Supporting Information to

# Ether Functionalisation, Ion Conformation and the Optimisation of Macroscopic Properties in Ionic Liquids

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# Contents

# 1 Syntheses

## 1.1. Cation precursors

Please refer to the supporting information of our previous publication for detailed information on the syntheses of [P5551][I], [P(2O2)$_3$1][I], as well as the underlying phosphines.[1]

### *Tris(2-ethoxyethyl)amine N(2O2)$_3$*

For the synthesis of tris(2-ethoxyethyl)amine, 30.0 g of triethanolamine (201 mmol / 1.00 eq / 26.5 mL) were dissolved in 500 mL of dry THF under argon atmosphere. To this solution 24.5 g of 60% sodium hydride dispersion in mineral oil (613 mmol / 3.05 eq) were added. The resulting suspension was heated to slight reflux and stirred with a KPG stirrer for two days. After cooling to ambient temperature, 45.8 mL of bromoethane (613 mmol /3.05 eq / 66.8 g) were added dropwise over 2 hours. After completion of the addition, the mixture was stirred for two days at ambient temperature and the organic solvent removed by rotary evaporation. The solid residue was dissolved in a minimal amount of water and extracted three times with about 300 mL of diethyl ether. The combined organic extracts were dried over magnesium sulphate and filtered, followed by removal of the solvent on a rotary evaporator. The residue was distilled in vacuum to obtain 29.1 g of the title compound (125 mmol / 62% isolated yield) as a colourless liquid (b.p.(N(2O2)$_3$) = 80°C at 0.3 mbar)

$^1$H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.75-3.30 (m, 12 H, N-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H + N-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 2.73 (t, $^3J_{H/H}$ = 6.3 Hz, 6H, N-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 1.13 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, N-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 69.09 (s, N-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 66.42 (s, N-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 54.81 (s, N-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 15.24 (s, N-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***).

### *Tris(2-ethoxyethyl)ammonium iodide [N(2O2)$_3$1][I]*

27.0 g of tris(2-ethoxyethyl)amine (116 mmol / 1.00 eq) were dissolved in 300 mL of dry acetonitrile and cooled to 0°C under an atmosphere of argon. To this solution were added dropwise 7.56 mL of iodomethane (121 mmol / 1.04 eq / 17.2 g). The solution was allowed to warm to ambient temperature and stirred for 4 days before the solvent was removed by rotary evaporation. The residue was dried in high vacuum for two days to obtain 41.8 g of the title compound (111 mmol / 96% isolated yield) as slightly yellow, highly viscous liquid.

$^1$H NMR (DMSO-d6, 400 MHz, δ in ppm): 3.82-3.75 (m, 6 H, N-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 3.64 (t, $^3J_{H/H}$ = 5.0 Hz, 6H, N-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 3.47 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, N-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 3.13 (s, 3H, N-***CH$_3$***) 1.11 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, N-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***).

$^{13}$C{$^1$H} NMR (DMSO-d6, 101 MHz, δ in ppm): 65.53 (s, N-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 63.17 (s, N-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 61.80 (s, N-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 49.52 (s, N-***CH$_3$***), 14.82 (s, N-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***).

### *Methyltripentylammonium iodide [N5551][I]*

Methyltripentylammonium iodide was prepared similar to tris(2-ethoxyethyl)ammonium iodide using 38.4 mL freshly distilled tripentylamine (132 mmol/ 1.00 eq / 30.0 g) and 7.4 mL methyliodide (145 mmol / 1.10 eq / 20.6 g). 47.3 g of the title compound (128 mmol / 97% isolated yield) were obtained as slightly yellow solid.

$^1$H NMR (DMSO-d6, 400 MHz, δ in ppm): 3.24-3.19 (m, 6 H, N-***CH$_2$***-(CH$_2$)$_4$-H), 2.97 (s, 3H, N-***CH$_3$***), 1.62 (p, $^3J_{H/H}$ = 7.8 Hz, 6H, N-CH$_2$-***CH$_2$***-(CH$_2$)$_3$-H), 1.42-1.19 (m, 12H, N-(CH$_2$)$_2$-***CH$_2$***-(CH$_2$)$_2$-H + N-(CH$_2$)$_3$-***CH$_2$***-CH$_3$) 0.90 (t, $^3J_{H/H}$ = 7.2 Hz, 9H, N-(CH$_2$)$_4$-***CH$_3$***).

$^{13}C\{^1H\}$ NMR (DMSO-d6, 101 MHz, δ in ppm): 60.50 (s, N-***CH₂***-(CH₂)₄-H), 47.48 (s, N-***CH₃***), 27.87 (s, N-CH₂-***CH₂***-(CH₂)₃-H), 21.56 (s, N-(CH₂)₂-***CH₂***-(CH₂)₂-H), 21.07 (s, N-(CH₂)₃-***CH₂***-CH₃), 13.69 (s, N-(CH₂)₄-***CH₃***).

## 1.2. Anion precursors

The syntheses of $KB(CN)_4$,[2] $CH_2Tf_2$,[3] and KNTfTFA[4] are based on literature protocols.

### *Potassium tetracyanoborate [K][B(CN)₄] (or [K][TCB])*

170.2 g potassium cyanide (2.61 mol), 116.2 g lithium chloride (2.74 mol), and 36.9 g potassium tetrafluoroborate (293 mmol) were weighed and roughly ground together inside a glovebox using mortar and pestle. The whole mass is finely ground five times using a manual burr coffee grinder inside the glovebox and transferred to a nickel crucible with nickel lid. The nickel crucible was put into a pre-heated muffle furnace at 315°C for 1.5 h. After cooling down, the resulting cake was roughly broken up inside a 5 L beaker. Water (150 mL) was added, followed by the slow addition of 350 mL $H_2O_2$ 30% together with ice to control the exothermic (and delayed) reaction. After complete addition of the hydrogen peroxide, 200 mL concentrated hydrochloric acid were added, followed by filtration. To the clear filtrate were added 28 mL concentrated hydrochloric acid together with 47 g tripropylamine and 250 mL methylene chloride. The mixture was stirred vigorously for 30 min, and the phases separated. The aqueous phase was extracted in the same manner with 150 mL of methylene chloride, followed by 100 mL of methylene chloride. The combined organic phases were washed with 200 mL of water, and the water reextracted with 50 mL of methylene chloride. To the combined methylene chloride phases were added 41.2 g potassium hydroxide 85% in 25 mL water. After stirring for 30 min, the supernatant is carefully decanted and the remainder extracted with 300 mL, 100 mL, and 50 mL tetrahydrofuran. The combined organic phases were dried over potassium carbonate, and the solvent removed under reduced pressure. The residue is washed with methylene chloride and dried in high vacuum to yield 20.9 g potassium tetracyanoborate (136 mmol / 46% yield based on $[K][BF_4]$). For the use as ionic liquid precursor, further purification is advisable. To this end, raw $[K][B(CN)_4]$ was dissolved in the minimum amount of acetonitrile. Activated charcoal powder was then added to the yellow solution, and the resulting suspension stirred for 3 h. The solution was then passed over a plug of $Al_2O_3$ for chromatography, acidic, Brookmann I, 50-200 µm (ACROS organics, New Jersey, USA). Approximately 10-20 mL of Alumina powder was used per 100 mL of suspension, and the plug eluted with twice the initial volume of acetonitrile. The clear colourless solution was filtered through a 0.2 µm PTFE syringe filter and the solvent removed under reduced pressure. The resulting solid was recrystallised from hot acetonitrile/toluene, with crystals being allowed to grow further by cooling to 4°C. Decanting of the solvent and drying in high vacuum gives pure $[K][B(CN)_4]$ suitable for the use as anion precursor in ionic liquids. Checking the purity with $^{11}B$ NMR using quartz NMR tubes is indispensable, as some batches contained significant amounts of an unidentified side product which was not observed in $^1H$, $^{13}C$ or $^{19}F$ NMR spectra. The predominant side product appears as broad singlet at −32.39 ppm in the $^{11}B$ spectrum and can be removed by the Alumina plug.

$^{13}C\{^1H\}$ NMR (DMSO-d6, 100 MHz, δ in ppm): 121.82 (q, $^1J_{C/B} = 70.9$ Hz, ***CN***).

$^{11}B$ NMR (DMSO-d6, 128 MHz, δ in ppm): −38.51 (s).

HRMS, ESI$^-$: m/z found 115.0211, calc. 115.0216 $(B(CN)_4)^-$

### *Potassium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide [K][NTfTFA] (or [K][TSAC])*

25.2 g $TfNH_2$ (169 mmol / 1.00 eq) were dissolved in 200 mL methanol (dried over MS 3Å prior to use) and cooled to 0°C in an ice bath. To this solution were carefully added 19.0 g tBuOK (169 mmol / 1.00 eq), and the resulting solution heated to 60°C for 3 h. The solvent is removed under reduced pressure, and to the resulting colourless solid were added 120 mL diethyl ether (distilled from sodium / benzophenone prior to use). The suspension is cooled to 0°C, and 25 mL trifluoroacetic anhydride (38.0 g / 181 mmol / 1.07 eq) dissolved in 80 mL dry diethyl ether were added slowly over 1 h. The reaction mixture is stirred at 0°C for 1 h, then at ambient temperature for 11 h. The precipitate is filtered off using a Schlenk-frit, washed with 100 mL dry diethyl ether, and dried in high vacuum to give the desired product as colourless, free-flowing powder (45.6 g / 161 mmol / 95% isolated yield).

$^{13}C\{^1H\}$ NMR (DMSO-d6, 100 MHz, δ in ppm): 160.16 (q, $^2J_{C/F}$ = 35.2 Hz, $\boldsymbol{CO}CF_3$), 119.57 (q, $^1J_{C/F}$ = 322.6 Hz, $SO_2\boldsymbol{CF_3}$), 116.36 (q, $^1J_{C/F}$ = 289.8 Hz, $CO\boldsymbol{CF_3}$).

$^{19}F\{^1H\}$ NMR (Acetone-d6, 377 MHz, δ in ppm): −76.46 (s, $SO_2\boldsymbol{CF_3}$), −80.02 (s, $CO\boldsymbol{CF_3}$).

HRMS, $ESI^-$: m/z found 243.9510, calc. 243.9503 $(NTfTFA)^-$

### *Methylene ditriflone $CH_2Tf_2$*

A 1000 mL three necked round bottom flask with internal thermometer, dropping funnel and nitrogen inlet was charged under Schlenk conditions with 570 mL of a 0.7 M solution of (trimethylsilyl)methyllithium (400 mmol, 2.02 eq) in hexanes (Fischer Scientific, LE11 5RG Leicestershire, United Kingdom). This solution was cooled in an ice/NaCl bath, and 33.2 mL triflic anhydride (55.7 g, 197 mmol, 1.00 eq) were added so that the temperature remained between 0°C and 5°C. Lower temperatures led to precipitation of the TMSLi and should be avoided. After complete addition, the solution was stirred at 0°C for 2 h and quenched by addition of 300 mL saturated sodium bicarbonate solution and 100 mL water. The aqueous layer was separated and washed three times with each 300 mL of methylene chloride. Then, 200 mL of concentrated hydrochlorid acid were added to the aqueous phase, followed by extraction with each 300 mL of methylene chloride. The combined organic phases were dried over magnesium sulphate and the solvent removed on a rotary evaporator under reduced pressure. The residue is transferred to a sublimation apparatus with dry ice cooled cold finger and water bath (40°C) and sublimed under high vacuum to give 16.2 g of methylene ditriflone (57.8 mmol / 59% yield based on $4\ TMSLi + 2\ Tf_2O \rightarrow CH_2Tf_2$). The methylene ditriflone obtained this way was further purified by a second sublimation, where approximately the same volume of concentrated sulfuric acid was added to the crude methylene ditriflone.

$^1H$ NMR (DMSO-d6, 400 MHz, δ in ppm): 12.58 (br s, 1H), 3.94 (br s, 1H).

$^{13}C\{^1H\}$ NMR (DMSO-d6, 100 MHz, δ in ppm): 120.96 (q, $^1J_{C/F}$ = 326.3 Hz, $\boldsymbol{CF_3}$), 54.13 (s, $\boldsymbol{CH_2}$).

$^{19}F\{^1H\}$ NMR (DMSO-d6, 377 MHz, δ in ppm): −76.00 (s).

HRMS, $ESI^-$: m/z found 278.9215, calc. 278.9220 $(CHTf_2)^-$

### *Sodium bis(trifluoromethylsulfonyl) methanide [Na][CHTf$_2$] (or [Na][TFSM])*

10.095 g methylene ditriflone (36.0 mmol / 1.00 eq) were dissolved in 40 mL water and cooled to 0°C in an ice bath. To this solution, 3.037 g $NaHCO_3$ (36.2 mmol / 1.00 eq) were slowly added, giving a neutral solution. The reaction mixture was then frozen in liquid nitrogen, freeze dried under high vacuum, and dried under high vacuum at ambient temperature for several days to give 10.03 g of sodium bis(trifluoromethylsulfonyl) methanide (33.2 mmol / 92% isolated yield) as a colourless solid.

$^1$H NMR (DMSO-d6, 400 MHz, δ in ppm): 3.90 (s, 1H).

$^{13}$C{$^1$H} NMR (DMSO-d6, 100 MHz, δ in ppm): 120.80 (q, $^1J_{C/F}$ = 326.3 Hz, ***$CF_3$***), 53.98 (s, ***$CH_2$***).

$^{19}$F{$^1$H} NMR (DMSO-d6, 377 MHz, δ in ppm): −80.75 (s).

## 1.3. Ionic Liquids

### *General procedure*

To 10-20 mmol of a cation precursor ([P5551][I], [P(2O2)$_3$1][I], [N5551][I], [N(2O2)$_3$1][I]) are added 1.15 to 1.20 equivalents of the desired anion precursor ([K][B(CN)4], [Na][CHTf$_2$], [Li][NTf$_2$], [K][NTfTFA]) as well as 20 mL of water and 200 mL of methylene chloride. The resulting mixture is then stirred for an hour, and the organic phase separated. The organic phase is then washed with water (20 mL each) until no further halide is detected in the washing water using silver nitrate solution. Since [Ag][B(CN)$_4$] precipitates in water, tetracyanoborate ionic liquids were checked for the absence of halides by means of ion chromatography. After removing the methylene chloride under reduced pressure, the resulting ionic liquids are dried by stirring under high vacuum at 40°C for several days. After each washing step, the separating funnel is thoroughly rinsed with ethanol and deionised water to avoid transfer of halides.

### *Tris(2-ethoxyethyl)methylphosphonium tetracyanoborate [P(2O2)$_3$1][B(CN)$_4$]*

6.82 g [P(2O2)$_3$1][I] (17.4 mmol / 1.00 eq) and 3.25 g $KB(CN)_4$ (21.2 mmol / 1.22 eq) were converted to 6.07 g of [P(2O2)$_3$1][B(CN)$_4$] (16.0 mmol / 92% yield) using the general procedure, washing the DCM phase 5 times with water.

