Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# Electronic Supporting Information

# How is Charge Transport Different in Ionic Liquids? : Effect of High Pressure

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## Experimental Section

### Chemicals

Paraformaldehyde (crystalline reagent grade), glyoxal trimer dihydrate (<97 %), *n*-butylamine (99.5 %), methylimidazole (99 %), 1-bromobutane (98 %) and ammonium carbonate (reagent grade) were purchased from Sigma-Aldrich and used as received. Sulfuric acid (95-98 %) was supplied by Alfa Aesar and used as received. All solvents used were HPLC grade purchased from Riedel de Haën. Lithium bis[(trifluoromethyl)sulfonyl]imide was purchased from 3M (> 98 %). $^{1}H$ and $^{13}C$ NMR spectra were recorded at 20 °C on a Bruker Avance DPX spectrometer at 300 MHz and 75 MHz, respectively and are reported herein in Figs. S1 to S6 of the electronic supporting information (ESI). Chemical shifts are given in ppm downfield from TMS.

### Synthesis of 1-butylimidazole

To a 200 $cm^3$ round-bottom flask was added 8.16 g (272 mmol) of paraformaldehyde and 40 $cm^3$ of methanol. After cooling to 0-5 °C, there was added, in order, 18.86 g (258 mmol) *n*-butylamine, 20 $cm^3$ methanol, 12.40 g (130 mmol) ammonium carbonate, 10 $cm^3$ methanol, 18.14 g (86 mmol) trimeric glyoxal dihydrate and 25 $cm^3$ methanol. The reaction was stirred overnight at room temperature. A small aliquot was removed for NMR analysis. Volatiles were removed under reduced pressure and the reaction mixture was vacuum distilled to yield 27.5 g (86 %) of 1-butylimidazole, b.p. 98-100 °C/6 mmHg.

$^{1}H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 7.45 (s, 1H), 7.04 (s, 1H), 6.90 (s, 1H), 3.93 (t, *J* = 7.1 Hz, 2H), 1.75 (dt, *J* = 14.7, 7.3 Hz, 2H), 1.51 – 1.12 (m, 2H), 0.91 (t, *J*= 7.3Hz, 3H).

### Synthesis of 1-butylimidazolium hydrogensulfate

A mixture of 1-butylimidazole (9.30 g, 0.075 mol) was dissolved in deionised water (20 $cm^3$) and cooled in an ice bath. To this solution was added slowly dropwise sulfuric acid (7.62 g, 0.075 mol). The reaction mixture was stirred for a further hour and then the excess water was removed under reduced pressure. After this trace amounts of water were removed under high vacuum. The highly viscous straw colored liquid was then characterized by NMR spectroscopy.

$^{1}H$ NMR (300 MHz, DMSO): δ (ppm) 9.22 (s, 1H), 7.87 (s, 1H), 7.75 (s, 1H), 5.95 (s, 1H), 4.27 (t, *J* = 7.2 Hz, 2H), 2.01 – 1.68 (m, 2H), 1.52 – 1.15 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

$^{13}C$ NMR (75 MHz, DMSO): δ (ppm) 135.62 (s), 122.38 (s), 120.32 (s), 48.57 (s), 31.82 (s), 19.17 (s), 13.64 (s).

### Synthesis of 1-butylimidazolium bis[(trifluoromethyl)sulfonyl]imide

A mixture of 1-butylimidazole (9.30 g, 0.075 mol) was dissolved in deionised water (20 $cm^3$) and cooled in an ice bath. To this solution was added slowly dropwise hydrochloric acid solution (7.40 g, 0.075 mol). The reaction mixture was stirred for a further hour.

A solution of lithium bis[(trifluoromethyl)sulfonyl]imide (21.81 g, 0.076 mol) in distilled water (20 $cm^3$) was added drop-wise to the rapidly stirred solution. After one hour dichloromethane (50 $cm^3$) was added to the biphasic reaction mixture and allowed to stir under ambient conditions overnight. The organic layer was then extracted and washed with distilled water (20 $cm^3$) repeatedly five times. The organic layer was then dried *in vacuo* to give the product as an off-white liquid in < 98% yield.

$^{1}H$ NMR (300 MHz, DMSO): δ (ppm) 9.13 (s, 1H), 7.80 (s, 1H), 7.70 (s, 1H), 4.20 (t, *J* = 7.2 Hz, 2H), 1.96 – 1.66 (m, 2H), 1.43 – 1.15 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

$^{13}$C NMR (75 MHz, DMSO): δ (ppm) 135.56 (s), 122.38 (s), 122.15 (d, *J* = 25.7 Hz), 120.30 (s), 117.71 (s), 113.45 (s), 48.63 (s), 31.74 (s), 19.17 (s), 13.57 (s).

