C8	1.517 (4)	C14—C15	1.465 (4)
C7—H7A	0.9700	C15—C16	1.362 (4)
C7—H7B	0.9700	C16—C17	1.384 (4)
C8—C9	1.517 (4)	C16—H16	0.9300
C8—H8A	0.9700	C17—C18	1.380 (4)
C8—H8B	0.9700	C18—C19	1.373 (4)
C9—H9A	0.9600	C18—H18	0.9300

Bond Angle

C2—N1—C5	108.4 (2)	C8—C9—H9A	109.5
C2—N1—C7	125.2 (3)	C8—C9—H9B	109.5
C5—N1—C7	126.1 (2)	H9A—C9—H9B	109.5
C2—N3—C4	108.9 (2)	C8—C9—H9C	109.5
C2—N3—C6	125.5 (3)	H9A—C9—H9C	109.5

C4—N3—C6	125.6 (3)	H9B—C9—H9C	109.5
C5—C4—N3	107.1 (3)	O2—N20—O3	121.9 (3)
C5—C4—H4	126.5	O2—N20—C15	120.1 (2)
N3—C4—H4	126.5	O3—N20—C15	118.0 (2)
N3—C2—N1	108.6 (3)	O5—N21—O4	123.4 (3)
N3—C2—H2	125.7	O5—N21—C17	118.9 (2)
N1—C2—H2	125.7	O4—N21—C17	117.6 (3)
C4—C5—N1	107.0 (3)	O7—N22—O6	122.4 (2)
C4—C5—H5	126.5	O7—N22—C19	119.6 (2)
N1—C5—H5	126.5	O6—N22—C19	118.1 (2)
N3—C6—H6A	108.5	(15) O1—C14—C19	125.0 (3)
N3—C6—H6B	110.4 (17)	O1—C14—C15	124.1 (3)
H6A—C6—H6B	105 (2)	C19—C14—C15	110.8 (2)
N3—C6—H6C	111.4 (16)	C16—C15—N20	116.6 (2)
H6A—C6—H6C	110 (2)	C16—C15—C14	124.8 (3)
H6B—C6—H6C	112 (2)	N20—C15—C14	118.6 (2)
N1—C7—C8	112.1 (2)	C15—C16—C17	119.3 (3)
N1—C7—H7A	109.2	C15—C16—H16	120.3
C8—C7—H7A	109.2	C17—C16—H16	120.3
N1—C7—H7B	109.2	C18—C17—C16	121.0 (3)
C8—C7—H7B	109.2	C18—C17—N21	119.7 (3)
H7A—C7—H7B	107.9	C16—C17—N21	119.3 (3)
C7—C8—C9	114.2 (3)	C19—C18—C17	119.7 (3)
C7—C8—H8A	108.7	C19—C18—H18	120.1
C9—C8—H8A	108.7	C17—C18—H18	120.1
C7—C8—H8B	108.7	C18—C19—C14	124.1 (2)
C9—C8—H8B	108.7	C18—C19—N22	115.9 (2)
H8A—C8—H8B	107.6	C14—C19—N22	120.0 (2)

Table 9 Cation-Anion Interactions Parameters of ILs from SCXRD data

ILs	C_2-H	C_2-H··O-C_{14}	C_7-H··O-N_{22}	C_6-H··O-N_{20}
mmimPic	0.93	2.25	2.60	2.84
pmimPic	0.93	2.24	2.75	2.50

Table 10 Hydrogen Bonding Parameters for ILs using DFT Results[25]

	H-C_2 (Å)	C_{14}-O··H(Å)	< C_{14}-O··H-C_2	<H··O··C_{14}
mmimPic	1.090	1.902	143.73	133.57
pmimPic	1.089	1.909	143.56	133.79
bmimPic	1.089	1.914	143.18	134.28
hmimPic	1.089	1.918	142.87	133.73

Table 11: C_{14}-O bond length of picrate anion from SCXRD and DFT calculation

	SCXRD	DFT Result
	C_{14}-O bond Length	
mmimPic	1.235	1.2434
pmimPic	1.237	1.2431

Table 12: Chemical Shift of Picrate ILs in D_2O and $CDCl_3$

		C_2-H	C_4-H	C_5-H	C_3-CH_3	NCH_2
mmim	D_2O	NA	7.23	7.23	3.72	3.72
	$CDCl_3$	10.41	7.18	7.18	4.10	4.10
pmim	D_2O	8.52	7.28	7.24	3.71	3.97
	$CDCl_3$	10.38	7.20	7.20	4.11	4.33
bmim	D_2O	NA	7.27	7.23	3.69	3.99