$^1$H NMR ($CDCl_3$, 400 MHz, δ in ppm): 3.81 (dt, $^3J_{H/P}$ = 20.4 Hz, $^3J_{H/H}$ = 6.0 Hz, 6H, P-$CH_2$-***$CH_2$***-O-$(CH_2)_2$-H), 3.54 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, P-$(CH_2)_2$-O-***$CH_2$***-$CH_3$), 2.51 (dt, $^2J_{H/P}$ = 12.4 Hz, $^3J_{H/H}$ = 6.0 Hz, 6H, P-***$CH_2$***-$CH_2$-O-$(CH_2)_2$-H), 1.90 (d, $^1J_{H/P}$ = 14.1 Hz, 3H, P-***$CH_3$***), 1.20 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, P-$(CH_2)_2$-O-$CH_2$-***$CH_3$***).

$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz, δ in ppm): 122.73 (q, $^1J_{C/B}$ = 71.4 Hz, B***$(CN)_4$***), 67.25 (s, P-$(CH_2)_2$-O-***$CH_2$***-$CH_3$), 63.17 (d, $^2J_{C/P}$ = 8.1 Hz, P-$CH_2$-***$CH_2$***-O-$(CH_2)_2$-H), 23.99 (d, $^1J_{C/P}$ = 51.7 Hz, P-***$CH_2$***-$CH_2$-O-$(CH_2)_2$-H), 15.03 (s, P-$(CH_2)_2$-O-$CH_2$-***$CH_3$***), 7.29 (d, $^1J_{C/P}$ = 52.6 Hz, P-***$CH_3$***).

$^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz, δ in ppm): 32.95 (s).

$^{11}$B NMR ($CDCl_3$, 128 MHz, δ in ppm): −38.20 (s).

### *Tris(2-ethoxyethyl)methylammonium tetracyanoborate [N(2O2)$_3$1][B(CN)$_4$]*

[N(2O2)$_3$1][B(CN)$_4$] was synthesized from 9.30 g of tris(2-ethoxyethyl)methylammonium iodide (24.7 mmol / 1.00 eq) and 4.50 g potassium tetracyanoborate (29.2 mmol / 1.18 eq) according to the general procedure. 8.26 g of the product (22.7 mmol / 92% isolated yield) were obtained as colourless liquid.

$^1$H NMR (DMSO-d6, 400 MHz, δ in ppm): 3.80-3.74 (m, 6H, N-$\boldsymbol{CH_2}$-CH$_2$-O-(CH$_2$)$_2$-H), 3.63 (t, $^3J_{H/H}$ = 4.7 Hz, 6H, N-$\boldsymbol{CH_2}$-CH$_2$-O-(CH$_2$)$_2$-H), 3.48 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, N-(CH$_2$)$_2$-O-$\boldsymbol{CH_2}$-CH$_3$), 3.11 (s, 3H, N-$\boldsymbol{CH_3}$) 1.13 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, N-(CH$_2$)$_2$-O-CH$_2$-$\boldsymbol{CH_3}$).

$^{13}$C{$^1$H} NMR (DMSO-d6, 101 MHz, δ in ppm): 122.75 (q, $^1J_{C/B}$ = 70.8 Hz, B$\boldsymbol{(CN)_4}$), 65.62 (s, N-CH$_2$-$\boldsymbol{CH_2}$-O-(CH$_2$)$_2$-H), 63.22 (s, N-(CH$_2$)$_2$-O-$\boldsymbol{CH_2}$-CH$_3$), 61.90 (s, N-$\boldsymbol{CH_2}$-CH$_2$-O-(CH$_2$)$_2$-H), 49.51 (s, N-$\boldsymbol{CH_3}$), 14.80 (s, N-(CH$_2$)$_2$-O-CH$_2$-$\boldsymbol{CH_3}$).

$^{11}$B NMR (DMSO-d6, 128 MHz, δ in ppm): −38.53 (s).

### *Methyltripentylphosphonium tetracyanoborate [P5551][B(CN)$_4$]*

7.49 g [P5551][I] (19.4 mmol / 1.00 eq) and 3.62 g KB(CN)$_4$ (23.5 mmol / 1.21 eq) were converted to 5.71 g of [P5551][B(CN)$_4$] (15.3 mmol / 79% yield) using the general procedure, washing the DCM phase 5 times with water.

$^1$H NMR (DMSO-d6, 400 MHz, δ in ppm): 2.24-2.05 (m, 6H, P-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 1.78 (d, $^2J_{H/P}$ = 13.9 Hz, 3H, P-$\boldsymbol{CH_3}$), 1.57-1.44 (m, 6H, P-CH$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_3$-H), 1.44-1.26 (m, 12H, P-(CH$_2$)$_2$-$\boldsymbol{(CH_2)_2}$-CH$_3$), 0.90 (t, $^3J_{H/H}$ = 7.1 Hz, 9H, P-(CH$_2$)$_4$-$\boldsymbol{CH_3}$).

$^{13}$C{$^1$H} NMR (DMSO-d6, 101 MHz, δ in ppm): 121.74 (q, $^1J_{C/B}$ = 70.8 Hz, B$\boldsymbol{(CN)_4}$), 32.13 (d, $^3J_{C/P}$ = 15.5 Hz, P-CH$_2$-CH$_2$-$\boldsymbol{CH_2}$-CH$_2$-CH$_3$), 21.33 (s, P-(CH$_2$)$_3$-$\boldsymbol{CH_2}$-CH$_3$), 20.19 (d, $^2J_{C/P}$ = 4.4 Hz, P-CH$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_3$-H), 19.10 (d, $^1J_{C/P}$ = 49.1 Hz, P-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 13.48 (s, P-(CH$_2$)$_4$-$\boldsymbol{CH_3}$), 3.08 (d, $^1J_{C/P}$ = 51.4 Hz, P-$\boldsymbol{CH_3}$).

$^{31}$P{$^1$H} NMR (DMSO-d6, 162 MHz, δ in ppm): 32.23 (s).

$^{11}$B NMR (DMSO-d6, 128 MHz, δ in ppm): −38.52 (s).

### *Methyltripentylammonium tetracyanoborate [N5551][B(CN)$_4$]*

The title compound was prepared according to the general procedure from 9.20 g of [N5551][I] (24.5 mmol / 1.00 eq) and 4.43 g of [K][B(CN)$_4$] (28.2 mmol / 1.15 eq). 8.46 g of the product (23.3 mmol / 95% yield) were obtained as colourless liquid.

$^1$H NMR (DMSO-d6, 400 MHz, δ in ppm): 3.24-3.14 (m, 6 H, N-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 2.94 (s, 3H, N-$\boldsymbol{CH_3}$), 1.62 (p, $^3J_{H/H}$ = 7.9 Hz, 6H, N-CH$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_3$-H), 1.39-1.19 (m, 12H, N-(CH$_2$)$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_2$-H + N-(CH$_2$)$_3$-$\boldsymbol{CH_2}$-CH$_3$) 0.89 (t, $^3J_{H/H}$ = 7.2 Hz, 9H, N-(CH$_2$)$_4$-$\boldsymbol{CH_3}$).

$^{13}$C{$^1$H} NMR (DMSO-d6, 101 MHz, δ in ppm): 121.73 (q, $^1J_{C/B}$ = 70.8 Hz, B$\boldsymbol{(CN)_4}$), 60.58 (s, N-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 47.46 (s, N-$\boldsymbol{CH_3}$), 27.90 (s, N-CH$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_3$-H), 21.59 (s, N-(CH$_2$)$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_2$-H), 21.06 (s, N-(CH$_2$)$_3$-$\boldsymbol{CH_2}$-CH$_3$), 13.66 (s, N-(CH$_2$)$_4$-$\boldsymbol{CH_3}$).

$^{11}$B NMR (DMSO-d6, 128 MHz, δ in ppm): −38.53 (s).

### *Tris(2-ethoxyethyl)methylphosphonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide [P(2O2)$_3$1][NTfTFA]*

6.62 g [P(2O2)$_3$1][I] (16.9 mmol / 1.00 eq) and 5.70 g KNTfTFA (20.1 mmol / 1.19 eq) were converted to 7.57 g of [P(2O2)$_3$1][NTfTFA] (14.9 mmol / 88% yield) using the general procedure, washing the DCM phase 4 times with water.

$^1$H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.72 (dt, $^3J_{H/P}$ = 20.3 Hz, $^3J_{H/H}$ = 6.0 Hz, 6H, P-CH$_2$-$\boldsymbol{CH_2}$-O-(CH$_2$)$_2$-H), 3.44 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, P-(CH$_2$)$_2$-O-$\boldsymbol{CH_2}$-CH$_3$), 2.51 (dt, $^2J_{H/P}$ = 13.2 Hz, $^3J_{H/H}$ = 6.0 Hz, 6H, P-$\boldsymbol{CH_2}$-CH$_2$-O-(CH$_2$)$_2$-H), 1.84 (d, $^1J_{H/P}$ = 14.4 Hz, 3H, P-$\boldsymbol{CH_3}$), 1.11 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, P-(CH$_2$)$_2$-O-CH$_2$-$\boldsymbol{CH_3}$).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 161.92 (q, $^2J_{C/F}$ = 35.9 Hz, $\boldsymbol{CO}$CF$_3$), 120.12 (q, $^1J_{C/F}$ = 322.9 Hz, SO$_2$$\boldsymbol{CF_3}$), 116.64 (q, $^1J_{C/F}$ = 289.2 Hz, CO$\boldsymbol{CF_3}$), 66.82 (s, P-(CH$_2$)$_2$-O-$\boldsymbol{CH_2}$-CH$_3$), 63.18 (d, $^2J_{C/P}$ = 7.9 Hz, P-CH$_2$-$\boldsymbol{CH_2}$-O-(CH$_2$)$_2$-H), 23.47 (d, $^1J_{C/P}$ = 51.7 Hz, P-$\boldsymbol{CH_2}$-CH$_2$-O-(CH$_2$)$_2$-H), 14.79 (s, P-(CH$_2$)$_2$-O-CH$_2$-$\boldsymbol{CH_3}$), 6.690 (d, $^1J_{C/P}$ = 52.3 Hz, P-$\boldsymbol{CH_3}$).

$^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 32.72 (s).

$^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz, δ in ppm): −75.84 (s, SO$_2$$\boldsymbol{CF_3}$), −78.39 (s, CO$\boldsymbol{CF_3}$).

### *Tris(2-ethoxyethyl)methylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide [N(2O2)$_3$1][NTfTFA]*

[N(2O2)$_3$1][NTfTFA] was synthesised from 6.10 g of [N(2O2)$_3$1][I] (16.2 mmol / 1.00 eq) and 5.52 g of [K][NTfTFA] (19.5 mmol / 1.20 eq) according to the standard procedure mentioned above. 7.26 g of the title compound (14.7 mmol / 91% yield) were obtained as colourless liquid.

$^1$H NMR (DMSO-d6, 400 MHz, δ in ppm): 3.81-3.74 (m, 6 H, N-CH$_2$-$\boldsymbol{CH_2}$-O-(CH$_2$)$_2$-H), 3.64 (t, $^3J_{H/H}$ = 5.8 Hz, 6H, N-$\boldsymbol{CH_2}$-CH$_2$-O-(CH$_2$)$_2$-H), 3.47 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, N-(CH$_2$)$_2$-O-$\boldsymbol{CH_2}$-CH$_3$), 3.11 (s, 3H, N-$\boldsymbol{CH_3}$) 1.12 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, N-(CH$_2$)$_2$-O-CH$_2$-$\boldsymbol{CH_3}$).

$^{13}$C{$^1$H} NMR (DMSO-d6, 101 MHz, δ in ppm): 160.37 (q, $^2J_{C/F}$ = 35.0 Hz, $\boldsymbol{CO}$CF$_3$), 120.12 (q, $^1J_{C/F}$ = 322.9 Hz, SO$_2$$\boldsymbol{CF_3}$), 66.06 (s, N-CH$_2$-$\boldsymbol{CH_2}$-O-(CH$_2$)$_2$-H), 63.68 (s, N-(CH$_2$)$_2$-O-$\boldsymbol{CH_2}$-CH$_3$), 62.35 (s, N-$\boldsymbol{CH_2}$-CH$_2$-O-(CH$_2$)$_2$-H), 49.96 (s, N-$\boldsymbol{CH_3}$), 15.23 (s, N-(CH$_2$)$_2$-O-CH$_2$-$\boldsymbol{CH_3}$).

$^{19}$F{$^1$H} NMR (DMSO-d6, 376 MHz, δ in ppm): −75.87 (s, SO$_2$$\boldsymbol{CF_3}$), −78.44 (s, CO$\boldsymbol{CF_3}$).

### *Methyltripentylphosphonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide [P5551][NTfTFA]*

5.77 g [P5551][I] (14.9 mmol / 1.00 eq) and 5.00 g KNTfTFA (17.7 mmol / 1.18 eq) were converted to 7.06 g of [P5551][NTfTFA] (14.0 mmol / 94% yield) using the general procedure, washing the DCM phase 3 times with water.

$^1$H NMR (CDCl$_3$, 400 MHz, δ in ppm): 2.19-2.02 (m, 6H, P-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 1.77 (d, $^2J_{H/P}$ = 13.3 Hz, 3H, P-$\boldsymbol{CH_3}$), 1.55-1.23 (m, 18H, P-CH$_2$-$\boldsymbol{(CH_2)_3}$-CH$_3$), 0.86 (t, $^3J_{H/H}$ = 7.2 Hz, 9H, P-(CH$_2$)$_4$-$\boldsymbol{CH_3}$).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 161.01 (q, $^2J_{C/F}$ = 35.8 Hz, $\boldsymbol{CO}$CF$_3$), 120.29 (q, $^1J_{C/F}$ = 323.2 Hz, SO$_2$$\boldsymbol{CF_3}$), 116.72 (q, $^1J_{C/F}$ = 289.4 Hz, CO$\boldsymbol{CF_3}$), 32.55 (d, $^3J_{C/P}$ = 15.2 Hz, P-CH$_2$-CH$_2$-$\boldsymbol{CH_2}$-CH$_2$-CH$_3$), 21.86 (s, P-(CH$_2$)$_3$-$\boldsymbol{CH_2}$-CH$_3$), 21.13 (d, $^2J_{C/P}$ = 4.5 Hz, P-CH$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_3$-H), 20.12 (d, $^1J_{C/P}$ = 48.7 Hz, P-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 13.60 (s, P-(CH$_2$)$_4$-$\boldsymbol{CH_3}$), 3.97 (d, $^1J_{C/P}$ = 52.7 Hz, P-$\boldsymbol{CH_3}$).

$^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 31.45 (s).

$^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz, δ in ppm): −75.73 (s, SO$_2$$\boldsymbol{CF_3}$), −78.05 (s, CO$\boldsymbol{CF_3}$).