**Synthesis of 1-methyl-3-butylimidazolium bromide**

A mixture of 1-methylimidazole 99 % Sigma-Aldrich (12.32 g, 0.15 mol) and 1-bromobutane 98 % Sigma-Aldrich (20.55 g, 0.15 mol) was placed in a Parr autoclave sealed reaction vessel along with 50 cm$^3$ of HPLC grade acetonitrile. The reaction mixture was heated up to 70 °C and then held at this temperature for 24 h with stirring at 500 rpm. After cooling of the reaction mixture the acetonitrile was removed under vacuum. The highly viscous yellow product was recrystallized from acetonitrile/ethyl acetate mixture to afford an off-white solid, 87 % yield.

$^1$H-NMR (300 MHz, CDCl$_3$): δ (ppm) 10.22 (s, 1H, Ar-H), 7.62 (d, 1H, Ar-H), 7.51 (s, 1H, Ar-H), 4.32 (t, *J* = 7.31 Hz, 2H, CH$_2$), 4.14 (s, 3H, N-CH$_3$), 1.97 (m, 2H, CH$_2$), 0.99 (t, *J* = 7.45 Hz, 3H, CH$_3$)

**Synthesis of 1-methyl-3-butylimidazolium bis[(trifluoromethyl)sulfonyl]imide**

A solution of lithium bis[(trifluoromethyl)sulfonyl]imide (28.71 g, 0.1 mol) in distilled water (50 cm$^3$) was added drop-wise to a rapidly stirred solution of 1-methyl-3-butylimidazolium bromide (15.68 g, 0.098 mol) in dichloromethane (40 cm$^3$) and allowed to stir under ambient conditions overnight. The organic layer was then extracted and washed with distilled water (100 cm$^3$) repeatedly five times. The organic layer was then dried *in vacuo* to give the product as an off-white liquid in < 98% yield.

$^1$H NMR (300 MHz, DMSO): δ (ppm) 9.15 (s, 1H), 7.81 (s, 1H), 7.75 (s, 1H), 4.39 – 4.05 (m, 2H), 3.90 (s, 3H), 2.02 – 1.58 (m, 2H), 1.50 – 1.11 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

$^{13}$C NMR (75 MHz, DMSO): δ (ppm) 136.85 (s), 126.24 (s), 123.95 (s), 122.59 (s), 121.97 (s), 117.70 (s), 113.39 (s), 48.86 (s), 36.04 (s), 31.69 (s), 19.09 (s), 13.52 (s).

