Supporting Information to:

Curled Cation Structures Accelerate the Dynamics of Ionic Liquid

Daniel Rauber,^{a)} Frederik Philippi,^{b)} Björn Kuttich,^{c)} Julian Becker,^{b)} Tobias Kraus,^{a),c)} Patricia Hunt,^{b),d)} Tom Welton,^{b)} Rolf Hempelmann^{a)} and Christopher W. M. Kay^{a),e)}

^{a)} Department of Chemistry, Saarland University, Campus B2.2, 66123 Saarbrücken, Germany.

^{b)} Department of Chemistry, Molecular Sciences Research Hub, Imperial College London, White City Campus, London W12 OBZ, United Kingdom.

^{c)} INM-Leibniz Institute for New Materials, Campus D2.2, 66123 Saarbrücken, Germany.

^{d)} School of Chemical and Physical Sciences, Victoria University of Wellington, New Zealand

^{e)} London Centre for Nanotechnology, University College London, 17-19 Gordon Street, London WC1H 0AH, United Kingdom.

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1. Synthesis of the ionic liquids

The syntheses of the precursors were carried out under inert atmosphere of argon using standard Schlenktechniques. Dried ionic liquids were handled using Schlenk line or glovebox to avoid the uptake of water. Sample purity of the ionic liquids was confirmed by multinuclear NMR spectroscopy and testing with AgNO₃ solution for halide impurities. NMR spectra were recorded on an AVANCE II 400 NMR spectrometer from Bruker (Billerica, USA). Samples were locked to the deuterium signal of the solvent and - where possible - referred to the (residual) ¹H or ¹³C solvent peak. Two-dimensional NMR spectroscopy (HSQC and COSY) was used for assignment of the peaks where necessary. The solvents used in the syntheses, acetonitrile (>99.9 %, gradient HPLC grade) and acetone (99.9 %) from Fisher Scientific (Nidderau, Germany) were dried using 4 Å and 3 Å molecular sieves. Triethanolamine (>99.0 %), tributylamine (>99.0 %), iodomethane (\geq 99.0 %) and trifluoromethanesulfonic acid (\geq 99.0 %) were purchased from Sigma Aldrich (St. Louis, USA) and used as received. Lithium bis(fluorosulfonyl)imide (99 %), lithium bis(trifluoromethanesulfonyl)imide (99 %) and lithium bis(pentafluoroethylsulfonyl)imide (99 %) supplied by IoLiTec (Heilbronn, Germany), as well as trifluoroacetic acid (\geq 99%) from VWR International (Radnor, USA) were used as received. Potassium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide [K][TSAC] was prepared as previously described.¹

1.1 Synthesis of the precursors

1.1.1 Tris(2-methoxyethyl)amine N(2O1)₃

The title amine was synthesised according to the published protocol for tris(2-ethoxyethyl)amine using the same equivalents of methyl iodide instead of bromoethane. The base was obtained in 63 % yield as a colourless liquid.¹

¹**H-NMR** (400 MHz, CDCl₃): δ / ppm = 3.45 (t, J = 6.1 Hz, 6H, N-CH₂-CH₂), 3.32 (s, 9H, CH₃), 2.75 (t, J = 6.1 Hz, 6H, N-CH₂).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ / ppm =71.25 (s, N-CH₂-CH₂), 58.91 (s, CH₃), 54.56 (s, N-CH₂-CH₂).

1.1.2 Tris(2-methoxylethyl)methylammonium iodide [N(2O1)₃1][I]

The quaternary cation with threefold ether-substitution was prepared by dissolving 1.0 e.q. tris(2-ethoxyethyl)amine in dry acetonitrile under argon and addition of about 1.1 equivalents of methyl iodide. The resulting solution was allowed to react for seven days at ambient temperature, followed by removal of the excess reagent and solvent by rotary evaporation. The residue was dried on a Schlenk line for two days at 45°C with stirring to obtain the product in 97 % yield as a highly viscous liquid.

¹**H-NMR** (400 MHz, DMSO-d6): δ / ppm = 3.79 – 3.71 (m, 6H, N-CH₂-C**H**₂), 3.69 – 3.57 (m, 6H, N-C**H**₂), 3.28 (s, 9H, O-C**H**₃), 3.10 (s, 3H, N-C**H**₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d6): δ / ppm = 65.25 (s, N-CH₂-*C*H₂), 61.77 (s, N-*C*H₂-CH₂), 58.13 (s, O-C*H*₃), 49.40 (s, N-*C*H₃).

1.1.3 Tributylmethylammonium iodide [N4441][I]

The alkylated ammonium cation was prepared by dissolving 1.0 eq. tributylamine in dry acetonitrile under argon. The mixture was cooled with an ice bath before 1.1 eq. methyl iodide in acetonitrile were added dropwise. The obtained clear solution was allowed to warm to ambient temperature and stirred for 3 days. The excess of reagents and the organic solvent were removed on a rotary evaporator and the residue dried for two days in high vacuum. The product was obtained as a colourless solid in 98 % yield.

¹**H-NMR** (400 MHz, DMSO-d6): δ / ppm = 3.24 - 3.15 (m, 6H, N-C*H*₂), 2.94 (s, 3H, N-C*H*₃), 1.67 - 1.54 (m, 6H, N-CH₂-C*H*₂), 1.30 (h, *J* = 7.4 Hz, 6H, N-(CH₂)₂-C*H*₂), 0.93 (t, *J* = 7.4 Hz, 9H, N-(CH₂)₃-C*H*₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d6): δ / ppm = 60.42 (s, N-CH₂), 47.55 (s, N-CH₃), 23.39 (s, N-CH₂-CH₂), 19.22 (s, N-(CH₂)₂-CH₂), 13.50 (s, N-(CH₂)₃-CH₃).

1.2 Synthesis of the ether-substituted ionic liquids

1.2.1 Tris(2-methoxylethyl)methylammonium bis(fluorosulfonyl)imide [N(2O1)₃1][FSI]

To a solution of 1.0 eq. of $[N(2O1)_31][I]$ in dry acetone were added 1.1 eq. of lithium bis(fluorosulfonyl)imide. The resulting clear, homogenous solution was stirred for 24 hours and the solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane, filtered and extracted several times with distilled water. The organic phase was dried over MgSO₄, filtered and the solvent removed using a rotary evaporator. The residuum was dried in high vacuum with stirring for two days to obtain the title compound in 97 % yield as slightly yellowish liquid.

¹**H-NMR** (400 MHz, CDCl₃): δ / ppm = 3.84 – 3.74 (m, 6H, N-CH₂-C**H**₂), 3.69 – 3.63 (m, 6H, N-C**H**₂), 3.36 (s, 9H, O-C**H**₃), 3.18 (s, 3H, N-C**H**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ / ppm = 66.09 (s, N-CH₂-CH₂), 63.65 (s, N-CH₂-CH₂), 59.19 (s, O-CH₃), 50.49 (s, N-CH₃).

¹⁹F{¹H}-NMR (377 MHz, CDCl₃): δ / ppm = 52.72 (s).

1.2.2 Tris(2-methoxylethyl)methylammonium bis(trifluoromethanesulfonyl)imide [N(2O1)₃1][NTf₂]

The title compound was synthesised analogous to [N(2O1)₃1][FSI] using lithium bis(trifluoromethanesulfonyl)imide instead of lithium bis(fluorosulfonyl)imide. The product was obtained as slightly yellowish liquid in 98 % yield.

¹**H-NMR** (400 MHz, CDCl₃): δ / ppm = 3.80 – 3.73 (m, 2H, N-CH₂-C**H**₂), 3.67 – 3.61 (m, 6H, N-C**H**₂), 3.34 (s, 9H, O-C**H**₃), 3.16 (s, 3H, N-C**H**₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ / ppm = 119.95 (q, J = 321.3 Hz, CF_3), 66.04 (s, N-CH₂- CH_2), 63.54 (s, N- CH_2 - CH_2), 59.07 (s, O-C H_3), 50.42 (s, N- CH_3).

¹⁹**F**{¹**H**}-**NMR** (377 MHz, CDCl₃): δ / ppm = -78.96 (s).

1.2.3 Tris(2-methoxylethyl)methylammonium bis(pentafluoroethylsulfonyl)imide [N(2O1)₃1][BETI]

 $[N(2O1)_{3}1][BETI]$ was synthesised analogous to $[N(2O1)_{3}1][FSI]$ using the lithium salt of the bis(pentafluoroethylsulfonyl)imide instead of lithium bis(fluorosulfonyl)imide. After drying for 3 days in high vacuum the product was obtained in 99 % yield as colourless liquid.

¹**H-NMR** (400 MHz, CDCl₃): δ / ppm = 3.79 – 3.71 (m, 2H, N-CH₂-CH₂), 3.67 – 3.61 (m, 6H, N-CH₂), 3.33 (s, 9H, O-CH₃), 3.15 (s, 3H, N-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ / ppm = 123.22 – 114.81 (m, CF_3), 114.81 – 107.97 (m, CF_2), 66.04 (s, N-CH₂- CH_2), 63.54 (s, N- CH_2 - CH_2), 59.04 (s, O- CH_3), 50.38 (s, N- CH_3).

¹⁹F{¹H}-NMR (377 MHz, CDCl₃): δ / ppm = -79.05 (s, 6F, -C**F**₃), -117.21 (s, 4F, C**F**₂).

1.2.4 Tris(2-methoxylethyl)methylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide [N(2O1)₃1][TSAC]

For the synthesis of the ionic liquid with asymmetric anion 1.0 eq. of the halide precursor $[N(2O1)_31][I]$ was dissolved in deionised water and 1.1 eq. potassium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide ([K][TSAC]) were added. After stirring for 16 hours the biphasic mixture was extracted twice with 200 mL dichloromethane per 5 g halide precursor. The combined organic phases were washed with small amounts of water for several times. After drying over MgSO₄ and filtration, the solvent was removed by rotary evaporation. The residue was further dried in high vacuum for two days with stirring to obtain the title compound in 97 % yield as colourless liquid.

¹**H-NMR** (400 MHz, DMSO-d6): δ / ppm = 3.81 – 3.67 (m, 2H, N-CH₂-C*H*₂), 3.67 – 3.58 (m, 6H, N-C*H*₂), 3.28 (s, 9H, O-C*H*₃), 3.09 (s, 3H, N-C*H*₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d6): δ / ppm = 159.90 (q, J = 34.81 Hz, *CO*-CF₃), 119.65 (q, J = 322.9 Hz, SO₂-*C*F₃), 116.44 (q, J = 290.36 Hz, CO-*C*F₃), 65.28 (s, N-CH₂-*C*H₂), 61.82 (s, N-*C*H₂-CH₂), 58.10 (s, O-C*H***₃), 49.37 (s, N-***C*H₃).

¹⁹F{¹H}-NMR (377 MHz, DMSO-d6): δ / ppm = -74.79 (s, 3F, CO-C*F*₃), -79.05 (s, 3F, SO₂-C*F*₃).

1.2.5 Tris(2-methoxylethyl)methylammonium trifluoromethyl sulfonate [N(2O1)₃1][OTf]

A concentrated aqueous solution of [N(2O1)₃1][I] was passed through Amberlyst A-27 anion exchange resin using roughly 150 g resin per 1.0 g of halide salt to obtain the cation with hydroxide anion. The aqueous solution was neutralised with diluted (approximately 0.2 molar) trifluoromethanesulfonic acid and the water removed by rotary evaporation. After drying in high vacuum for two days at 50°C with stirring the product was obtained in 98 % yield as slightly yellowish liquid.

¹**H-NMR** (400 MHz, DMSO-d6): δ / ppm = 3.77 – 3.67 (m, 2H, N-CH₂-C**H**₂), 3.67 – 3.59 (m, 6H, N-C**H**₂), 3.28 (s, 9H, O-C**H**₃), 3.09 (s, 3H, N-C**H**₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d6): δ / ppm = 120.68 (q, *J* = 322.4 Hz, *C*F₃), 65.27 (s, N-CH₂-*C*H₂), 61.81 (s, N-*C*H₂-CH₂), 58.10 (s, O-C*H*₃), 49.35 (s, N-*C*H₃).