### *Methyltripentylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide [N5551][NTfTFA]*

For the preparation according to the general protocol 6.07 g of tripentylmethylammonium iodide (16.4 mmol / 1.00 eq) and 5.59 g of [K][NTfTFA] (19.7 mmol / 1.20 eq) were used. After purification and drying, 7.66 g of the product (15.7 mmol / 96% yield) were obtained as colourless liquid.

$^1$H NMR ($CDCl_3$, 400 MHz, δ in ppm): 3.23-3.15 (m, 6 H, N-***CH₂***-(CH₂)₄-H), 3.00 (s, 3H, N-***CH₃***), 1.64 (p, $^3J_{H/H}$ = 7.8 Hz, 6H, N-CH₂-***CH₂***-(CH₂)₃-H), 1.42-1.26 (m, 12H, N-(CH₂)₂-***CH₂***-(CH₂)₂-H + N-(CH₂)₃-***CH₂***-CH₃) 0.89 (t, $^3J_{H/H}$ = 6.9 Hz, 9H, N-(CH₂)₄-***CH₃***).

$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz, δ in ppm): 162.16 (q, $^2J_{C/F}$ = 35.8 Hz, ***CO***CF₃), 120.35 (q, $^1J_{C/F}$ = 323.3 Hz, SO₂***CF₃***), 61.90 (s, N-***CH₂***-(CH₂)₄-H), 48.46 (s, N-***CH₃***), 28.21 (s, N-CH₂-***CH₂***-(CH₂)₃-H), 22.13 (s, N-(CH₂)₂-***CH₂***-(CH₂)₂-H), 21.96 (s, N-(CH₂)₃-***CH₂***-CH₃), 13.71 (s, N-(CH₂)₄-***CH₃***).

$^{19}$F{$^1$H} NMR ($CDCl_3$, 376 MHz, δ in ppm): −75.74 (s, SO₂***CF₃***), −78.06 (s, CO***CF₃***).

### *Tris(2-ethoxyethyl)methylphosphonium bis(trifluoromethylsulfonyl)imide [P(2O2)₃1][NTf₂]*

10.2 g [P(2O2)₃1][I] (26.0 mmol / 1.00 eq) and 10.0 g LiNTf₂ (34.8 mmol / 1.34 eq) were converted to 13.58 g of [P(2O2)₃1][NTf₂] (24.9 mmol / 96% yield) using the general procedure, washing the DCM phase 3 times with water.

$^1$H NMR ($CDCl_3$, 400 MHz, δ in ppm): 3.76 (dt, $^3J_{H/P}$ = 20.3 Hz, $^3J_{H/H}$ = 6.0 Hz, 6H, P-CH₂-***CH₂***-O-(CH₂)₂-H), 3.49 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, P-(CH₂)₂-O-***CH₂***-CH₃), 2.51 (dt, $^2J_{H/P}$ = 13.0 Hz, $^3J_{H/H}$ = 6.0 Hz, 6H, P-***CH₂***-CH₂-O-(CH₂)₂-H), 1.86 (d, $^1J_{H/P}$ = 14.3 Hz, 3H, P-***CH₃***), 1.16 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, P-(CH₂)₂-O-CH₂-***CH₃***).

$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz, δ in ppm): 119.94 (q, $^1J_{C/F}$ = 321.4 Hz, ***CF₃***), 66.99 (s, P-(CH₂)₂-O-***CH₂***-CH₃), 63.24 (d, $^2J_{C/P}$ = 7.9 Hz, P-CH₂-***CH₂***-O-(CH₂)₂-H), 23.62 (d, $^1J_{C/P}$ = 51.4 Hz, P-***CH₂***-CH₂-O-(CH₂)₂-H), 14.93 (s, P-(CH₂)₂-O-CH₂-***CH₃***), 6.88 (d, $^1J_{C/P}$ = 52.7 Hz, P-***CH₃***).

$^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz, δ in ppm): 32.69 (s).

$^{19}$F{$^1$H} NMR ($CDCl_3$, 376 MHz, δ in ppm): −78.96 (s).

### *Tris(2-ethoxyethyl)methylammonium bis(trifluoromethylsulfonyl)imide [N(2O2)₃1][NTf₂]*

The title compound was prepared from 9. 00 g [N(2O2)₃1][I] (24.0 mmol / 1.00 eq) and 8.26 g lithium bis(trifluoromethylsulfonyl)imide (28.8 mmol / 1.20 eq) according to the general protocol. 12.2 g of the ionic liquid (23.0 mmol / 96% yield) were obtained as colourless liquid.

$^1$H NMR (DMSO-d6, 400 MHz, δ in ppm): 3.81-3.74 (m, 6 H, N-CH₂-***CH₂***-O-(CH₂)₂-H), 3.63 (t, $^3J_{H/H}$ = 4.8 Hz, 6H, N-***CH₂***-CH₂-O-(CH₂)₂-H), 3.48 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, N-(CH₂)₂-O-***CH₂***-CH₃), 3.11 (s, 3H, N-***CH₃***) 1.12 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, N-(CH₂)₂-O-CH₂-***CH₃***).

$^{13}$C{$^1$H} NMR (DMSO-d6, 101 MHz, δ in ppm): 119.50 (q, $^1J_{C/F}$ = 321.9 Hz, ***CF₃***), 65.61 (s, N-CH₂-***CH₂***-O-(CH₂)₂-H), 63.22 (s, N-(CH₂)₂-O-***CH₂***-CH₃), 61.91 (s, N-***CH₂***-CH₂-O-(CH₂)₂-H), 49.52 (s, N-***CH₃***), 14.75 (s, N-(CH₂)₂-O-CH₂-***CH₃***).

$^{z19}$F{$^1$H} NMR (DMSO-d6, 376 MHz, δ in ppm): −78.81 (s).

### *Methyltripentylphosphonium bis(trifluoromethylsulfonyl)imide [P5551][NTf$_2$]*

15.0 g [P5551][I] (38.9 mmol / 1.00 eq) and 12.9 g LiNTf$_2$ (45.0 mmol / 1.16 eq) were converted to 20.6 g of [P5551][NTf$_2$] (38.1 mmol / 98% yield) using the general procedure, washing the DCM phase 3 times with water.

$^1$H NMR (DMSO-d6, 400 MHz, δ in ppm): 2.23-2.05 (m, 6H, P-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 1.78 (d, $^2J_{H/P}$ = 14.0 Hz, 3H, P-$\boldsymbol{CH_3}$), 1.57-1.42 (m, 6H, P-CH$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_3$-H), 1.42-1.24 (m, 12H, P-(CH$_2$)$_2$-$\boldsymbol{(CH_2)_2}$-CH$_3$), 0.88 (t, $^3J_{H/H}$ = 7.1 Hz, 9H, P-(CH$_2$)$_4$-$\boldsymbol{CH_3}$).

$^{13}$C{$^1$H} NMR (DMSO-d6, 101 MHz, δ in ppm): 321.93 (q, $^1J_{C/F}$ = 321.9 Hz, $\boldsymbol{CF_3}$), 32.15 (d, $^3J_{C/P}$ = 15.5 Hz, P-CH$_2$-CH$_2$-$\boldsymbol{CH_2}$-CH$_2$-CH$_3$), 21.32 (s, P-(CH$_2$)$_3$-$\boldsymbol{CH_2}$-CH$_3$), 20.19 (d, $^2J_{C/P}$ = 4.3 Hz, P-CH$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_3$-H), 19.07 (d, $^1J_{C/P}$ = 49.2 Hz, P-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 13.49 (s, P-(CH$_2$)$_4$-$\boldsymbol{CH_3}$), 3.04 (d, $^1J_{C/P}$ = 51.4 Hz, P-$\boldsymbol{CH_3}$).

$^{31}$P{$^1$H} NMR (DMSO-d6, 162 MHz, δ in ppm): 32.22 (s).

$^{19}$F{$^1$H} NMR (DMSO-d6, 376 MHz, δ in ppm): −78.87 (s).

### *Methyltripentylammonium bis(trifluoromethylsulfonyl)imide [N5551][NTf$_2$]*

For the preparation of [N5551][NTf$_2$] following the general procedure 8.5 g of methyltripentylammonium iodide (23.0 mmol / 1.00 eq) and 7.59 g [Li][NTf$_2$] (26.5 mmol / 1.15 eq) were used to obtain 11.8 g of the product (22.5 mmol / 98% yield) as slightly yellowish liqud.

$^1$H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.24-3.16 (m, 6 H, N-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 3.00 (s, 3H, N-$\boldsymbol{CH_3}$), 1.65 (p, $^3J_{H/H}$ = 7.7 Hz, 6H, N-CH$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_3$-H), 1.44-1.27 (m, 12H, N-(CH$_2$)$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_2$-H + N-(CH$_2$)$_3$-$\boldsymbol{CH_2}$-CH$_3$) 0.89 (t, $^3J_{H/H}$ = 6.9 Hz, 9H, N-(CH$_2$)$_4$-$\boldsymbol{CH_3}$).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 321.93 (q, $^1J_{C/F}$ = 321.8 Hz, $\boldsymbol{CF_3}$), 61.87 (s, N-$\boldsymbol{CH_2}$-(CH$_2$)$_4$-H), 48.42 (s, N-$\boldsymbol{CH_3}$), 28.22 (s, N-CH$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_3$-H), 22.2 (s, N-(CH$_2$)$_2$-$\boldsymbol{CH_2}$-(CH$_2$)$_2$-H), 21.95 (s, N-(CH$_2$)$_3$-$\boldsymbol{CH_2}$-CH$_3$), 13.70 (s, N-(CH$_2$)$_4$-$\boldsymbol{CH_3}$).

$^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz, δ in ppm): −78.82 (s)

### *Tris(2-ethoxyethyl)methylphosphonium bis(trifluoromethylsulfonyl)methanide [P(2O2)$_3$1][CHTf$_2$]*

6.56 g [P(2O2)$_3$1][I] (16.7 mmol / 1.00 eq) and 6.13 g NaCHTf$_2$ (20.3 mmol / 1.22 eq) were converted to 8.76 g of [P(2O2)$_3$1][CHTf$_2$] (16.1 mmol / 96% yield) using the general procedure washing the DCM phase 4 times with water.

$^1$H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.83 (br s, 1H, $\boldsymbol{CH}$Tf$_2$), 3.72 (dt, $^3J_{H/P}$ = 20.3 Hz, $^3J_{H/H}$ = 6.0 Hz, 6H, P-CH$_2$-$\boldsymbol{CH_2}$-O-(CH$_2$)$_2$-H), 3.45 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, P-(CH$_2$)$_2$-O-$\boldsymbol{CH_2}$-CH$_3$), 2.48 (dt, $^2J_{H/P}$ = 13.2 Hz, $^3J_{H/H}$ = 6.0 Hz, 6H, P-$\boldsymbol{CH_2}$-CH$_2$-O-(CH$_2$)$_2$-H), 1.82 (d, $^1J_{H/P}$ = 14.3 Hz, 3H, P-$\boldsymbol{CH_3}$), 1.12 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, P-(CH$_2$)$_2$-O-CH$_2$-$\boldsymbol{CH_3}$).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 120.96 (q, $^1J_{C/F}$ = 325.96 Hz, $\boldsymbol{CF_3}$), 66.84 (s, P-(CH$_2$)$_2$-O-$\boldsymbol{CH_2}$-CH$_3$), 63.14 (d, $^2J_{C/P}$ = 7.9 Hz, P-CH$_2$-$\boldsymbol{CH_2}$-O-(CH$_2$)$_2$-H), 53.73 (s, $\boldsymbol{CH}$Tf$_2$), 23.44 (d, $^1J_{C/P}$ = 51.5 Hz, P-$\boldsymbol{CH_2}$-CH$_2$-O-(CH$_2$)$_2$-H), 14.80 (s, P-(CH$_2$)$_2$-O-CH$_2$-$\boldsymbol{CH_3}$), 6.70 (d, $^1J_{C/P}$ = 52.7 Hz, P-$\boldsymbol{CH_3}$).

$^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 32.68 (s).

$^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz, δ in ppm): −81.32 (s).

### *Tris(2-ethoxyethyl)methylammonium bis(trifluoromethylsulfonyl)methanide [N(2O2)$_3$1][CHTf$_2$]*

The title compound was synthesised from 6.62 g [N(2O2)$_3$1][I] (16.6 mmol / 1.00 eq) and 5.51 g [Na][CHTf$_2$] (18.2 mmol / 1.10 eq) according to the general protocol. 8.41 g of the product (15.9 mmol / 96% yield) were obtained as colourless liquid.

$^1$H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.93 (br s, 1H, ***CH***Tf$_2$), 3.84-3.78 (m, 6 H, N-CH$_2$-***CH***$_2$-O-(CH$_2$)$_2$-H), 3.68 (t, $^3J_{H/H}$ = 4.6 Hz, 6H, N-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 3.51 (q, $^3J_{H/H}$ = 7.0 Hz, 6H, N-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 3.20 (s, 3H, N-***CH$_3$***) 1.18 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, N-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 121.16 (q, $^1J_{C/F}$ = 325.42 Hz, ***CF$_3$***), 67.13 (s, N-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 63.60 (s, N-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 61.80 (s, N-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 53.64 (s, ***CH***Tf$_2$), 50.61 (s, N-***CH$_3$***), 14.95 (s, N-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***).

$^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz, δ in ppm): −81.24 (s).

### *Methyltripentylphosphonium bis(trifluoromethylsulfonyl)methanide [P5551][CHTf$_2$]*

5.60 g [P5551][I] (14.5 mmol / 1.00 eq) and 5.21 g NaCHTf$_2$ (17.2 mmol / 1.19 eq) were converted to 7.45 g of [P5551][CHTf$_2$] (13.8 mmol / 95% yield) using the general procedure washing the DCM phase 4 times with water.

$^1$H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.79 (br s, 1H, ***CH***Tf$_2$), 2.14-1.97 (m, 6H, P-***CH$_2$***-(CH$_2$)$_4$-H), 1.71 (d, $^2J_{H/P}$ = 13.2 Hz, 3H, P-***CH$_3$***), 1.58-1.21 (m, 18H, P-CH$_2$-***(CH$_2$)$_3$***-CH$_3$), 0.86 (t, $^3J_{H/H}$ = 7.2 Hz, 9H, P-(CH$_2$)$_4$-***CH$_3$***).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 120.99 (q, $^1J_{C/F}$ = 325.61 Hz, ***CF$_3$***), 53.85 (s, ***CH***Tf$_2$), 32.47 (d, $^3J_{C/P}$ = 14.9 Hz, P-CH$_2$-CH$_2$-***CH$_2$***-CH$_2$-CH$_3$), 21.81 (s, P-(CH$_2$)$_3$-***CH$_2$***-CH$_3$), 21.07 (d, $^2J_{C/P}$ = 4.8 Hz, P-CH$_2$-***CH$_2$***-(CH$_2$)$_3$-H), 20.08 (d, $^1J_{C/P}$ = 49.1 Hz, P-***CH$_2$***-(CH$_2$)$_4$-H), 13.56 (s, P-(CH$_2$)$_4$-***CH$_3$***), 3.84 (d, $^1J_{C/P}$ = 51.4 Hz, P-***CH$_3$***).