	$CDCl_3$	10.27	7.23	7.23	4.11	4.36
hmim	D_2O	8.52	7.29	7.24	3.71	4.01
	$CDCl_3$	10.29	7.22	7.22	4.11	4.35

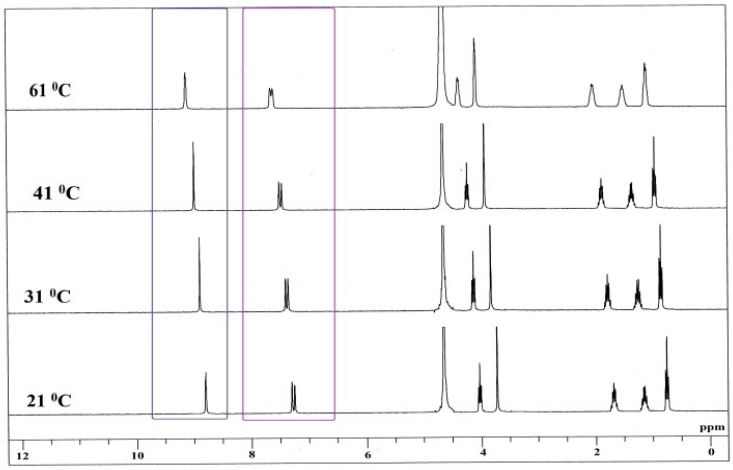


Fig. 2 Temperature dependent ^{1}H-NMR of bmimPic in D_2O solvent.

Table 13 Selected bond lengths, bond angles and dihedral angles of ILs from DFT calculation.

Ionic liquids	mmimpic	pmimpic	bmimpic	hmimpic
Dipole Moment	17.57 D	17.62 D	17.60 D	17.47 D
C_2-H	1.09037 Å	1.0898	1.0894	1.0892
C_2-H…O-C_{14}	1.90227 Å	1.9095	1.9148	1.9189
C_6-H···O-N_{20}	2.2389	2.3700	2.3649	2.3564
C_7-H…O-N_{22}	2.2389	2.2754	2.2723	2.2852
N_1-C_2	1.3392 Å	1.3392	1.3389	1.3390
N_3-C_2	1.33741 Å	1.3376	1.3379	1.3379
C_4-C_5	1.3597 Å	1.3602	1.3600	1.3600
N_3-C_4	1.3824 Å	1.3825	1.3824	1.3824
N_1-C_5	1.3837 Å	1.3832	1.3834	1.3835
<N_1-C-N_3	108.27˚	108.35	108.37	108.38
<C_2-H…Pic	143.73˚	143.56	143.18	142.87
<C_2H..O-C_{14}	133.57	133.79	134.28	133.73

Table 14 Hydrogen bonding parameters using DFT calculation.

	C_2-H (Å)	C_2H··O-C_{14} (Å)	< C_2H··O	<H··O··C_{14}
mmimPic	1.090	1.902	143.73	133.57
pmimPic	1.089	1.909	143.56	133.79
bmimPic	1.089	1.914	143.18	134.28
hmimPic	1.089	1.918	142.87	133.73

Table 15 Binding energy from DFT calculation

	BE(Kcalmol^{-1})	CPCBE(Kcalmol^{-1})	BSSE(Kcalmol^{-1})	ZPE(Kcalmol^{-1})
mmimpic	-769.43379x10^3	-769.43277x10^3	1.0209	150.29462
pmimpic	-818.78927x10^3	-818.78820x10^3	1.0691	185.86062
bmimpic	-843.4668x10^3	-843.46438x10^3	1.1269	203.68951
hmimpic	-892.81852x10^5	-892.81731x10^3	1.2079	239.26993

UV-Vis Spectra of picrate ILs

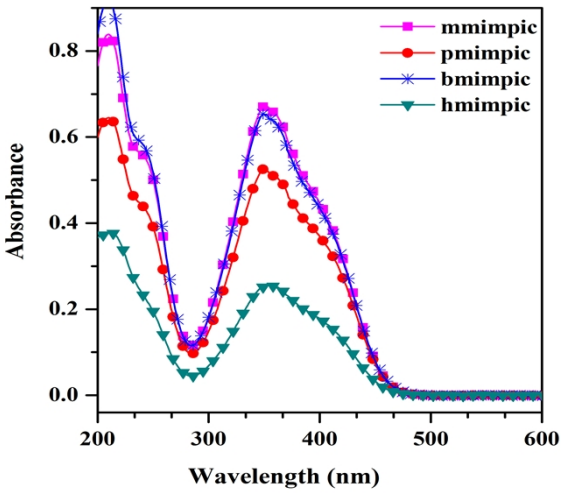
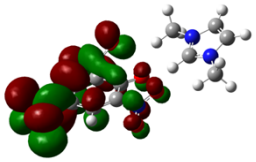
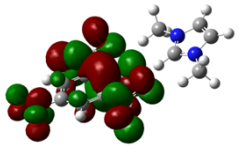