¹⁹**F**{¹**H**}-**NMR** (377 MHz, DMSO-d6): δ / ppm = -77.76 (s).

1.2.6 Tris(2-methoxylethyl)methylammonium trifluoroacetate [N(2O1)₃1][TFA]

The title compound was prepared similar to [N(2O1)₃1][OTf] using the anion exchanger method to obtain the product in 98 % yield as slightly yellow liquid after drying in vacuum.

¹**H-NMR** (400 MHz, DMSO-d6): δ / ppm = 3.77 – 3.69 (m, 2H, N-CH₂-C*H*₂), 3.69 – 3.60 (m, 6H, N-C*H*₂), 3.28 (s, 9H, O-C*H*₃), 3.10 (s, 3H, N-C*H*₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d6): δ / ppm = 157.68 (q, J = 30.08, CO_2 -CF₃), 117.44 (q, J = 301.5 Hz, CO₂- CF_3), 65.29 (s, N-CH₂- CH_2), 61.79 (s, N- CH_2 -CH₂), 58.08 (s, O-C H_3), 49.33 (s, N- CH_3).

¹⁹**F**{¹**H**}-**NMR** (377 MHz, DMSO-d6): δ / ppm = -73.44 (s).

1.3 Synthesis of the alkyl-substituted ionic liquids

1.3.1 Tributylmethylammonium bis(fluorosulfonyl)imide [N4441][FSI]

[N4441][FSI] was prepared analogous to the ether substituted ionic liquid [N(2O1)₃1][FSI] using [N4441][I] and [Li][FSI] to obtain a slightly yellowish liquid in 98 % yield.

¹**H-NMR** (400 MHz, DMSO-d6): δ / ppm = 3.23 - 3.15 (m, 6H, N-C*H*₂), 2.94 (s, 3H, N-C*H*₃), 1.67 - 1.54 (m, 6H, N-CH₂-C*H*₂), 1.30 (h, *J* = 7.4 Hz, 6H, N-(CH₂)₂-C*H*₂), 0.94 (t, *J* = 7.3 Hz, 9H, N-(CH₂)₃-C*H*₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d6): δ / ppm = 60.45 (s, N- CH_2), 47.52 (s, N- CH_3), 23.37 (s, N- CH_2 - CH_2), 19.20 (s, N-(CH_2)₂- CH_2), 13.44 (s, N-(CH_2)₃- CH_3).

¹⁹**F**{¹**H**}-**NMR** (377 MHz, DMSO-d6): δ / ppm = 53.17 (s).

1.3.2 Tributylmethylammonium bis(trifluoromethanesulfonyl)imide [N4441][NTf₂]

[N4441]NTf2] was prepared similar to $[N(2O1)_31][NTf_2]$ using the alkylated cation instead of the ethersubstituted to obtain a slightly yellowish liquid in 97 % yield.

¹**H-NMR** (400 MHz, CDCl₃): δ / ppm = 3.22 - 3.13 (m, 6H, N-CH₂), 2.97 (s, 3H, N-CH₃), 1.69 - 1.57 (m, 6H, N-CH₂-CH₂), 1.39 (h, *J* = 7.4 Hz, 6H, N-(CH₂)₂-CH₂), 0.98 (t, *J* = 7.3 Hz, 9H, N-(CH₂)₃-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ / ppm = 119.99 (s, J = 321.3 Hz, CF₃), 61.83 (s, N-CH₂), 48.50 (s, N-CH₃), 24.22 (s, N-CH₂-CH₂), 19.57 (s, N-(CH₂)₂-CH₂), 13.52 (s, N-(CH₂)₃-CH₃).

¹⁹**F**{¹**H**}-**NMR** (377 MHz, CDCl₃): δ / ppm = -78.93 (s).

1.3.3 Tributylmethylammonium bis(pentafluoroethylsulfonyl)imide [N4441][BETI]

The title compound was synthesised in analogous way to [N(2O1)₃1][BETI] by replacing the halide precursor with [N4441][I]. The alkylated [BETI]⁻-IL was obtained in 99 % yield as colourless, viscous liquid.

¹**H-NMR** (400 MHz, CDCl₃): δ / ppm = 3.25 - 3.12 (m, 6H, N-CH₂), 2.95 (s, 3H, N-CH₃), 1.68 - 1.55 (m, 6H, N-CH₂-CH₂), 1.38 (h, J = 7.4 Hz, 6H, N-(CH₂)₂-CH₂), 0.97 (t, J = 7.3 Hz, 9H, N-(CH₂)₃-CH₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ / ppm = 122.48 – 113.90 (m, *C*F₃), 114.90 – 108.68 (m, *C*F₂), 61.77 (s, N-*C*H₂), 48.42 (s, N-*C*H₃), 24.19 (s, N-CH₂-*C*H₂), 19.51 (s, N-(CH₂)₂-*C*H₂), 13.43 (s, N-(CH₂)₃-*C*H₃).

¹⁹F{¹H}-NMR (377 MHz, CDCl₃): δ / ppm = -78.93 (s, 6F, CF₃), -117.21 (s, 4F, CF₂).

1.3.4 Tributylmethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide [N4441][TSAC]

[N4441][TSAC] was prepared similar to $[N(2O1)_31]$ [TSAC] using [N4441][I] instead of $[N(2O1)_31]$ [I] for the anion metathesis reaction. The title compound was isolated in 98 % yield as a colourless liquid.

¹**H-NMR** (400 MHz, DMSO-d6): δ / ppm = 3.25 - 3.12 (m, 6H, N-C*H*₂), 2.95 (s, 3H, N-C*H*₃), 1.68 - 1.55 (m, 6H, N-CH₂-C*H*₂), 1.38 (h, *J* = 7.4 Hz, 6H, N-(CH₂)₂-C*H*₂), 0.93 (t, *J* = 7.3 Hz, 9H, N-(CH₂)₃-C*H*₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d6): δ / ppm = 159.93 (q, J = 34.89 Hz, CO-CF₃), 119.67 (q, J = 323.0 Hz, SO₂- CF_3), 116.45 (q, J = 290.06 Hz, CO- CF_3), 60.47 (s, N- CH_2), 47.51 (s, N- CH_3), 23.38 (s, N- CH_2 - CH_2), 19.19 (s, N-(CH₂)₂- CH_2), 13.37 (s, N-(CH₂)₃- CH_3).

¹⁹F{¹H}-NMR (377 MHz, DMSO-d6): δ / ppm = -74.88 (s, 3F, CO-CF₃), -78.44(s, 3F, SO₂-CF₃).

1.3.5 Tributylmethylammonium trifluoromethyl sulfonate [N4441][OTf]

The alkylated trifluoromethanesulfonate IL was prepared similar to the ether-substituted [N(2O1)₃1][OTf] sample by the anion exchanger method. The product was obtained as a colourless solid in 98 % yield.

¹**H-NMR** (400 MHz, DMSO-d6): δ / ppm = 3.24 - 3.15 (m, 6H, N-C*H*₂), 2.94 (s, 3H, N-C*H*₃), 1.67 - 1.54 (m, 6H, N-CH₂-C*H*₂), 1.30 (h, *J* = 7.4 Hz, 6H, N-(CH₂)₂-C*H*₂), 0.93 (t, *J* = 7.4 Hz, 9H, N-(CH₂)₃-C*H*₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d6): δ / ppm = 120.68 (q, J = 322.4 Hz, CF_3), 60.43 (s, N- CH_2), 47.52 (s, N- CH_3), 23.38 (s, N- CH_2 - CH_2), 19.21 (s, N-(CH_2)₂- CH_2), 13.46 (s, N-(CH_2)₃- CH_3).

¹⁹**F**{¹**H**}-**NMR** (377 MHz, DMSO-d6): δ / ppm = -77.77 (s).

1.3.6 Tributylmethylammonium trifluoroacetate [N4441][TFA]

[N4441][TFA] was prepared analogous to $[N(2O1)_31][TFA]$ by exchanging the iodide anion with $[OH]^-$ by means of an anion exchanger and neutralising the aqueous solution with diluted trifluoroacetic acid. The title compound was obtained in 97 % yield as viscous, colourless liquid.

¹**H-NMR** (400 MHz, DMSO-d6): δ / ppm = 3.25 - 3.12 (m, 6H, N-C*H*₂), 2.96 (s, 3H, N-C*H*₃), 1.67 - 1.54 (m, 6H, N-CH₂-C*H*₂), 1.30 (h, *J* = 7.4 Hz, 6H, N-(CH₂)₂-C*H*₂), 0.93 (t, *J* = 7.4 Hz, 9H, N-(CH₂)₃-C*H*₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d6): δ / ppm = 157.64 (q, J = 30.29 Hz, CO_2 -CF₃), 117.41 (q, J = 301.6 Hz, CO₂- CF_3), 60.39 (s, N- CH_2), 47.47 (s, N- CH_3), 23.38 (s, N- CH_2 - CH_2), 19.19 (s, N-(CH_2)₂- CH_2), 13.42 (s, N-(CH_2)₃- CH_3).

¹⁹**F**{¹**H**}-**NMR** (377 MHz, DMSO-d6): δ / ppm = -73.48 (s).

2. Density

Temperature dependent densities for the ammonium ionic liquids investigated in this work are given in Table S1 and Fig. S1 and were fitted with Equation (S1).

$$\rho = a + b \cdot T \,\mathrm{K}^{-1} \tag{S1}$$

The fitting results are given in Table S2.

Table S1 Experimental values for the densities ρ of the ammonium ionic liquids given in g mL⁻¹ at the specified temperatures.

| | Temperature / °C | | | | | | | | | | |
|--|------------------|--------|--------|--------|--------|--------|--------|--|--|--|--|
| Ionic liquid | 25 | 35 | 45 | 55 | 65 | 75 | 85 | | | | |
| [N(2O1) ₃ 1][FSI] | 1.3172 | 1.3093 | 1.3012 | 1.2935 | 1.2853 | 1.2764 | 1.2693 | | | | |
| [N(2O1) ₃ 1][NTf ₂] | 1.3911 | 1.3821 | 1.3734 | 1.3647 | 1.3550 | 1.3455 | 1.3373 | | | | |
| [N(2O1)₃1][BETI] | 1.4572 | 1.4486 | 1.4389 | 1.4283 | 1.4173 | 1.4071 | 1.3989 | | | | |
| [N(2O1)₃1][TSAC] | 1.3346 | 1.3251 | 1.3164 | 1.3062 | 1.2959 | 1.2849 | 1.2772 | | | | |
| [N(2O1)₃1][OTf] | 1.2757 | 1.2679 | 1.2609 | 1.2531 | 1.2439 | 1.2359 | 1.2278 | | | | |
| [N(2O1) ₃ 1][TFA] | 1.2101 | 1.2028 | 1.1951 | 1.1870 | 1.1791 | 1.1709 | 1.1645 | | | | |
| [N4441][FSI] | 1.1776 | 1.1693 | 1.1599 | 1.1518 | 1.1443 | 1.1358 | 1.1289 | | | | |
| [N4441][NTf ₂] | 1.2648 | 1.2568 | 1.2482 | 1.2396 | 1.2298 | 1.2214 | 1.2131 | | | | |
| [N4441][BETI] | 1.3513 | 1.3429 | 1.3334 | 1.3231 | 1.3137 | 1.3039 | 1.2940 | | | | |
| [N4441][TSAC] | 1.2045 | 1.1969 | 1.1886 | 1.1803 | 1.1718 | 1.1631 | 1.1542 | | | | |
| [N4441][TFA] | 1.0616 | 1.0546 | 1.0488 | 1.0407 | 1.0335 | 1.0271 | 1.0202 | | | | |



Fig. S1 Temperature dependent densities of a) the ether-substituted and b) the alkyl substituted ionic liquids. Drawn lines are the linear fits.

| Table S2 Linear fitting parameters a and b (Equation (S1)) for the IL's densities $ ho$ on absolute temperature |
|---|
| scale including errors and coefficient of determination R^2 . |

| Ionic liquid | a / g mL ⁻¹ | $\Delta a / 10^{-3} \mathrm{g mL^{-1}}$ | $b / 10^{-4} \mathrm{g mL^{-1}}$ | Δb / 10 ⁻⁶ g mL ⁻¹ | <i>R</i> ² |
|--|------------------------|--|-----------------------------------|--|-----------------------|
| [N(2O1) ₃ 1][FSI] | 1.557 | 2.36 | -8.047 | 0.717 | 0.9996 |
| [N(2O1) ₃ 1][NTf ₂] | 1.661 | 2.48 | -9.031 | 0.754 | 0.9997 |
| [N(2O1)₃1][BETI] | 1.756 | 5.58 | -9.984 | 1.697 | 0.9986 |
| [N(2O1) ₃ 1][TSAC] | 1.626 | 5.29 | -9.756 | 1.608 | 0.9986 |
| [N(2O1)₃1][OTf] | 1.516 | 3.77 | -8.028 | 1.146 | 0.9990 |
| [N(2O1)₃1][TFA] | 1.441 | 3.02 | -7.738 | 0.919 | 0.9993 |
| [N4441][FSI] | 1.420 | 4.54 | -8.161 | 1.380 | 0.9986 |
| [N4441][NTf ₂] | 1.525 | 2.83 | -8.722 | 0.859 | 0.9995 |
| [N4441][BETI] | 1.639 | 3.05 | -9.630 | 0.928 | 0.9995 |
| [N4441][TSAC] | 1.456 | 2.83 | -8.400 | 0.861 | 0.9995 |
| [N4441][TFA] | 1.269 | 3.10 | -6.945 | 0.941 | 0.9991 |

3. Thermogravimetric Analysis

Experimental traces of the thermogravimetric analysis (TGA) are shown in Fig. S2. The obtained decomposition temperature as extrapolated onsets are given in the main manuscript.