$^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 31.39 (s).

$^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz, δ in ppm): −81.26 (s).

### *Methyltripentylammonium bis(trifluoromethylsulfonyl)methanide [N5551][CHTf$_2$]*

For the synthesis of [N5551][CHTf$_2$] 5.61 g of methyltripentylammonium iodide (15.2 mmol / 1.00 eq) 5.50 g of [Na][CHTf$_2$] (18.2 mmol / 1.20 eq) were used following the synthesis protocol mentioned above. 7.69 g of the product (14.7 mmol / 97% yield) were obtained as colourless liquid.

$^1$H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.92 (s, 1H, ***CH***Tf$_2$), 3.23-3.16 (m, 6 H, N-***CH$_2$***-(CH$_2$)$_4$-H), 3.01 (s, 3H, N-***CH$_3$***), 1.67 (p, $^3J_{H/H}$ = 7.8 Hz, 6H, N-CH$_2$-***CH$_2$***-(CH$_2$)$_3$-H), 1.45-1.29 (m, 12H, N-(CH$_2$)$_2$-***CH$_2$***-(CH$_2$)$_2$-H + N-(CH$_2$)$_3$-***CH$_2$***-CH$_3$) 0.94 (t, $^3J_{H/H}$ = 6.9 Hz, 9H, N-(CH$_2$)$_4$-***CH$_3$***).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 121.17 (q, $^1J_{C/F}$ = 325.43 Hz, ***CF$_3$***), 61.93 (s, N-***CH$_2$***-(CH$_2$)$_4$-H), 53.67 (s, ***CH***Tf$_2$), 48.51 (s, N-***CH$_3$***), 28.25 (s, N-CH$_2$-***CH$_2$***-(CH$_2$)$_3$-H), 22.21 (s, N-(CH$_2$)$_2$-***CH$_2$***-(CH$_2$)$_2$-H), 22.04 (s, N-(CH$_2$)$_3$-***CH$_2$***-CH$_3$), 13.78 (s, N-(CH$_2$)$_4$-***CH$_3$***).

$^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz, δ in ppm): −81.24 (s).

# 2 Physicochemical measurements

The physicochemical data for molar conductivity ($\Lambda_M$, $B < 0$), specific conductivity ($\kappa$, $B < 0$), and viscosity ($\eta$, $B > 0$) was fitted to the commonly used Vogel-Fulcher-Tammann (VFT) equation (1).[5–9]

$$A = A_0 \exp\left(\frac{B}{T - T_0}\right) \tag{1}$$

[P5551][NTf$_2$] and [P(2O2)$_3$1][NTf$_2$] have been synthesised and measured independently of our previous publication. The errors given in this work for density, viscosity, specific conductivity, molar conductivity and diffusion coefficients are the averages of the difference between the two data sets.

## 2.1. Thermogravimetric analysis

The experimental thermogravimetric analysis (TGA) traces for the phosphonium and ammonium ILs are shown in **Figure S1** and **Figure S2**, respectively.

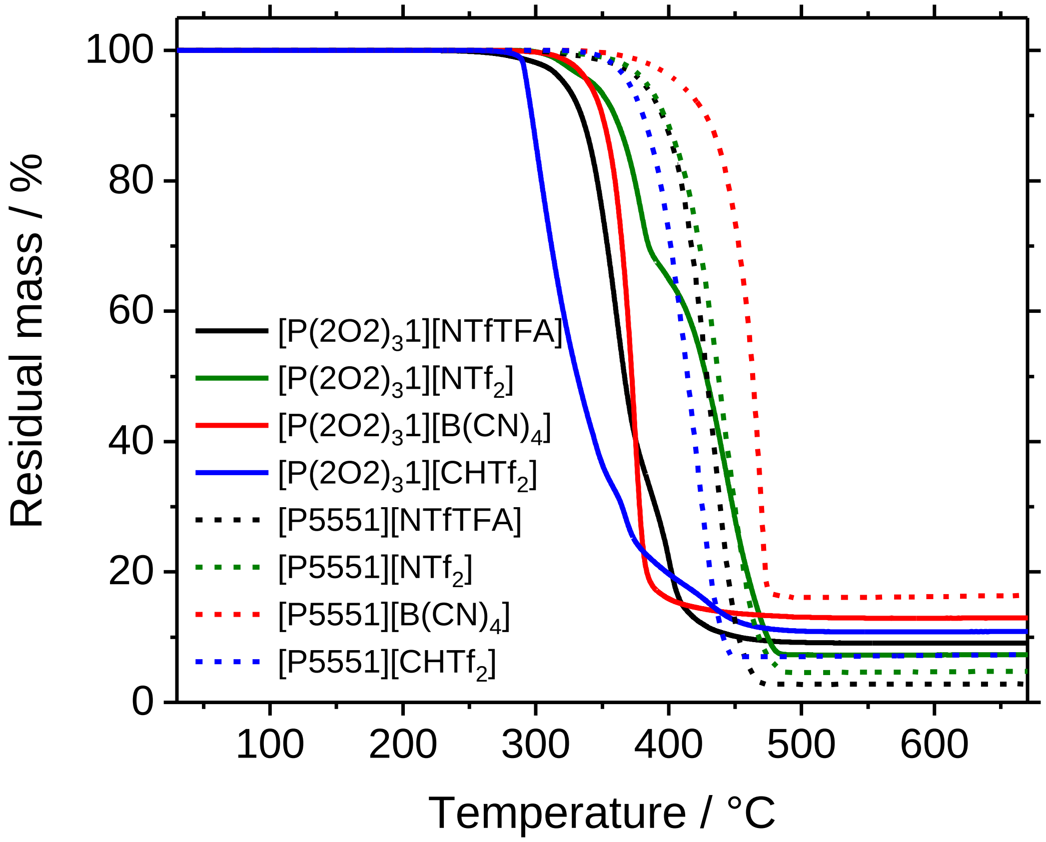

**Figure S1**: TGA traces for phosphonium ionic liquids under nitrogen flow measured at +10°C min$^{-1}$ heating rate .

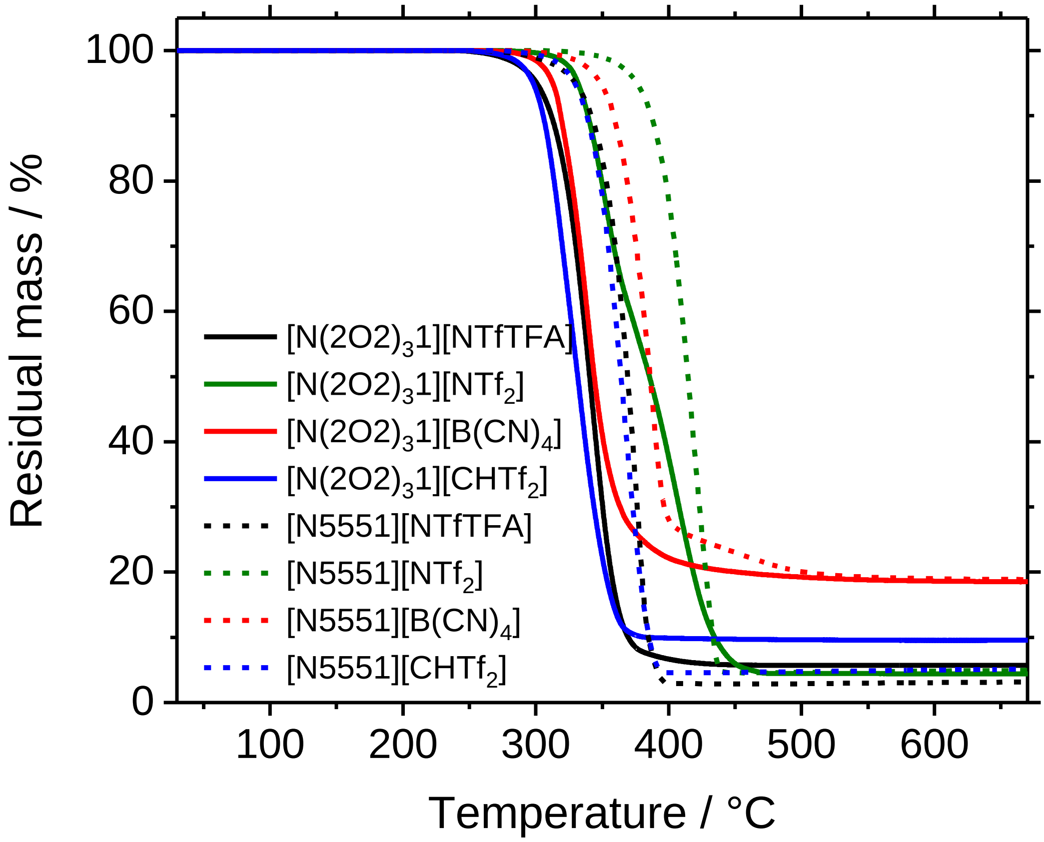

**Figure S2:** TGA traces for ammonium ionic liquids under nitrogen flow measured at +10°C min$^{-1}$ heating rate.

## 2.2. Density

The temperature dependent experimental density values, **Table S1**, were fitted with the linear equation (2).

$$\rho = a + b \times T/K \qquad (2)$$

Fit parameters for $a$ and $b$ as well as the square of Pearson's R$^2$ are given in **Table S2**. Both experimental data and fits are shown in **Figure S3** (phosphonium cations) and **Figure S4** (ammonium cations). The average deviation of experimental values from fit is 0.032%, the maximum deviation from fit is 0.12%.

**Table S1:** Experimental values for the density in g mL$^{-1}$.

| System | Temperature / °C<br>25 | 35 | 45 | 55 | 65 | 75 | 85 | 95 |
|---|---|---|---|---|---|---|---|---|
| $[P(2O2)_31][B(CN)_4]$ | 0.995 | 0.988 | 0.981 | 0.973 | 0.966 | 0.959 | 0.952 | 0.945 |
| $[N(2O2)_31][B(CN)_4]$ | 0.989 | 0.982 | 0.975 | 0.967 | 0.959 | 0.952 | 0.945 | 0.939 |
| $[P5551][B(CN)_4]$ | 0.907 | 0.901 | 0.895 | 0.889 | 0.882 | 0.876 | 0.870 | 0.865 |
| $[N5551][B(CN)_4]$ | 0.907 | 0.901 | 0.895 | 0.889 | 0.882 | 0.876 | 0.870 | 0.865 |
| $[P(2O2)_31][NTfTFA]$ | 1.245 | 1.237 | 1.228 | 1.219 | 1.209 | 1.200 | 1.192 | 1.183 |
| $[N(2O2)_31][NTfTFA]$ | 1.246 | 1.237 | 1.228 | 1.219 | 1.210 | 1.200 | 1.192 | 1.183 |
| $[P5551][NTfTFA]$ | 1.152 | 1.146 | 1.137 | 1.129 | 1.121 | 1.112 | 1.104 | 1.097 |
| $[N5551][NTfTFA]$ | 1.156 | 1.148 | 1.140 | 1.132 | 1.124 | 1.115 | 1.108 | 1.100 |
| $[P(2O2)_31][NTf_2]$ | 1.293 | 1.284 | 1.275 | 1.266 | 1.257 | 1.248 | 1.240 | 1.232 |
| $[N(2O2)_31][NTf_2]$ | 1.297 | 1.288 | 1.280 | 1.270 | 1.261 | 1.251 | 1.243 | 1.234 |
| $[P5551][NTf_2]$ | 1.202 | 1.193 | 1.185 | 1.177 | 1.169 | 1.161 | 1.154 | 1.146 |
| $[N5551][NTf_2]$ | 1.206 | 1.198 | 1.190 | 1.182 | 1.174 | 1.165 | 1.158 | 1.149 |
| $[P(2O2)_31][CHTf_2]$ | 1.284 | 1.275 | 1.266 | 1.258 | 1.249 | 1.241 | 1.232 | 1.224 |
| $[N(2O2)_31][CHTf_2]$ | 1.286 | 1.277 | 1.268 | 1.259 | 1.250 | 1.241 | 1.232 | 1.223 |
| $[P5551][CHTf_2]$ | 1.191 | 1.182 | 1.175 | 1.167 | 1.158 | 1.150 | 1.142 | 1.135 |
| $[N5551][CHTf_2]$ | 1.193 | 1.185 | 1.178 | 1.169 | 1.161 | 1.153 | 1.146 | 1.138 |

**Table S2:** Fit parameters for the linear equation (2).

| System | a / g mL$^{-1}$ | $10^3 \times \Delta a$ / g mL$^{-1}$ | $10^4 \times b$ / g mL$^{-1}$ | $10^6 \times \Delta b$ / g mL$^{-1}$ | $R^2$ |
|---|---|---|---|---|---|
| $[P(2O2)_31][B(CN)_4]$ | 1.207 | 1.270 | −7.130 | 3.810 | 0.9998 |
| $[N(2O2)_31][B(CN)_4]$ | 1.206 | 2.060 | −7.280 | 6.160 | 0.9996 |
| $[P5551][B(CN)_4]$ | 1.089 | 1.860 | −6.100 | 5.560 | 0.9995 |
| $[N5551][B(CN)_4]$ | 1.089 | 1.860 | −6.100 | 5.560 | 0.9995 |
| $[P(2O2)_31][NTfTFA]$ | 1.512 | 2.010 | −8.930 | 6.010 | 0.9997 |
| $[N(2O2)_31][NTfTFA]$ | 1.515 | 1.680 | −9.040 | 5.030 | 0.9998 |
| $[P5551][NTfTFA]$ | 1.394 | 3.810 | −7.280 | 5.700 | 0.9996 |
| $[N5551][NTfTFA]$ | 1.396 | 1.910 | −8.170 | 4.250 | 0.9998 |
| $[P(2O2)_31][NTf_2]$ | 1.552 | 2.550 | −8.720 | 7.630 | 0.9995 |
| $[N(2O2)_31][NTf_2]$ | 1.566 | 2.140 | −9.040 | 6.390 | 0.9997 |
| $[P5551][NTf_2]$ | 1.440 | 3.766 | −7.991 | 3.766 | 0.9999 |
| $[N5551][NTf_2]$ | 1.450 | 1.420 | −8.170 | 4.250 | 0.9998 |
| $[P(2O2)_31][CHTf_2]$ | 1.541 | 1.420 | −8.620 | 4.250 | 0.9999 |
| $[N(2O2)_31][CHTf_2]$ | 1.552 | 1.490 | −8.930 | 4.460 | 0.9999 |
| $[P5551][CHTf_2]$ | 1.430 | 2.170 | −8.020 | 6.510 | 0.9996 |
| $[N5551][CHTf_2]$ | 1.428 | 2.690 | −7.890 | 8.070 | 0.9994 |

