Electronic Supplementary Information

Imidazolium-Based Ionic Liquids with Different Fatty Acid Anions: Phase Behavior, Electronic Structure and Ionic Conductivity Investigation

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Synthesis of imidazolium-based ionic liquids of different long alkyl chain containing fatty acid anions. A series of different chain length of fatty acids, fatty acid-ascorbic acid and fatty acid-amino acid conjugates such as ($C_{17}H_{35}$-CO_2H/ $C_{15}H_{31}$-CO_2H/ $C_{13}H_{27}$-CO_2H and $C_{15}H_{31}$-As-OH/$C_{15}H_{31}$-Trp-OH respectively) were utilized to prepare 1-alkyl-3-methylimidazolium based ionic liquids. The synthesis involved first the preparation of 1-alkyl-3-methylimidazolium bromide ionic liquid from 1-methylimmidazole and 1-bromoalkane using microwave heating. 1-Alkyl-3-methylimidazolium bromides ILs were then converted into their corresponding hydroxide through ion exchange. The final ionic liquids were prepared by the neutralization 1-alkyl-3-methylimidazolium hydroxide with fatty acids and fatty acid conjugates.

Synthesis of 1-alkyl-3-methylimidazolium bromide. In a typical synthesis of 1-butyl-3-methylimidazolium bromide [BMIM][Br], an homogeneous mixture of 1-methylimidazole (10 mm) and 1-bromobutane (10 mm) was heated intermittently in an unmodified household MW oven (Haier HR 2485EG 230V-50 Hz) at 340 W (40 s irradiation with 10 s mixing) until a clear single phase was obtained. The bulk temperature recorded was in the range of 70 °C. The resulting yellowish viscous compound was then cooled, repeatedly washed with diethyl ether (3 x 10 mL) to remove unreacted components. Purified waxy product was dried under vacuum at 80 °C and characterized by 300 MHz ^{1}H NMR spectroscopy ($CDCl_3$) and ESI mass spectroscopy. Similarly, we have also prepared 1-decyl-3-methylimidazolium bromide [DMIM][Br].

[BMIM][Br]: ^{1}HNMR (300 MHz, $CDCl_3$, TMS): δ = 10.25 (s, imidazole ring H), 7.61 (s, imidazole ring H), 7.49 (s, imidazole ring H), 4.37–4.32 (t, J=7.5 Hz, -NCH_2), 4.15 (s, -NCH_3), 1.96–1.86 (m, -CH_2), 1.43–1.36 (m, -CH_2), 0.99–0.94 ppm (t, J=7.3 Hz, -CH_3).

MS (35eV): m/z: 139 ($BMIM^+$ 100%).

[DMIM][Br]: ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ =10.61 (s, 1 H), 7.31 (s, 1 H), 7.24 (s, 1 H), 4.34–4.29 (t, J=7.4 Hz, 2 H), 4.13 (s, 3 H), 1.92 (m, 2 H), 1.25 (bs, 14H), 0.90–0.85 ppm (t, J=6.3 Hz, 3H). MS (35 eV): m/z: 223 ($DMIM^+$ 100%).

Synthesis of 1-alkyl-3-methylimidazolium bromide [BMIM][OH]. 1-Alkyl-3-methylimidazolium hydroxides were prepared by passing the corresponding aqueous 1-alkyl-3-methylimidazolium bromide solution (5 mM) through anio444n exchange resin (Amberlite IRA-400Cl, Aldrich). For this, a glass column was first packed with the resin followed by washing with plenty of water. The column was charged with an aqueous NaOH solution (2 M) to modify the resin beads with hydroxide ions. The column was then washed thoroughly with water to remove any traces of unexchanged hydroxide ion (tested with Litmus paper). Finally, an aqueous solution of 1-alkyl-3-methylimidazolium bromide was passed through the column to exchange the bromide ions with hydroxide ions. The exchange reaction was confirmed by means of thin layer chromatography (TLC).

Synthesis of methyl ester of tryptophan (H_2N-Trp-OMe). First, 20 mmol of tryptophan (3.62 gm) was dissolved in of 20 mL ice cold dry methanol containing 2 mL $SOCl_2$ and allowed to stand for 8h to obtain the chloride salt of methyl ester ($Cl^-NH_3^+$-Trp-OMe). The subsequent neutralization of these compounds with saturated Na_2CO_3 solution and extraction with ethyl acetate results the required H_2N-Trp-OMe. Using this purified ester, the following methyl esters of amphiphiles were synthesized.

Synthesis of methyl ester of fatty acid-tryptophan conjugate ($C_{15}H_{31}$-Trp-OMe): The methyl ester of tryptophan was coupled with palmitic acid by using DCC and HOBt. Typically, 12 mmol of palmitic acid (3.5 g) is taken in DCM (10 ml) and cooled in an ice-water bath. DCM solution of purified methyl ester of tryptophan (10 mmol) was then added separately to this fatty acid solution. Finally, DCC (2.06 g, 10 mmol) and HOBt (0.135 g, 1 mmol) were added consecutively to the reaction mixture and stirred magnetically for 3 days. Final reaction mixture, collected in ethyl acetate (30 ml) was filtered through sintered funnel to remove the formed

dicyclohexyl urea (DCU). The filtrate containing the actual compound was washed with 2N HCl (3 × 20 mL), brine (1 × 20 mL), saturated sodium carbonate (3 × 20 mL), water (1 × 20 mL) and finally dried over anhydrous sodium sulfate. The crude compound was isolated by evaporating the solvent in rotary evaporator and finally dried under vacuum. Final purification was done on a silica gel column (100-200 mesh) using mixture of ethyl acetate and toluene as eluent. $C_{15}H_{31}$-Trp-OMe is finally characterized through ESI mass spectroscopy, 300 MHz ^{1}H NMR spectroscopy, the details of which are given below.