Fig. S2 TGA traces for a) the ether-substituted and b) the alkylated ammonium ionic liquids under nitrogen flow and heating rate of +10 °C min⁻¹.

4. Viscosity

The experimental values for the temperature-dependent viscosities are given in Table S3. Additional details for the fits according to the Vogel-Fulcher-Tammann (VFT) Equation (7) are given in Table S4.

| | Temperature / °C | | | | | | | | | | | | | | | | |
|--|------------------|-------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ionic liquid | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 | 105 |
| [N(2O1)₃1][FSI] | 73.69 | 57.88 | 46.22 | 37.49 | 31.00 | 25.95 | 22.00 | 18.83 | 16.30 | 14.22 | 12.51 | 11.09 | 9.89 | 8.88 | 8.03 | 7.30 | 6.66 |
| [N(2O1) ₃ 1][NTf ₂] | 90.54 | 69.08 | 53.75 | 42.63 | 34.48 | 28.27 | 23.50 | 19.78 | 16.80 | 14.53 | 12.60 | 11.03 | 9.75 | 8.67 | 7.76 | 7.00 | 6.35 |
| [N(2O1)₃1][BETI] | 163.5 | 119.2 | 89.36 | 68.33 | 53.34 | 42.48 | 34.30 | 28.20 | 23.47 | 19.77 | 16.88 | 14.48 | 12.55 | 10.98 | 9.71 | 8.62 | 7.69 |
| [N(2O1)₃1][TSAC] | 69.71 | 53.31 | 41.55 | 33.14 | 26.95 | 22.26 | 18.62 | 15.78 | 13.55 | 11.72 | 10.25 | 9.04 | 8.03 | 7.18 | 6.49 | 5.90 | 5.38 |
| [N(2O1)₃1][OTf] | 299.9 | 211.3 | 152.5 | 113.1 | 86.15 | 66.9 | 53.01 | 42.76 | 34.93 | 29.05 | 24.39 | 20.76 | 17.81 | 15.43 | 13.48 | 11.90 | 10.57 |
| [N(2O1)₃1][TFA] | 205.2 | 147.2 | 108.2 | 81.45 | 63.19 | 50.09 | 40.53 | 33.50 | 27.70 | 23.09 | 19.27 | 16.48 | 14.35 | 12.33 | 10.79 | 9.52 | 8.44 |
| [N4441][FSI] | 399.0 | 289.5 | 214.7 | 162.6 | 125.8 | 98.98 | 79.06 | 64.08 | 52.45 | 43.69 | 36.67 | 31.09 | 26.63 | 23.00 | 20.00 | 17.57 | 15.52 |
| [N4441][NTf ₂] | 550.8 | 376.9 | 264.3 | 190.5 | 141.0 | 106.58 | 82.27 | 64.71 | 51.55 | 41.92 | 34.45 | 28.69 | 24.14 | 20.51 | 17.64 | 15.31 | 13.39 |
| [N4441][BETI] | 1186 | 774.2 | 519.1 | 358.7 | 255.5 | 185.9 | 138.2 | 104.9 | 80.91 | 63.85 | 51.11 | 41.50 | 34.09 | 28.34 | 23.88 | 20.32 | 17.46 |
| [N4441][TSAC] | 293.0 | 208.1 | 150.9 | 112.2 | 85.66 | 66.71 | 52.85 | 42.58 | 34.60 | 28.73 | 24.02 | 20.38 | 17.44 | 15.06 | 13.12 | 11.55 | 10.21 |
| [N4441][TFA] | 1048 | 682.4 | 457.3 | 316.3 | 225.4 | 164.7 | 123.1 | 94.1 | 73.35 | 58.49 | 47.39 | 39.01 | 32.24 | 26.72 | 22.44 | 18.97 | 16.41 |

Table S3 Experimental values for the temperature dependent viscosities η of the ionic liquids given in mPa s.

| Ionic liquid | η_0 / mPa s | $\Delta \eta_0$ / 10 ⁻³ mPa s | В / К | ∆В / К | Т ₀ / К | Δ <i>T</i> ₀ / K | <i>R</i> ² |
|-------------------------------|------------------|--|-------|--------|--------------------|-----------------------------|-----------------------|
| [N(2O1)₃1][FSI] | 0.2031 | 3.59 | 684.6 | 4.81 | 182.0 | 0.47 | 1.00000 |
| [N(2O1)₃1][NTf ₂] | 0.1446 | 3.05 | 729.6 | 5.55 | 184.9 | 0.50 | 1.00000 |
| [N(2O1)₃1][BETI] | 0.1126 | 2.65 | 801.6 | 5.95 | 188.0 | 0.47 | 1.00000 |
| [N(2O1)₃1][TSAC] | 0.1857 | 3.29 | 620.5 | 4.36 | 193.5 | 0.43 | 1.00000 |
| [N(2O1)₃1][OTf] | 0.1280 | 6.62 | 811.0 | 12.3 | 193.6 | 0.90 | 0.99999 |
| [N(2O1)₃1][TFA] | 0.1483 | 1.34 | 746.5 | 21.4 | 194.9 | 1.69 | 0.99997 |
| [N4441][FSI] | 0.1004 | 2.45 | 1024 | 6.81 | 174.5 | 0.46 | 1.00000 |
| [N4441][NTf ₂] | 0.0651 | 5.03 | 1021 | 19.5 | 185.2 | 1.20 | 0.99999 |
| [N4441][BETI] | 0.0297 | 3.08 | 1252 | 27.0 | 180.0 | 1.39 | 0.99999 |
| [N4441][TSAC] | 0.0896 | 5.77 | 904.7 | 16.3 | 186.4 | 1.14 | 0.99999 |
| [N4441][TFA] | 0.0512 | 5.64 | 1087 | 26.7 | 188.7 | 1.48 | 0.99999 |

Table S4 Vogel-Fulcher-Tammann (VFT Equation (7)) fitting parameters η_0 , B, T_0 for the viscosity data including errors of the fits and coefficient of determination R^2 .

5. Specific conductivity

Table S5 contains the values for the specific conductivities obtained by experiment which are plotted in Fig. S3. The corresponding VFT fitting parameters are given in Table S6.

| Table S5 Experimental values for the specific conductivity κ at ϵ | different temperatures given in mS cm ⁻¹ . | ••• |
|--|---|-----|
|--|---|-----|

| | Temperature / °C | | | | | | | | | | |
|--|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ionic liquid | 25 | 35 | 45 | 55 | 65 | 75 | 85 | 95 | 105 | 115 | 125 |
| [N(2O1)₃1][FSI] | 2.506 | 3.690 | 5.473 | 7.458 | 9.772 | 12.58 | 15.54 | 18.78 | 22.30 | 26.04 | 29.92 |
| [N(2O1) ₃ 1][NTf ₂] | 1.528 | 2.368 | 3.690 | 5.206 | 7.054 | 9.307 | 11.77 | 14.47 | 17.40 | 20.36 | 23.49 |
| [N(2O1)₃1][BETI] | 0.649 | 1.091 | 1.814 | 2.709 | 3.829 | 5.227 | 6.871 | 8.668 | 10.70 | 12.93 | 15.31 |
| [N(2O1)₃1][TSAC] | 1.946 | 2.961 | 4.529 | 6.244 | 8.304 | 10.75 | 13.44 | 16.33 | 19.57 | 22.93 | 26.30 |
| [N(2O1)₃1][OTf] | 0.574 | 1.057 | 1.769 | 2.738 | 4.005 | 5.612 | 7.509 | 9.708 | 12.23 | 14.99 | 17.88 |
| [N(2O1)₃1][TFA] | 0.735 | 1.323 | 2.169 | 3.313 | 4.741 | 6.544 | 8.635 | 11.06 | 13.78 | 16.81 | 20.00 |
| [N4441][FSI] | 0.551 | 0.975 | 1.594 | 2.432 | 3.529 | 4.959 | 6.620 | 8.593 | 10.84 | 13.35 | 16.12 |
| [N4441][NTf ₂] | 0.267 | 0.520 | 0.915 | 1.482 | 2.246 | 3.299 | 4.559 | 6.034 | 7.789 | 9.741 | 11.94 |
| [N4441][BETI] | 0.092 | 0.202 | 0.393 | 0.688 | 1.119 | 1.723 | 2.486 | 3.449 | 4.584 | 5.896 | 7.444 |
| [N4441][TSAC] | 0.448 | 0.819 | 1.369 | 2.121 | 3.113 | 4.420 | 5.915 | 7.703 | 9.709 | 11.98 | 14.46 |
| [N4441][TFA] | 0.122 | 0.272 | 0.530 | 0.936 | 1.512 | 2.321 | 3.371 | 4.681 | 6.224 | 8.075 | 10.22 |



Fig. S3 Specific conductivity of the ammonium ionic liquids for a) the ether containing and b) the alkylated ammonium samples. Drawn lines are the VFT fits.