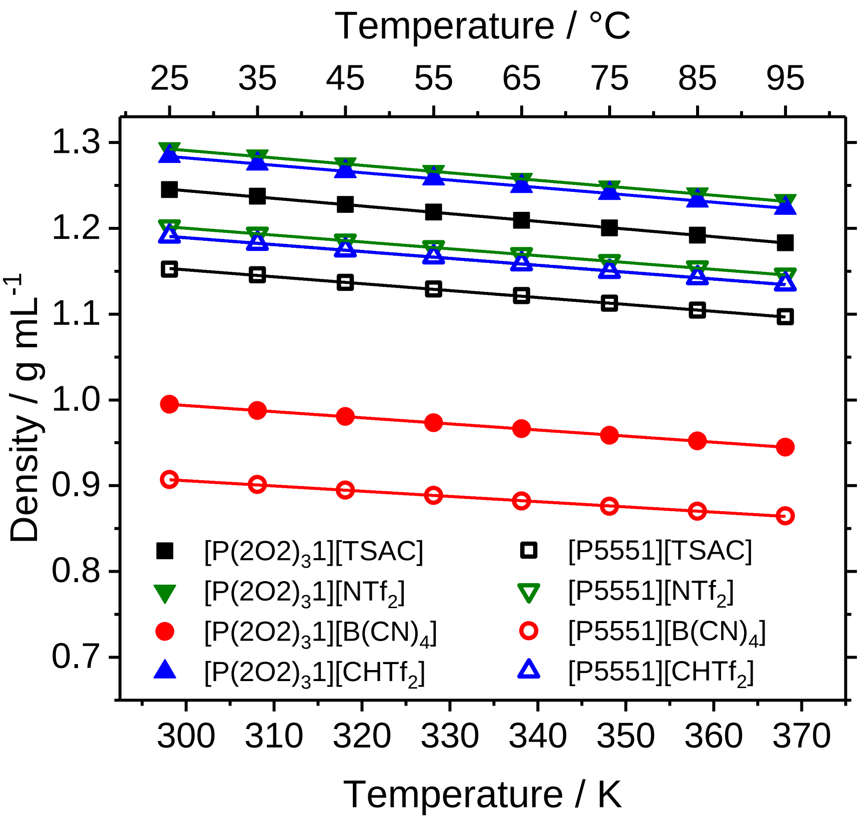

**Figure S3:** Experimental densities and linear fits for phosphonium ionic liquids.

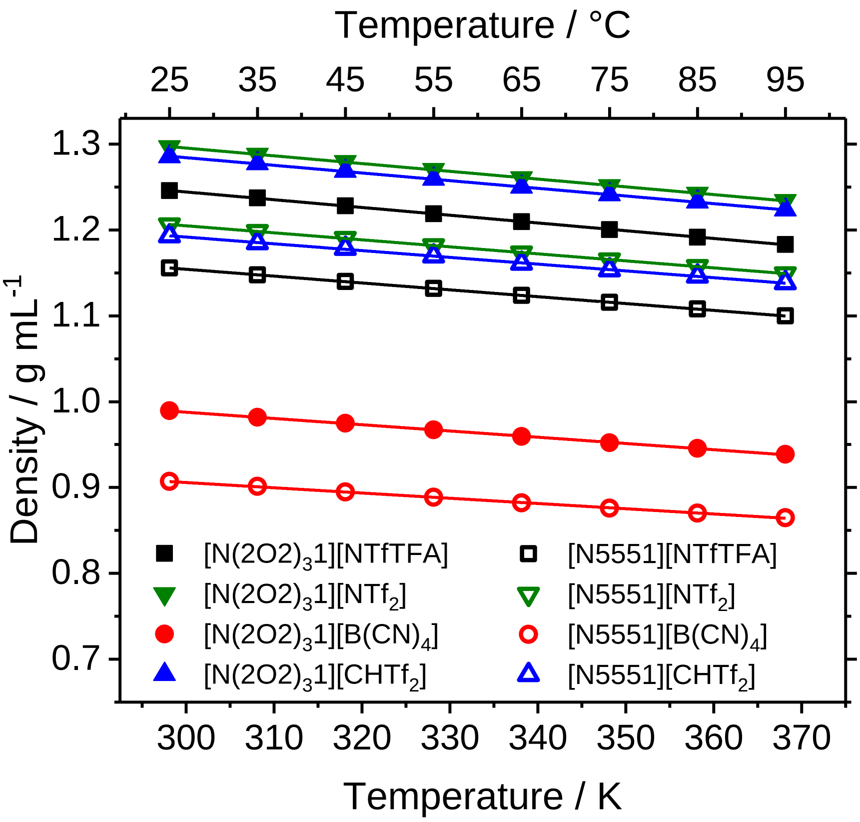

**Figure S4:** Experimental densities and linear fits for ammonium ionic liquids.

## 2.3. Rheology

The temperature dependent viscosity values, **Table S3**, were fitted with the VFT equation (1). Fit paremeters are given in **Table S4**. Experimental data and fits are shown in **Figure S5** (trialkyl functionalised cations) and **Figure S6** (triether functionalised cations). The average deviation of experimental values from fit is 0.047%, the maximum deviation from fit is 4.27%.

**Table S3:** Experimental values for the viscosity in mPa s.

| | Temperature / °C | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| System | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 |
| [P(2O2)$_3$1][B(CN)$_4$] | 28.2 | 23.0 | 19.1 | 16.1 | 13.8 | 11.9 | 10.4 | 9.13 | 8.08 |
| [N(2O2)$_3$1][B(CN)$_4$] | 56.8 | 43.5 | 34.2 | 27.5 | 22.5 | 18.6 | 15.6 | 13.3 | 11.5 |
| [P5551][B(CN)$_4$] | 148 | 111 | 86.0 | 67.5 | 53.8 | 43.6 | 35.8 | 29.7 | 25.0 |
| [N5551][B(CN)$_4$] | 290 | 206 | 151 | 113 | 86.7 | 67.4 | 53.6 | 43.3 | 35.4 |
| [P(2O2)$_3$1][NTfTFA] | 30.6 | 25.1 | 20.9 | 17.7 | 15.1 | 13.0 | 11.3 | 9.94 | 8.81 |
| [N(2O2)$_3$1][NTfTFA] | 54.0 | 42.1 | 33.7 | 27.5 | 22.7 | 19.1 | 16.2 | 13.9 | 12.1 |
| [P5551][NTfTFA] | 141 | 107 | 83.2 | 65.7 | 52.5 | 42.7 | 35.1 | 29.3 | 24.7 |
| [N5551][NTfTFA] | 316 | 227 | 168 | 126 | 97.0 | 75.8 | 60.2 | 48.5 | 39.6 |
| [P(2O2)$_3$1][NTf$_2$] | 32.8 | 26.8 | 22.3 | 18.7 | 15.9 | 13.7 | 11.9 | 10.4 | 9.17 |
| [N(2O2)$_3$1][NTf$_2$] | 61.2 | 47.8 | 38.0 | 30.7 | 25.2 | 21.0 | 17.8 | 15.1 | 13.0 |
| [P5551][NTf$_2$] | 206 | 155 | 119 | 92.4 | 73.1 | 58.7 | 47.8 | 39.3 | 32.7 |
| [N5551][NTf$_2$] | 480 | 339 | 245 | 181 | 137 | 105 | 82.4 | 65.4 | 52.7 |
| [P(2O2)$_3$1][CHTf$_2$] | 65.7 | 50.9 | 40.2 | 32.2 | 26.3 | 21.9 | 18.4 | 15.7 | 13.5 |
| [N(2O2)$_3$1][CHTf$_2$] | 181 | 129 | 94.7 | 71.1 | 54.8 | 43.1 | 34.6 | 28.2 | 23.3 |
| [P5551][CHTf$_2$] | 390 | 281 | 207 | 156 | 120 | 93.3 | 74.0 | 59.4 | 48.4 |
| [N5551][CHTf$_2$] | 1070 | 716 | 487 | 341 | 245 | 181 | 136 | 104 | 81.4 |

**Table S3:** Experimental values for the viscosity in mPa s – continued.

| | Temperature / °C | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| System | 70 | 75 | 80 | 85 | 90 | 95 | 100 | 105 |
| [P(2O2)$_3$1][B(CN)$_4$] | 7.22 | 6.49 | 5.88 | 5.35 | 4.88 | 4.48 | 4.14 | 3.84 |
| [N(2O2)$_3$1][B(CN)$_4$] | 9.98 | 8.75 | 7.77 | 6.92 | 6.22 | 5.62 | 5.12 | 4.68 |
| [P5551][B(CN)$_4$] | 21.2 | 18.2 | 15.7 | 13.7 | 12.0 | 10.7 | 9.49 | 8.50 |
| [N5551][B(CN)$_4$] | 29.4 | 24.7 | 20.9 | 17.9 | 15.5 | 13.5 | 11.9 | 10.5 |
| [P(2O2)$_3$1][NTfTFA] | 7.85 | 7.04 | 6.36 | 5.77 | 5.26 | 4.83 | 4.43 | 4.13 |
| [N(2O2)$_3$1][NTfTFA] | 10.6 | 9.30 | 8.25 | 7.38 | 6.64 | 6.02 | 5.46 | 4.99 |
| [P5551][NTfTFA] | 21.0 | 18.0 | 15.6 | 13.7 | 12.0 | 10.7 | 9.48 | 8.50 |
| [N5551][NTfTFA] | 32.7 | 27.3 | 23.1 | 19.7 | 16.9 | 14.7 | 12.9 | 11.3 |
| [P(2O2)$_3$1][NTf$_2$] | 8.15 | 7.28 | 6.57 | 5.94 | 5.41 | 4.93 | 4.52 | 4.17 |
| [N(2O2)$_3$1][NTf$_2$] | 11.3 | 9.93 | 8.78 | 7.81 | 6.99 | 6.29 | 5.67 | 5.17 |
| [P5551][NTf$_2$] | 27.5 | 23.3 | 20.0 | 17.2 | 15.0 | 13.1 | 11.6 | 10.3 |
| [N5551][NTf$_2$] | 43.0 | 35.5 | 29.6 | 25.0 | 21.3 | 18.3 | 15.8 | 13.8 |
| [P(2O2)$_3$1][CHTf$_2$] | 11.7 | 10.3 | 9.08 | 8.06 | 7.22 | 6.48 | 5.87 | 5.36 |
| [N(2O2)$_3$1][CHTf$_2$] | 19.5 | 16.5 | 14.2 | 12.3 | 10.7 | 9.43 | 8.35 | 7.47 |
| [P5551][CHTf$_2$] | 39.9 | 33.3 | 28.0 | 23.8 | 20.4 | 17.6 | 15.3 | 13.4 |
| [N5551][CHTf$_2$] | 64.5 | 52.0 | 42.4 | 35.1 | 29.4 | 24.9 | 21.2 | 18.2 |

**Table S4:** VFT fit parameters for the viscosity.

| System | A / mPa s | ΔA / % | B / K | ΔB / % | $T_0$ / K | $\Delta T_0$ / % |
|---|---|---|---|---|---|---|
| [P(2O2)$_3$1][B(CN)$_4$] | 0.20953 | 1.64 | 573.33 | 0.80 | 181.17 | 0.30 |
| [N(2O2)$_3$1][B(CN)$_4$] | 0.18917 | 1.25 | 585.78 | 0.52 | 195.47 | 0.16 |
| [P5551][B(CN)$_4$] | 0.09173 | 2.14 | 932.52 | 0.66 | 171.87 | 0.28 |
| [N5551][B(CN)$_4$] | 0.09785 | 2.49 | 897.01 | 0.71 | 185.95 | 0.24 |
| [P(2O2)$_3$1][NTfTFA] | 0.17276 | 1.64 | 653.58 | 0.75 | 171.90 | 0.32 |
| [N(2O2)$_3$1][NTfTFA] | 0.18971 | 3.94 | 625.1 | 1.65 | 187.50 | 0.57 |
| [P5551][NTfTFA] | 0.09438 | 2.06 | 933.2 | 0.64 | 170.54 | 0.27 |
| [N5551][NTfTFA] | 0.06110 | 2.31 | 1067.1 | 0.61 | 173.36 | 0.24 |
| [P(2O2)$_3$1][NTf$_2$] | 0.14543 | 1.14 | 705.47 | 0.49 | 167.93 | 0.22 |
| [N(2O2)$_3$1][NTf$_2$] | 0.13458 | 1.81 | 723.75 | 0.69 | 179.90 | 0.26 |
| [P5551][NTf$_2$] | 0.05928 | 0.99 | 1118.6 | 0.27 | 160.98 | 0.13 |
| [N5551][NTf$_2$] | 0.05020 | 2.29 | 1154.9 | 0.56 | 172.16 | 0.23 |
| [P(2O2)$_3$1][CHTf$_2$] | 0.16173 | 2.43 | 670.75 | 0.95 | 186.49 | 0.33 |
| [N(2O2)$_3$1][CHTf$_2$] | 0.12843 | 3.53 | 734.98 | 1.12 | 196.83 | 0.33 |
| [P5551][CHTf$_2$] | 0.05241 | 3.57 | 1168.1 | 0.89 | 167.13 | 0.39 |
| [N5551][CHTf$_2$] | 0.03220 | 14.5 | 1265.8 | 3.06 | 176.62 | 1.15 |

