

Supplementary Material (ESI) for Chemical Communications

A new family of Ionic liquids based on N, N-dialkyl 3-azabicyclo[3.2.2]-nonaneium cations: organic plastic crystal behaviour and lithium metal electrodeposition

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Experimental Section

General: Commercially available reagents were purchased from Aldrich, Merck (solvents and 1-butyl-4methyl pyrrolidinium bis(trifluoromethanesulfonyl)amide high purity grade) and 3M [lithiumbis(trifluoromethylsulfonyl)amide]. 3-azabicyclo(3.2.2)nonane (City Chemicals, USA) was sublimed prior to use. All solvents used in the synthetic procedures were commercial high purity (HPLC or p.a. grade) products and activated carbon (Norit SX Ultra, Fluka) was of pharmaceutical grade purity. All glassware was pre-rinsed with the solvent used in individual synthetic procedures prior to reactions which were carried out on a vacuum Schlenk line under dry nitrogen. Products were dried under vacuum ($\sim 1\text{--}5 \times 10^{-2}$ mbar at 40 to 50 °C) for at least two days. Prior to measurement of cyclic voltammograms the glass electrochemical cell and the reference electrode tubing was (i) soaked in $\sim 30\%$ HNO₃, (ii) soaked in and rinsed with deionised water, (iii) rinsed with HPLC grade acetone and finally dried in an oven over night. Cyclic voltammetry and sample preparation for other physicochemical measurements was carried out in an argon filled glove box (dew point in chamber approximately -50 °C).

Measurements

¹H, ¹⁹F, and ¹³C NMR spectra were recorded on a BRUKER spectrometer operating at 200.13, 50.33, and 188.31 MHz, respectively. Chemical shift values are reported relative to CDCl₃ solutions of TMS (¹H, ¹³C) and CFCI₃ (¹⁹F) respectively as the external references. Positive and negative ion electrospray mass spectra were acquired on a VG Platform mass spectrometer using a cone voltage of 50 or 30V and the source was maintained at 80°C. The solvent system used was a water, CH₃CN, CH₃OH (1:1:2) mixture with a flow rate of 0.04ml/min. Elemental analysis (C, H, and N) was carried out by the Microanalytical Unit of the Research School of Chemistry at the Australian National University in Canberra.

Water content and impurity: The water content in the room-temperature liquid salts was determined by coulometric Karl-Fischer titration (Methrom 756 KF Coulometer). The levels of residual lithium and halide ions in the ionic liquid were estimated by inductively-coupled plasma mass spectrometry (Thermo Elemental X Series ICP-MS) and ion chromatography (Dionex DX 300 ion-chromatograph) respectively.

Thermal stability: Thermal gravimetric analysis (TGA) was performed on a thermal analysis system (TA Instruments, TGA 2050). An average sample weight of 10 mg was loaded into a platinum pan and heated at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ over a range of approximately $25 - 600\text{ }^{\circ}\text{C}$ under a slow stream of nitrogen gas. The decomposition temperature (T_{dec}) was obtained by using the TG-onset temperature which is the intersection of the baseline below the decomposition temperature with the tangent to the slope of mass loss in the TGA experiment.

Phase transition: Calorimetric measurements were performed on a differential scanning calorimeter (TA instruments, DSC 2910). The temperature calibration was performed with the following standard samples: cyclopentane (solid–solid transitions: -151.16 and $-135.06\text{ }^{\circ}\text{C}$), n-heptane (-90.56), n-octane ($-56.76\text{ }^{\circ}\text{C}$), cyclohexane (solid–solid transition: $-87.06\text{ }^{\circ}\text{C}$; melting point: 6.54), n-decane ($-29.64\text{ }^{\circ}\text{C}$), n-dodecane ($-9.65\text{ }^{\circ}\text{C}$), water ($0\text{ }^{\circ}\text{C}$), n-octadecane ($28.24\text{ }^{\circ}\text{C}$) p-nitrotoluene (melting point: $51.64\text{ }^{\circ}\text{C}$), hexatriacontan (solid–solid transitions: 72.14 and $73.94\text{ }^{\circ}\text{C}$; melting point: $75.94\text{ }^{\circ}\text{C}$) and indium (melting point: $156.6\text{ }^{\circ}\text{C}$) used as reference. An average weight of $1-5\text{ mg}$ of each sample was hermetically sealed in an aluminum pan (glove box) and cooled to $-140\text{ }^{\circ}\text{C}$ then heated again at a rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$, under a flow of helium gas.