**Figure S1:** $^1$H-NMR of 1-butylimidazolium hydrogensulfate

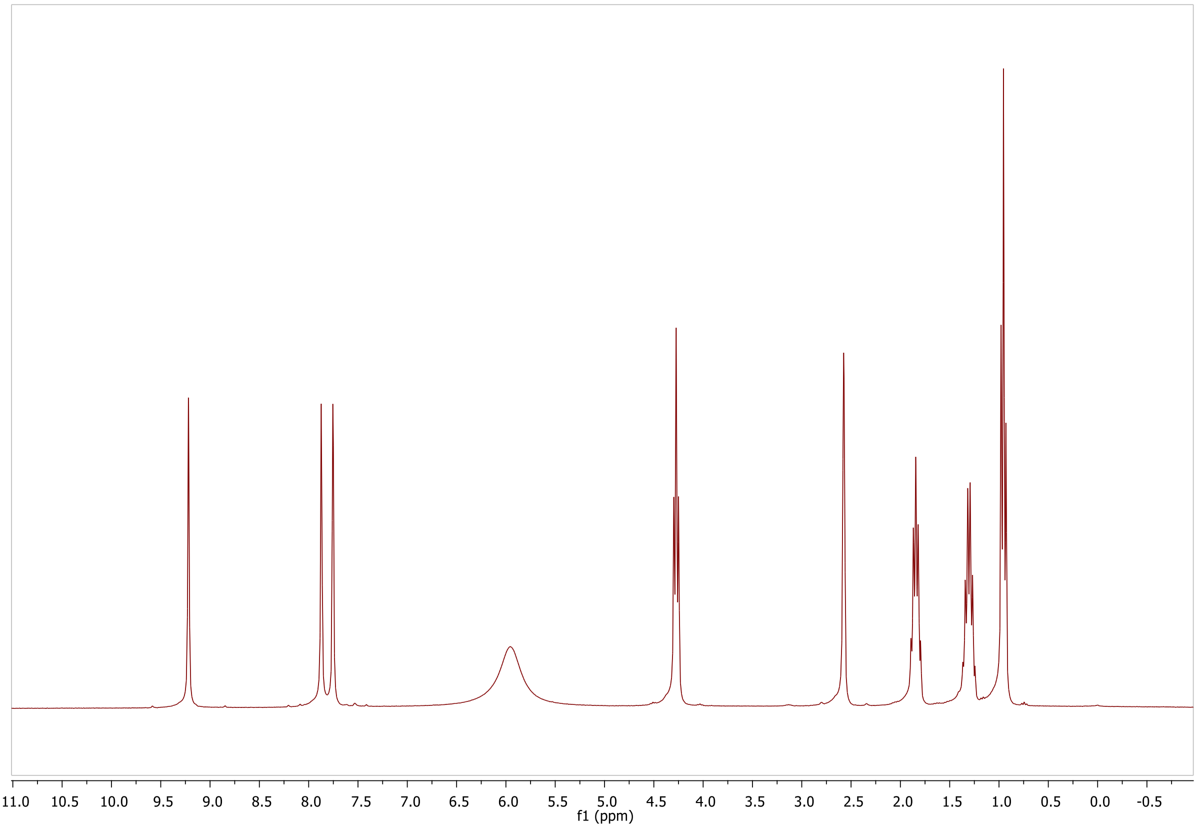

**Figure S2:** $^{13}$C-NMR of 1-butylimidazolium hydrogensulfate

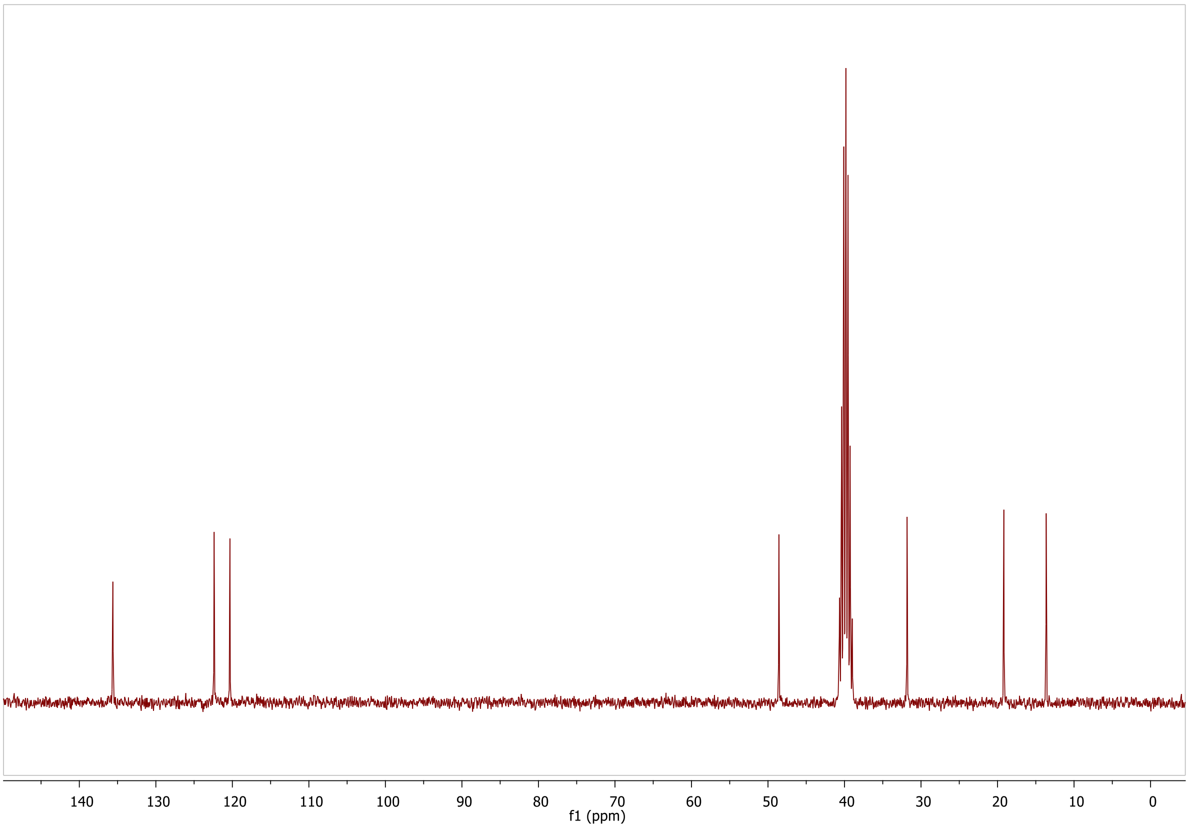

**Figure S3:** $^{1}$H-NMR of 1-butylimidazolium bis[(trifluoromethyl)sulfonyl]imide

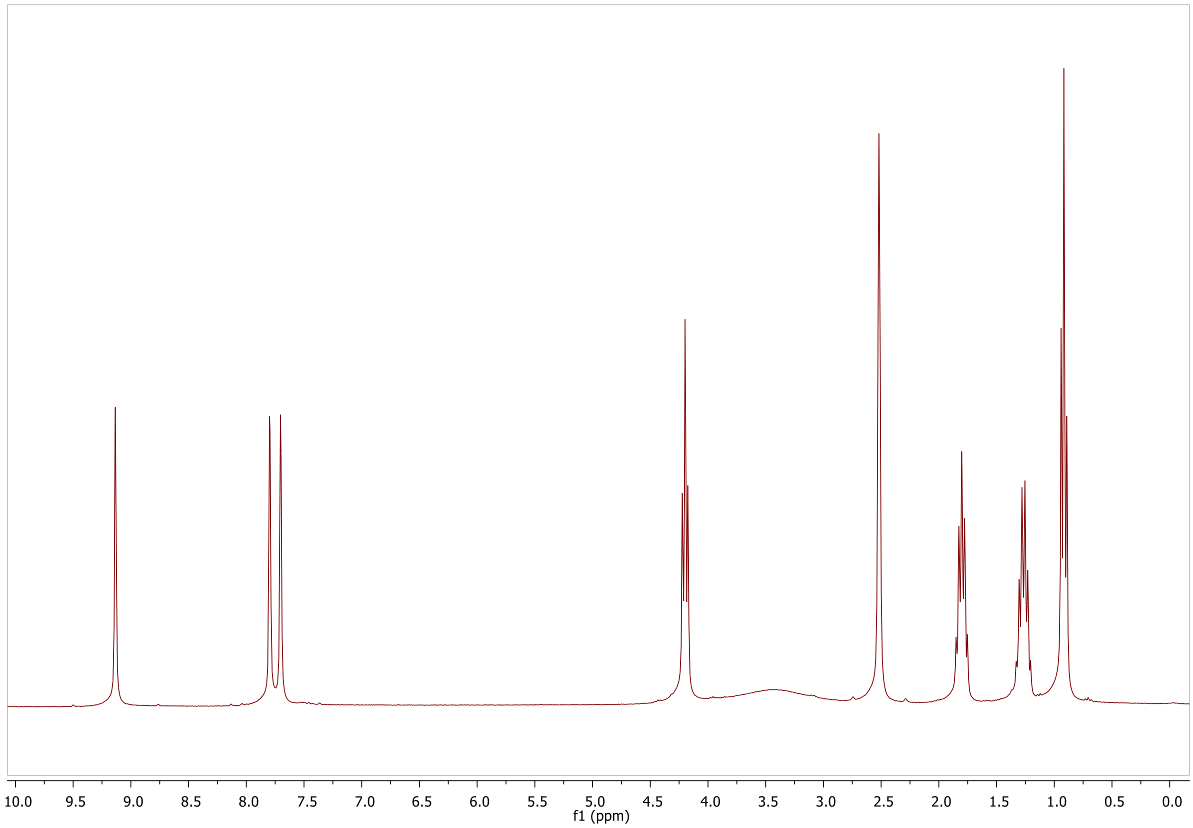

**Figure S4:** $^{13}$C-NMR of 1-butylimidazolium bis[(trifluoromethyl)sulfonyl]imide

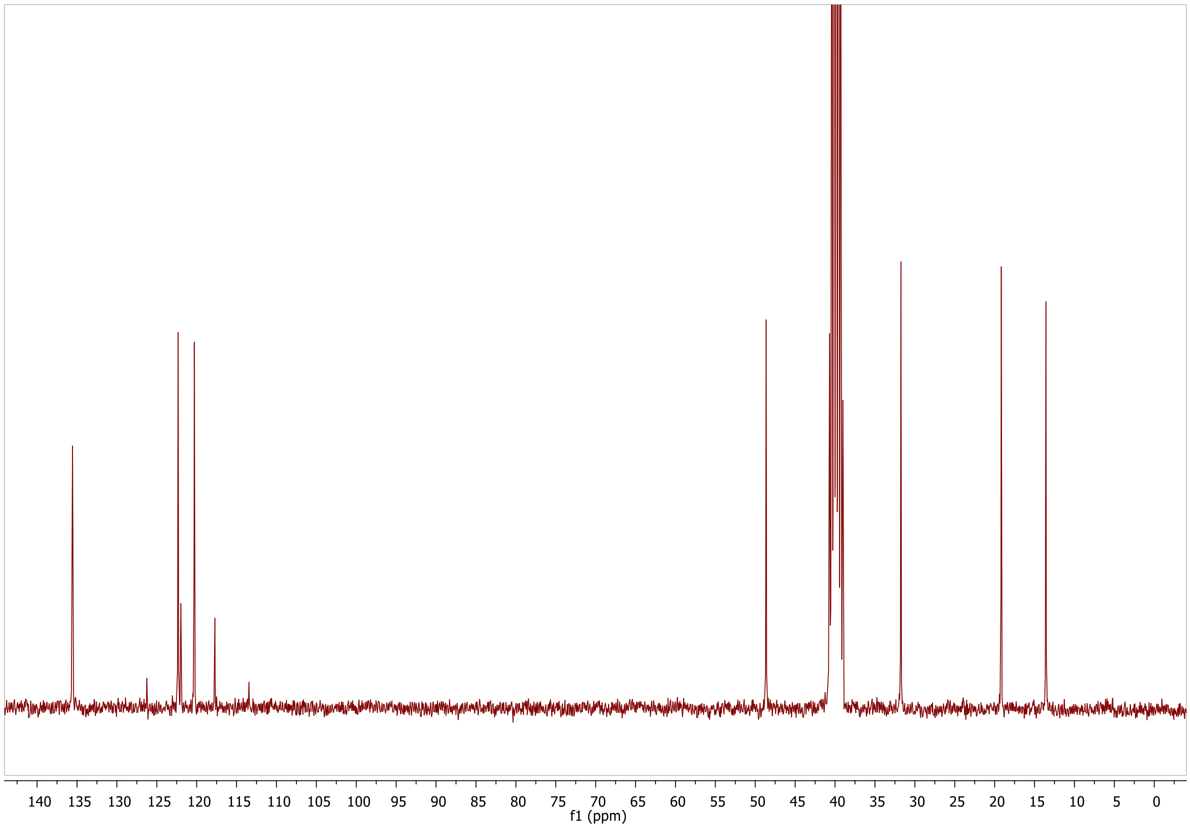

**Figure S5:** $^1$H-NMR of 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide

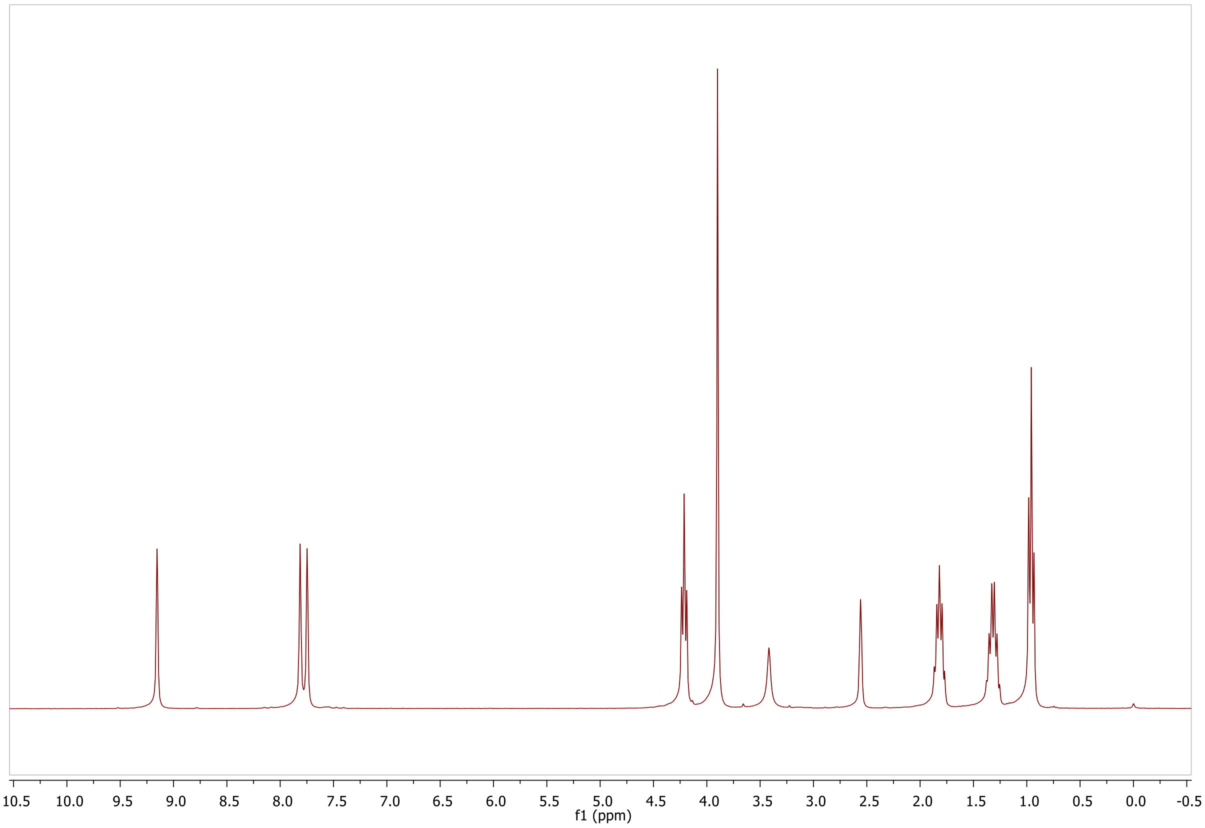