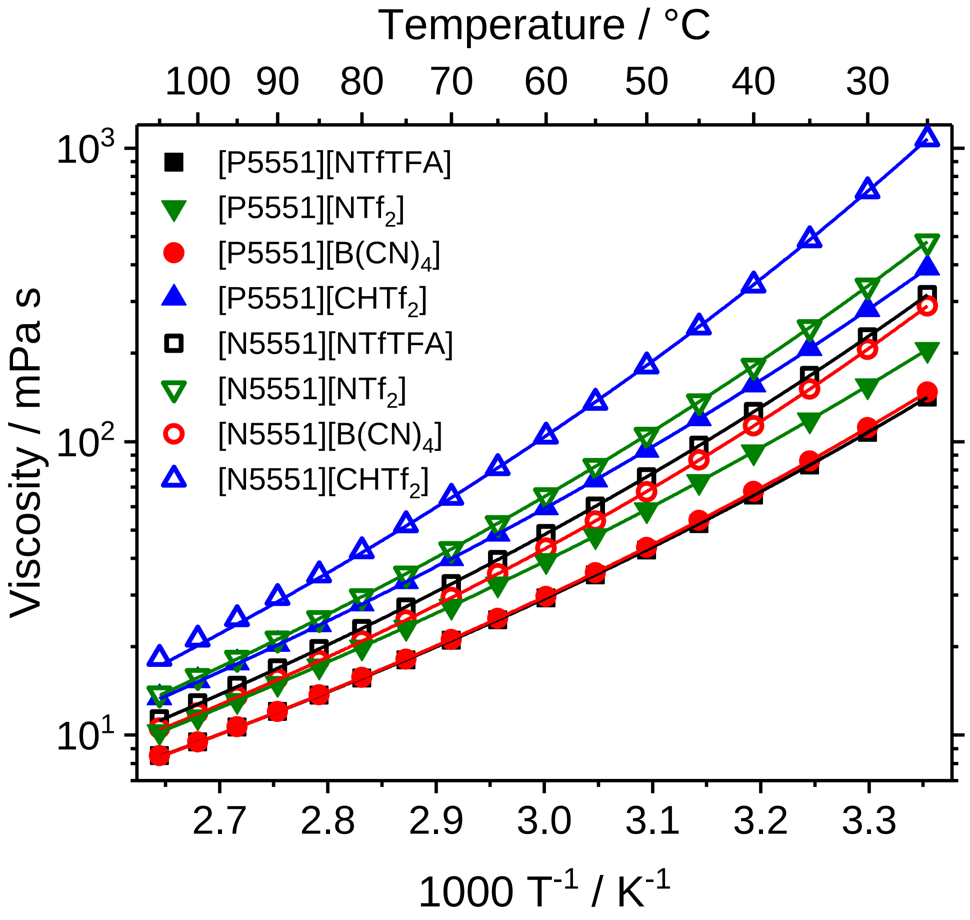

**Figure S5:** experimental viscosities and VFT fits for ionic liquids with trialkyl functionalised cations.

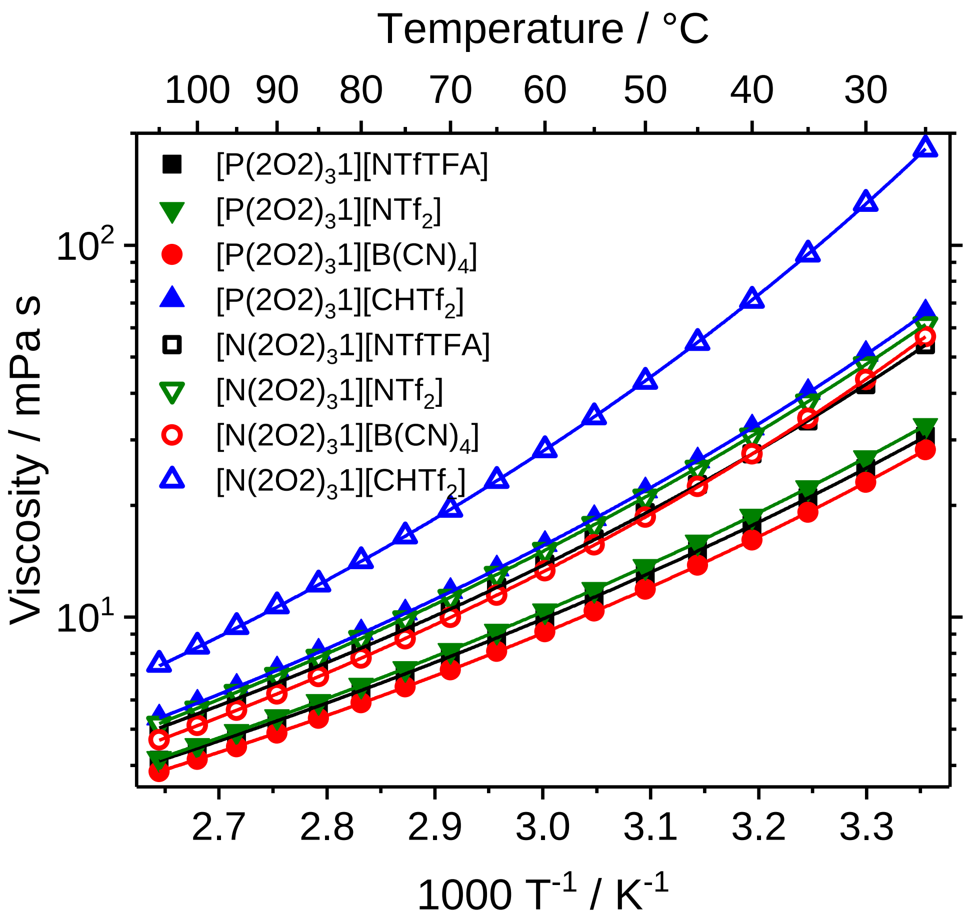

**Figure S6:** experimental viscosities and VFT fits for ionic liquids with triether functionalised cations.

## 2.4. Ionic conductivity

The temperature dependent specific conductivities, **Table S5**, were fitted with the VFT equation (1). Fit parameters are given in **Table S6**. The average deviation of experimental values from fit is 0.29%. The maximum deviation from fit is 2.89%.

The temperature dependent molar conductivities, **Table S7**, were fitted with the VFT equation (1). Fit parameters are given in**Table S8**. The average deviation of experimental values from fit is 0.51%. The maximum deviation from fit is 3.69%.

**Table S5:** Experimental values for the specific conductivity in mS cm$^{-1}$.

| | Temperature / °C | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| System | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| [P(2O2)$_3$1][B(CN)$_4$] | 4.548 | 5.418 | 6.391 | 7.491 | 8.608 | 9.814 | 11.11 | 12.48 |
| [N(2O2)$_3$1][B(CN)$_4$] | 2.416 | 3.047 | 3.786 | 4.633 | 5.550 | 6.631 | 7.725 | 8.922 |
| [P5551][B(CN)$_4$] | 0.954 | 1.226 | 1.547 | 1.916 | 2.337 | 2.827 | 3.383 | 4.001 |
| [N5551][B(CN)$_4$] | 0.535 | 0.729 | 0.971 | 1.262 | 1.605 | 2.011 | 2.483 | 3.019 |
| [P(2O2)$_3$1][NTfTFA] | 3.107 | 3.724 | 4.400 | 5.123 | 5.911 | 6.767 | 7.679 | 8.637 |
| [N(2O2)$_3$1][NTfTFA] | 1.686 | 2.111 | 2.584 | 3.136 | 3.749 | 4.421 | 5.145 | 5.939 |
| [P5551][NTfTFA] | 0.531 | 0.674 | 0.859 | 1.069 | 1.319 | 1.601 | 1.914 | 2.274 |
| [N5551][NTfTFA] | 0.260 | 0.355 | 0.472 | 0.616 | 0.791 | 1.001 | 1.248 | 1.530 |
| [P(2O2)$_3$1][NTf$_2$] | 3.080 | 3.685 | 4.353 | 5.076 | 5.835 | 6.700 | 7.616 | 8.578 |
| [N(2O2)$_3$1][NTf$_2$] | 1.436 | 1.812 | 2.244 | 2.736 | 3.293 | 3.892 | 4.594 | 5.323 |
| [P5551][NTf$_2$] | 0.396 | 0.513 | 0.658 | 0.827 | 1.027 | 1.261 | 1.519 | 1.819 |
| [N5551][NTf$_2$] | 0.189 | 0.257 | 0.346 | 0.459 | 0.597 | 0.766 | 0.964 | 1.201 |
| [P(2O2)$_3$1][CHTf$_2$] | 1.564 | 1.964 | 2.413 | 2.927 | 3.515 | 4.157 | 4.861 | 5.621 |
| [N(2O2)$_3$1][CHTf$_2$] | 0.603 | 0.824 | 1.095 | 1.415 | 1.771 | 2.199 | 2.679 | 3.229 |
| [P5551][CHTf$_2$] | 0.210 | 0.286 | 0.381 | 0.496 | 0.636 | 0.802 | 0.994 | 1.223 |
| [N5551][CHTf$_2$] | 0.094 | 0.137 | 0.196 | 0.272 | 0.370 | 0.493 | 0.622 | 0.799 |

**Table S5:** Experimental values for the specific conductivity in mS cm$^{-1}$ – continued.

| | Temperature / °C | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| System | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| [P(2O2)$_3$1][B(CN)$_4$] | 13.90 | 15.39 | 16.91 | 18.44 | 20.07 | 21.61 | 23.28 | 24.92 |
| [N(2O2)$_3$1][B(CN)$_4$] | 10.20 | 11.53 | 12.99 | 14.49 | 16.01 | 17.60 | 19.27 | 21.02 |
| [P5551][B(CN)$_4$] | 4.681 | 5.402 | 6.202 | 7.058 | 7.975 | 8.952 | 9.941 | 11.08 |
| [N5551][B(CN)$_4$] | 3.638 | 4.304 | 5.032 | 5.852 | 6.680 | 7.629 | 8.626 | 9.656 |
| [P(2O2)$_3$1][NTfTFA] | 9.640 | 10.71 | 11.83 | 12.98 | 14.19 | 15.43 | 16.68 | 18.03 |
| [N(2O2)$_3$1][NTfTFA] | 6.779 | 7.690 | 8.652 | 9.650 | 10.75 | 11.86 | 13.05 | 14.25 |
| [P5551][NTfTFA] | 2.677 | 3.126 | 3.622 | 4.155 | 4.756 | 5.357 | 6.004 | 6.709 |
| [N5551][NTfTFA] | 1.851 | 2.218 | 2.619 | 3.078 | 3.588 | 4.141 | 4.728 | 5.373 |
| [P(2O2)$_3$1][NTf$_2$] | 9.587 | 10.66 | 11.80 | 12.95 | 14.15 | 15.40 | 16.67 | 17.99 |
| [N(2O2)$_3$1][NTf$_2$] | 6.122 | 6.975 | 7.882 | 8.844 | 9.850 | 10.93 | 12.07 | 13.25 |
| [P5551][NTf$_2$] | 2.157 | 2.537 | 2.961 | 3.420 | 3.916 | 4.437 | 5.013 | 5.614 |
| [N5551][NTf$_2$] | 1.484 | 1.795 | 2.107 | 2.493 | 2.928 | 3.409 | 3.932 | 4.495 |
| [P(2O2)$_3$1][CHTf$_2$] | 6.410 | 7.281 | 8.195 | 9.156 | 10.12 | 11.19 | 12.32 | 13.43 |
| [N(2O2)$_3$1][CHTf$_2$] | 3.840 | 4.509 | 5.224 | 5.983 | 6.817 | 7.693 | 8.586 | 9.557 |
| [P5551][CHTf$_2$] | 1.478 | 1.765 | 2.093 | 2.449 | 2.860 | 3.311 | 3.791 | 4.317 |
| [N5551][CHTf$_2$] | 1.003 | 1.246 | 1.518 | 1.826 | 2.188 | 2.575 | 3.016 | 3.504 |

**Table S6:** VFT fit parameters for the specific conductivity.

| System | A / mS cm$^{-1}$ | ΔA / % | B / K | ΔB / % | T$_0$ / K | ΔT$_0$ / % |
|---|---|---|---|---|---|---|
| [P(2O2)$_3$1][B(CN)$_4$] | 300.2 | 3.30 | −457.3 | 2.17 | 189.29 | 0.85 |
| [N(2O2)$_3$1][B(CN)$_4$] | 371.8 | 2.24 | −500.9 | 1.28 | 198.88 | 0.45 |
| [P5551][B(CN)$_4$] | 574.1 | 4.88 | −770.9 | 2.11 | 177.92 | 0.98 |
| [N5551][B(CN)$_4$] | 511.9 | 4.66 | −702.1 | 1.99 | 196.26 | 0.75 |
| [P(2O2)$_3$1][NTfTFA] | 363.5 | 1.76 | −611.0 | 0.98 | 169.79 | 0.49 |
| [N(2O2)$_3$1][NTfTFA] | 406.7 | 2.10 | −646.4 | 1.06 | 180.27 | 0.47 |
| [P5551][NTfTFA] | 598.5 | 8.00 | −927.0 | 3.08 | 166.67 | 1.64 |
| [N5551][NTfTFA] | 711.5 | 4.11 | −954.6 | 1.46 | 177.73 | 0.69 |
| [P(2O2)$_3$1][NTf$_2$] | 370.8 | 2.25 | −615.1 | 1.25 | 169.84 | 0.62 |
| [N(2O2)$_3$1][NTf$_2$] | 425.2 | 2.56 | −666.7 | 1.25 | 180.99 | 0.55 |
| [P5551][NTf$_2$] | 568.7 | 7.06 | −943.4 | 2.65 | 168.78 | 1.38 |
| [N5551][NTf$_2$] | 744.7 | 11.5 | −995.9 | 3.92 | 178.27 | 1.85 |
| [P(2O2)$_3$1][CHTf$_2$] | 323.8 | 3.10 | −591.0 | 1.62 | 187.43 | 0.66 |
| [N(2O2)$_3$1][CHTf$_2$] | 323.1 | 3.64 | −598.7 | 1.72 | 203.05 | 0.60 |
| [P5551][CHTf$_2$] | 759.6 | 4.22 | −1051.8 | 1.43 | 169.70 | 0.74 |
| [N5551][CHTf$_2$] | 837.3 | 6.57 | −1032.7 | 2.10 | 184.58 | 0.94 |

**Table S7:** Experimental values for the molar conductivity in S cm$^2$ mol$^{-1}$.

| | Temperature / °C | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| System | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| [P(2O2)$_3$1][B(CN)$_4$] | 1.739 | 2.078 | 2.461 | 2.895 | 3.338 | 3.820 | 4.339 | 4.891 |
| [N(2O2)$_3$1][B(CN)$_4$] | 0.887 | 1.123 | 1.401 | 1.720 | 2.069 | 2.481 | 2.901 | 3.364 |
| [P5551][B(CN)$_4$] | 0.394 | 0.508 | 0.643 | 0.799 | 0.978 | 1.187 | 1.425 | 1.691 |
| [N5551][B(CN)$_4$] | 0.211 | 0.288 | 0.385 | 0.503 | 0.641 | 0.806 | 0.999 | 1.218 |
| [P(2O2)$_3$1][NTfTFA] | 1.271 | 1.529 | 1.813 | 2.118 | 2.453 | 2.818 | 3.210 | 3.624 |
| [N(2O2)$_3$1][NTfTFA] | 0.640 | 0.837 | 1.029 | 1.253 | 1.504 | 1.780 | 2.079 | 2.408 |
| [P5551][NTfTFA] | 0.225 | 0.286 | 0.366 | 0.457 | 0.565 | 0.689 | 0.826 | 0.985 |
| [N5551][NTfTFA] | 0.110 | 0.150 | 0.200 | 0.262 | 0.338 | 0.429 | 0.536 | 0.660 |
| [P(2O2)$_3$1][NTf$_2$] | 1.300 | 1.561 | 1.850 | 2.164 | 2.497 | 2.876 | 3.281 | 3.708 |
| [N(2O2)$_3$1][NTf$_2$] | 0.585 | 0.741 | 0.921 | 1.126 | 1.361 | 1.614 | 1.912 | 2.223 |
| [P5551][NTf$_2$] | 0.178 | 0.231 | 0.297 | 0.375 | 0.467 | 0.576 | 0.696 | 0.836 |
| [N5551][NTf$_2$] | 0.082 | 0.112 | 0.151 | 0.201 | 0.262 | 0.338 | 0.426 | 0.533 |
| [P(2O2)$_3$1][CHTf$_2$] | 0.664 | 0.836 | 1.030 | 1.254 | 1.511 | 1.793 | 2.104 | 2.442 |
| [N(2O2)$_3$1][CHTf$_2$] | 0.247 | 0.339 | 0.452 | 0.587 | 0.737 | 0.918 | 1.122 | 1.358 |
| [P5551][CHTf$_2$] | 0.095 | 0.130 | 0.174 | 0.227 | 0.292 | 0.369 | 0.459 | 0.567 |
| [N5551][CHTf$_2$] | 0.041 | 0.060 | 0.086 | 0.120 | 0.164 | 0.219 | 0.278 | 0.358 |