Viscosity and specific conductivity: The dynamic viscosity (η) was examined by an automated micro viscometer (Anton Parr AMVn) at $40\text{ }^{\circ}\text{C}$. The specific conductivity (σ) was measured with a conductivity meter (Agilent precision LCR meter 4284A) coupled with a PC controlled temperature controller (Eurotherm) in a custom made glass cell in combination with a custom made electrode. The glass cell/electrode combination was housed in the centre of a custom made brass block next to a thermocouple. Data were collected at each step of individual temperature programs using a temperature equilibration time of 1 min and a temperature deviation of $\Delta T = 0.5\text{ }^{\circ}\text{C}$. The cell/electrode combination was calibrated prior to each measurement over a temperature range of 20 to $70\text{ }^{\circ}\text{C}$ with 0.01M KCl solutions. The assembly and method was validated by measuring 1-butyl-4-methyl pyrrolidinium bis(trifluoromethanesulfonyl)amide (Merck, high purity grade) and comparing results with reported values. The data were recorded over a frequency range of 20 to $1,000,000\text{ Hz}$ between 20 and $135\text{ }^{\circ}\text{C}$.

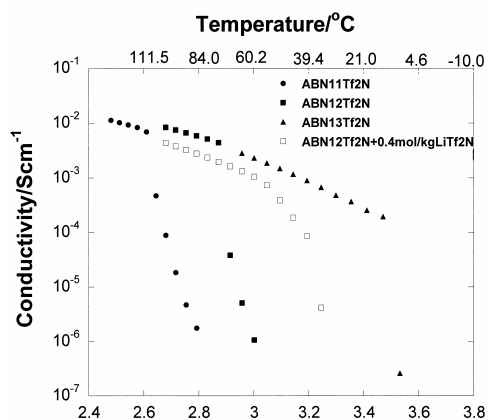


Fig. S1 Conductivity vs temperature for **4a-c** and **4b** + $0.4\text{ mol kg}^{-1}\text{ LiTf}_2\text{N}$.

Electrochemical measurements: Linear-sweep voltammetry was performed (dry box) on potentiostats Autolab PGSTAT 302 and μ Autolab Type III respectively, interfaced and monitored with a PC. The standard three-electrode configuration consisted of: a Pt electrode (surface area: $3 \cdot 10^{-3} \text{ cm}^2$, determined from the Randles-Sevcik equation, using $D = 2.3 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and 5 mM ferrocene/0.1M tetrabutylammonium hexafluorophosphate) served as the working electrode, a Pt wire was used as the counterelectrode, and the reference electrode was a Ag wire immersed in 10 mM solution of AgTf in 1-butyl-3-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide and contained in a teflon tube with a glass sinter tip. All potentials are given versus the Ag/AgTf redox couple as the internal standard in each salt. The data for each salt were collected in the liquid state; prior to each scan the working electrode was washed with (i) methanol, (ii) deionised water in presence of $3 \mu\text{m}$ alumina, (iv) polished with 0.3 to $1 \mu\text{m}$ alumina, (v) rinsed with HPLC grade acetone and finally dried. The cathodic and anodic limits were arbitrarily defined as the potential at which the current density reached $0.8 \cdot 10^{-3} \text{ A cm}^{-2}$. For lithium electrodeposition, a Pt and Cu electrode were used as working electrodes, and LiTf_2N dissolved in the IL (0.4 mol kg^{-1}) was used as the source of Li^+ ion.

Synthetic procedures

Sublimation of 3-azabicyclo[3.2.2]nonane 1. The sticky brownish material was placed into a round bottom Schlenk flask equipped with tube which had an outer mantle fitted in the middle part and a hose adapter at the top part. The mantle was filled with dry ice, the flask immersed into an oil bath and the sublimation apparatus connected to a high-vacuum Schlenk line. Sublimation was carried out at 55 to 65 °C and 1 to $5 \cdot 10^{-2}$ mbar when a crystalline white material condensed in the lower part of the glass tube. Under these conditions 10 to 20 g lots of crude 3-ABN could be sublimed within one day. Most of the material was removed from the apparatus mechanically by means of a long spatula and difficult to remove remainders were rinsed off with methanol which was subsequently allowed to evaporate in a fume cupboard (rotary evaporation is more difficult because the water bath temperature must be kept below the sublimation temperature at a given vacuum, e.g. 30 /~20 mbar). Typical recoveries from the commercial material after exhaustive sublimation were in the order of 70-80 wt%. The pure compound is best stored under an inert atmosphere at 4 °C (fridge) to prevent the development of a yellow brown colour over time.