Table S6 Vogel-Fulcher-Tammann (VFT Equation (7)) fitting parameters, κ_0 , B and T_0 for the specific conductivity κ data including errors, coefficient of determination R^2 and Angell's strength parameter δ_{κ} for the specific conductivity.

| Ionic liquid | κ_0 / mS cm ⁻¹ | $\Delta \kappa_0 / \text{mS cm}^{-1}$ | <i>B /</i> K | Δ <i>B /</i> K | <i>T</i> ₀ / K | Δ <i>T</i> ₀ / K | R^2 | δ_{κ} |
|--|----------------------------------|---------------------------------------|--------------|----------------|---------------------------|-----------------------------|---------|-------------------|
| [N(2O1) ₃ 1][FSI] | 512.3 | 21.4 | -609.6 | 14.4 | 184.4 | 2.02 | 0.99998 | 3.31 |
| [N(2O1) ₃ 1][NTf ₂] | 359.4 | 23.7 | -537.3 | 20.9 | 201.0 | 3.03 | 0.99994 | 2.67 |
| [N(2O1)₃1][BETI] | 396.1 | 15.1 | -655.3 | 12.7 | 196.7 | 1.58 | 0.99999 | 3.33 |
| [N(2O1)₃1][TSAC] | 436.0 | 23.6 | -579.3 | 18.1 | 191.7 | 2.57 | 0.99996 | 3.02 |
| [N(2O1)₃1][OTf] | 558.1 | 35.9 | -681.9 | 21.2 | 199.8 | 2.52 | 0.99997 | 3.41 |
| [N(2O1)₃1][TFA] | 616.7 | 21.2 | -696.6 | 11.6 | 194.9 | 1.38 | 0.99999 | 3.57 |
| [N4441][FSI] | 745.0 | 30.7 | -813.5 | 14.7 | 185.9 | 1.60 | 0.99999 | 4.38 |
| [N4441][NTf ₂] | 567.3 | 30.7 | -771.7 | 18.3 | 198.3 | 1.97 | 0.99999 | 3.89 |
| [N4441][BETI] | 528.1 | 29.8 | -834.1 | 18.9 | 202.5 | 1.87 | 0.99999 | 4.12 |
| [N4441][TSAC] | 576.8 | 24.4 | -755.0 | 14.6 | 193.3 | 1.64 | 0.99999 | 3.91 |
| [N4441][TFA] | 872.8 | 39.2 | -890.6 | 15.4 | 197.9 | 1.48 | 0.99999 | 4.50 |

6. Molar conductivity

The calculated values for molar conductivity $\Lambda_{\rm M}$ in dependence on temperature are summarized in Table S7 and the corresponding data for the VFT fits are given Table S8.

| | | | Те | mperature / | °C | | |
|--|-------|-------|-------|-------------|-------|-------|-------|
| Ionic liquid | 25 | 35 | 45 | 55 | 65 | 75 | 85 |
| [N(2O1) ₃ 1][FSI] | 0.736 | 1.089 | 1.623 | 2.228 | 2.938 | 3.811 | 4.731 |
| [N(2O1) ₃ 1][NTf ₂] | 0.534 | 0.833 | 1.307 | 1.856 | 2.532 | 3.365 | 4.281 |
| [N(2O1)₃1][BETI] | 0.261 | 0.442 | 0.739 | 1.112 | 1.584 | 2.178 | 2.878 |
| [N(2O1)₃1][TSAC] | 0.657 | 1.006 | 1.549 | 2.153 | 2.886 | 3.769 | 4.739 |
| [N(2O1)₃1][OTf] | 0.160 | 0.296 | 0.498 | 0.777 | 1.144 | 1.614 | 2.174 |
| [N(2O1) ₃ 1][TFA] | 0.194 | 0.351 | 0.580 | 0.890 | 1.284 | 1.785 | 2.368 |
| [N4441][FSI] | 0.178 | 0.317 | 0.523 | 0.804 | 1.173 | 1.662 | 2.231 |
| [N4441][NTf ₂] | 0.102 | 0.199 | 0.352 | 0.574 | 0.878 | 1.298 | 1.806 |
| [N4441][BETI] | 0.039 | 0.088 | 0.171 | 0.302 | 0.494 | 0.767 | 1.115 |
| [N4441][TSAC] | 0.165 | 0.304 | 0.512 | 0.799 | 1.181 | 1.689 | 2.278 |
| [N4441][TFA] | 0.036 | 0.081 | 0.158 | 0.282 | 0.458 | 0.708 | 1.036 |

Table S7 Calculated values for the molar conductivity $\Lambda_{\rm M}$ at different temperatures given in S cm² mol⁻¹.

Table S8 VFT fitting parameters (following Equation (7)) $\Lambda_{M,0}$, B and T_0 for the molar conductivity Λ_M of the ammonium ionic liquids including errors of the fittings and coefficients of determination R^2 .

| Ionic liquid | $\Lambda_{\rm M,0}$ / S cm ² mol ⁻¹ | $\Delta \Lambda_{\rm M,0}$ / S cm ² mol ⁻¹ | <i>B /</i> K | Δ <i>B /</i> K | <i>T</i> ₀ / K | Δ <i>T</i> ₀ / K | <i>R</i> ² |
|------------------------------|--|---|--------------|----------------|---------------------------|-----------------------------|-----------------------|
| [N(2O1) ₃ 1][FSI] | 219.1 | 24.4 | -698.8 | 11.0 | 175.9 | 4.91 | 0.99988 |
| $[N(2O1)_31][NTf_2]$ | 203.6 | 21.9 | -723.0 | 9.31 | 181.4 | 3.90 | 0.99992 |
| [N(2O1)₃1][BETI] | 173.8 | 17.4 | -777.7 | 6.71 | 186.0 | 2.69 | 0.99996 |
| [N(2O1)₃1][TSAC] | 184.4 | 20.8 | -667.3 | 9.41 | 183.2 | 3.84 | 0.99991 |
| [N(2O1)₃1][OTf] | 304.3 | 7.25 | -834.1 | 2.62 | 186.4 | 1.05 | 0.99999 |
| [N(2O1)₃1][TFA] | 262.9 | 8.12 | -760.7 | 3.14 | 189.8 | 1.20 | 0.99999 |
| [N4441][FSI] | 422.5 | 22.3 | -960.4 | 7.58 | 174.4 | 3.52 | 0.99996 |
| [N4441][NTf ₂] | 401.7 | 22.5 | -995.7 | 7.14 | 181.0 | 3.09 | 0.99997 |
| [N4441][BETI] | 267.0 | 16.9 | -972.7 | 5.12 | 192.9 | 1.95 | 0.99998 |
| [N4441][TSAC] | 331.4 | 23.8 | -904.8 | 8.23 | 181.4 | 3.52 | 0.99995 |
| [N4441][TFA] | 512.0 | 9.91 | -1005.0 | 2.96 | 190.5 | 1.16 | 0.99999 |

7. Electrochemical stability

Electrochemical stability was obtained by cyclic voltammetry (CV) using glassy carbon electrodes in rodshape with 5 mm diameter (HTW Hochtemperatur-Werkstoffe, Thierhaupten, Germany) and Ag/Ag⁺ reference electrode. The reference electrode, which was separated from studied compound by a porous glass frit, was created from silver wire immersed into a solution of silver triflate (AgOTf) dissolved in the ionic liquid under investigation. Moisture and oxygen uptake were prevented by nitrogen flow through the cell. Cyclic voltammograms were recorded using a P-150 potentiostat (BioLogic, Seysinnet-Pariset, France) with a scan speed of 10 mV s^{-1} . Cut-off current densities of 0.1 mA cm^2 . The electrochemical stability of [N4441][NTf₂] on glassy carbon has already been investigated before and was found to be 5.5 V.²

| Ionic liquid | Cathodic limit $E_{\rm C}$ / V | Anodic limit <i>E</i> _A / V | Electrochemical window $\Delta E / V$ |
|--|--------------------------------|---|---------------------------------------|
| [N(2O1)₃1][FSI] | -3.3 | 1.4 | 4.7 |
| [N(2O1) ₃ 1][NTf ₂] | -3.6 | 1.6 | 5.2 |
| [N(2O1)₃1][BETI] | -3.6 | 1.5 | 5.1 |
| [N(2O1)₃1][TSAC] | -2.7 | 1.9 | 4.6 |
| [N(2O1)₃1][OTf] | -3.1 | 1.7 | 4.8 |
| [N(2O1)₃1][TFA] | -3.2 | 1.6 | 4.8 |
| [N4441][FSI] | -3.6 | 1.7 | 5.3 |
| [N4441][NTf ₂] | -3.6 | 2.1 | 5.7 |
| [N4441][BETI] | -3.6 | 1.6 | 5.2 |
| [N4441][TSAC] | -2.9 | 2.0 | 4.9 |
| [N4441][TFA] | -3.3 | 1.5 | 4.8 |

Table S9 Cathodic and anodic limits of the ammonium ionic liquids obtained by cyclic voltammetry and corresponding electrochemical windows on glassy carbon electrodes.

8. Walden relation

Fitting results for the linear fits of the logarithm inverse viscosity in Poise vs. logarithm of the molar conductivity in S cm² mol⁻¹ (Walden plot) following Equation (S2) are given in Table S10.³

$$\log\left(\frac{\Lambda_0}{\mathrm{S\ cm^2mol^{-1}}}\right) = \log C + t \cdot \log\left(\frac{0.1\ \mathrm{Pa\ s}}{\eta^{-1}}\right) \tag{S2}$$

The temperature-dependent ionicities $I_W(T)$ calculated from the Walden relation as given in the literature^{4,5} using Equation (S3) are plotted in Fig. S4.

$$I_{\rm W}(T) = \frac{\Lambda_{\rm M}}{\Lambda_{\rm M}^0} = \frac{\Lambda_{\rm M}^{\rm exp}(T)}{\rm S \ cm^2 \ mol^{-1}} \cdot \frac{\eta^{\rm exp}(T)}{0.1 \ \rm Pa \ s}$$
(S3)

| Ionic liquid | log C / 1 | $\Delta \log C / 10^{-3}$ | t / 1 | $\Delta t / 10^{-3}$ | <i>R</i> ² |
|--|-----------|---------------------------|-------|------------------------|-----------------------|
| [N(2O1) ₃ 1][FSI] | -0.265 | 5.66 | 0.934 | 8.28 | 0.99961 |
| [N(2O1) ₃ 1][NTf ₂] | -0.321 | 5.39 | 0.940 | 8.08 | 0.99963 |
| [N(2O1)₃1][BETI] | -0.390 | 3.57 | 0.940 | 6.44 | 0.99977 |
| [N(2O1)₃1][TSAC] | -0.336 | 6.74 | 0.920 | 8.96 | 0.99953 |
| [N(2O1)₃1][OTf] | -0.359 | 1.77 | 0.923 | 3.84 | 0.99991 |
| [N(2O1)₃1][TFA] | -0.421 | 1.47 | 0.942 | 2.87 | 0.99995 |
| [N4441][FSI] | -0.189 | 0.80 | 0.934 | 2.03 | 0.99998 |
| [N4441][NTf ₂] | -0.315 | 1.57 | 0.919 | 3.46 | 0.99993 |
| [N4441][BETI] | -0.389 | 1.65 | 0.939 | 2.97 | 0.99995 |
| [N4441][TSAC] | -0.351 | 1.73 | 0.929 | 3.73 | 0.99992 |
| [N4441][TFA] | -0.462 | 1.54 | 0.960 | 2.91 | 0.99995 |

Table S10 Linear fitting parameters log *C* and *t* for the fractional Walden relation (Equation (S2)).

Table S11 Calculated values for the 'ionicities' $I_W(T)$ obtained from the Walden plot at the specified temperatures.

| | | | Temp | eratur | e/°C | | |
|----------------------------|------|------|------|--------|------|------|------|
| Ionic liquid | 25 | 35 | 45 | 55 | 65 | 75 | 85 |
| [N(2O1)₃1][FSI] | 54.2 | 50.3 | 50.3 | 49.0 | 47.9 | 47.7 | 46.8 |
| [N(2O1)₃1][NTf₂] | 48.4 | 44.8 | 45.1 | 43.6 | 42.5 | 42.4 | 41.7 |
| [N(2O1)₃1][BETI] | 42.7 | 39.5 | 39.4 | 38.1 | 37.2 | 36.8 | 36.1 |
| [N(2O1)₃1][TSAC] | 45.8 | 41.8 | 41.8 | 40.1 | 39.1 | 38.6 | 38.1 |
| [N(2O1)₃1][OTf] | 48.0 | 45.2 | 42.9 | 41.2 | 40.0 | 39.4 | 38.7 |
| [N(2O1)₃1][TFA] | 39.8 | 38.0 | 36.6 | 36.1 | 35.6 | 34.4 | 34.0 |
| [N4441][FSI] | 71.0 | 68.1 | 65.8 | 63.5 | 61.5 | 61.0 | 59.4 |
| [N4441][NTf ₂] | 55.9 | 52.5 | 49.6 | 47.2 | 45.3 | 44.7 | 43.6 |
| [N4441][BETI] | 46.8 | 45.4 | 43.7 | 41.7 | 40.0 | 39.2 | 38.0 |
| [N4441][TSAC] | 48.5 | 45.9 | 43.9 | 42.2 | 40.9 | 40.6 | 39.7 |
| [N4441][TFA] | 37.9 | 37.0 | 35.7 | 34.7 | 33.6 | 33.6 | 33.4 |



Fig. S4 Progression of the 'ionicity' obtained from the Walden plot with temperature for a) the ether-ILs and b) the alkylated analogues.

9. Self-diffusion coefficients

Experimental values of the temperature dependent self-diffusion coefficients are given in Table S12 and the calculated inverse Haven ratios in Table S13. The obtained VFT fitting parameters are given in Table S14.