$C_{15}H_{31}$-Trp-OMe: ^{1}HNMR (300MHz, $CDCl_3$, TMS): δ = 8.06 (s, 1H, Trp ring -NH), 7.54-7.52 (d, 1H, J = 6, Trp ring H), 7.37-7.34 (d, 1H, J = 6, Trp ring H), 7.21-7.08 (m, 1H, Trp ring Hs), 6.97-6.96 (d, 1H, J = 3, Trp ring H), 5.94-5.92 (d, 1H, J = 6, amide -NH), 5.00-4.94 (m, 1H, Trp $C^{\alpha}H$), 3.69 (s, 3H, OCH_3), 3.33-3.31(d, 2H, J=6, Trp C^{β} Hs) 2.16-2.11 (t, 2H, J = 9, -CO-CH_2), 1.56 (br., 6H, -CH_2), 1.25 (br. 20H, -$(CH_2)_7$-), 0.90-0.85 (t, 3H, J = 9, -CH_3).

MS (35 eV): m/z (%): 372 [M+Na^+]

Synthesis of fatty acid-tryptophan conjugate ($C_{15}H_{31}$-Trp-OH). Finally, for the synthesis of tryptophan based amphiphile ($C_{15}H_{31}$-Trp-OH), an aqueous NaOH (10 mL, 2N) solution was added dropwise to the methanolic solution (25 mL) of purified ester of amphiphile ($C_{15}H_{31}$-Trp-OMe) and the progress of this basic hydrolysis was monitored via thin layer chromatography (TLC). The reaction mixture was then stirred further for 12 h and subsequently methanol was removed. The rest alkaline aqueous part containing sodium salt of amphiphiles was mixed with 30 mL of water followed by washing with diethyl ether (2 × 20 mL) to remove any unreacted ester. Then the pH of the aqueous layer was adjusted to 2 using 2N HCl and organic compound (amphiphile) was further extracted with ethyl acetate (3 × 20 mL). The extract was dried over anhydrous sodium sulphate, and evaporated by rotary evaporator and finally dried under vacuum to isolate the amphiphile. ^{1}H NMR spectroscopy, ESI mass spectroscopy are used to characterize the resultant amphiphiles, the details of which are mentioned below.

$C_{15}H_{31}$-Trp-OH: ^{1}HNMR (300MHZ, $CDCl_3$, TMS): δ = 8.21 (s, 1H, Trp ring -NH), 7.58-7.56 (d, 2H, J = 6, Trp ring H), 7.38-7.35 (d, 2H, J = 8.01, Trp ring H), 7.23-7.09 (m, 2H, Trp ring Hs), 7.03 (s, 1H, Trp ring H), 6.00-5.98 (d, 1H, J = 6, amide -NH), 4.94-4.92 (m, 1H, Trp $C^{\alpha}H$), 3.41-3.30 (m, 2H, Trp C^{β}), 2.14-2.09 (t, 2H, J = 9, -CO-CH_2), 1.51 (br. 2H, -CH_2), 1.25 (br. 24H, -CH_2), 0.88-0.85 (t, 3H, J = 6, -CH_3).MS (35eV): m/z (%): 470 [M+Na^+]

Synthesis of fatty acid-based 1-alkyl-3-methylimidazolium ionic liquids. Typically, as prepared aqueous solution of 1-alkyl-3-methylimidazolium hydroxide (5 mM) was added to the methanolic solution of different fatty acids and fatty acid conjugates (5 mM) and the reaction mixture was stirred magnetically for 12h at room temperature. The neutralization process was monitored via pH measurement. At pH~8, the resulting solution was evaporated to remove methanol under vacuum. Subsequently, the resultant organic compound was extracted to DCM and dried over Na_2SO_4 to remove water. The DCM solution was evaporated to collect the viscous ionic liquid, which was dried in vacuum at 60 ºC. The purity of the compounds was verified using ^{1}H NMR and ^{13}C NMR spectroscopy and CHN elemental analysis.

[BMIM][$C_{15}H_{31}$-CO_2]: ^{1}HNMR (300 MHz, $CDCl_3$, TMS): δ = 10.344 (s, imidazole ring C_2-H), 7.23-7.1 (s, imidazole ring $C_{4,5}$-H), 4.28–4.23 (t, J=7.2 Hz, -NCH_2), 4.02 (s, -NCH_3), 1.86–1.79 (m, cation-CH_2), 1.39–1.36 (m, anion-CH_2), 0.941 (t, J=7.2 Hz, -CH_3), 0.904 (t, J=6.3 Hz, anion -CH_3), 1.234 (m, 24H), 1.59-1.52 (m, anion β-CH_2), 2.51(t, anion α-CH_2) (spectra is shown in Figure 1; intensity ratio calculated of cation and anion 1:1.07); elemental analysis found (%) for $C_{24}H_{46}N_2O_2$ (395): C 73.16, H 11.61, N 7.27.

[BMIM][$C_{17}H_{35}$-CO_2]: ^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ = 10.68 (s, imidazole ring C_2-H), 7.19-7.16 (d, imidazole ring $C_{4,5}$-H), 4.31–4.28 (t, J=7.5 Hz, -NCH_2), 4.08 (s, -NCH_3), 1.875 (t, cation -CH_2), 1.40–1.35 (dd, anion-CH_2), 0.97–0.94 (t, J=7 Hz, -CH_3), 0.88-0.85 (t, J=6.5 Hz, anion -CH_3), 1.27-1.24 (m, 28H), 1.61-1.58 (m, β-CH_2), 2.30-2.27(m, α-CH_2) (spectra is shown in Figure 2; intensity ratio calculated cation:anion 1:1.1); elemental analysis found: (%) for $C_{26}H_{50}N_2O_2$ (422): C 73.71, H 11.84, N 6.54.