**Figure S6:** $^{13}$C-NMR of 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide

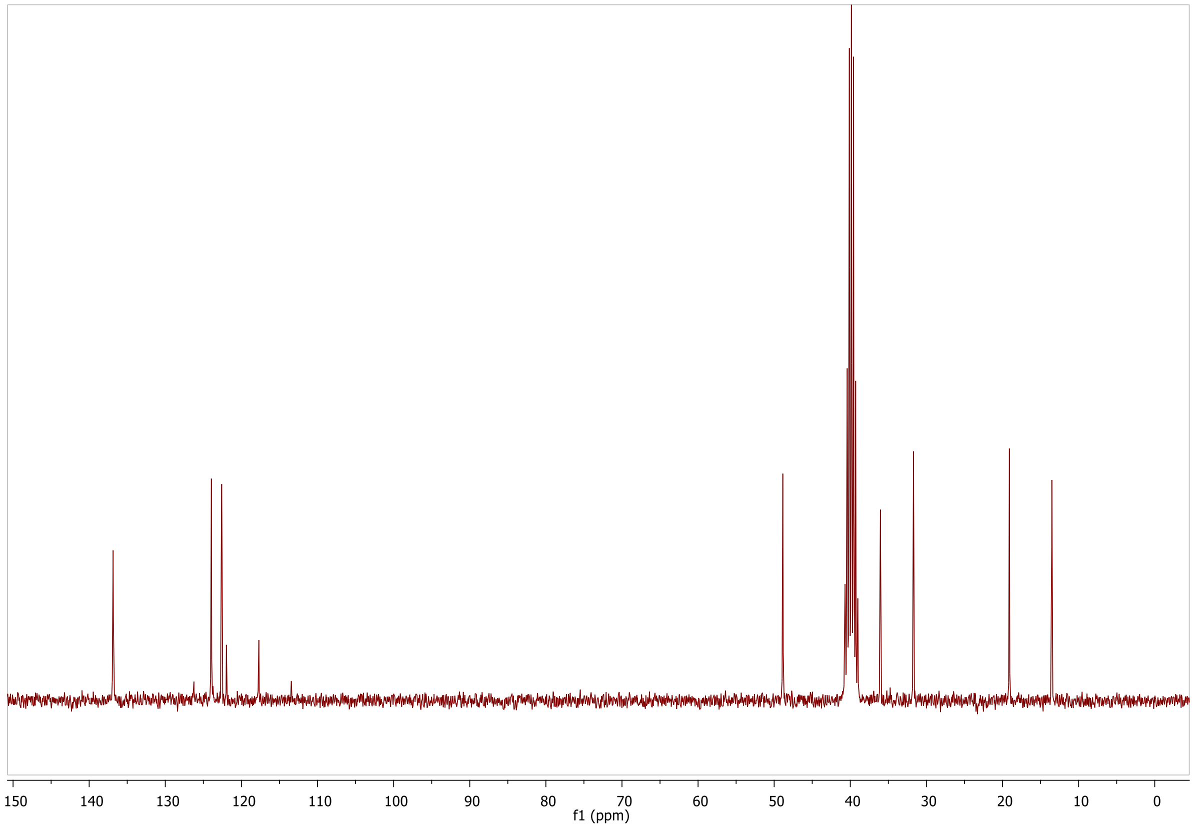

**Table S1:** Purity, molecular weight, water, lithium and halide contents in selected ILs.

| Ionic Liquid | Purity Mol% | Mw $g \cdot mol^{-1}$ | $H_2O$ ppm | Li ppm | Br ppm | Cl ppm |
|---|---|---|---|---|---|---|
| $[C_4Him]$ $[HSO_4]$ | >99.3 | 222.26 | 551 | - | - | - |
| $[C_4Him]$ $[NTf_2]$ | >99.4 | 405.33 | 187 | 24 | - | 19 |
| $[C_4mim]$ $[NTf_2]$ | >99.7 | 419.36 | 34 | 16 | 6 | - |