General procedure for the synthesis of 3-alkyl-3-azabicyclo[3.2.2]nonanes 2a-d. A mixture of 1-butyl-4-methylimidazolium hexafluorophosphate, 3-ABN, KOH (2 equiv.) and the appropriate alkyl iodide or alkyl bromide (1.1 equiv.) was stirred in a Schlenk flask at 25 to 60 °C for 24 to 48h. The amine product was removed from the reaction mixture by extraction into diethyl ether or ethyl acetate. The obtained products are usually of acceptable purity but further purification can be achieved by flash chromatography through a plug of activated alumina giving faint yellow oils in 70 – 75% yield.

Further details of the synthesis will be reported in a separate paper.

3-methyl-3-azabicyclo[3.2.2]nonane 2a

δ_{H} (200 MHz; $\text{d}_3\text{-CDCl}_3$): 1.58 (4 H, m, ring- CH_2), 1.75 (4 H, m, ring- CH_2), 1.85 (2H, m, bridgehead- CH), 2.29 (3H, s, N- CH_3), 2.55 (4H, "d", ring- $(\text{CH}_2)_2\text{N}$); δ_{C} (200 MHz; $\text{d}_3\text{-CDCl}_3$): 25.78 (ring CH_2), 30.27 (bridgehead CH), 46.65 (N- CH_3) and 65.67 (N- CH_2 -ring).

3-ethyl-3-azabicyclo[3.2.2]nonane 2b

δ_{H} (200 MHz; $\text{d}_3\text{-CDCl}_3$): 1.03 (3 H, t, J 7 Hz, $-\text{CH}_2\text{CH}_3$), 1.4 to 1.9 (10 H, m, ring- CH), 2.43 (2H, q, J 7 Hz, N- CH_2CH_3), 2.54 (4H, "d", J 4.4 Hz, ring- $(\text{CH}_2)_2\text{N}$); δ_{C} (200 MHz; $\text{d}_3\text{-CDCl}_3$): 12.44 ($-\text{CH}_2\text{CH}_3$), 25.74 (ring CH_2), 30.33 (bridgehead CH), 52.11 (N- CH_2CH_3) and 62.29 (N- CH_2 -ring); elemental analysis found: C, 77.85 H, 7.41 N, 10.39%. calcd. for $\text{C}_{10}\text{H}_{19}\text{N}$: C, 78.37; H, 12.50; N, 9.14%.

3-propyl-3-azabicyclo[3.2.2]nonane 2c

δ_{H} (200 MHz; $\text{d}_3\text{-CDCl}_3$): 0.88 (3 H, t, J 7.2 Hz, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.3 to 1.9 (12 H, m, ring- CH and side chain $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.30 (2H, t/d, J 7 Hz, N- $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.53 (4H, "d", J 4.2 Hz, ring- $(\text{CH}_2)_2\text{N}$); δ_{C} (200 MHz; $\text{d}_3\text{-CDCl}_3$): 14.02 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.63 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 25.71 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.44 (ring CH_2), 30.38 (bridgehead CH), 58.03 (N- $\text{CH}_2\text{CH}_2\text{CH}_3$) and 62.80 (N- CH_2 -ring).

3-butyl-3-azabicyclo[3.2.2]nonane 2d

δ_{H} (200 MHz; $\text{d}_3\text{-CDCl}_3$): 0.91 (3 H, t, J 7 Hz, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.60 to 2.0 (14 H, m, ring- CH and side chain $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.36 (2H, t/d, J 7 Hz, N- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.54 (4H, "d", J 4.2 Hz, N- CH_2 -ring); δ_{C} (200 MHz; $\text{d}_3\text{-CDCl}_3$): 14.02 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.63 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 25.71 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 29.44 (ring CH_2), 30.38 (bridgehead CH), 58.03 (N- $\text{CH}_2\text{CH}_2\text{CH}_3$) and 62.80 (N- CH_2 -ring).