Table S12 Temperature-dependent self-diffusion coefficients D_{Si} (i = +: cation; i = -: anion) for the ionic liquids given in 10^{-11} m² s⁻¹.

| 0 | | | | | | | | | | |
|--|---|------|------|------|------|-----------|------|-------|-------|-------|
| | | | | | Ten | nperature | e∕°C | | | |
| Ionic liquid | i | 25 | 30 | 35 | 45 | 55 | 65 | 75 | 78.9 | 85 |
| [N(2O1)₃1][FSI] | + | 1.39 | 1.84 | 2.34 | 3.66 | 5.40 | 7.43 | 9.89 | 11.27 | 13.03 |
| [N(2O1)₃1][FSI] | - | 1.78 | 2.33 | 2.97 | 4.62 | 6.81 | 9.46 | 12.46 | 14.12 | 16.32 |
| [N(2O1) ₃ 1][NTf ₂] | + | 1.15 | 1.62 | 2.09 | 3.43 | 5.30 | 7.42 | 10.16 | 11.51 | 13.47 |
| [N(2O1) ₃ 1][NTf ₂] | _ | 1.16 | 1.63 | 2.12 | 3.46 | 5.33 | 7.53 | 10.27 | 11.66 | 13.64 |
| [N(2O1)₃1][TSAC] | + | 1.48 | 2.00 | 2.65 | 4.25 | 6.39 | 9.01 | 12.20 | 13.64 | 16.28 |
| [N(2O1)₃1][TSAC] | - | 1.58 | 2.12 | 2.78 | 4.47 | 6.69 | 9.44 | 12.76 | 14.36 | 16.73 |
| [N4441][FSI] | + | 0.28 | 0.39 | 0.55 | 0.98 | 1.62 | 2.46 | 3.66 | 4.26 | 5.18 |
| [N4441][FSI] | - | 0.38 | 0.54 | 0.76 | 1.36 | 2.27 | 3.48 | 5.11 | 5.93 | 7.21 |
| [N4441][NTf ₂] | + | 0.20 | 0.30 | 0.44 | 0.85 | 1.50 | 2.42 | 3.65 | 4.31 | 5.38 |
| [N4441][NTf ₂] | - | 0.22 | 0.34 | 0.49 | 0.96 | 1.73 | 2.75 | 4.14 | 4.87 | 6.16 |
| [N4441][TSAC] | + | 0.34 | 0.52 | 0.73 | 1.34 | 2.25 | 3.42 | 5.09 | 5.82 | 7.34 |
| [N4441][TSAC] | - | 0.39 | 0.61 | 0.84 | 1.55 | 2.62 | 3.95 | 5.86 | 6.80 | 8.52 |

| | | Temperature / °C | | | | | | | | |
|--|------|------------------|------|------|------|------|------|------|------|--|
| Ionic liquid | 25 | 30 | 35 | 45 | 55 | 65 | 75 | 78.9 | 85 | |
| [N(2O1)₃1][FSI] | 0.61 | 0.59 | 0.58 | 0.55 | 0.53 | 0.53 | 0.53 | 0.51 | 0.52 | |
| [N(2O1) ₃ 1][NTf ₂] | 0.60 | 0.56 | 0.56 | 0.53 | 0.51 | 0.51 | 0.51 | 0.50 | 0.51 | |
| [N(2O1)₃1][TSAC] | 0.56 | 0.54 | 0.52 | 0.50 | 0.48 | 0.47 | 0.47 | 0.46 | 0.46 | |
| [N4441][FSI] | 0.72 | 0.70 | 0.66 | 0.63 | 0.61 | 0.60 | 0.59 | 0.58 | 0.58 | |
| [N4441][NTf ₂] | 0.64 | 0.60 | 0.58 | 0.55 | 0.52 | 0.52 | 0.52 | 0.51 | 0.50 | |
| [N4441][TSAC] | 0.60 | 0.54 | 0.53 | 0.50 | 0.48 | 0.49 | 0.48 | 0.47 | 0.46 | |

Table S13 Calculated temperature-dependent inverse Haven ratios $H_{\rm R}^{-1}$ (Equation (4)).

Table S14 VFT fitting parameters $D_{Si,0}$, B and T_0 following Equation (7) for the self-diffusion coefficients D_{Si} of the ammonium ionic liquids including errors of the fittings and coefficient of determination R^2 .

| Ionic liquid | i | D _{Si,0} / 10 ⁻⁹ m ² s ⁻¹ | $\Delta D_{\rm Si,0}$ / 10^{-9} m ² s ⁻¹ | <i>B /</i> K | Δ <i>B /</i> K | <i>T</i> ₀ / K | Δ <i>T</i> ₀ / K | R ² |
|--|---|--|--|--------------|----------------|---------------------------|-----------------------------|----------------|
| [N(2O1) ₃ 1][FSI] | + | 12.46 | 4.90 | -834.9 | 128 | 175.1 | 12.0 | 0.99975 |
| [N(2O1)₃1][FSI] | — | 11.84 | 3.52 | -754.4 | 90.3 | 182.1 | 9.00 | 0.99983 |
| [N(2O1) ₃ 1][NTf ₂] | + | 9.94 | 2.44 | -713.5 | 70.1 | 192.3 | 6.93 | 0.99988 |
| [N(2O1) ₃ 1][NTf ₂] | _ | 10.43 | 2.38 | -722.3 | 65.4 | 191.6 | 6.42 | 0.99990 |
| [N(2O1)₃1][TSAC] | + | 17.28 | 5.43 | -835.4 | 97.8 | 179.3 | 9.02 | 0.99985 |
| [N(2O1)₃1][TSAC] | _ | 11.18 | 1.40 | -701.1 | 36.0 | 191.2 | 3.64 | 0.99997 |
| [N4441][FSI] | + | 20.68 | 7.52 | -1096 | 118 | 175.1 | 8.71 | 0.99991 |
| [N4441][FSI] | _ | 19.24 | 4.19 | -971.8 | 66.8 | 184.2 | 5.24 | 0.99996 |
| [N4441][NTf ₂] | + | 26.71 | 9.08 | -1084 | 106 | 183.5 | 7.54 | 0.99993 |
| [N4441][NTf ₂] | _ | 41.04 | 24.9 | -1176 | 196 | 177.5 | 13.4 | 0.99980 |
| [N4441][TSAC] | + | 50.18 | 37.7 | -1260 | 259 | 165.3 | 17.7 | 0.99970 |
| [N4441][TSAC] | _ | 69.16 | 51.0 | -1318 | 260 | 161.7 | 17.34 | 0.99974 |

10. Stokes-Einstein relation

Fitting parameters for the Stokes-Einstein plots according to Equation (S4) are given in Table S15.

$$\log\left(\frac{D_{\mathrm{S}i}}{\mathrm{m}^{2}\mathrm{s}^{-1}} \cdot \frac{\mathrm{K}}{T}\right) = a + u \cdot \log(\eta^{-1} \mathrm{mPa} \mathrm{s}) \tag{S4}$$

Calculated values for the Stokes radius $r_{h,i}$ and correction factor f at the specified temperatures are summed up in Table S16 and Table S17.

| Ionic liquid | i | a / 1 | $\Delta a / 10^{-3}$ | u / 1 | Δu / 10^{-3} | R^2 |
|--|---|--------|----------------------|-------|------------------------|--------|
| [N(2O1)₃1][FSI] | + | -11.42 | 6.88 | 1.020 | 4.84 | 0.9998 |
| [N(2O1)₃1][FSI] | _ | -11.33 | 6.14 | 1.013 | 4.32 | 0.9999 |
| [N(2O1) ₃ 1][NTf ₂] | + | -11.41 | 13.2 | 1.014 | 9.03 | 0.9995 |
| [N(2O1) ₃ 1][NTf ₂] | - | -11.41 | 11.8 | 1.015 | 8.07 | 0.9996 |
| [N(2O1)₃1][TSAC] | + | -11.42 | 5.94 | 1.017 | 4.36 | 0.9999 |
| [N(2O1)₃1][TSAC] | - | -11.41 | 4.22 | 1.008 | 3.10 | 0.9999 |
| [N4441][FSI] | + | -11.39 | 9.04 | 1.014 | 4.52 | 0.9999 |
| [N4441][FSI] | - | -11.24 | 11.8 | 1.019 | 5.93 | 0.9998 |
| [N4441][NTf ₂] | + | -11.46 | 10.4 | 0.988 | 5.08 | 0.9998 |
| [N4441][NTf ₂] | - | -11.39 | 12.8 | 0.993 | 6.26 | 0.9997 |
| [N4441][TSAC] | + | -11.44 | 15.8 | 1.006 | 8.58 | 0.9995 |
| [N4441][TSAC] | - | -11.38 | 16.1 | 1.005 | 8.76 | 0.9995 |

Table S15 Linear fitting parameters *a* and *u* for the Stokes Einstein relation (Equation (S4)).

| | | | | | Tem | perature | / °C | | | |
|--|---|-------|-------|-------|-------|----------|-------|-------|-------|-------|
| Ionic liquid | i | 25 | 30 | 35 | 45 | 55 | 65 | 75 | 78.9 | 85 |
| [N(2O1)₃1][FSI] | + | 2.130 | 2.092 | 2.086 | 2.051 | 2.027 | 2.047 | 2.062 | 2.012 | 2.034 |
| [N(2O1)₃1][FSI] | - | 1.662 | 1.650 | 1.644 | 1.625 | 1.605 | 1.607 | 1.637 | 1.606 | 1.624 |
| [N(2O1) ₃ 1][NTf ₂] | + | 2.099 | 1.987 | 2.006 | 1.965 | 1.926 | 1.977 | 1.989 | 1.972 | 1.997 |
| [N(2O1) ₃ 1][NTf ₂] | - | 2.073 | 1.972 | 1.979 | 1.952 | 1.916 | 1.947 | 1.968 | 1.947 | 1.971 |
| [N(2O1)₃1][BETI] | + | 2.154 | - | - | - | - | - | - | _ | - |
| [N(2O1)₃1][BETI] | - | 2.559 | - | - | - | - | - | - | _ | - |
| [N(2O1)₃1][TSAC] | + | 2.113 | 2.086 | 2.044 | 2.032 | 2.019 | 2.030 | 2.037 | 2.034 | 2.003 |
| [N(2O1)₃1][TSAC] | - | 1.981 | 1.971 | 1.949 | 1.935 | 1.930 | 1.937 | 1.947 | 1.932 | 1.949 |
| [N(2O1)₃1][OTf] | + | 1.721 | - | - | - | - | - | - | _ | - |
| [N(2O1)₃1][OTf] | - | 1.713 | - | - | - | - | - | - | _ | - |
| [N(2O1)₃1][TFA] | + | 2.130 | _ | - | - | _ | _ | - | _ | - |
| [N(2O1)₃1][TFA] | - | 2.113 | - | - | - | - | - | - | _ | - |
| [N4441][FSI] | + | 1.967 | 1.965 | 1.917 | 1.891 | 1.869 | 1.912 | 1.894 | 1.879 | 1.902 |
| [N4441][FSI] | - | 1.430 | 1.427 | 1.372 | 1.359 | 1.335 | 1.350 | 1.357 | 1.348 | 1.365 |
| [N4441][NTf ₂] | + | 1.985 | 1.940 | 1.932 | 1.935 | 1.935 | 1.972 | 2.028 | 2.012 | 2.032 |
| [N4441][NTf ₂] | _ | 1.763 | 1.729 | 1.725 | 1.719 | 1.676 | 1.737 | 1.787 | 1.783 | 1.775 |
| [N4441][BETI] | + | - | _ | - | 1.978 | _ | _ | - | _ | - |
| [N4441][BETI] | - | - | - | - | 1.966 | - | - | - | _ | - |
| [N4441][TSAC] | + | 2.188 | 2.066 | 2.050 | 2.016 | 2.018 | 2.081 | 2.081 | 2.104 | 2.056 |
| [N4441][TSAC] | - | 1.883 | 1.753 | 1.785 | 1.750 | 1.730 | 1.803 | 1.809 | 1.799 | 1.773 |
| [N4441][TFA] | + | - | _ | - | 2.131 | - | - | - | _ | - |
| [N4441][TFA] | _ | _ | _ | _ | 2.039 | _ | _ | _ | _ | |