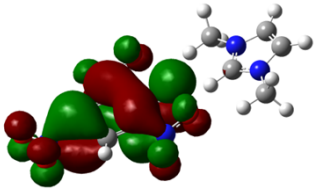
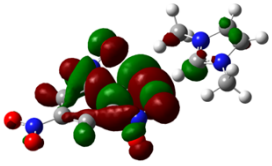
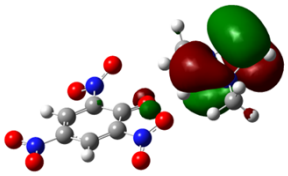
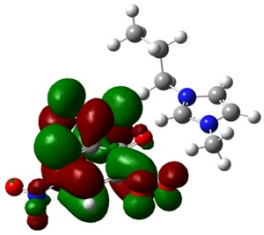
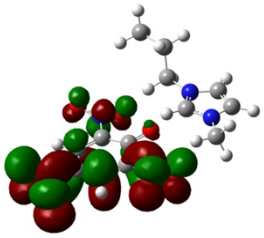
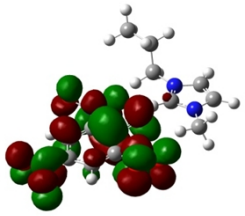
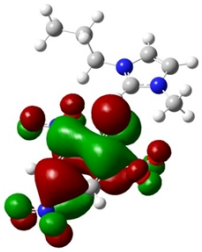
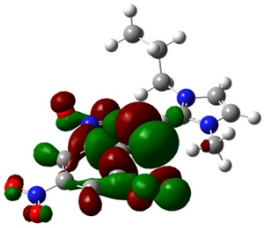
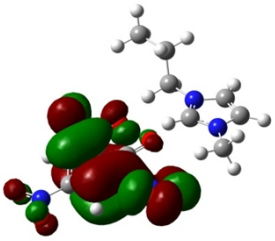
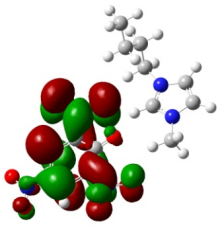
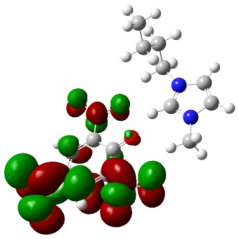
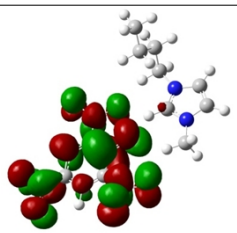
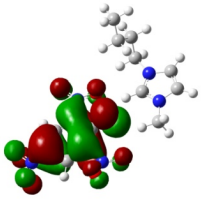
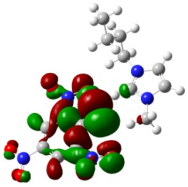
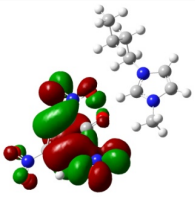
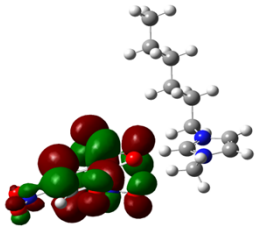
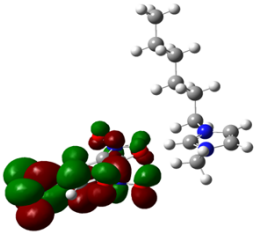
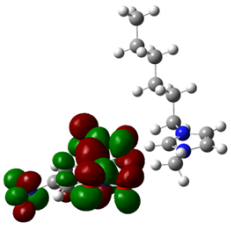
Fig. 3 UV-Vis Spectra of Picrate ILs in H_2O. [mmimpic]=1.13x10^{-4}(M); [pmimpic]= 2.47x10^{-4}(M);[bmimpic]=1.07x10^{-7}(M); [hmimpic]=1.26x10^{-4}(M).