**Table S7:** Experimental values for the molar conductivity in S cm2 mol$^{-1}$ – continued.

| | Temperature / °C | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| System | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| [P(2O2)$_3$1][B(CN)$_4$] | 5.469 | 6.078 | 6.706 | 7.336 | 8.017 | 8.662 | 9.369 | 10.07 |
| [N(2O2)$_3$1][B(CN)$_4$] | 3.860 | 4.381 | 4.953 | 5.546 | 6.153 | 6.788 | 7.463 | 8.169 |
| [P5551][B(CN)$_4$] | 1.985 | 2.299 | 2.649 | 3.025 | 3.430 | 3.864 | 4.306 | 4.816 |
| [N5551][B(CN)$_4$] | 1.473 | 1.749 | 2.052 | 2.395 | 2.743 | 3.144 | 3.567 | 4.007 |
| [P(2O2)$_3$1][NTfTFA] | 4.060 | 4.527 | 5.018 | 5.529 | 6.066 | 6.622 | 7.182 | 7.795 |
| [N(2O2)$_3$1][NTfTFA] | 2.759 | 3.142 | 3.548 | 3.972 | 4.440 | 4.917 | 5.432 | 5.957 |
| [P5551][NTfTFA] | 1.164 | 1.364 | 1.585 | 1.825 | 2.097 | 2.370 | 2.665 | 2.989 |
| [N5551][NTfTFA] | 0.801 | 0.964 | 1.142 | 1.347 | 1.576 | 1.825 | 2.092 | 2.386 |
| [P(2O2)$_3$1][NTf$_2$] | 4.159 | 4.639 | 5.156 | 5.678 | 6.224 | 6.796 | 7.386 | 7.999 |
| [N(2O2)$_3$1][NTf$_2$] | 2.566 | 2.934 | 3.328 | 3.747 | 4.189 | 4.663 | 5.170 | 5.697 |
| [P5551][NTf$_2$] | 0.995 | 1.175 | 1.375 | 1.594 | 1.831 | 2.083 | 2.361 | 2.654 |
| [N5551][NTf$_2$] | 0.661 | 0.802 | 0.945 | 1.122 | 1.322 | 1.545 | 1.788 | 2.051 |
| [P(2O2)$_3$1][CHTf$_2$] | 2.794 | 3.184 | 3.597 | 4.033 | 4.475 | 4.965 | 5.486 | 5.998 |
| [N(2O2)$_3$1][CHTf$_2$] | 1.620 | 1.910 | 2.220 | 2.552 | 2.918 | 3.305 | 3.703 | 4.136 |
| [P5551][CHTf$_2$] | 0.687 | 0.824 | 0.980 | 1.151 | 1.349 | 1.567 | 1.800 | 2.057 |
| [N5551][CHTf$_2$] | 0.451 | 0.561 | 0.686 | 0.829 | 0.996 | 1.176 | 1.383 | 1.611 |

**Table S8:** VFT fit parameters for the molar conductivity.

| System | A / S cm$^2$ mol$^{-1}$ | ΔA / % | B / K | ΔB / % | $T_0$ / K | Δ$T_0$ / % |
|---|---|---|---|---|---|---|
| [P(2O2)$_3$1][B(CN)$_4$] | 148.2 | 3.19 | −508.29 | 1.96 | 184.065 | 0.82 |
| [N(2O2)$_3$1][B(CN)$_4$] | 176.1 | 2.46 | −548.40 | 1.32 | 194.614 | 0.50 |
| [P5551][B(CN)$_4$] | 305.2 | 4.74 | −828.37 | 2.09 | 174.003 | 1.02 |
| [N5551][B(CN)$_4$] | 255.6 | 4.62 | −747.31 | 1.89 | 193.262 | 0.74 |
| [P(2O2)$_3$1][NTfTFA] | 199.3 | 2.05 | −678.93 | 1.07 | 163.743 | 0.58 |
| [N(2O2)$_3$1][NTfTFA] | 199.9 | 4.82 | −685.34 | 2.32 | 178.119 | 1.06 |
| [P5551][NTfTFA] | 348.4 | 8.15 | −994.50 | 3.00 | 162.592 | 1.68 |
| [N5551][NTfTFA] | 394.4 | 4.11 | −1015.45 | 1.41 | 174.321 | 0.69 |
| [P(2O2)$_3$1][NTf$_2$] | 205.3 | 2.14 | −677.65 | 1.12 | 164.330 | 0.59 |
| [N(2O2)$_3$1][NTf$_2$] | 227.0 | 2.98 | −724.98 | 1.37 | 176.485 | 0.64 |
| [P5551][NTf$_2$] | 334.5 | 7.04 | −1005.84 | 2.54 | 165.117 | 1.38 |
| [N5551][NTf$_2$] | 424.7 | 12.13 | −1057.26 | 3.99 | 174.915 | 1.97 |
| [P(2O2)$_3$1][CHTf$_2$] | 176.0 | 3.37 | −641.80 | 1.68 | 183.222 | 0.72 |
| [N(2O2)$_3$1][CHTf$_2$] | 167.3 | 3.50 | −640.73 | 1.59 | 199.967 | 0.57 |
| [P5551][CHTf$_2$] | 456.4 | 4.57 | −1118.60 | 1.49 | 166.078 | 0.81 |
| [N5551][CHTf$_2$] | 474.0 | 6.80 | −1087.78 | 2.11 | 181.782 | 0.97 |

## 2.5. Hole Theory

Experimental molar conductivity $\Lambda_{exp}$ at 25°C and comparison to the molar conductivity as predicted by hole theory, $\Lambda_{HT}$, using the deviation of the experimental from the predicted value, **Table S9**.

**Table S9:** Experimental molar conductivity, molar conductivity obtained from hole theory, deviation of experiment from hole theory at 25°C and 100°C.

| System | $\Lambda_{exp}$ | $\Lambda_{HT}$ | dev. from HT at 25°C | dev. from HT at 100 °C |
|---|---|---|---|---|
| $[P(2O2)_31][B(CN)_4]$ | 1.739 | 1.519 | 14% | −3% |
| $[N(2O2)_31][B(CN)_4]$ | 0.887 | 0.759 | 17% | −3% |
| $[P5551][B(CN)_4]$ | 0.390 | 0.286 | 36% | 7% |
| $[N5551][B(CN)_4]$ | 0.211 | 0.147 | 44% | 12% |
| $[P(2O2)_31]$[NTfTFA] | 1.271 | 1.346 | −6% | −16% |
| $[N(2O2)_31]$[NTfTFA] | 0.640 | 0.769 | −17% | −22% |
| [P5551][NTfTFA] | 0.232 | 0.288 | −19% | −28% |
| [N5551][NTfTFA] | 0.110 | 0.130 | −16% | −25% |
| $[P(2O2)_31][NTf_2]$ | 1.300 | 1.235 | 5% | −11% |
| $[N(2O2)_31][NTf_2]$ | 0.585 | 0.666 | −12% | −21% |
| $[P5551][NTf_2]$ | 0.178 | 0.194 | −8% | −23% |
| $[N5551][NTf_2]$ | 0.082 | 0.084 | −2% | −19% |
| $[P(2O2)_31][CHTf_2]$ | 0.663 | 0.613 | 8% | −13% |
| $[N(2O2)_31][CHTf_2]$ | 0.247 | 0.223 | 11% | −15% |
| $[P5551][CHTf_2]$ | 0.095 | 0.102 | −7% | −21% |
| $[N5551][CHTf_2]$ | 0.041 | 0.037 | 10% | −14% |

## 2.6. Walden plot

The Walden plots for ammonium ionic liquids, **Figure S7**, and phosphonium ionic liquids, **Figure S8**, are shown below.

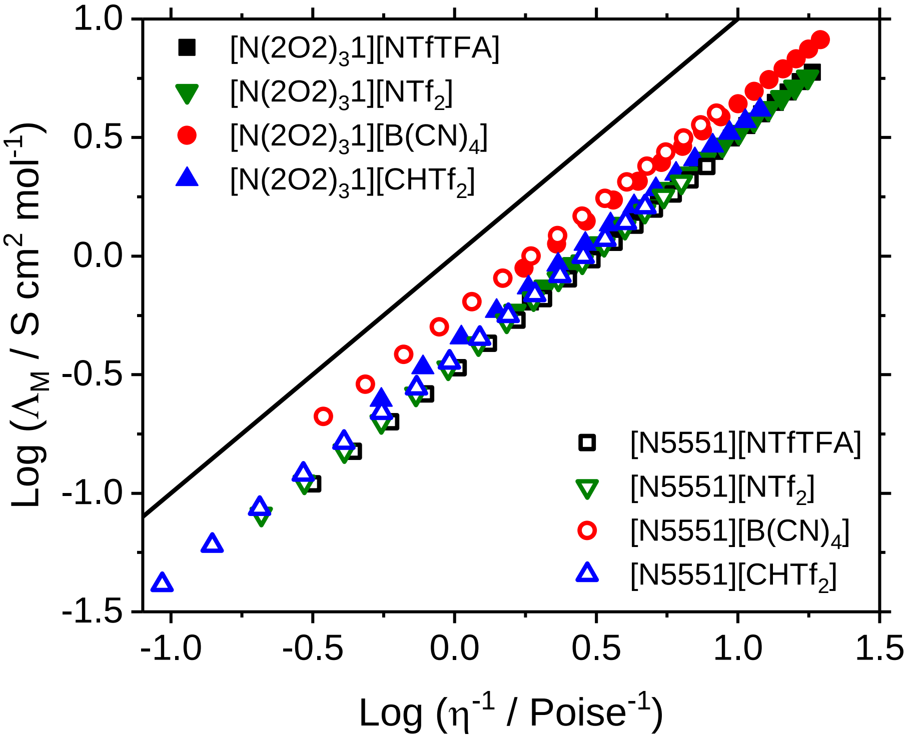

**Figure S7:** Walden plot for ammonium ionic liquids.

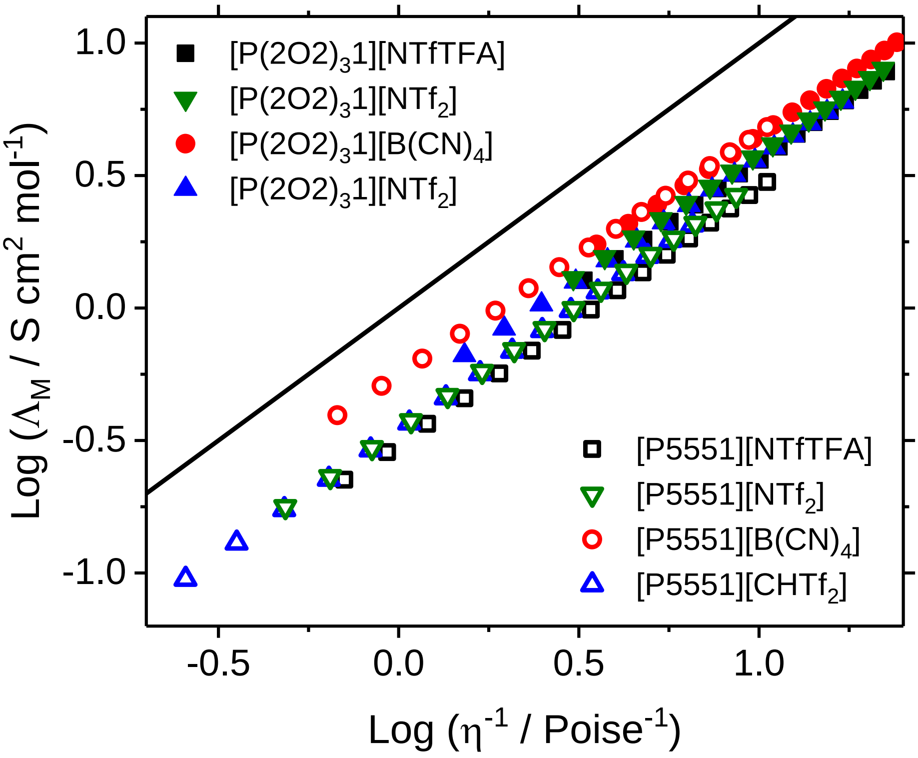

**Figure S8:** Walden plot for phosphonium ionic liquids.

## 2.7. NMR diffusometry

Self-diffusion coefficients for cations and anions, the ratio of cation to anion diffusion, and the ionicity from the Haven ratio as defined in reference [1] are given in **Table S10**.

**Table S10:** Experimental values for self-diffusion coefficients, their relative ratio, and the Haven ratio ionicity.

| System | $D^+$ / cm$^2$ s$^{-1}$ | $D^-$ / cm$^2$ s$^{-1}$ | $D^+$ / $D^-$ | $I_{HR}$ / % |
|---|---|---|---|---|
| [P(2O2)$_3$1][B(CN)$_4$] | 3.29E−07 | — | — | — |
| [N(2O2)$_3$1][B(CN)$_4$] | 1.71E−07 | — | — | — |
| [P5551][B(CN)$_4$] | 6.27E−08 | — | — | — |
| [N5551][B(CN)$_4$] | 3.31E−08 | — | — | — |
| [P(2O2)$_3$1][NTfTFA] | 2.79E−07 | 3.45E−07 | 0.808 | 54 |
| [N(2O2)$_3$1][NTfTFA] | 1.65E−07 | 1.98E−07 | 0.836 | 47 |
| [P5551][NTfTFA] | 5.91E−08 | 7.46E−08 | 0.793 | 46 |
| [N5551][NTfTFA] | 2.85E−08 | 3.44E−08 | 0.829 | 46 |
| [P(2O2)$_3$1][NTf$_2$] | 2.62E−07 | 3.16E−07 | 0.828 | 60 |
| [N(2O2)$_3$1][NTf$_2$] | 1.32E−07 | 1.57E−07 | 0.842 | 54 |
| [P5551][NTf$_2$] | 4.25E−08 | 5.33E−08 | 0.798 | 49 |
| [N5551][NTf$_2$] | 1.90E−08 | 2.31E−08 | 0.821 | 52 |
| [P(2O2)$_3$1][CHTf$_2$] | 1.27E−07 | 1.65E−07 | 0.767 | 60 |
| [N(2O2)$_3$1][CHTf$_2$] | 5.20E−08 | 6.55E−08 | 0.793 | 56 |
| [P5551][CHTf$_2$] | 2.14E−08 | 2.84E−08 | 0.752 | 51 |
| [N5551][CHTf$_2$] | 8.50E−09 | 1.09E−08 | 0.778 | 56 |

## 2.8. Small-angle X-ray scattering

The scattering intensity profiles for the [CHTf$_2$] and [NTfTFA] anions are shown in **Figure S9** and **Figure S10**, respectively. Values for the scattering vectors at peak positions for the observed peaks are given in **Table S11**. The corresponding real space distances are given in **Table S12**.