**Table S2**: Structure, abbreviation, sigma profile and Cosmo volume evaluated by COSMOthermX interface of studied ions and ILs.

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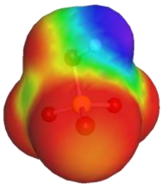
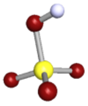
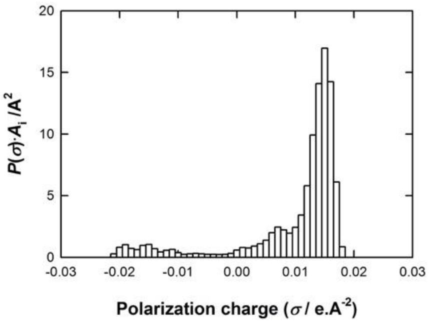
<tr><td></td><td></td><td rowspan="2">
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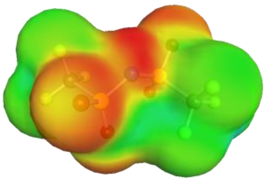
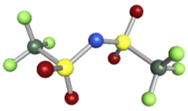
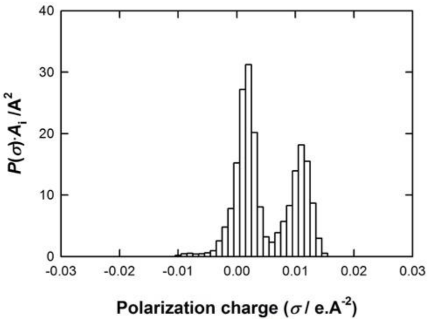