[BMIM][$C_{13}H_{27}$-CO_2]: ^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ = 10.445 (s, imidazole ring C_2-H), 7.2 (s, imidazole ring $C_{4,5}$-H), 4.296 (t, J=7 Hz, -NCH_2), 4.2 (s, -NCH_3), 1.88-1.85 (m, cation-CH_2), 1.41–1.33 (m, anion –$C_{13}H_2$), 0.97–0.94 (t, J=7 Hz, -CH_3), 0.88-0.85 (t, J=6.5 Hz, anion -CH_3), 1.27-1.24 (m, 20H), 1.60-1.56 (m, β-CH_2), 2.3-2.27(m, α-CH_2) (spectra is shown in Figure 3; intensity ratio of cation and anion calculated 1:1.1) elemental analysis found (%) for $C_{22}H_{42}N_2O_2$ (366): C 71.96, H 11.81, N 7.27

[DMIM][$C_{15}H_{31}$-CO_2]: ^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ = 10.213 (s, imidazole ring C_2-H), 7.19 (s, imidazole ring $C_{4,5}$-H), 4.29–4.26 (t, J=7 Hz, -NCH_2), 4.06 (s, -NCH_3), 1.883 (s, -

CH_2), 1.32–1.31 (m, -$C_{15}H_2$), 0.88-0.86 (t, , two -CH_3 of cation and anion), 1.249 (m, 24H), 1.63-1.58 (m, anion β-CH_2), 2.34-2.29(m, anion α-CH_2) (spectra is shown in Figure 4; cation anion intensity ratio 1:1) elemental analysis calcd(%) for $C_{30}H_{58}N_2O_2$ (478): C 75.26, H 12.21, N 5.85; found: C 75.42, H 12.04, N 5.62

[BMIM][$C_{15}H_{31}$-As-O]: ^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ = 7.06 (s, imidazole ring $C_{4,5}$-H), 8.10, 7.91(s, O-H of anion), 4.3–4.1 (m, J=7.5 Hz, -NCH_2), 4.07 (s, -NCH_3), 1.88–1.85 (m, -CH_2), 1.38–1.36 (d, -$C_{15}H_2$), 0.98–0.94 (t, J=7.3 Hz, -CH_3), 0.89-0.845 (t, J=6.5 Hz, palmitate -CH_3), 1.27-1.24 (m, 24H), 1.61-1.54 (m, ester β-CH_2), 2.33-2.27(m, ester α-CH_2), 5.29(s, ring CH of ascorbate), 4.4 (s, *t*-CH of ascorbate), 4.3-4.2 (m, *s*-CH_2 of ascorbate) (spectra is shown in Figure 5; cation anion intensity ratio 1:1); elemental analysis found for $C_{30}H_{52}N_2O_7$ (552): C 65.34, H 9.33, N 5.16

[BMIM][$C_{15}H_{31}$-Trp-O]: ^{1}HNMR (400 MHz, $CDCl_3$, TMS): δ = 10.1(s, imidazole ring H), 7.35-7.31 (s, imidazole ring H), 4.49 (m, J=7.5 Hz, -NCH_2), 4.08 (s, -NCH_3), 0.97–0.93 (t, J=7.3 Hz, -CH_3), 8.21 (s, 1H, Trp ring -NH), 7.65-7.63 (d, 2H, J = 6, Trp ring H), 7.38-7.35 (d, 2H, J = 8.01, Trp ring H), 7.23-7.09 (m, 2H, Trp ring Hs), 7.03 (s, 1H, Trp ring H), 6.00-5.98 (d, 1H, J = 6, amide -NH), 4.74-4.72 (m, 1H, Trp C^{α}H), 3.45-3.40 (m, 2H, Trp C^{β}-H), 2.15 (t, 2H, J = 9 Hz, -CO-CH_2), 1.53 (s. 2H, -CH_2), 1.25-1.22 (s. 24H, -CH_2), 0.92-0.85 (t, 3H, J = 6, -CH_3) (spectra is shown in Figure 6; intensity ratio calculated of cation and anion 1:1.1) elemental analysis found (%) for $C_{35}H_{56}N_4O_3$ (580): C 72.2, H 9.63, N 9.32

[DMIM][$C_{13}H_{27}$-CO_2]: ^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ = 10.71 (s, imidazole ring C_2-H), 7.19-7.15 (s, imidazole ring $C_{4,5}$-H), 4.3–4.27 (m, J=7.5 Hz, -NCH_2), 4.08 (s, -NCH_3), 1.88–1.86 (d, cation -CH_2), 1.63-1.57 (m, anion -$^{\beta}CH_2$), 0.88-0.857 (t, -CH_3 of both anion and cation), 1.31-1.24 (m, 20H), 2.3-2.28(m, anion α-CH_2) (spectra is shown in Figure 7; intensity ratio of cation and anion calculated 1:1) elemental analysis found (%) for $C_{28}H_{54}N_2O_2$ (451): C 74.76, H 12.15, N 6.17

Preparation of $C_{15}H_{31}$-CO_2Na. Typically, 10 mg of $C_{15}H_{31}$-CO_2H was first dissolved in 3 mL of methanol in a small beaker; subsequently water (5 mL) was added with swirling. 0.025 N NaOH was then added to it dropwise with subsequent pH measurement. At certain point, pH abruptly increases to 8.3. The salt is collected after solvent removal under vacuum.

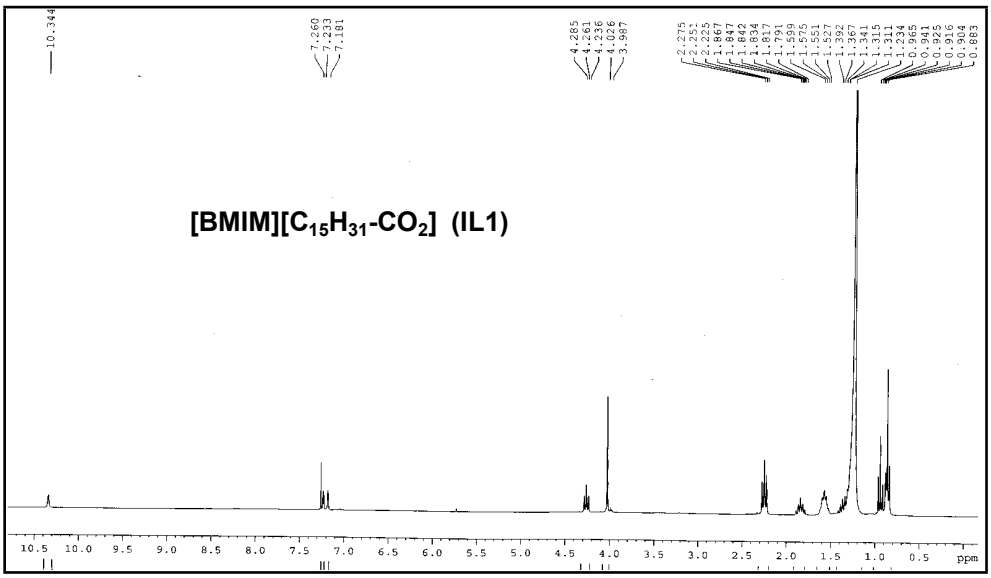


Figure S1: NMR spectrum of [BMIM][$C_{15}H_{31}$-CO_2].