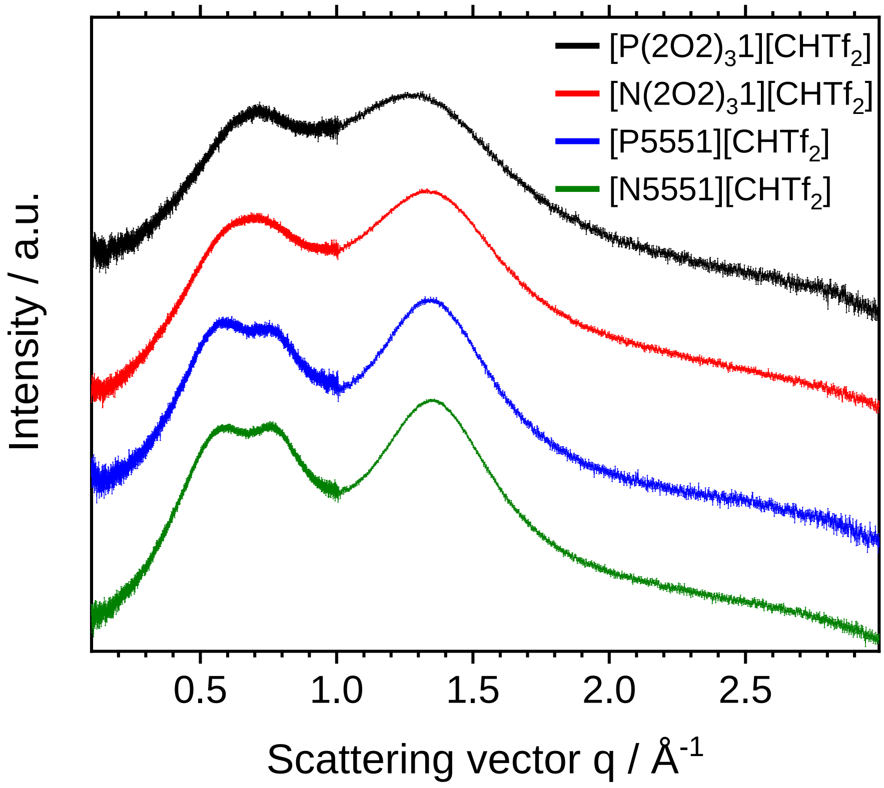

**Figure S9**: Radially averaged SAXS data for the ionic liquids with [CHTf$_2$] anion. The curves are shifted vertically and include error bars of the (small) experimental error.

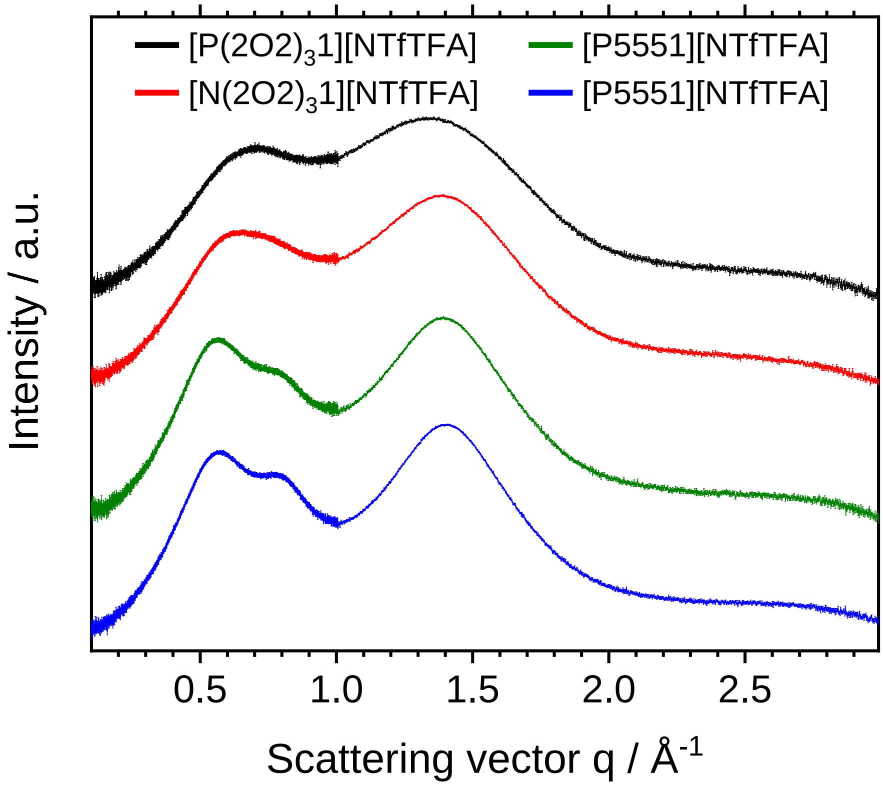

**Figure S10**: Radially averaged SAXS data for the ionic liquids with [NTfTFA] anion. The curves are shifted vertically and include error bars of the (small) experimental error.

**Table S11**: Values of the scattering vector q in reciprocal space and experimental errors Δq for the up to three observed peaks.

| System | $q_1$ / Å$^{-1}$ | $\Delta q_1$ / Å$^{-1}$ | $q_2$ / Å$^{-1}$ | $\Delta q_2$ / Å$^{-1}$ | $q_3$ / Å$^{-1}$ | $\Delta q_3$ / Å$^{-1}$ |
|---|---|---|---|---|---|---|
| [P(2O2)$_3$1][B(CN)$_4$] | 0.7233 | 0.0001 | 1.1082 | 0.0006 | 1.7839 | 0.0008 |
| [N(2O2)$_3$1][B(CN)$_4$] | 0.7211 | 0.0001 | 1.1563 | 0.0003 | 1.7347 | 0.0006 |
| [P5551][B(CN)$_4$] | 0.7450 | 0.0004 | 1.2255 | 0.0002 | 1.6482 | 0.0012 |
| [N5551][B(CN)$_4$] | 0.7497 | 0.0003 | 1.2237 | 0.0002 | 1.6321 | 0.0009 |
| [P(2O2)$_3$1][NTfTFA] | 0.6681 | 0.0005 | 1.3402 | 0.0004 | — | — |
| [N(2O2)$_3$1][NTfTFA] | 0.6718 | 0.0002 | 1.3870 | 0.0002 | — | — |
| [P5551][NTfTFA] | 0.5382 | 0.0008 | 0.7864 | 0.0017 | 1.3927 | 0.0002 |
| [N5551][NTfTFA] | 0.5508 | 0.0006 | 0.8035 | 0.0008 | 1.4024 | 0.0001 |
| [P(2O2)$_3$1][NTf$_2$] | 0.6898 | 0.0013 | 1.3056 | 0.0013 | — | — |
| [N(2O2)$_3$1][NTf$_2$] | 0.6905 | 0.0003 | 1.3375 | 0.0003 | — | — |
| [P5551][NTf$_2$] | 0.5746 | 0.0007 | 0.8120 | 0.0005 | 1.3622 | 0.0004 |
| [N5551][NTf$_2$] | 0.5655 | 0.0008 | 0.8043 | 0.0007 | 1.3622 | 0.0004 |
| [P(2O2)$_3$1][CHTf$_2$] | 0.6640 | 0.0006 | 1.2792 | 0.0007 | — | — |
| [N(2O2)$_3$1][CHTf$_2$] | 0.6822 | 0.0003 | 1.3374 | 0.0003 | — | — |
| [P5551][CHTf$_2$] | 0.5449 | 0.0023 | 0.7759 | 0.0032 | 1.3297 | 0.0011 |
| [N5551][CHTf$_2$] | 0.5460 | 0.0013 | 0.7778 | 0.0015 | 1.3409 | 0.0006 |

**Table S12**: Values of the corresponding real space distance r and experimental errors Δr for the up to three observed peaks.

| System | $r_1$ / Å | $\Delta r_1$ / Å | $r_2$ / Å | $\Delta r_2$ / Å | $r_3$ / Å | $\Delta r_3$ / Å |
|---|---|---|---|---|---|---|
| [P(2O2)$_3$1][B(CN)$_4$] | 8.6868 | 0.0014 | 5.6696 | 0.0029 | 3.5222 | 0.0016 |
| [N(2O2)$_3$1][B(CN)$_4$] | 8.7127 | 0.0017 | 5.4339 | 0.0015 | 3.6221 | 0.0012 |
| [P5551][B(CN)$_4$] | 8.4335 | 0.0042 | 5.1269 | 0.0007 | 3.8122 | 0.0027 |
| [N5551][B(CN)$_4$] | 8.3809 | 0.0031 | 5.1345 | 0.0007 | 3.8497 | 0.0021 |
| [P(2O2)$_3$1][NTfTFA] | 9.4040 | 0.0064 | 4.6884 | 0.0012 | — | — |
| [N(2O2)$_3$1][NTfTFA] | 9.3533 | 0.0033 | 4.5300 | 0.0006 | — | — |
| [P5551][NTfTFA] | 11.6747 | 0.0171 | 7.9902 | 0.0174 | 4.5114 | 0.0007 |
| [N5551][NTfTFA] | 11.4072 | 0.0126 | 7.8198 | 0.0079 | 4.4802 | 0.0004 |
| [P(2O2)$_3$1][NTf$_2$] | 9.1085 | 0.0170 | 4.8124 | 0.0047 | — | — |
| [N(2O2)$_3$1][NTf$_2$] | 9.0994 | 0.0042 | 4.6976 | 0.0010 | — | — |
| [P5551][NTf$_2$] | 10.9356 | 0.0131 | 7.7382 | 0.0047 | 4.6126 | 0.0013 |
| [N5551][NTf$_2$] | 11.1113 | 0.0156 | 7.8123 | 0.0066 | 4.6126 | 0.0013 |
| [P(2O2)$_3$1][CHTf$_2$] | 9.4628 | 0.0091 | 4.9118 | 0.0027 | — | — |
| [N(2O2)$_3$1][CHTf$_2$] | 9.2100 | 0.0040 | 4.6981 | 0.0009 | — | — |
| [P5551][CHTf$_2$] | 11.5312 | 0.0489 | 8.0978 | 0.0329 | 4.7254 | 0.0038 |
| [N5551][CHTf$_2$] | 11.5071 | 0.0266 | 8.0781 | 0.0159 | 4.6857 | 0.0020 |

# 3 Ab initio calculations

This supporting information is accompanied by the Gaussian job files required to reproduce the ab initio calculations.

## 3.1. Ion Volumes

The volume confined by the 0.001 electrons/Bohr$^3$ electron density isosurface obtained from the RB3LYP-GD3BJ/6-311+G(d,p) wavefunction is given in TABLEXX, together with the radii of a sphere with the same volume. The volumes of the [NTf$_2$] (210.8 Å$^3$) and [NFs$_2$] (142.6 Å$^3$) were taken from the Literature.[10]

**Table S13:** Ion volumes obtained from the electron density and the radii obtained therefrom.

| Ion | Charge | Volume / Å$^3$ | Radius / Å |
|---|---|---|---|
| [P(2O2)$_3$1] | +1 | 381.0 | 4.50 |
| [N(2O2)$_3$1] | +1 | 362.1 | 4.42 |
| [P5551] | +1 | 415.9 | 4.63 |
| [N5551] | +1 | 396.5 | 4.56 |
| [P1111] | +1 | 141.6 | 3.23 |
| [B(CN)$_4$] | −1 | 155.8 | 3.34 |
| [NTfTFA] | −1 | 190.6 | 3.57 |
| [CHTf$_2$] | −1 | 217.3 | 3.73 |

### 3.2. Electrostatic surface potential

ESP surface analysis was performed on the wavefunction used for the ion volumes using multiwfn with the input given in multiwfn_inp.inp.[11,12] The electrostatic surface potential shows the more efficient shielding of positive charge for the multiple ether-functionalised [P(2O2)$_3$1] cation compared to [P5551], **Figure S11**.[13]

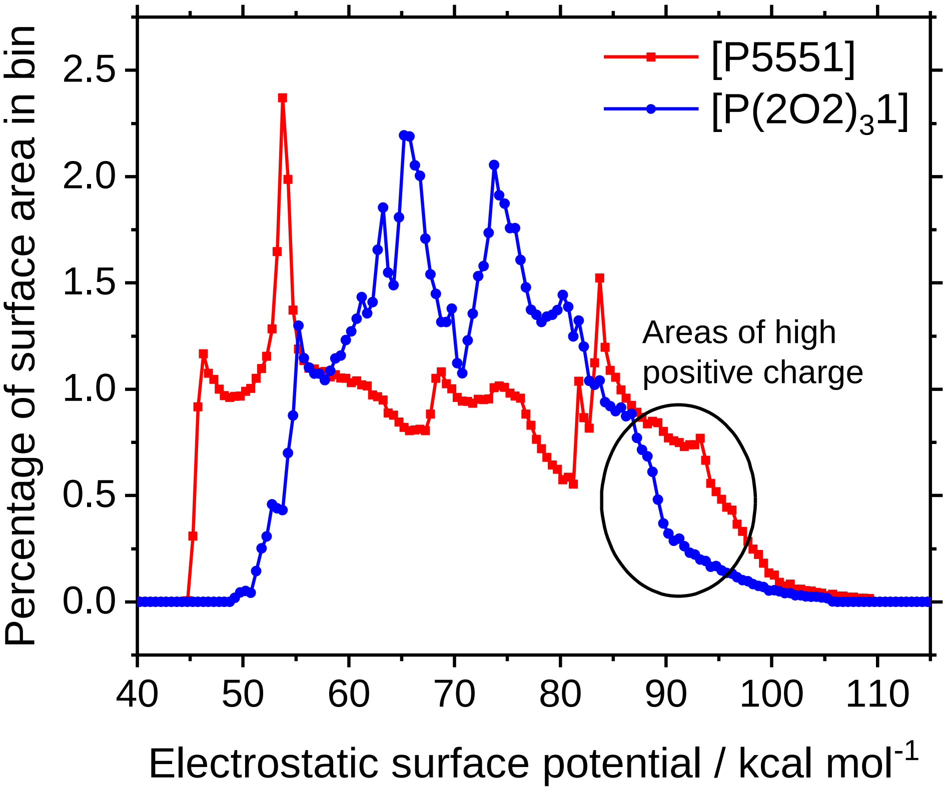

**Figure S11:** Histogram of the electrostatic potential at the 0.001 a.u. isodensity surface.

## 4 Relative Reaction Rates

The relative ratio of rate constants for barrier crossings can be estimated from the Arrhenius equation, using the activation energies $E_A$ for the rotation driven by the dihedral C-N-C-C compared to C-P-C-C in the small model cations.[14,15]

$$\frac{k^{\mathrm{C-N-C-C}}}{k^{\mathrm{C-P-C-C}}} = \exp\left(\frac{E_A^{\mathrm{C-P-C-C}} - E_A^{\mathrm{C-N-C-C}}}{RT}\right) \approx 40 \qquad (3)$$

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