<tr><td></td><td></td><td rowspan="2">
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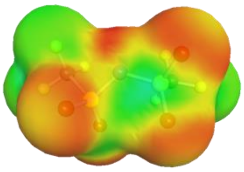
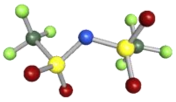
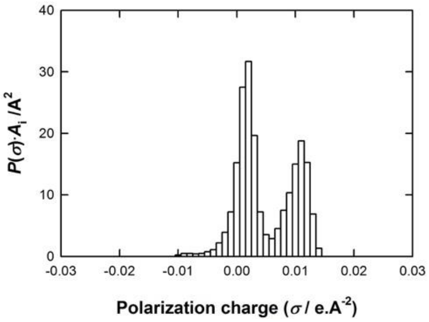
<tr><td></td><td></td><td rowspan="2">
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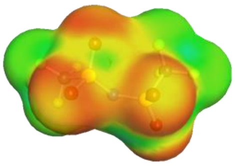
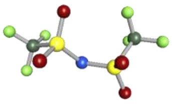
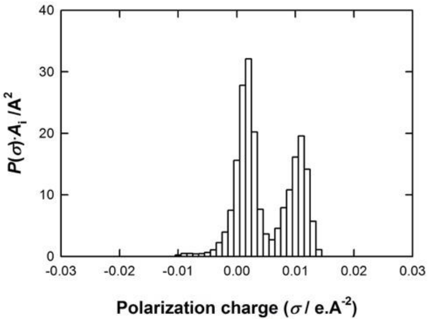
<tr><td></td><td></td><td rowspan="2">
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**Table S2**: *Continued…*