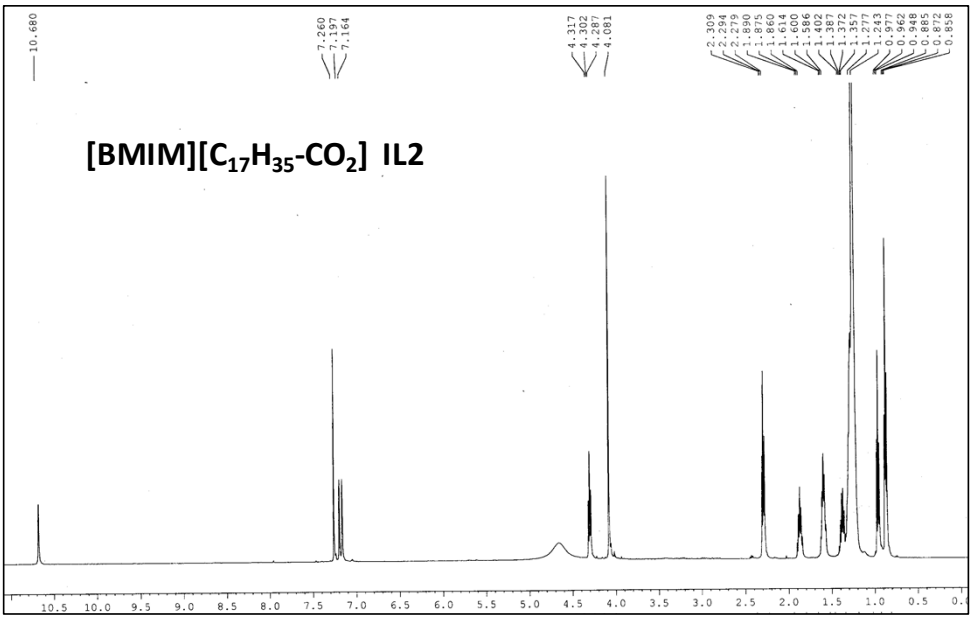


Figure S2: NMR spectrum of [BMIM][$C_{17}H_{35}$-CO_2].

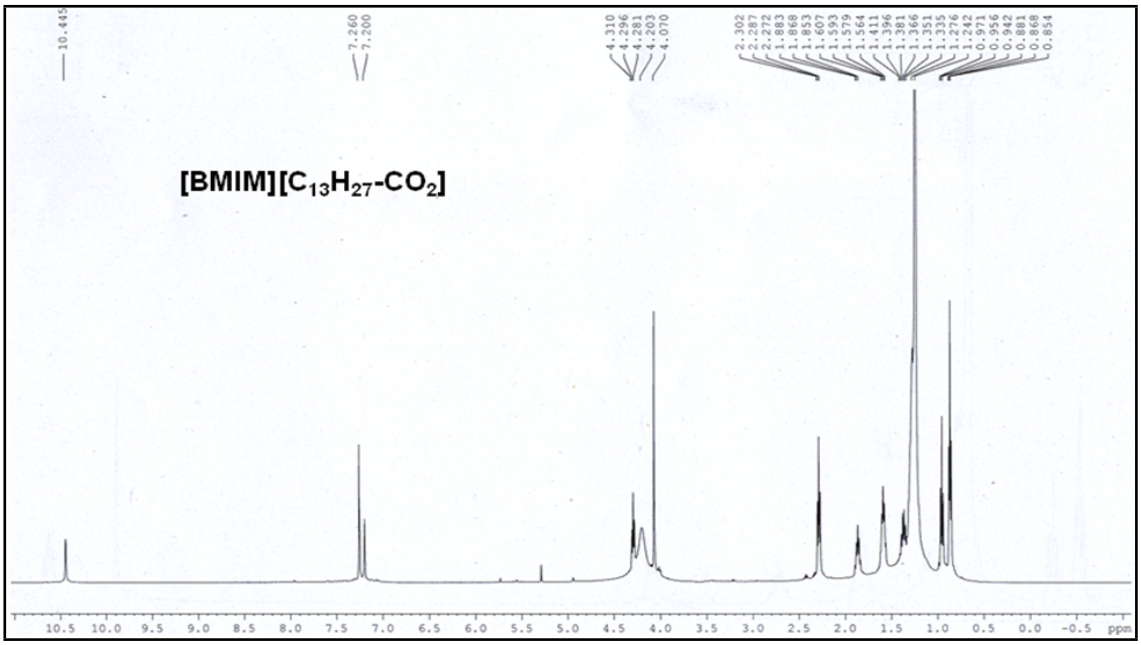


Figure S3: NMR spectrum of [BMIM][$C_{13}H_{27}$-CO_2].