General procedure for the synthesis of 3, 3-dialkyl-3-azoniabicyclo[3.2.2]nonane iodides 3a-d. Alkylamines **2** were placed in a Schlenk flask and dissolved in ~10 volumes of acetonitrile. Methyl iodide (1.1 equiv.) was slowly added via a dropping funnel under good stirring. The reaction mixture was subsequently heated at 40 °C for 48h after which time the product was precipitated by the slow addition of ethyl acetate (typically approximately the same volume as reaction solvent) under good stirring. The white solid product was collected on a sinter, washed with ethyl acetate /acetonitrile (2:1) followed by a final wash with ethyl acetate and dried under vacuum at 40 °C. At this stage the products are obtained in good purity and yields of 75 to 85%. High purity crystalline materials are obtained by recrystallisation from ethyl acetate /acetonitrile (2:1 to 3:2) mixtures with 75 – 80% recovery.

3, 3-dimethyl-3-azoniabicyclo[3.2.2]nonaneium iodide 3a

δ_{H} (200 MHz; $\text{d}_6\text{-DMSO}$): 1.7(4 H, m, ring- CH_2), 1.90 (4 H, m, ring- CH_2), 2.08 (2H, m, ring- CH), 3.25 (6H, s, N- CH_3), 3.64 (4H, d, J 3.6 Hz N- CH_2 -ring); m/z (+ES): 154 (100%, A+) and 435 (7%, A2B+ cluster); m/z (-ES): 126.9 (100%, B-), 408 (63%, AB2-cluster).

3-ethyl-3-methyl-3-azoniabicyclo[3.2.2]nonaneium iodide 3b (mp/dec. 248 °C)
 δ_{H} (200 MHz; d_6 -DMSO): 1.29 (3 H, t, J 7.2 Hz, $-\text{CH}_2\text{CH}_3$), 1.69 to 2.1 (10 H, m, ring-CH), 3.18 (3H, s, N- CH_3), 3.57 (6H, m, ring- $(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_3)$ -sidechain); δ_{C} (200 MHz; d_6 -DMSO): 8.90 ($-\text{CH}_2\text{CH}_3$), 23.61 and 26.11 (ring CH_2), 29.47 (bridgehead CH), 53.18 (N- CH_3), 65.79 (N- CH_2CH_3) and 70.15 (N- CH_2 -ring); m/z (+ES): 168 (100%, A+) and 463 (2%, A2B+ cluster); m/z (-ES): 126.9 (100%, B-), 422 (2%, AB2- cluster); elemental analysis found: C, 44.79 H, 7.41 N, 4.48%. calcd. for $\text{C}_{11}\text{H}_{22}\text{IN}$: C, 44.75; H, 7.51; N, 4.74%.

3-propyl-3-methyl-3-azoniabicyclo[3.2.2]nonaneium iodide 3c (mp/dec. 217 °C)
 δ_{H} (200 MHz; d_6 -DMSO): 0.9 (3 H, t, J 7.2 Hz, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.65 to 2.1 (12 H, m, ring-CH and side chain - $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.21 (3H, s, N- CH_3), 3.35 to 3.8 (6H, m, ring- $(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{CH}_3)$ -sidechain); δ_{C} (200 MHz; d_6 -DMSO): 10.94 ($-\text{CH}_2\text{CH}_2\text{CH}_3$), 16.31 ($-\text{CH}_2\text{CH}_2\text{CH}_3$) 23.38 and 26.32 (ring CH_2), 29.56 (bridgehead CH), 53.73 (N- CH_3), 70.72 (N- $\text{CH}_2\text{CH}_2\text{CH}_3$) and 71.89 (N- CH_2 -ring); m/z (+ES): 182.1 (100%, A+) and 491 (8%, A2B+ cluster); m/z (-ES): 126.9 (100%, B-), 435.9 (5%, AB2- cluster); elemental analysis found: C, 46.44 H, 7.84 N, 4.32%. calcd. for $\text{C}_{11}\text{H}_{22}\text{IN}$ C, 46.61; H, 7.82; N, 4.53%.