| Structure<br>and abbreviation | Cosmo Volume<br>(Å$^3$) | Sigma Profile |
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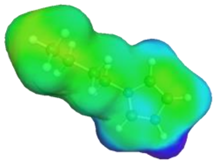
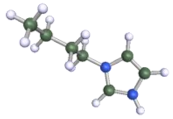
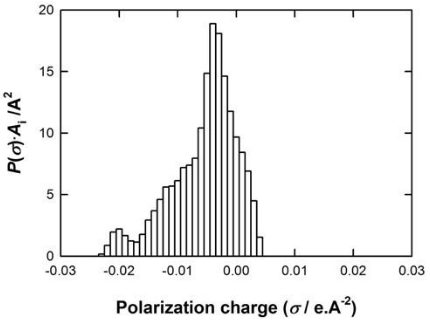
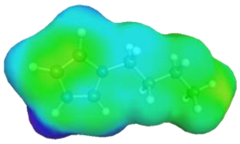
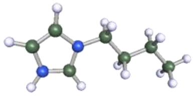
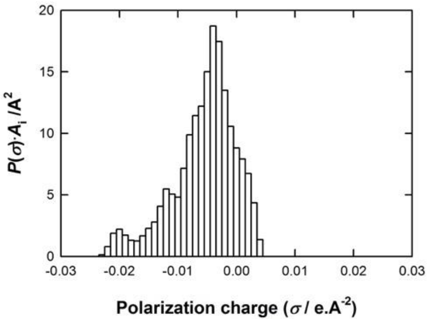
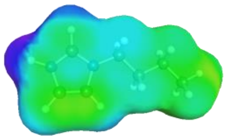
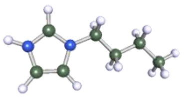
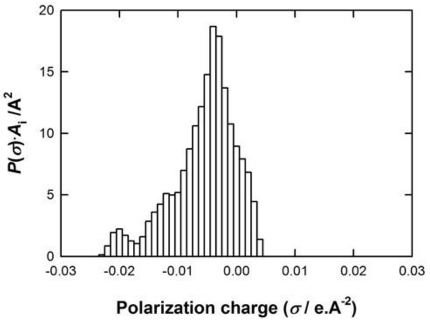
|  |  |  |
| [C$_4$Him]$^+$ conformer 1 | 176.7355 | |
|  |  |  |
| [C$_4$Him]$^+$ conformer 2 | 174.9824 | |
|  |  |  |
| [C$_4$Him]$^+$ conformer 3 | 174.8594 | |