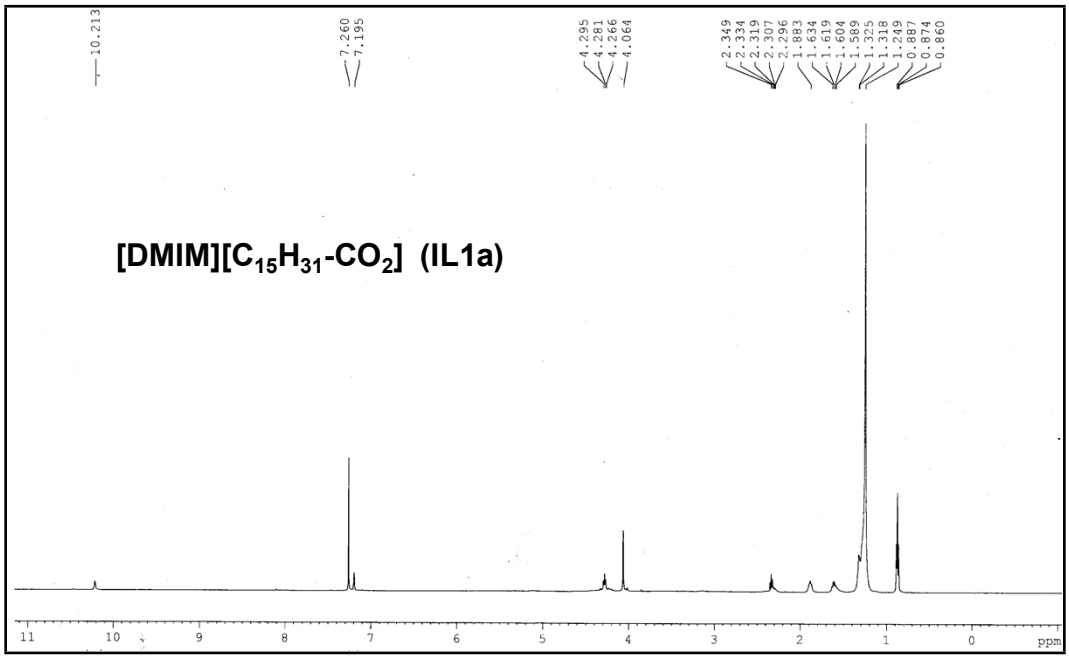


Figure S4: NMR spectrum of [DMIM][$C_{15}H_{31}$-CO_2].

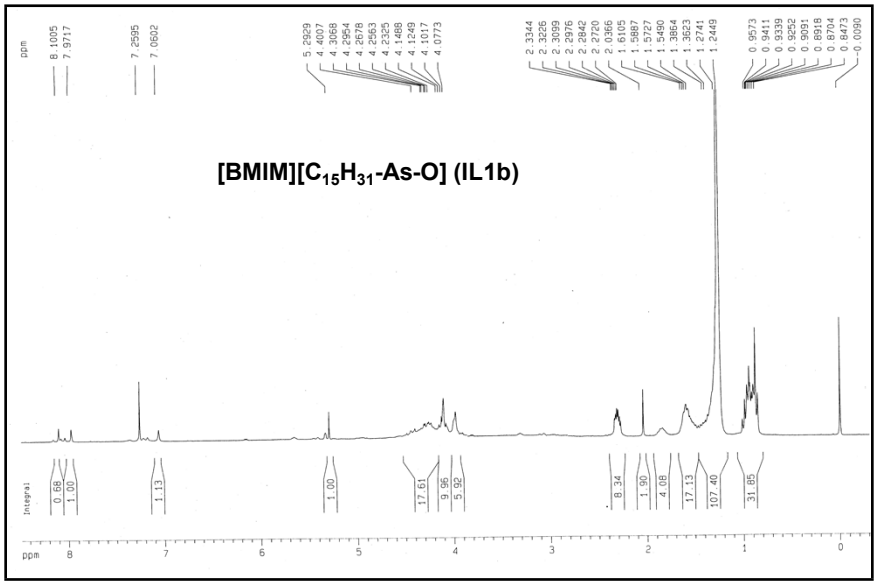


Figure S5: NMR spectrum of [BMIM][$C_{15}H_{31}$-As-O].

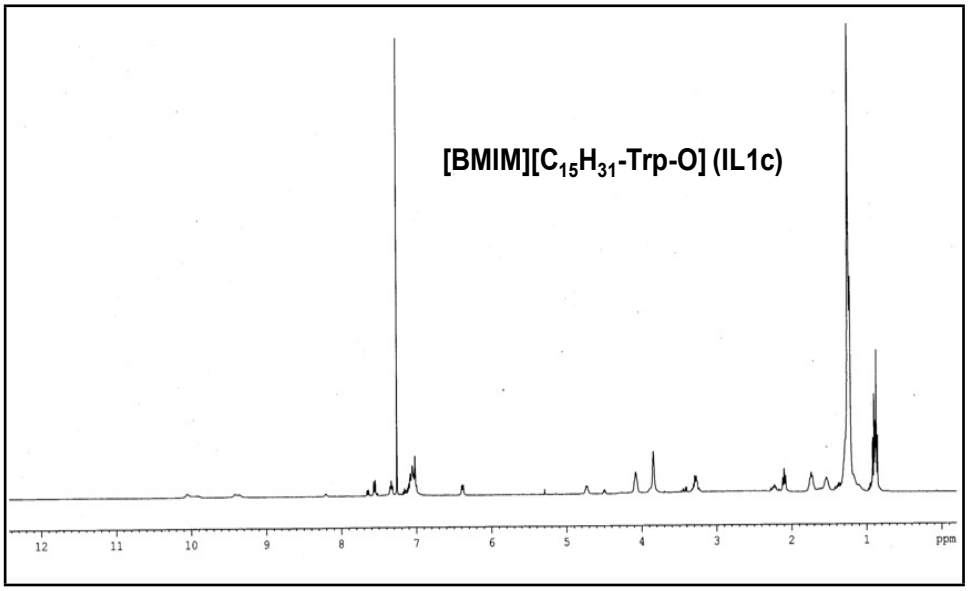


Figure S6: NMR spectrum of [BMIM][$C_{15}H_{31}$-Trp-O].