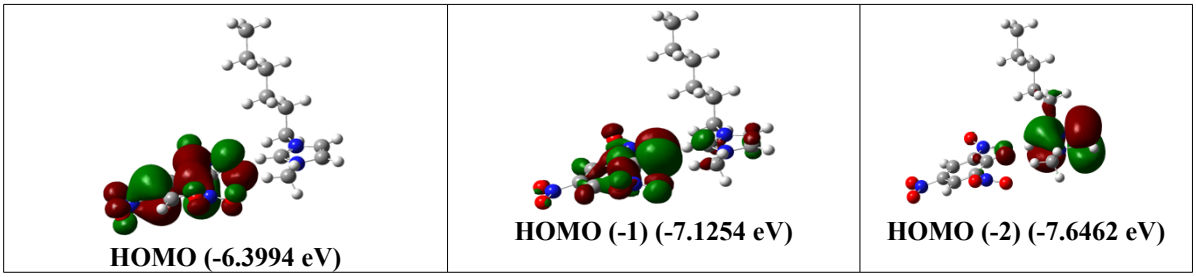
Table 16 Molar extinction coefficient of picrate ILs in ACN and H_2O solvent

	$\varepsilon(\lambda max)/10^3 dm^3 mol^{-1} cm^{-1}$			
	ACN (D= 37.5)		H_2O (D= 78.4)	
	at 429 nm	at 375 nm	at 408 nm	at 353 nm
mmimPic	(4.14±0.2)	(8.0±0.3)	(3.64±0.2)	(5.9±0.3)
pmimPic	(6.94±0.3)	(11.3±0.2)	(1.3±0.2)	(2.1±0.2)
bmimPic	(4.99±0.2)	(9.53±0.2)	(3.3±0.2)	(6.0±0.3)
hmimPic	(5.48±0.3)	(10.3±0.3)	(1.3±0.3)	(2.0±0.2)

Table 17 HOMO-LUMO of picrate ILs

mmimpic Ionic Liquid		
 **LUMO (-2.8207 eV)**	 **LUMO (+1) (-2.3682 eV)**	 **LUMO (+2) (-2.1437 eV)**

 HOMO (-6.4348 eV)	 HOMO(-1)(-7.1624 eV)	 HOMO (-2) (-7.6781 eV)
pmimpic Ionic Liquid		
 LUMO (-2.7968 eV)	 LUMO (+1) (-2.3483 eV)	 LUMO (+2) (-2.1198 eV)
 HOMO (-6.4089 eV)	 HOMO (-1) (-7.1303 eV)	 HOMO (-2) (-7.6547 eV)
bmimpic Ionic Liquid		
 LUMO (-2.7881 eV)	 LUMO (+1) (-2.3443 eV)	 LUMO (+2) (-2.1173 eV)
 HOMO (-6.4021 eV)	 HOMO (-1) (7.1276 eV)	 HOMO (-2) (-7.6479 eV)
hmimpic Ionic Liquid		
 LUMO (-2.7862 eV)	 LUMO(+1) (-2.3437 eV)	 LUMO (+2) (-2.1160 eV)