**Table S2**: *Continued…*

| Structure and abbreviation | | Cosmo Volume (Å$^3$) | Sigma Profile |
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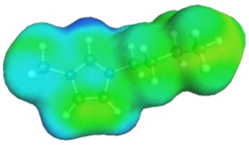
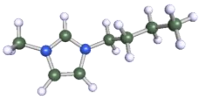
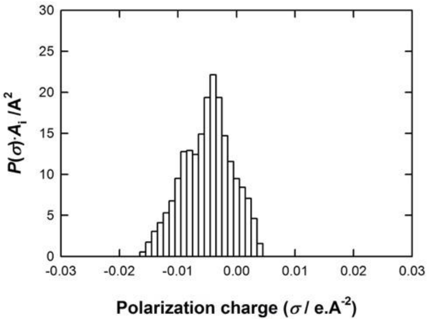
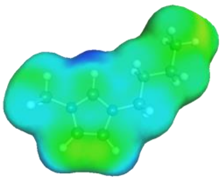
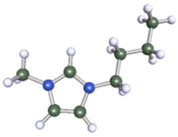
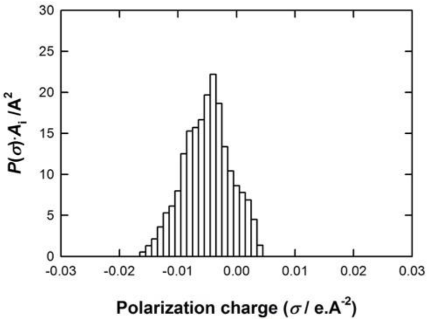
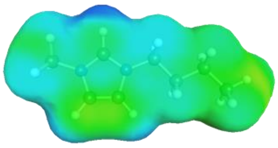
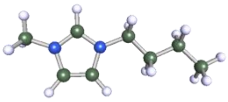
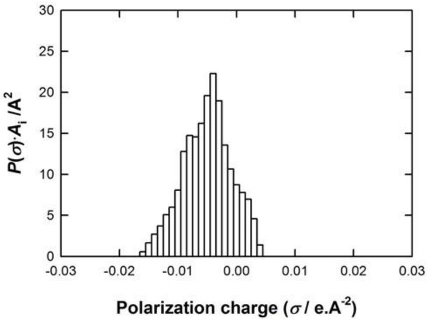
|  |  | |  |
| [C$_4$mim]$^+$ conformer 1 | | 199.8626 | |
|  |  | |  |
| [C$_4$mim]$^+$ conformer 2 | | 197.7214 | |
|  |  | |  |
| [C$_4$mim]$^+$ conformer 3 | | 197.8473 | |

**Table S2**: *Continued…*

| Structure and abbreviation | Cosmo Volume (Å$^3$) | Sigma Profile |
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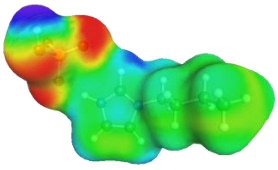
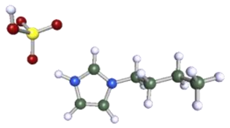
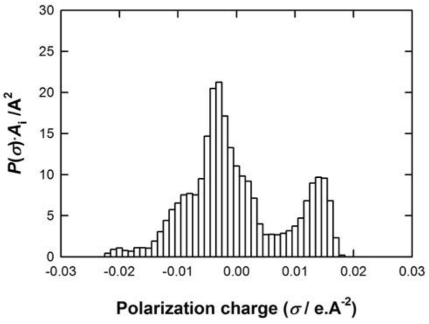
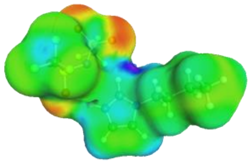
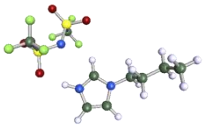
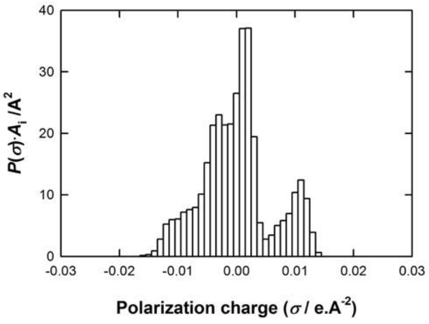
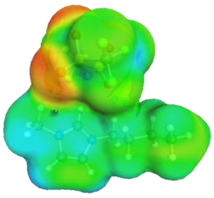
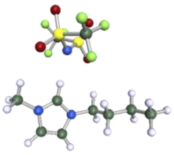
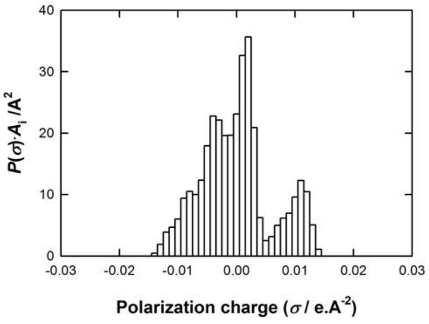
|  |  |  |
| [$C_4$Him] [$HSO_4$] | 254.5517 | |
|  |  |  |
| [$C_4$Him] [$NTf_2$] | 394.0972 | |
|  |  |  |
| [$C_4$mim] [$NTf_2$] | 430.2795 | |

**Table S3**: Molar volume ($V_m$) and free volume ($V_f$) of selected ILs determined by COSMOthermX at 25 °C and 0.1 MPa.

| Ionic Liquid | $V_m$ $cm^3 \cdot mol^{-1}$ | $V_f$ $cm^3 \cdot mol^{-1}$ |
|---|---|---|
| [$C_4$Him] [$HSO_4$] | 174.67 | 18.62 |
| [$C_4$Him] [$NTf_2$] | 270.00 | 28.08 |
| [$C_4$mim] [$NTf_2$] | 288.88 | 31.93 |