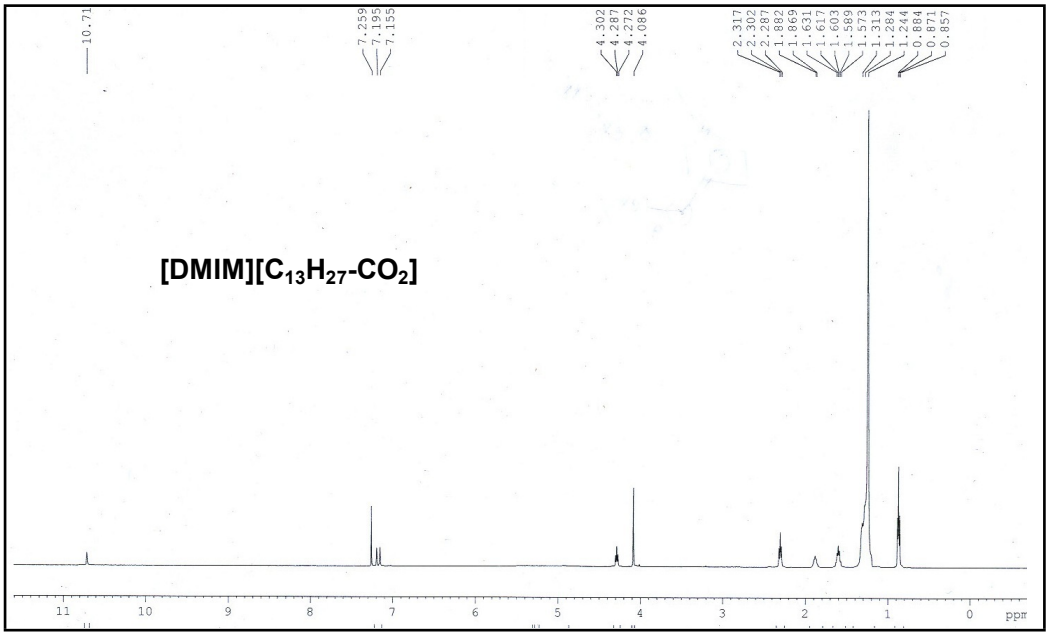
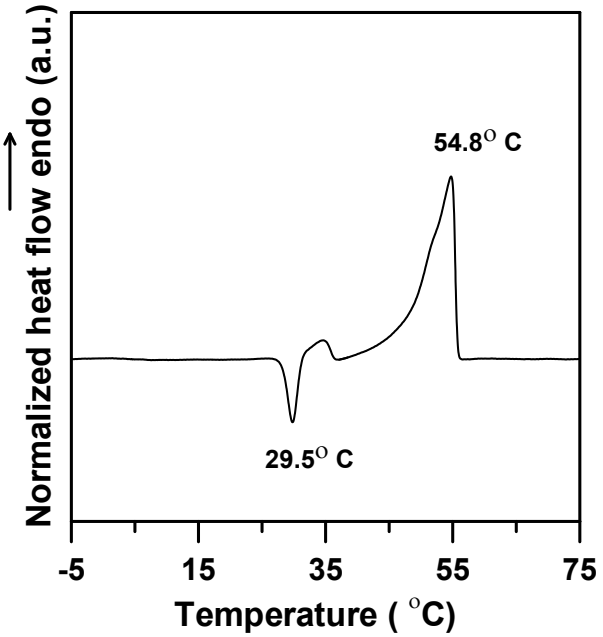
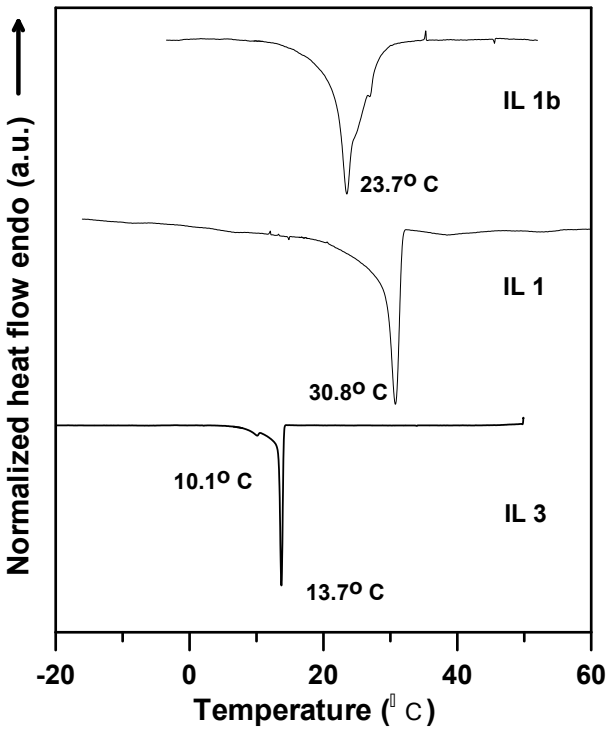


Figure S7: NMR spectrum of [DMIM][$C_{13}H_{27}$-CO_2].



FigureS8. DSC thermogram of [DMIM][$C_{13}H_{27}$-CO_2] on heating at 2° C/ min.



FigureS9. DSC thermograms during cooling (2° C/min) of different ILs.

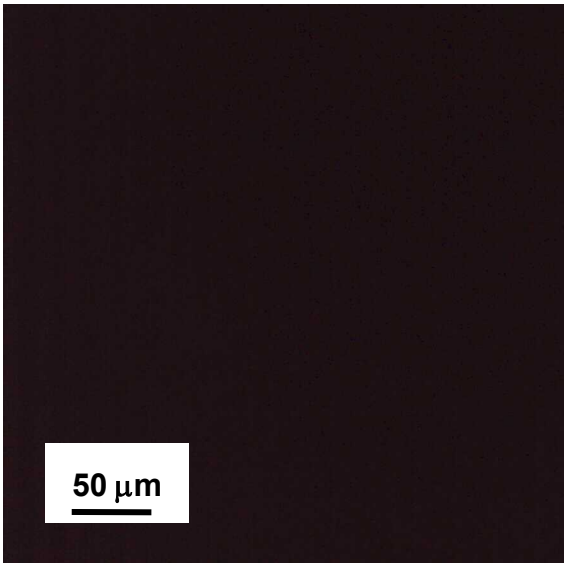


Figure S10: POM images of **IL1** at 70° C.

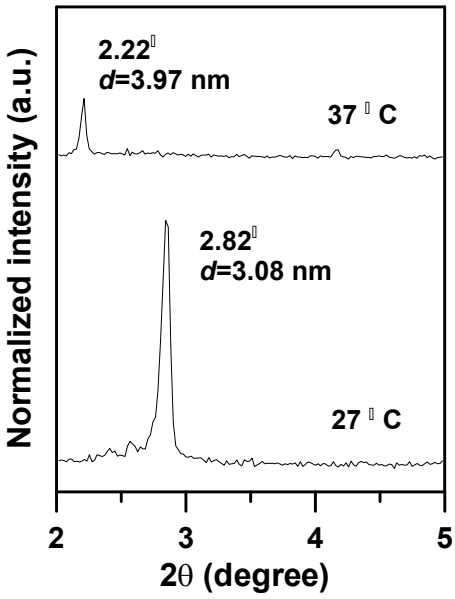


Figure S11. The low angle XRD pattern of **IL1 at** 27 °C and at 37 °C.