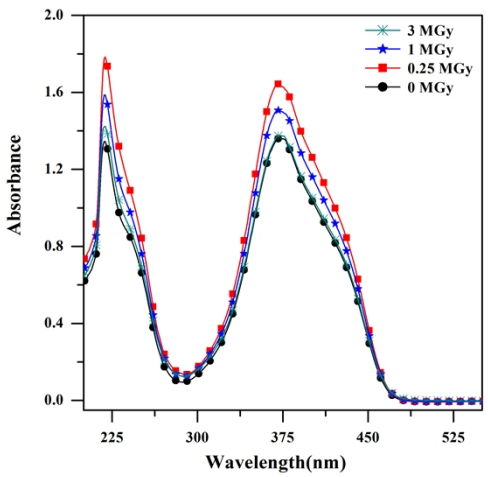


Fig. 4 UV-Vis spectra of irradiated mmimPic in ACN at different dose

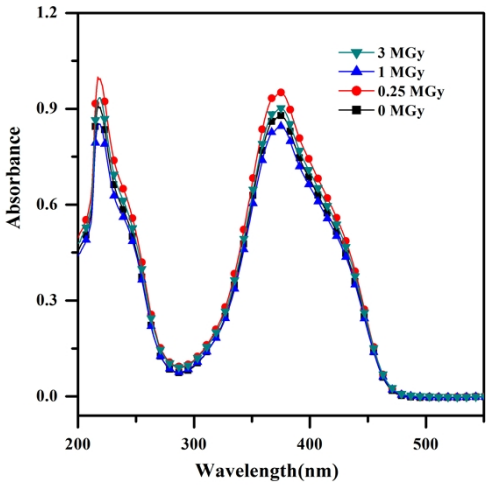


Fig 5 UV-Vis Spectra of irradiated bmimpic at different dose in ACN Solvent

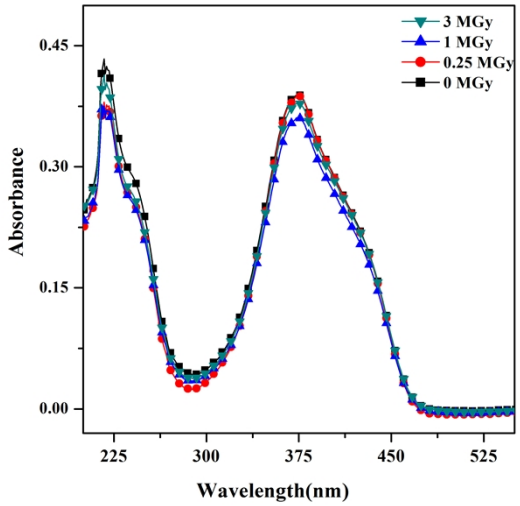


Fig 6 UV-Vis Spectra of Irradiated hmimpic at Different Dose in ACN Solvent

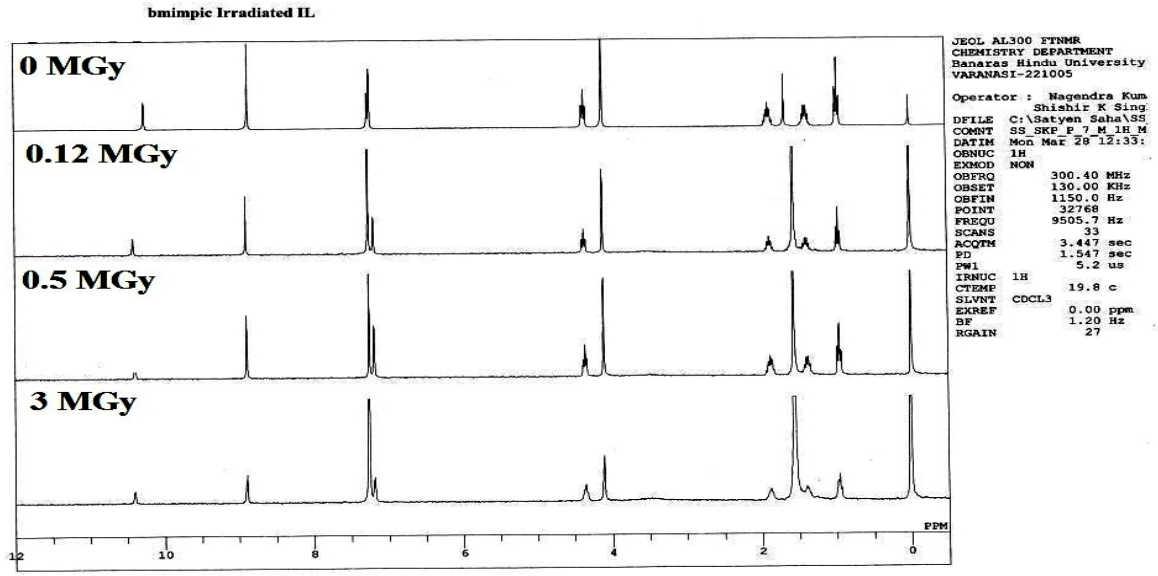