3-butyl-3-methyl-3-azoniabicyclo[3.2.2]nonaneium iodide 3d (mp/dec. 210 °C)
 δ_{H} (200 MHz; d_6 -DMSO): 0.95 (3 H, t, J 7.2 Hz, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.31 (2H, sx, J 7.4 Hz, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.60 to 2.2 (12 H, m, ring-CH and side chain $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.21 (3H, s, N- CH_3), 3.35 to 3.8 (6H, m, ring- $(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ -sidechain); δ_{C} (200 MHz; d_6 -DMSO): 13.97 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.63 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 23.4 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 24.65 and 26.31 (ring CH_2), 29.56 (bridgehead CH), 53.70 (N- CH_3), 70.36 (N- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) and 70.69 (N- CH_2 -ring); m/z (+ES): 196.1 (100%, A+) and 519.2 (5%, A2B+ cluster); m/z (-ES): 126.9 (100%, B-), 449.9 (3%, AB2- cluster); elemental analysis found: C, 48.13 H, 7.95 N, 4.13 %. Calcd. for $\text{C}_{13}\text{H}_{26}\text{IN}$: C, 48.30; H, 8.11; N, 4.33%.

General procedure for the synthesis of 3, 3-dialkyl-3-azoniabicyclo[3.2.2]nonaneium bis(trifluoromethanesulfonyl)amides 4a-d. The precursors **3** were placed in a Schlenk flask and dissolved in the minimum amount of water. A solution of LiTf_2N (1.05 equiv) in water (1:1 w/v) was added slowly via a dropping funnel upon which immediate separation of the product occurred. In the case of the solid materials 4a and 4b extra water may be added during the addition of LiTf_2N in order to maintain stirring. The reaction mixture was stirred for 0.5 to 1h at ambient temperature.

Isolation procedure A:

The reaction mixture was allowed to settle and the aqueous phase was decanted. The crude product was repeatedly extracted (8 – 10 extractions, AgNO_3 test) with water using contact times of at least 20 min. In case of 4a and 4b which are somewhat water soluble, concentration of the aqueous phase on a rotary evaporator resulted in precipitation of additional product. The bulk of the water was removed from the product on a rotary evaporator (45 – 50 °C /10 – 20 mbar) and the resulting solid was dried at 45 – 50 °C and 1 – 5 10^{-2} mbar for a minimum of 2 days.

Isolation procedure B:

Dichloromethane was added, the aqueous layer separated and the dichloromethane layer repeatedly washed with water (AgNO₃ test). The solvent was removed on a rotary evaporator and the resulting solid dried at 45 – 50 °C and 1 – 5 10⁻² mbar for a minimum of 2 days.

In the event that the isolated products were slightly yellow an extra purification step was conducted prior to final drying under high vacuum. The solution of the product in acetonitrile was stirred in presence of 5 wt% activated carbon over night. The mixture was filtered through a 0.5 μm membrane filter and the solvent removed on a rotary evaporator. The products were stored in a drying tube against lithium and kept in an argon filled glove box. Yield 75 – 80%.

3, 3-dimethyl-3-azoniabicyclo[3.2.2]nonaneium bis(trifluoromethylsulfonyl)amide 4a
(mp 105 °C)

δ_H (200 MHz; d₆-DMSO): 1.72(4 H, m, ring-CH₂), 1.89 (4 H, m, ring-CH₂), 2.09 (2H, m, ring-CH), 3.24 (6H, s, N-CH₃), 3.63 (4H, d, *J* 3.6 Hz, N-CH₂-ring); δ_C (200 MHz; d₆-DMSO): 24.78 (ring CH₂), 29.52 (bridgehead CH), 58.42 (N-CH₃), 72.34 (N-CH₂-ring); δ_F (200 MHz; d₆-DMSO): -79.18 (CF₃); *m/z* (+ES): 154 (100%, A+); *m/z* (-ES): 280 (100%, B-); elemental analysis found: C, 33.42 H, 4.70 N, 6.48%. Calcd. for C₁₂H₂₀F₆N₂O₄S₂: C, 33.18; H, 4.64; N, 6.45%; (isolation procedure A) residual Li⁺ (ICP-MS): 16 ppm; residual I⁻ (IC): 0.1%; (isolation procedure B) residual Li⁺ (ICP-MS): 1 ppm; residual I⁻ and Cl⁻ (IC): 65 and <25 ppm respectively.