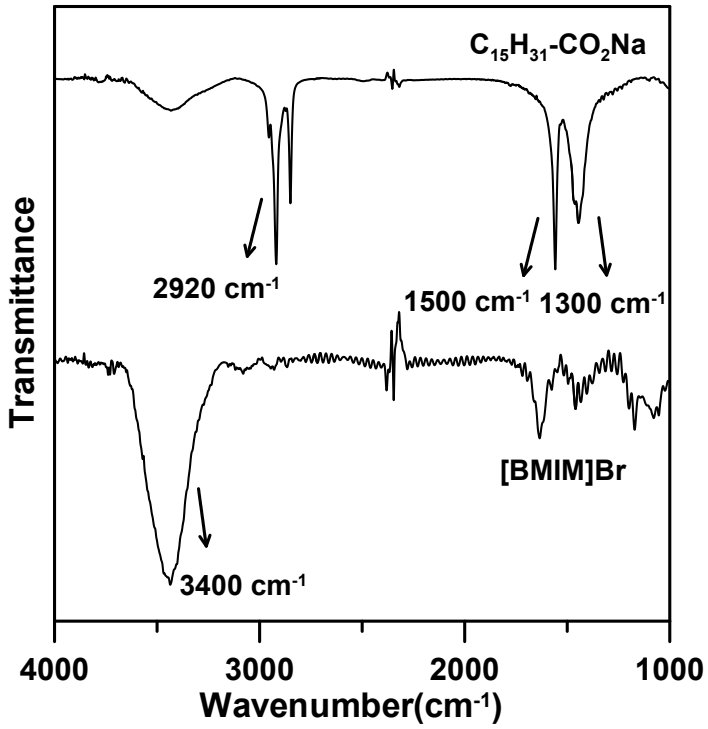


Figure S12: FTIR spectra of $C_{15}H_{31}$-CO_2Na and [BMIM]Br.

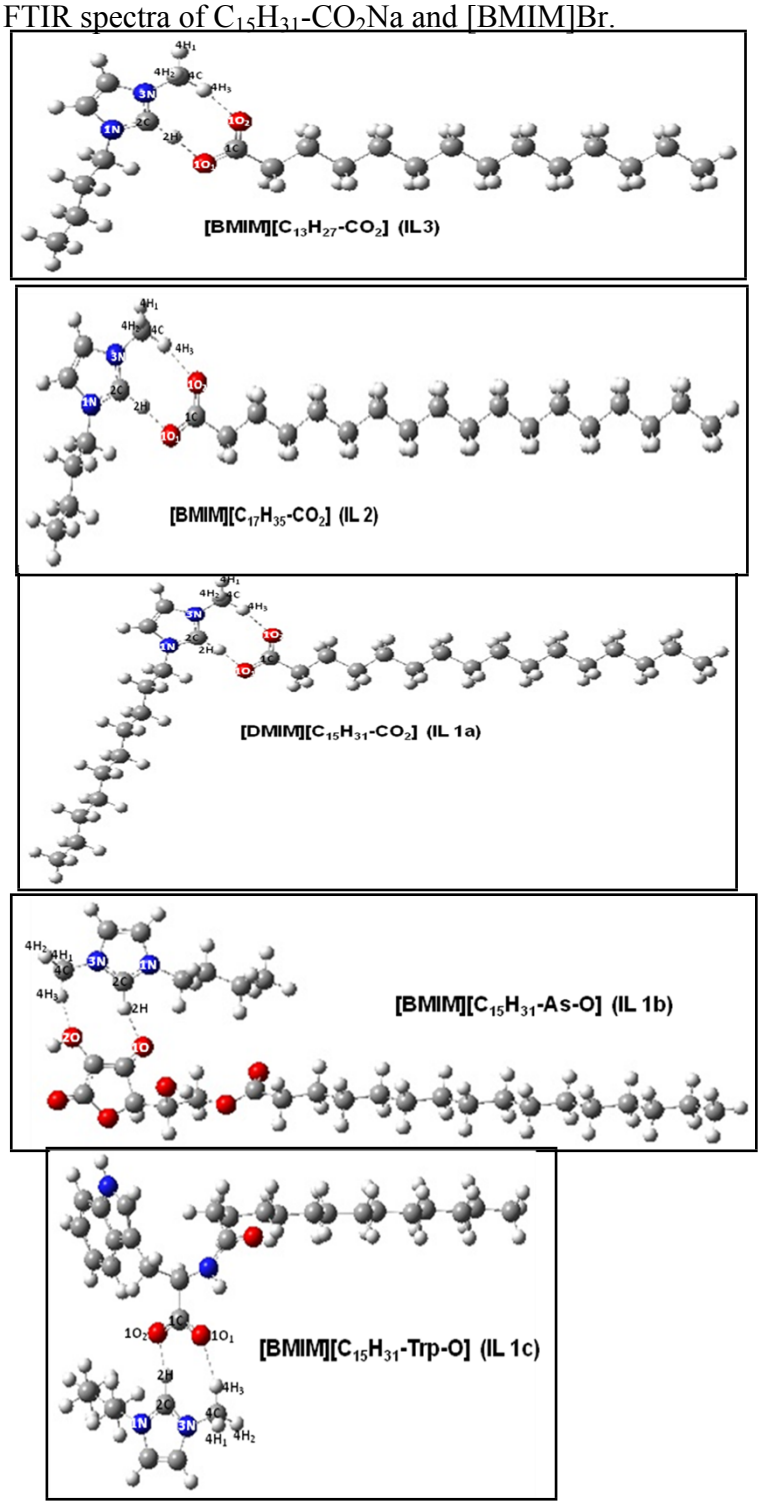


Figure S13. Optimized geometry of ionic liquids (**IL2, IL3, IL1a, IL1b** and **IL1c**) at the B3LYP/6-31G(d) level of theory. The red, blue, grey and white color signifies oxygen, nitrogen, carbon and hydrogen atom respectively.