Fig. 7 ^{1}H-NMR Spectra of Irradiated bmimpic in $CDCl_3$

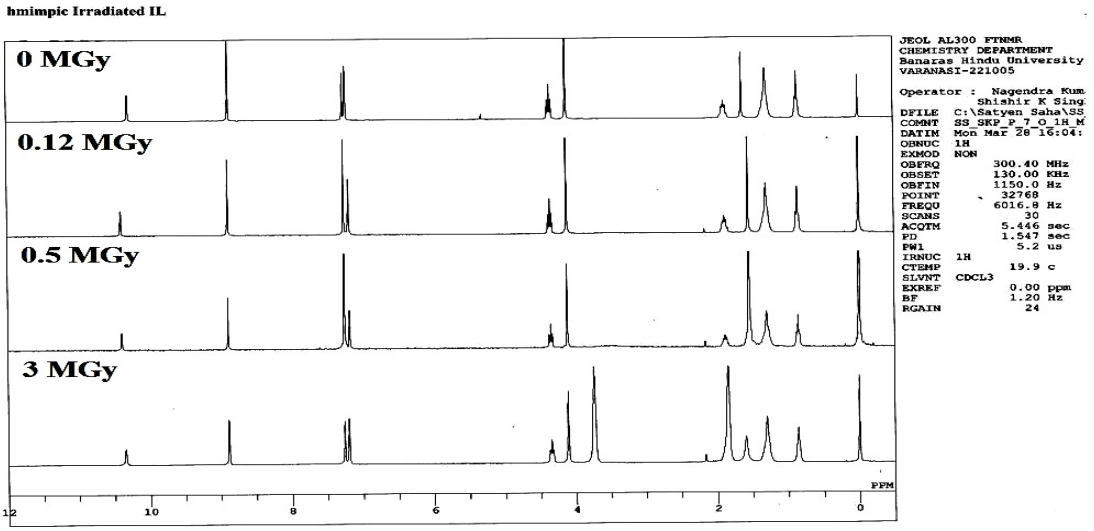


Fig. 8 ^{1}H-NMR Spectra of Irradiated hmimpic in $CDCl_3$

MAS Spectra of pure and Irradiated ILs

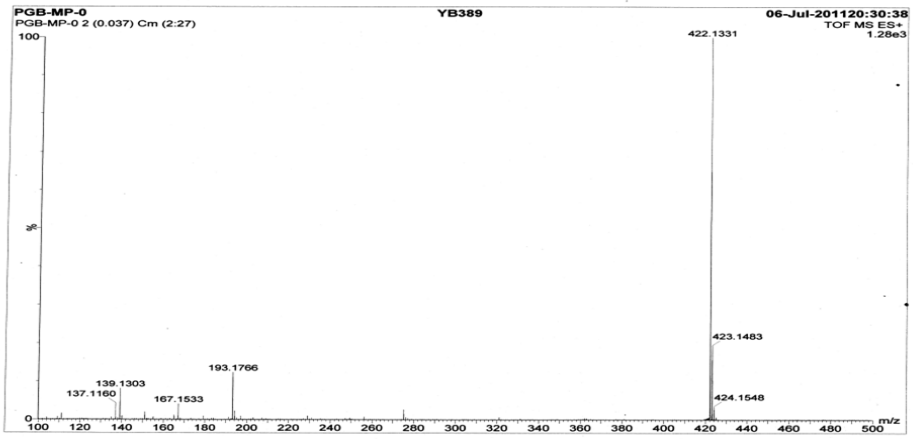


Figure 9 ESI-MASS of mmimpic (Pure IL)

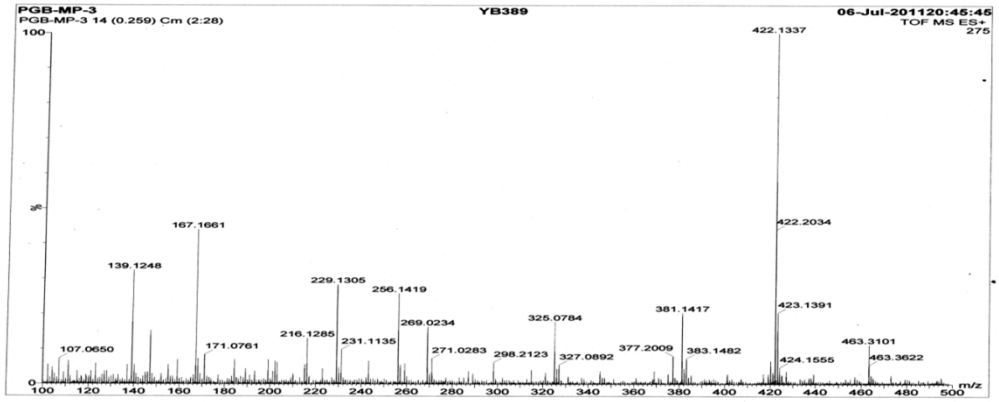


Figure 10 ESI-MASS of mmimpic (3 MGy)