Table S16 Calculated values for the Stokes radius $r_{h,i}$ at the specified temperatures when assuming a friction factor of 1 and sticky boundary conditions given the Stokes–Einstein relation in the conventional form $D_{Si} = \frac{k_B T}{6\pi \eta r_{h,i}}$ Reported values of $r_{h,i}$ are given in 10^{-10} m.

| | | | | | Tem | perature | e / °C | | | |
|--|---|-------|-------|-------|-------|----------|--------|-------|-------|-------|
| Ionic liquid | i | 25 | 30 | 35 | 45 | 55 | 65 | 75 | 78.9 | 85 |
| [N(2O1) ₃ 1][FSI] | + | 0.516 | 0.506 | 0.505 | 0.497 | 0.491 | 0.496 | 0.499 | 0.487 | 0.492 |
| [N(2O1)₃1][FSI] | _ | 0.513 | 0.509 | 0.507 | 0.502 | 0.495 | 0.496 | 0.505 | 0.496 | 0.501 |
| [N(2O1) ₃ 1][NTf ₂] | + | 0.508 | 0.481 | 0.486 | 0.476 | 0.466 | 0.479 | 0.481 | 0.477 | 0.483 |
| [N(2O1) ₃ 1][NTf ₂] | _ | 0.561 | 0.534 | 0.536 | 0.529 | 0.519 | 0.527 | 0.533 | 0.527 | 0.534 |
| [N(2O1) ₃ 1][BETI] | + | 0.522 | - | - | - | - | - | _ | _ | - |
| [N(2O1) ₃ 1][BETI] | - | 0.633 | - | - | - | - | _ | _ | _ | - |
| [N(2O1) ₃ 1][TSAC] | + | 0.512 | 0.505 | 0.495 | 0.492 | 0.489 | 0.492 | 0.493 | 0.493 | 0.485 |
| [N(2O1) ₃ 1][TSAC] | _ | 0.555 | 0.552 | 0.546 | 0.542 | 0.541 | 0.543 | 0.545 | 0.541 | 0.546 |
| [N(2O1)₃1][OTf] | + | 0.417 | - | - | - | - | - | _ | _ | - |
| [N(2O1)₃1][OTf] | - | 0.600 | - | - | - | - | - | _ | _ | - |
| [N(2O1) ₃ 1][TFA] | + | 0.516 | - | - | - | - | _ | _ | _ | - |
| [N(2O1) ₃ 1][TFA] | - | 0.733 | - | - | - | - | - | _ | _ | - |
| [N4441][FSI] | + | 0.458 | 0.458 | 0.447 | 0.440 | 0.435 | 0.445 | 0.441 | 0.438 | 0.443 |
| [N4441][FSI] | — | 0.441 | 0.440 | 0.423 | 0.419 | 0.412 | 0.417 | 0.419 | 0.416 | 0.421 |
| [N4441][NTf ₂] | + | 0.462 | 0.452 | 0.450 | 0.451 | 0.451 | 0.459 | 0.472 | 0.469 | 0.473 |
| [N4441][NTf ₂] | - | 0.477 | 0.468 | 0.467 | 0.466 | 0.454 | 0.470 | 0.484 | 0.483 | 0.481 |
| [N4441][BETI] | + | - | - | - | 0.461 | - | - | _ | _ | - |
| [N4441][BETI] | - | - | - | - | 0.487 | - | - | _ | _ | - |
| [N4441][TSAC] | + | 0.510 | 0.481 | 0.477 | 0.470 | 0.470 | 0.485 | 0.485 | 0.490 | 0.479 |
| [N4441][TSAC] | - | 0.528 | 0.491 | 0.500 | 0.490 | 0.485 | 0.505 | 0.507 | 0.504 | 0.497 |
| [N4441][TFA] | + | - | - | - | 0.496 | - | - | - | - | - |
| [N4441][TFA] | — | _ | _ | _ | 0.708 | _ | _ | _ | _ | _ |

Table S17 Calculated values for the correction factor f at the specified temperatures when using ion radii r_i obtained by *ab initio* methods⁶ and the Stokes–Einstein relation in the form $D_{Si} = \frac{k_B T}{6f \pi \eta r_i}$.

11. Molecular dynamics simulations and liquid structure

The charges obtained for the atoms in different cations, Fig. S5, obtained by different methods following the procedure described in the main manuscript, Table S18 to Table S20. For the molecular dynamics the MP2 ADCH charges are used, rounded to three decimal places. Nitrogen charges were adjusted to yield +1.



Fig. S5. B3LYP-GD3BJ/6-311+G(d,p) optimised geometries of [N(2O1)₃1]⁺ and [N4441]⁺.

| | B3LYP | | I | MP2 | | | | |
|--------------------|--------|--------|--------|--------|--------|--|--|--|
| | CHELPG | ADCH | CHELPG | ADCH | Used | | | |
| Ammonium N | -0.147 | 0.073 | -0.127 | 0.046 | 0.050 | | | |
| α-methyl-C | -0.045 | -0.200 | -0.070 | -0.190 | -0.190 | | | |
| α-methyl-H | 0.093 | 0.118 | 0.100 | 0.123 | 0.123 | | | |
| α-methylene-C | -0.234 | -0.128 | -0.204 | -0.115 | -0.115 | | | |
| α-methylene-H | 0.187 | 0.122 | 0.177 | 0.122 | 0.122 | | | |
| β-methylene-C | 0.113 | -0.036 | 0.076 | -0.025 | -0.025 | | | |
| β-methylene-H | 0.062 | 0.105 | 0.067 | 0.105 | 0.105 | | | |
| γ-ether-O | -0.269 | -0.231 | -0.252 | -0.263 | -0.263 | | | |
| δ -methyl-C | -0.074 | -0.143 | -0.086 | -0.127 | -0.127 | | | |
| δ -methyl-H | 0.090 | 0.113 | 0.093 | 0.111 | 0.111 | | | |

Table S18 Charges for the $[N(2O1)_31]^+$ cation in curled geometry obtained by different computational methods.

| | B3LYP | | M | 2 | |
|--------------------|--------|--------|--------|--------|--------|
| | CHELPG | ADCH | CHELPG | ADCH | Used |
| Ammonium N | 0.389 | 0.107 | 0.363 | 0.066 | 0.063 |
| α-methyl-C | -0.249 | -0.222 | -0.267 | -0.209 | -0.209 |
| α-methyl-H | 0.131 | 0.146 | 0.138 | 0.145 | 0.145 |
| α-methylene-C | -0.195 | -0.134 | -0.186 | -0.123 | -0.123 |
| α-methylene-H | 0.088 | 0.124 | 0.095 | 0.127 | 0.127 |
| β-methylene-C | 0.303 | -0.029 | 0.229 | -0.020 | -0.020 |
| β-methylene-H | 0.017 | 0.094 | 0.029 | 0.094 | 0.094 |
| γ-ether-O | -0.383 | -0.258 | -0.338 | -0.278 | -0.278 |
| δ -methyl-C | -0.018 | -0.131 | -0.046 | -0.117 | -0.117 |
| δ -methyl-H | 0.079 | 0.114 | 0.085 | 0.111 | 0.111 |

Table S19 Charges for the $[N(2O1)_31]^+$ cation in linear geometry obtained by different computational methods.

Table S20 Charges for the [N4441]⁺ cation in linear geometry obtained by different computational methods.

| | B3L | YP | MF | 2 | |
|--------------------|--------|--------|--------|--------|--------|
| | CHELPG | ADCH | CHELPG | ADCH | Used |
| Ammonium N | 0.388 | 0.089 | 0.421 | 0.059 | 0.055 |
| α-methyl-C | -0.246 | -0.221 | -0.256 | -0.207 | -0.207 |
| α-methyl-H | 0.132 | 0.141 | 0.135 | 0.140 | 0.140 |
| α-methylene-C | -0.269 | -0.121 | -0.285 | -0.108 | -0.108 |
| α-methylene-H | 0.121 | 0.116 | 0.123 | 0.116 | 0.116 |
| β-methylene-C | 0.013 | -0.165 | 0.003 | -0.162 | -0.162 |
| β-methylene-H | 0.027 | 0.096 | 0.031 | 0.095 | 0.095 |
| γ-methylene-C | 0.156 | -0.144 | 0.153 | -0.142 | -0.142 |
| γ-methylene-H | -0.006 | 0.093 | -0.002 | 0.090 | 0.090 |
| δ -methyl-C | -0.250 | -0.250 | -0.270 | -0.243 | -0.243 |
| δ -methyl-H | 0.073 | 0.101 | 0.079 | 0.099 | 0.099 |

The general procedure for equilibration was as follows. First, the initial topology was minimised using a conjugate gradient algorithm, with a maximum of 100 iterations. The atoms were then assigned random velocities corresponding to 400 K. The pressure was kept at 1 bar / raised to 1000 bar / lowered to 1 bar / kept at 1 bar in an NPT ensemble for 10000 steps for each of these intervals. Similarly, the temperature was then raised to 600 K in 10000 steps, kept at 600 K for 500000 steps, lowered to 400 K for 10000, and kept at 400 K for 10000 steps in an NPT ensemble. After this pre-equilibration we determined the cell volume. To this end, we first let the system relax for 300000 steps in an NVT ensemble, followed by 500000 steps in an NPT ensemble, during which we recorded the cell volume every 10 steps for the first 300000 steps. After the NPT run, the cell vector obtained from the average of these values, Table S21, was printed

to a file, and the box deformed to the obtained box size over 100000 steps. This procedure, totalling for 900000 steps or 0.9 ns, was repeated 10 times to ensure absence of drift in the cell vector. After that, all obtained cell vectors were averaged and the box deformed to the target value over 100000 steps. Then followed the final equilibration for 10 ns.

| Ionic Liquid | Cation structure | Temp. / K | Charges | Box length / Å | Standard deviation / ${\rm \AA}$ |
|--|------------------|-----------|----------|----------------|----------------------------------|
| [N(2O1) ₃ 1][NTf ₂] | curled | 298 | scaled | 85.00 | 0.02 |
| [N(2O1)₃1][NTf₂] | curled | 400 | unscaled | 86.39 | 0.01 |
| [N(2O1)₃1][NTf₂] | linear | 298 | scaled | 84.75 | 0.03 |
| [N(2O1)₃1][NTf₂] | linear | 400 | unscaled | 85.96 | 0.02 |
| [N4441][NTf ₂] | | 298 | scaled | 87.10 | 0.03 |
| [N4441][NTf ₂] | | 400 | unscaled | 88.59 | 0.03 |

Table S21 Cell vectors / box lengths for the different simulation setups using different cation structures and temperatures.

After equilibration, we performed the production runs in the microcanonical ensemble for 15 ns, writing to a trajectory every 5000 steps or 5 ps. To further validate results, another production run of 15 ns was performed after that, starting from the last point of the previous run. The datafiles (effectively equilibrated for \approx 50 ns) and input files are given in the supporting information. We also repeated the whole procedure – cell vector determination, equilibration, and two consecutive production runs – for the same system with scaled charges at 298 K. The energy drift during the NVE simulation (obtained from the slope of the total energy vs. time during the first production run) was around -0.1 kJ mol⁻¹ over 1 ns, or less than 0.4 % of the total energy over the whole length of the simulation.