Table S1. Bragg reflections data collected from the X-ray diffractograms of different ionic liquids

Ionic liquids	Angle of diffraction (2θ)	Layer-spacing value (nm)
IL1	2.85, 5.72, 21.4	3.08
IL2	2.72, 5.45, 8.16, 10.9	3.24
IL3	5.69	3.27
IL1a	5.83, 6.97,10.1, 10.5	-
IL1b	2.82, 5.64, 21.4	3.13

Table S2. Estimated length of the IL fully extended molecules

Ionic liquids	Estimated molecular length(nm)
IL1	2.67
IL2	3.10
IL3	2.20
IL1a	2.45
IL1b	2.72
IL1c	2.61

Table S3.

Isolated ions	Calculated(cm^{-1})	Experimental(cm^{-1})
$[BMIM]^+$	3312(C-H str)	3400
$[C_{15}H_{35}\text{-}CO_2]^-$	2978 (CH_2 sym st)	2920
	1546(CH_2 bend)	1500
	1366(CO_2 sym strr)	1400

Comparison between calculated and experimental IR stretching frequencies of isolated $[BMIM]^+$ cation and $[C_{15}H_{35}\text{-}CO_2]^-$ anion.

Ionic liquid	ΔE (kJmol^{-1})		ΔH(kJmol^{-1})		ΔG(kJmol^{-1})	
	6-31G(d)	6-311++G(d,p)	6-31G(d)	6-311++G(d,p)	6-31G(d)	6-311++G(d,p)
IL1	-441.32	-401.53	-440.02	-401.28	-392.41	-344.29
IL2	-441.57	-401.49	-442.95	-400.02	-383.13	-351.62
IL3	-441.70	-401.60	-440.44	-400.94	-392.50	-347.05
IL1a	-439.35		-440.27		-383.51	
IL1b	-377.45		-375.82		-329.30	

Table S4. Computed interaction energies (Δ*E*), enthalpy change (Δ*H*) and Gibbs free energy change (Δ*G*) for single ion-pair formation in ionic liquids.

IL1c	-382.01		-382.38		-332.85	

Table S5. Computed bond lengths and Mülliken Charge distributions on atoms of optimized geometries of **IL1** at the B3LYP/6-31G(d) level of theory.

Atom No.	**Mülliken Charge**	**Bond No.**	**Bond distance**
1N	-0.409	2C-2H	**1.141**
2C	0.261	2H-$1O_1$	**1.614**
3N	-0.410	$4H_3$-$1O_2$	**2.025**
2H	0.346	4C-$4H_3$	**1.099**
4C	-0.378	-	-
$4H_1$ and $4H_2$	0.173	-	-
$4H_3$	0.285	-	-
$1O_1$	-0.652	-	-
$1O_2$	-0.594	-	-
1C	0.607	-	-

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Table S6. Computed bond lengths and Mülliken Charge distributions on atoms of optimized geometries of **IL2** at the B3LYP/6-31G(d) level of theory.

Atom No.	Mülliken Charge	Bond No.	Bond distance(Å)
1N	-0.409	2C-2H	1.143
2C	0.261	2H-$1O_1$	1.602
3N	-0.41	$4H_3$-$1O_2$	2.024
2H	0.345	4C-$4H_3$	1.099
4C	-0.378	-	-
$4H_1$ and $4H_2$	0.173	-	-
$4H_3$	0.285	-	-
$1O_1$	-0.651	-	-
$1O_2$	-0.593	-	-
1C	0.605	-	-

Table S7. Computed bond lengths and Mülliken Charge distributions on atoms of optimized geometries of **IL3** at the B3LYP/6-31G(d) level of theory.

Atom No.	Mülliken Charge	Bond No.	Bond distance(Å)
1N	-0.409	2C-2H	1.14
2C	0.262	2H-$1O_1$	1.626
3N	-0.410	$4H_3$-$1O_2$	2.034
2H	0.343	4C-$4H_3$	1.099
4C	-0.377	-	-
$4H_1$ and $4H_2$	0.173	-	-
$4H_3$	0.285	-	-
$1O_1$	-0.649	-	-
$1O_2$	-0.596	-	-
1C	0.603	-	-

Table S8. Computed bond lengths and Mülliken Charge distributions on atoms of optimized geometries of **IL1a** at the B3LYP/6-31G(d) level of theory.

Atom No.	Mülliken Charge	Bond No.	Bond distance(Å)

1N	-0.409	2C-2H	1.139
2C	0.264	2H-$1O_1$	1.622
3N	-0.409	$4H_3$-$1O_2$	2.028
2H	0.340	4C-$4H_3$	1.099
4C	-0.376	-	-
$4H_1$ and $4H_2$	0.172	-	-
$4H_3$	0.284	-	-
$1O_1$	-0.647	-	-
$1O_2$	-0.595	-	-
1C	0.602	-	-

Table S9. Computed bond lengths and Mülliken Charge distributions on atoms of optimized geometries of **IL1b** at the B3LYP/6-31G(d) level of theory.

Atom No.	**Mülliken Charge**	**Bond No.**	**Bond distance(Å)**
1N	-0.409	2C-2H	1.114
2C	0.288	2H-1O	1.727
3N	-0.410	$4H_3$-2O	2.203
2H	0.318	4C-$4H_3$	1.092
4C	-0.352	-	-
$4H_1$	0.180	-	-
$4H_2$	0.188	-	-
$4H_3$	0.255	-	-
1O	-0.683	-	-
2O	-0.713	-	-

Table S10. Computed bond lengths and Mülliken Charge distributions on atoms of optimized geometries of **IL1c** at the B3LYP/6-31G(d) level of theory.

Atom No.	Mülliken Charge	Bond No.	Bond distance(Å)
1N	-0.408	2C-2H	1.118
2C	0.267	2H-$1O_1$	1.700
3N	-0.409	$4H_3$-$1O_2$	2.064
2H	0.338	4C-$4H_3$	1.097
4C	-0.376	-	-
$4H_1$	0.180	-	-
$4H_2$	0.181	-	-
$4H_3$	0.283	-	-
$1O_1$	-0.626	-	-
$1O_2$	-0.593	-	-
1C	0.595	-	-