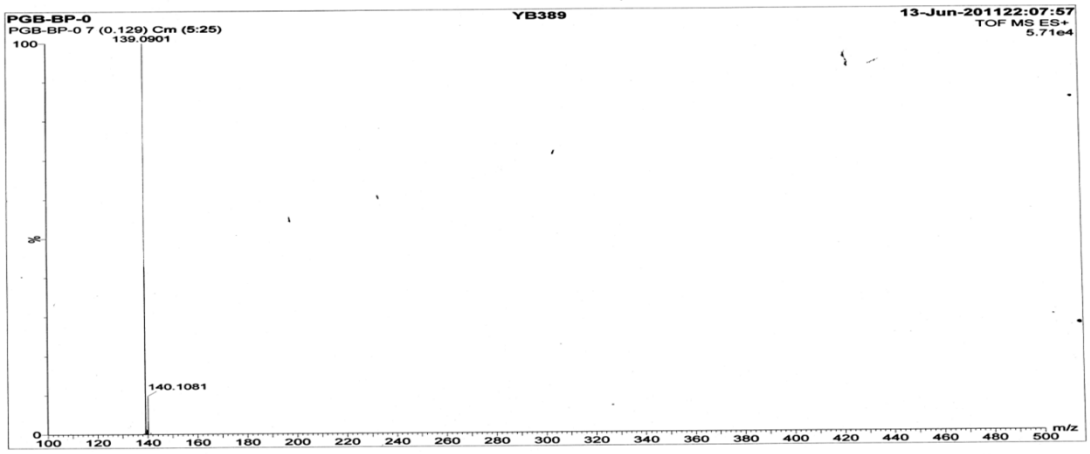


Figure 11 ESI-MASS of bmimpic (Pure IL)

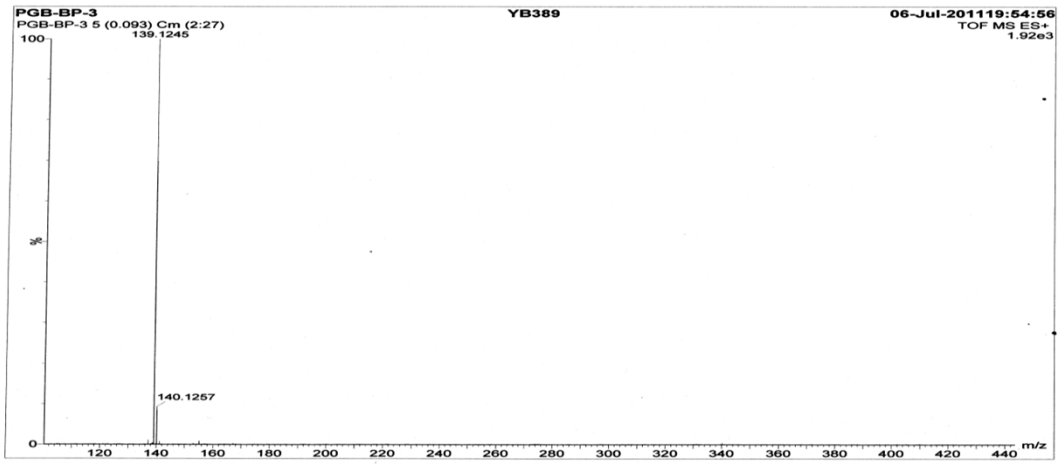


Figure 12 ESI-MASS of bmimpic (3 MGy)

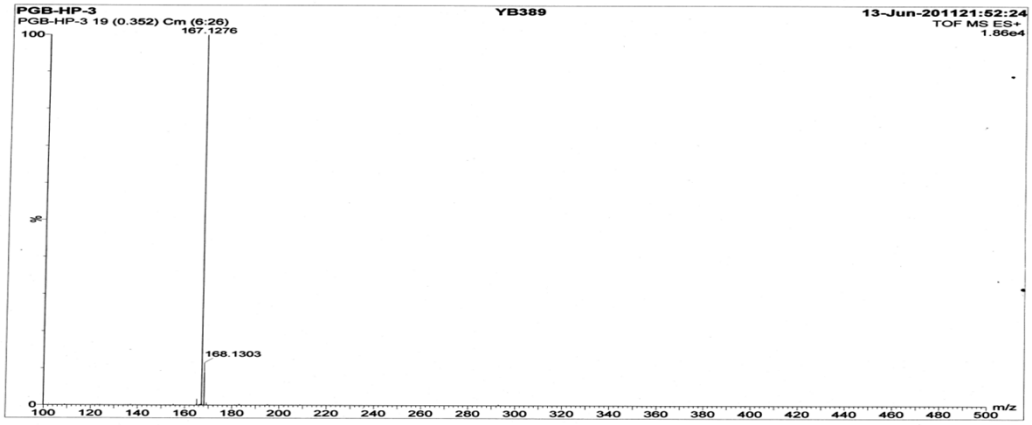


Figure 13 ESI-MASS of hmimpic (Pure IL)