The calculated self-diffusion coefficients from the molecular dynamics (MD) simulations are given in Table S22 for both of the two consecutive runs. For each of the 15 ns runs, we calculated the ensemble averages of the mean squared displacements $\langle r^2(t) \rangle$ using a sliding window algorithm and fitted the mean squared displacement times of 3-7 ns. For t < 3 ns the regime of Gaussian diffusion is not reached; for t > 7 ns the statistics become insufficient.

| | | | Unscaled simulation | | Scaled si | mulation |
|--|---|---------------------|--|--|--|--|
| lonic Liquid | i | Cation structure | Run 1 D_{Si} / 10^{-11} m ² s ⁻¹ | Run 2 D_{Si} / 10^{-11} m ² s ⁻¹ | Run 1 D_{Si} / 10^{-12} m ² s ⁻¹ | Run 2 D_{Si} / 10^{-12} m ² s ⁻¹ |
| [N(2O1) ₃ 1][NTf ₂] | + | Curled | 7.75 | 7.50 | 7.44 | 7.28 |
| [N(2O1) ₃ 1][NTf ₂] | + | Linear | 2.76 | 3.00 | 2.61 | 2.84 |
| [N4441][NTf ₂] | + | | 3.14 | 2.70 | 1.96 | 2.83 |
| [N(2O1) ₃ 1][NTf ₂] | _ | Curled | 6.52 | 7.23 | 6.99 | 7.01 |
| [N(2O1) ₃ 1][NTf ₂] | _ | Linear | 2.69 | 2.41 | 2.29 | 2.31 |
| [N4441][NTf ₂] | _ | | 2.86 | 2.07 | 2.05 | 1.93 |

Table S22 Calculated self-diffusion coefficients obtained from MD-simulations.

Obtained peak positions calculated from the MD simulations for the charge and adjacency peak as well as corresponding real space distances in comparison with the experimental values are given in Table S23. The plots of the scattering data are shown in Fig. S6. The calculated radial distribution functions for the different ion combinations are shown in Fig. S7 while the energy as a function of different dihedral angles of the different side chains are plotted in Fig. S8. The energies shown in Fig. S8 were obtained from the population of the dihedral angles as the potential of mean force, demonstrating the successful parameterization.

| | | Peak | position | Real space | e distances |
|--|----------------------|----------------------------------|-------------------------------------|--------------------|-----------------------|
| Ionic Liquid | Method | Charge peak / Å ⁻¹ | Adjacency peak / Å ^{–1} | Charge peak / Å | Adjacency peak / Å |
| [N(2O1) ₃ 1][NTf ₂] | SAXS Experi- ment | 0.80 | 1.32 | 7.82 | 4.77 |
| [N(2O1) ₃ 1][NTf ₂] | MD unscaled | 0.82 | 1.30 | 7.64 | 4.83 |
| [N(2O1) ₃ 1][NTf ₂] | MD scaled | 0.83 | 1.41 | 7.53 | 4.79 |
| [N4441][NTf ₂] | SAXS Experi- ment | 0.79 | 1.38 | 7.94 | 4.56 |
| [N4441][NTf ₂] | MD unscaled | 0.79 | 1.36 | 7.92 | 4.68 |
| [N4441][NTf ₂] | MD scaled | 0.79 | 1.38 | 7.97 | 4.55 |

Table S23 Comparison of the peak positions obtained from small angle X-ray scattering experiments (SAXS) and molecular dynamics simulations under different conditions.



Fig. S6 Plots of the SAXS profiles with normalised intensity from experiment and molecular dynamics simulations.



Fig. S7 Radial distribution functions g(r) of a) cation-anion b) cation-cation and c) anion-anion.



Fig. S8 Energy (potential of mean force) as a function of the dihedral angles from the MD simulations of the cation for a) the C-N-C-C, b) the N-C-C-X and c) the C-C-X-C dihedral angles where X = O, CH₂.

12. Electronic structure analysis

12.1 Introduction to QTAIM

The quantum theory of atoms in molecules (QTAIM) links concepts of chemical bonding with electron density distributions ($\rho(r)$). The underlying concept of QTAIM is the topological analysis of ($\rho(r)$) which produces information about stationary points of $\rho(r)$). Specific types of saddle points (those being a minimum along one direction in space and a maximum for the two perpendicular directions) of $\rho(r)$ are called bond critical points (BCPs), which are indicative for the presence of localised bonding interactions. BCPs are found between pair-wise interacting atoms and have been basis for the study of covalent bonds and localised non-covalent interactions such as hydrogen bonding (H-bonding). $\rho(r)$ at intermolecular BCPs ($\rho_{\rm BCP}$) has been correlated successfully to interaction strength. Further insight into an interaction is accessible via the Laplacian of the electron density [$\nabla^2 \rho = (\partial^2 / \partial x^2 + \partial^2 / \partial z^2)\rho$ with x, y, and z being the three directions in cartesian space] and the total energy density (H) at the BCP. If both $\nabla^2 \rho_{\rm BCP}$ and $H_{\rm BCP}$ are positive numbers, a closed-shell interaction is observed while negative $\nabla^2 \rho$ and H values indicate a covalent bond. However, systems with $\nabla^2 \rho_{\rm BCP}$ and $H_{\rm BCP}$ values of different sign are known and characterise an intermediate situation on the sliding scale between closed shell and covalent interactions.^{7,8}

QTAIM also provides a physically meaningful atomic charge scheme. The space occupied by an atom can be defined by surfaces consisting of a set of electron density gradient $[\nabla \rho = (\partial/\partial x + \partial/\partial y + \partial/\partial z)\rho]$ paths with steepest ascent which originate at the BCP between two atoms and terminate at infinity. The portions of space which are defined by those surfaces are called atomic basins and represent a definition of an atom in a molecule. QTAIM atomic charges (Q_{QTAIM}) can be calculated by knowledge of the nuclei and integrating the electron density over the corresponding basin space.^{7,8}

12.2 Introduction to NCI

NCI reveals areas defined by both localised and delocalised non-covalent interactions. Basis of the NCI framework is the dimensionless reduced electron density gradient (*s*), Equation (S5), which describes the deviation of ρ from a homogenous distribution.⁹

$$s = \frac{\nabla \rho}{2(3\pi^2)^{1/3} \rho^{4/3}}$$
(S5)

Non-covalent interactions can be defined by points in space which have low *s* and low ρ values at the same time. Therefore, *s*- ρ scatter plots are a typical representation to identify non-covalent interactions. Often ρ is multiplied with the sign of the second eigenvalue of the electron density Hessian matrix (λ_2), which allows to differentiate between attractive ($\lambda_2 < 0$) and repulsive ($\lambda_2 > 0$) interactions. Additionally, three-dimensional representations can be generated if the *s*-isosurface is plotted (often with a *s*-isovalue of 0.5 or 0.6) and colour-coded according to sign(λ_2) ρ in order to differentiate repulsive and attractive interactions visually.⁹ The NCI framework allows for a quantitative analysis of non-covalent interactions by integrating sign(λ_2) ρ within the volumes enclosed by a NCI surface which results in charges connected to attractive (att) and repulsive (rep) interactions (Q_{att} and Q_{rep} , Equation (S6) and (S7)). The sum of these two charges (Q_{bind} , Equation (S8)) has previously been linked to interaction energies and reveals overall attractive ($Q_{bind} < 0$) or repulsive ($Q_{bind} > 0$) non-covalent interactions.^{10,11}

$$Q_{\text{att}} = \int \operatorname{sign}(\lambda_2) \rho^n dr$$
 for $\lambda_2 < 0$ (S6)

$$Q_{\rm rep} = \int {\rm sign}(\lambda_2) \rho^n dr \quad \text{for} \quad \lambda_2 > 0$$
 (S7)

$$Q_{\rm bind} = Q_{\rm att} - Q_{\rm rep} \tag{S8}$$

The exponent *n* has been introduced to allow for a flexible correlation of Q_{bind} with interaction energies. The cut-off value for *s* is another important factor determining the values of NCI integrals. One study suggests a combination of n = 4/3, and a cut-off value of s = 0.06.¹⁰ Another study reports *n* values between 2 and 3 in combination with a cut-off of s = 1.0 to recover the most accurate interaction energies, if contributions from electron densities not stemming from non-covalent interactions can eliminated.¹¹ Therefore, n = 1.0; 4/3 were used in this report because no such elimination is available for intramolecular interactions. A cut-off of 0.5 for *s* was employed, as lifting this value further led to significant integration over NCI isosurfaces in the periphery of the molecules.

12.3 Introduction to NBO

NBOs are a localised representation of molecular orbitals and provide the best Lewis-like orbital structures. Typically, NBOs are localised on one or two atomic centres.¹² Within this report NBOs are used to characterise H-bonds. In the NBO approach traditional H-bonds consist of a H-bond donor group (D-H) and a H-bond acceptor (A). The H-bond acceptor donates electron density from its lone-pair orbitals to the antibonding σ^* D-H orbital. This interaction is accompanied by a stabilisation which can be measured through the second order stabilisation energy $E^{(2)}$, Equation (S9),¹³ q is the orbital occupancy, ε is the orbital energy, F is the off-diagonal NBO Fock matrix element, i refers to the donor orbital and j to the acceptor orbital.

$$E^{(2)} = q_i \frac{F_{i,j}^2}{\varepsilon_j - \varepsilon_i}$$
(S9)

12.4 Introduction to SAPT

Symmetry-adapted perturbation theory (SAPT) provides an energy decomposition scheme which allows for understanding the physical origins of interactions between two fragments. Different levels of SAPT are available.¹⁴ However, intramolecular interactions are the centre of this report, thus, only the simplest SAPT methodology – SAPT(0) – will be introduced as no higher-level intramolecular SAPT methods are yet available in the Psi4 program.

SAPT partitions the Hamiltonian of a system (\hat{H}) into contributions from fragments and contributions from interactions between the fragments, Equation (S10). Fragment contributions are the fragment Fock operators ($\hat{F}_A \otimes \hat{F}_B$) and the fluctuation potential operators ($\hat{W}_A \otimes \hat{W}_B$) of the two interacting fragments A and B. The interaction between the fragments is captured by the interaction potential (\hat{V}). SAPT interaction energies are computed through a perturbative expansion in \hat{V} , \hat{W}_A and \hat{W}_B . SAPT(0) does not include any perturbation in \hat{W}_A and \hat{W}_B . Therefore, SAPT(0) basically treats the system on a Hartree-Fock level and corrects for dispersive terms obtained from a second-order perturbation in \hat{V} .^{14,15}

$$\widehat{H} = \widehat{F}_A + \widehat{F}_B + \widehat{W}_A + \widehat{W}_B + \widehat{V}$$
(S10)

Physically meaningful components to SAPT interaction energies can be obtained: E_{elst} , E_{exch} , E_{ind} , and E_{disp} , Equation (S11). E_{elst} is the quasi-classical electrostatic interaction between the charge distributions of the fragments. The Pauli-exclusion principle causes an exchange energy (E_{exch}) which has to be repulsive (positive) at all times. E_{ind} is a result of induction through polarisation in one fragment by the electric field generated by the other fragment and *vice versa*. E_{disp} is the London dispersion energy contribution.^{14,15} SAPT(0) is the computationally least expensive and most inaccurate version of SAPT. An extensive benchmark study employing different basis sets showed a mean average error of roughly 5 kJ mol⁻¹ for H-bond energies evaluated across the S22, NC10, HBC6, and HSG benchmark datasets. However, SAPT(0) can still be a valuable semi-quantitative tool for characterising intramolecular interactions.^{14,16}

$$E_{\text{SAPT}(0)} = E_{\text{elst}} + E_{\text{exch}} + E_{\text{ind}} + E_{\text{disp}}$$
(S11)

12.5 Model systems and conformations

The DFT optimised linear and curled geometries for [N111(2O1)]⁺ and C111(2O1) are depicted in Fig. S9. Relative energies at different levels of theories for all cations and the charge neutral analogue are reported in Table S24.



Fig. S9 B3LYP-GD3BJ/6-311+G(d,p) energy optimised linear and curled geometries of [N111(2O1)]⁺, and C111(2O1).