3-ethyl-3-methyl-3-azoniabicyclo[3.2.2]nonaneium bis(trifluoromethylsulfonyl)-amide 4b (mp 73 °C)

δ_H (200 MHz; d₆-DMSO): 1.29 (3 H, t, *J* 7.2 Hz, -CH₂CH₃), 1.69 to 2.1 (10 H, m, ring-CH), 3.17 (3H, s, N-CH₃), 3.53 (6H, m, ring-(CH₂)₂N(CH₂CH₃)-sidechain); δ_C (200 MHz; d₆-DMSO): 8.90 (-CH₂CH₃), 23.61 and 26.11 (ring CH₂), 29.47 (bridgehead CH), 53.18 (N-CH₃), 65.79 (N-CH₂CH₃) and 70.15 (N-CH₂-ring), 119.4 (q, CF₃); δ_F (200 MHz; d₆-DMSO): -79.20 (CF₃); *m/z* (+ES): 168 (100%, A+) and 616.5 (3%, A2B+ cluster); *m/z* (-ES): 279.9 (100%, B-); elemental analysis found: 6.25 C, 34.98 H, 5.09 N, 6.31%. Calcd. for C₁₃H₂₂F₆N₂O₄S₂: C, 34.82; H, 4.94; N, 6.25%; (isolation procedure A) residual Li⁺ (ICP-MS): 12 ppm; residual I⁻ (IC): 0.04%; residual water <10 ppm; (isolation procedure B) residual Li⁺ (ICP-MS): 2 ppm; residual I⁻ and Cl⁻ (IC): 14 and 16 ppm respectively; residual water <10 ppm.

3-propyl-3-methyl-3-azoniabicyclo[3.2.2]nonaneium bis(trifluoromethylsulfonyl)-amide 4c (mp -1 °C)

(isolation procedure B) δ_H (200 MHz; d₆-DMSO): 0.91 (3 H, t, *J* 7.2 Hz, -CH₂CH₂CH₃), 1.6 to 2.1 (12 H, m, ring-CH and side chain -CH₂CH₂CH₃), 3.20 (3H, s, N-CH₃), 3.33 (2H, m, (N-CH₂CH₂CH₃), 3.59 (4H, m, (N-CH₂-ring); δ_C (200 MHz; d₆-DMSO): 10.87 (-CH₂CH₂CH₃), 16.26 (-CH₂CH₂CH₃) 23.35 and 26.28 (ring CH₂), 29.57 (bridgehead CH), 53.69 (N-CH₃), 70.76 (N-CH₂CH₂CH₃) and 72.01 (N-CH₂-ring), 120.3 (q, CF₃); δ_F (200 MHz; d₆-DMSO): -79.23 (CF₃); *m/z* (+ES): 181.9 (100%, A+) and 644.1 (15%, A2B+ cluster); *m/z* (-ES): 279.9 (100%, B-); elemental analysis found: C, 36.31 H, 5.36

N, 6.11%. Calcd. for $C_{14}H_{24}F_6N_2O_4S_2$: C, 36.36; H, 5.23; N, 6.06%; (isolation procedure B) residual Li^+ (ICP-MS): 0.2 ppm; residual Γ (IC): 9 ppm; residual water: 26 ppm.

3-butyl-3-methyl-3-azoniabicyclo[3.2.2]nonaneium bis(trifluoromethylsulfonyl)-amide 4d (mp 35 °C)

δ_H (200 MHz; d_6 -DMSO): 0.93 (3 H, t, J 7.0 Hz, $-CH_2CH_2CH_2CH_3$), 1.31 (2H, sx, J 7.4 Hz, $-CH_2CH_2CH_2CH_3$), 1.50 to 2.1 (12 H, m, ring-CH and side chain $-CH_2CH_2CH_2CH_3$), 3.18 (3H, s, N- CH_3), 3.35 (2H, m, N- CH_2 -sidechain), 3.58 (4H, m, N- CH_2 -ring); δ_C (200 MHz; d_6 -DMSO): 13.86 ($-CH_2CH_2CH_2CH_3$), 19.62 ($-CH_2CH_2CH_2CH_3$), 23.36 ($-CH_2CH_2CH_2CH_3$), 24.62 and 26.28 (ring CH_2), 29.57 (bridgehead CH), 53.65 (N- CH_3), 70.46 (N- $CH_2CH_2CH_3$) and 70.73 (N- CH_2 -ring), 119.5 (q, CF_3); δ_F (200 MHz; d_6 -DMSO): -79.19 (CF_3); m/z (+ES): 196.1 (100%, A+) and 672.2 (8%, A2B+ cluster); m/z (-ES): 279.9 (100%, B-); elemental analysis found: C, 37.97 H, 5.61 N, 5.55%. Calcd. for $C_{15}H_{26}F_6N_2O_4S_2$: C, 37.81; H, 5.50; N, 5.88%; (isolation procedure B) residual Li^+ (ICP-MS): 37 ppm; residual Γ and Cl^- (IC): 10 and <25 ppm respectively.