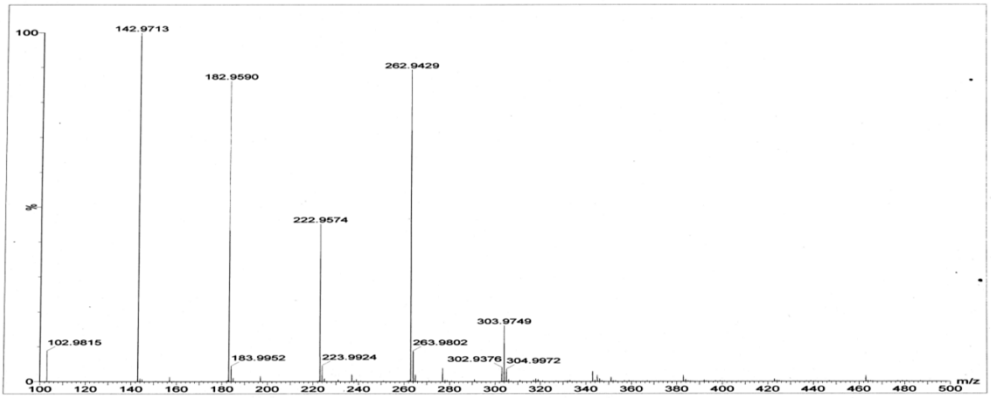


Figure 14 ESI-MASS of hmimpic (3 MGy)

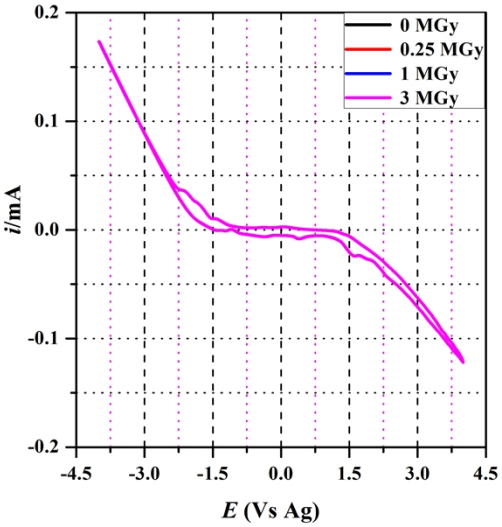


Fig. 15 Cyclic voltagram of Irradiated mmimPic

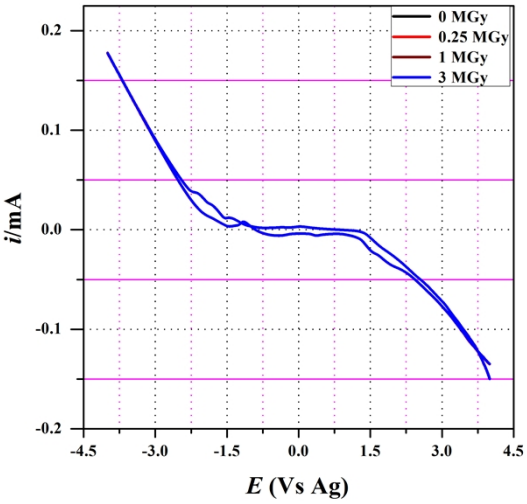


Fig. 16 Cyclic voltagram of Irradiated bmimpic

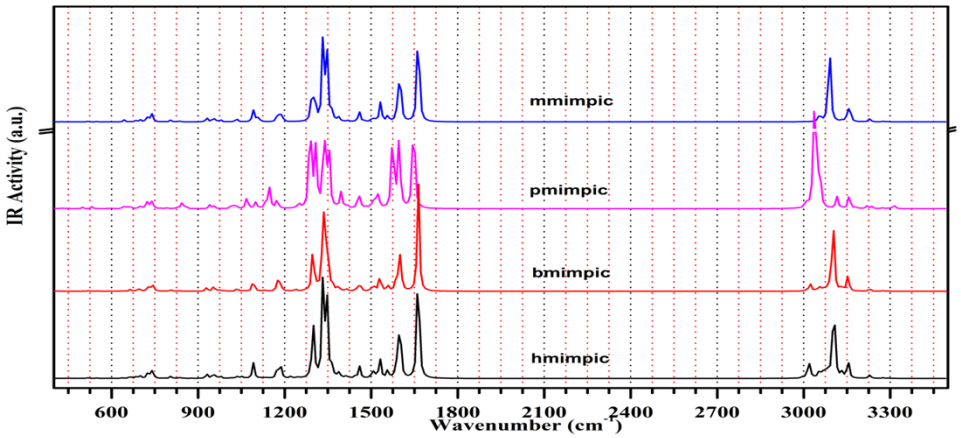


Fig. 17 Theoretical IR Activity of Picrate ILs from DFT Calculation

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