Table S24 Relative energies in kJ mol⁻¹ of the DFT optimised linear and curled geometries of [N111(201)]⁺, C111(201) and [N(201)₃1]⁺ at different levels of theory.

| Cation | B3LYP-GD3BJ/6-311+G(d,p) | | HF/co | :-pVTZ | MP2/c | MP2/cc-pVTZ | |
|--------------------------|--------------------------|--------|--------|--------|--------|-------------|--|
| | linear | curled | linear | curled | linear | curled | |
| [N111(201)] ⁺ | 20 | 0 | 13 | 0 | 22 | 0 | |
| C111(2O1) | 0 | 0 | 0 | 3 | 2 | 0 | |
| [N(2O1)₃1]⁺ | 46 | 0 | 27 | 0 | 49 | 0 | |

12.6 Characterisation of intramolecular interactions

12.6.1 H-bonds

A common approach to identify H-bonds is the presence of BCPs within the QTAIM framework. H-bonding BCPs were found in all geometries but no such BCPs are present in the linear geometries, Fig. S10. A set of electronic structure properties obtained from QTAIM and NBO calculations has been previously established for the quantitative characterisation of H-bonds, Table S25.¹³



Fig. S10 QTAIM molecular graphs for $[N111(201)]^+$, C111(201) and $[N(201)_31]^+$ obtained from wavefunctions at the B3LYP-GD3BJ/6-311+G(d,p) level of theory. H-bonding BCPs are highlighted with red circles.

| | Strong | Medium | Weak |
|-------------------------------------|--------|-----------|------------------------|
| $ ho_{ m BCP}$ / a.u. | > 0.05 | 0.02-0.05 | 0.02-0.002 |
| $ abla^2 ho_{ m BCP}$ / a.u. | -ve | +ve or-ve | +ve and small (< 0.01) |
| $H_{ m BCP}$ / a.u. | < 0 | < 0 | > 0 |
| $E^{(2)}$ / kJ mol ⁻¹ | > 150 | 30-150 | < 30 |
| $E_{\rm HB}$ / kJ mol ⁻¹ | 63-167 | 17-63 | < 17 |

Table S25 Electronic structure property criteria for the quantitative characterisation of H-bonds.¹³

H-bond energies (E_{HB}) are usually estimated from supramolecular association energies if the H-bond under study is the most predominant interaction. However, intramolecular interactions are studied in this report, thus, E_{HB} was estimated from electronic structure properties at H-bonding BCPs instead. A rather old approach is based on the kinetic energy density (V) at BCPs (E_{HB}^1), Equation (S12).¹⁷ Another study used ρ_{BCP} values instead - three different equations, Equation (S13) through Equation (S15), are provided: E_{HB}^2 is based on the complete set of complexes studied, E_{HB}^3 only takes neutral complexes into account while E_{HB}^4 is based on a subset of charged H-bond complexes.¹⁸ All equations have been derived from intermolecularly H-bonded complexes but can be expected to produce reasonable numbers for intramolecular H-bonds as well.

$$E_{\rm HB}^{1}/(\rm kJ/mol) = \frac{V_{\rm BCP}}{2}$$
(S12)

$$E_{\rm HB}^2/(\rm kJ/mol) = (-357.73 \cdot \rho_{\rm BCP} + 2.6182) \cdot 4.184$$
 (S13)

$$E_{HB}^{3}/(\text{kJ/mol}) = (-223.08 \cdot \rho_{BCP} + 0.7423) \cdot 4.184$$
 (S14)

$$E_{\rm HB}^4/(\rm kJ/mol) = (-332.34 \cdot \rho_{\rm BCP} - 1.0661) \cdot 4.184$$
 (S15)

 E_{HB}^1 , E_{HB}^2 , and E_{HB}^3 all produce H-bond energies in the same numerical range, Table S26. Only E_{HB}^4 results in H-bond energies which are roughly 2 to 6 times more negative than the other three values. This is most probably an artefact from the subset of charged complexes used to derive Equation (S15). If only E_{HB}^1 , E_{HB}^2 , and E_{HB}^3 are evaluated in conjunction with other electronic structure properties, Table S25, all Hbonds can be classified as weak in nature.

Table S26 Electronic structure properties at the B3LYP-GD3BJ/6-311+G(d,p) level of theory for the characterisation of intramolecular H-bond strength in the curled geometries of $[N111(201)]^+$, C111(201) and $[N(201)_31]^+$.

| | ρ _{BCP} / a.u. | $ abla^2 ho_{ m BCP}$ / a.u. | H _{BCP} / a.u. | V _{BCP} / a.u. | E ⁽²⁾ / kJ mol ⁻¹ | E ¹ _{HB} / kJ mol ⁻¹ | E ² _{HB} / kJ mol ⁻¹ | $E_{\rm HB}^{3}$ / kJ mol ⁻¹ | $E_{\rm HB}^4$ / kJ mol ⁻¹ |
|------------------------|----------------------------|------------------------------|----------------------------|----------------------------|---|---|---|---|---------------------------------------|
| [N1112O1] ⁺ | 0.0177 | 0.0662 | 0.0022 | -0.0120 | 5.86 | -15.8 | -15.5 | -13.4 | -29.1 |
| C1112O1 | 0.0125 | 0.0433 | 0.0094 | -0.0081 | - | -10.6 | -7.8 | -8.6 | -21.8 |
| [N(2O1)₃1]⁺ | 0.0177 | 0.0665 | 0.0024 | -0.0121 | 6.15 | -15.9 | -15.5 | -13.4 | -29.1 |

12.6.2 Delocalised interactions

NCI plots were generated for all cation and charge-neutral analogue geometries, Fig. S11, to study the total non-covalent interactions instead of localised H-bonds only. All geometries show NCI isosurfaces between neighbouring hydrogen atoms which are either attributed to attractive dispersion or repulsive steric interactions. All curled geometries show NCI isosurfaces between the oxygen atoms and the hydrogen atoms involved in the previously discussed intramolecular H-bonds. Since all NCI isosurfaces are green in colour, none of the interactions are strongly attractive nor repulsive which is also reflected by the spike positions in the *s*-sign(λ_2) ρ scatter plots, Fig. S11. Integrals of ρ over NCI volumes are given in Table S27.



Fig. S11 NCI scatter plots and NCI isosurfaces (both with a grid spacing of 0.05 Å) for $[N111(201)]^+$, C111(201) and $[N(201)_31]^+$ at the B3LYP-GD3BJ/6-311+G(d,p) level of theory. NCI isosurfaces have been generated at an isovalue of s = 0.5 and with a cut-off of $\rho = 0.05$ a.u.

| Structure | Geometry | Q_{type} | $n = 1 / (10^4 \text{ a.u.})$ | <i>n</i> = 4/3 / (10 ⁴ a.u.) |
|--------------------------------------|----------|---------------------|-------------------------------|---|
| | | $Q_{\rm att}$ | -97.727 | -23.073 |
| | curled | $Q_{ m rep}$ | 119.689 | 25.765 |
| | | $Q_{\rm bind}$ | 21.963 | 2.691 |
| [N111(201)] ⁺ | | $Q_{\rm att}$ | -39.142 | -8.138 |
| | linear | $Q_{ m rep}$ | 40.329 | 8.641 |
| | | $Q_{\rm bind}$ | 1.187 | 0.503 |
| | | | | |
| | curled | $Q_{\rm att}$ | -63.978 | -14.066 |
| | | $Q_{ m rep}$ | 50.825 | 10.691 |
| (111/201) | | $Q_{\rm bind}$ | -13.153 | -3.375 |
| C111(201) | linear | $Q_{\rm att}$ | -37.141 | -7.503 |
| | | $Q_{ m rep}$ | 31.825 | 6.626 |
| | | $Q_{\rm bind}$ | -5.316 | -0.877 |
| | | | | |
| | | $Q_{\rm att}$ | -321.811 | -75.425 |
| | curled | $Q_{ m rep}$ | 412.699 | 89.741 |
| [N(2O1) ₃ 1] ⁺ | | $Q_{\rm bind}$ | 90.889 | 14.316 |
| | linear | $Q_{\rm att}$ | -138.115 | -29.056 |
| | | $Q_{ m rep}$ | 197.090 | 42.415 |
| | | $Q_{\rm bind}$ | 58.975 | 13.359 |

Table S27 NCI integrals for $[N111(201)]^+$, C111(201) and $[N(201)_31]^+$ at the B3LYP-GD3BJ/6-311+G(d,p) level of theory evaluated within the -0.05 to 0.05 a.u. sign(λ_2) ρ range with a s cut-off of 0.5 and a grid spacing of 0.05 Å.

12.6.3 Long-range interactions

Long-range intramolecular interactions in the two curled model compounds were studied within the SAPT(0) approach. Intramolecular SAPT(0) calculations require to partition a molecule into two interacting fragments (A, B) and a linker fragment (C) which connects A and B.¹⁶ [N111(2O1)]⁺ and C111(2O1) have been assigned to the fragments in two different ways: 1) the methoxy group is fragment A, the trime-thylammonium/*tert*-butyl moiety is fragment B, and the two methylene groups represent the linker. 2) The methoxy group is fragment A, the methyl group involved in hydrogen bonding is fragment B and the methylene groups plus the remaining part of the molecule is the linker, Fig. S12. Assignment 1 allows for studying the total interactions of the methoxy group with the molecule core and the alkyl periphery. Assignment 2 mostly reflects the intramolecular H-bond interaction.



Fig. S12 Schematic representation of the different fragment assignments during the intramolecular SAPT(0) calculations.

The contributions to the intramolecular stabilisation as calculated within the SAPT(0) scheme is shown in Fig. S13. The energy resulting from a long-range interaction between the methoxy group and the nitrogen core plus the alkyl periphery can be estimated from the difference between the sum of attractive terms for assignment 1 (-40 kJ mol^{-1}) and the sum of attractive term for assignment 2 (-18 kJ mol^{-1}) – leading to a value of -22 kJ mol^{-1} . The sum of attractive terms for assignment 2 should mostly reflect the H-bond interactions. Within the error margin of the method, both H-bonding and non-specific long-range attraction can be estimated as equally important for the overall stabilisation of the model cation.



Fig. S13 Intramolecular SAPT(0) energy decomposition for [N111(201)]⁺ and C111(201) performed with the cc-pVTZ basis set on B3LYP-GD3BJ/6-311+G(d,p) optimised geometries.

12.6.4 QTAIM atomic charges

The calculated QTAIM atomic charges are given in Table S28 following the numbering scheme in Fig. S14.



Fig. S14: Numbering scheme for the QTAIM atomic charges of [N111(201)]⁺ and C111(201).

| | [N111(| [201)]+ | C111(2O1) | | |
|-----------------|--------|---------|-----------|--------|--|
| | curled | linear | curled | linear | |
| N^1/C^1 | -0.918 | -0.930 | 0.094 | 0.093 | |
| C ² | 0.269 | 0.267 | 0.022 | 0.024 | |
| C ³ | 0.266 | 0.267 | 0.019 | 0.020 | |
| C ⁴ | 0.248 | 0.267 | 0.020 | 0.020 | |
| C⁵ | 0.256 | 0.263 | 0.050 | 0.051 | |
| C ₆ | 0.528 | 0.546 | 0.493 | 0.495 | |
| O ⁷ | -1.057 | -1.028 | -1.046 | -1.040 | |
| C ⁸ | 0.457 | 0.463 | 0.506 | 0.507 | |
| H ⁹ | 0.068 | 0.072 | -0.016 | -0.013 | |
| H^{11} | 0.064 | 0.072 | -0.020 | -0.013 | |
| H ¹² | 0.069 | 0.068 | -0.015 | -0.016 | |
| H ¹³ | 0.060 | 0.072 | -0.021 | -0.013 | |
| H^{14} | 0.067 | 0.069 | -0.013 | -0.013 | |
| H ¹⁵ | 0.085 | 0.067 | -0.011 | -0.018 | |
| H^{16} | 0.059 | 0.072 | -0.019 | -0.013 | |
| H ¹⁷ | 0.125 | 0.067 | 0.025 | -0.018 | |
| H ¹⁸ | 0.057 | 0.070 | -0.025 | -0.013 | |
| H ¹⁹ | 0.056 | 0.068 | -0.019 | -0.007 | |
| H ²⁰ | 0.064 | 0.067 | -0.007 | -0.007 | |
| H ²¹ | 0.018 | 0.009 | -0.013 | -0.016 | |
| H ²² | 0.045 | 0.009 | -0.015 | -0.016 | |
| H ²³ | 0.032 | 0.064 | -0.005 | 0.024 | |
| H ²⁴ | 0.058 | 0.020 | 0.024 | -0.007 | |
| | | | | | |

Table S28 QTAIM atomic charges (Q_{QTAIM} / e) at the B3LYP-GD3BJ/6-311+G(d,p) level of theory.

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