Preparation of the 4b + 0.4 mol kg⁻¹ LiTf₂N mixture:

4b (3g, 6.7 mmol) and LiTf₂N (0.384g, 1.34 mmol) was weighed into a sample vial equipped with a stir bar. The solid mixture was slowly heated to 75 °C and the resulting clear melt stirred over night at this temperature. Upon cooling to ambient temperature the solution settled into a wax-like solid.

DSC measurement:

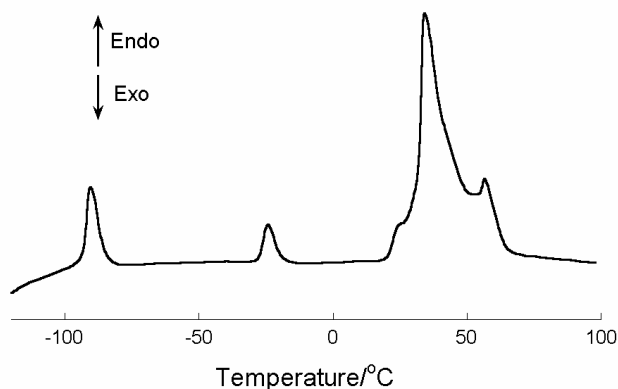


Fig. S2 differential scanning calorimeter thermogram of 4b + 0.4 mol kg⁻¹ LiTf₂N recorded at a heating rate of 10 °C min⁻¹ after cooling from room temperature to 120 °C.

Table S1 Selected bond lengths, bond angles and dihedral angles calculated (Ab-initio simulation program Gaussian 03 using B3LYP/6-311++G**) ¹ for the cation 3-ABN12 shown in Fig 1.

	Bond distance, Å		Bond Angle, °		Dihedral Angle, °
N-1C	1.508	21C-N-22C	114.798	9C-21C-N-1C	85.135
N-21C	1.532	1C-N-28C	104.809	6C-22C-N-1C	-85.138
N-22C	1.532	1C-N-21C	109.389	9C-21C-N-22C	-38.252
N-28C	1.539	1C-N-22C	109.389	6C-22C-N-21C	38.249
6C-21C	1.539	28C-N-21C	108.991	6C-7C-8C-9C	-0.003
9C-22C	1.539	28C-N-22C	108.990	5C-6C-7C-8C	-54.308
6C-5C	1.537	N-28C-31C	117.842		
6C-7C	1.537	N-22C-6C	119.355		
9C-10C	1.537	N21C-9C	119.355		
9C-8C	1.537	5C-6C-7C	109.772		
5C-10C	1.553	8C-9C-10C	109.772		
7C-8C	1.547	6C-5C-10	112.258		
		6C-7C-8C	112.389		
		9C-10C-5C	112.258		
		9C-8C-7C	112.389		

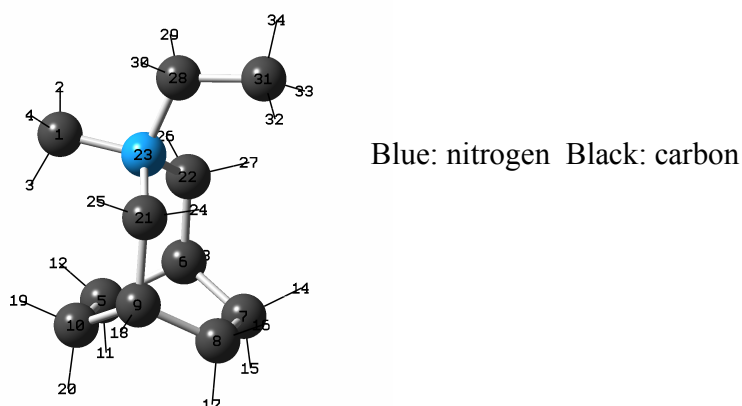


Fig S3 Atom labelling for the cation 3-ABN12

¹ Gaussian 03, Revision D.01,
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