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Ionic liquids and plastic crystals with a symmetrical pyrrolidinium cation

Ruhamah Yunis,‡ Timothy W. Newbiggin‡, Anthony F. Hollenkamp§ and Jennifer M. Pringle‡∗

Solid and liquid salts utilising the N-methyl-N-alkyl pyrrolidinium cation, [C₄mepy]⁺, and their use in electrochemical devices, are well established. However, new materials with enhanced properties, such as higher conductivity, lower viscosity or more favourable thermal phase behaviour, are still required. Here we report the synthesis and characterisation of new ionic liquids and plastic crystals using the N,N-diethylpyrrolidinium cation ([C₄epyr]⁺) with six different anions. With the fluorosulfonyl(trifluoromethanesulfonyl)imide ([FTFSI]⁻) and dicyanamide ([DCA]) anions, room temperature ionic liquids with low viscosity are formed. With the bis(trifluoromethanesulfonyl)imide ([NTf₂]⁻), bis(fluorosulfonyl)imide ([FSI]⁻) hexafluorophosphate ([PF₆]⁻) and tetrafluoroborate ([BF₄]⁻) anions, organic ionic plastic crystals are produced. Of the new solid salts, [C₄epyr][FSI] has the highest conductivity, higher than the well-established methyl-substituted analogue, giving 1.9×10⁻⁵ S cm⁻¹ at 30 °C. Thermal analysis, conductivity and the Walden relationship are used to compare the new N,N-diethylpyrrolidinium salts across the different anions and with some previously reported N-methyl-N-alkylpyrrolidinium salts.

Introduction

There is increasing demand to replace the current flammable liquid battery electrolytes with less volatile or solidified materials, particularly for applications such as electric vehicles where safety is paramount.1, 2 Ionic liquids (ILs) and organic ionic plastic crystals (OIPCs) generally show high decomposition temperatures, non-volatility and negligible vapour pressure, making them potentially safer electrolytes for applications such as batteries, fuel cells and solar cells.3, 4 Both materials are composed entirely of ions; ILs that are liquid at room temperature are often referred to as room temperature ionic liquids (RTILs), while OIPCs are a specific type of salt structurally analogous to ILs but solid at room temperature and with significant disorder within the crystal lattice.5, 6 The term “plastic crystal”, described in detail by Timmermans in the 1960s with respect to the molecular species,7 indicates that these materials have rotational, translational and/or conformational motions that allow them to flow under stress. The most plastic phase of OIPCs, denoted as phase I (the phase immediately before the melt), is reached via one or more solid-solid phase transition. In electrochemical applications, the plasticity of OIPCs can provide better contact with electrodes during volume change compared to brittle solid electrolytes, while also preventing the leakage problems associated with liquid electrolytes. OIPCs can be used to produce relatively conductive solid-state electrolytes, particularly when doped with an additional salt, e.g. lithium salts for use in Li batteries,6, 10 or sodium salts for Na batteries,11 and so forth depending on the target ion required for the application. Examples of high conductivity OIPCs include diethyl(methyl)(isobutyl)phosphonium thiocyanate, [P₃tetra][SCN], with a solid state conductivity approaching 10⁻⁵ S cm⁻¹ at 40 °C,12 and the tetraethylphosphonium fluoro hydrogenate salt, [P₆tetra][FH]F, with a conductivity of 3x10⁻⁵ S cm⁻¹ at 25 °C (phase II).13 Although ILs have been known for more than 100 years, and OIPCs for more than a decade, the exact structure-property relationships that define the thermal and transport behaviour of these salts are still poorly understood. In comparison to the plethora of cations and anions previously explored to make ionic liquids, the range of known OIPC-forming ions is significantly smaller. The most commonly used cations include pyrrolidinium, tetraalkyl ammonium and phosphoniums, combined with anions such as dicyanamide ([DCA]⁻), bis(trifluoromethanesulfonyl)imide ([NTf₂]⁻), hexafluorophosphate ([PF₆]⁻), bis(fluorosulfonyl)imide ([FSI]⁻)14 and tetrafluoroborate ([BF₄]⁻).12, 15, 16, 17 Alternative OIPC cations include trialkylsulfonium,18, 19 and pyrazolium.20, 21 Relatively new anions include (fluorosulfonyl)(trifluoromethanesulfonyl)imide ([FTFSI]⁻),22 and the six-membered cyclic N(SO₂CF₂)₂CF₂ anion.23 Many combinations of these cations and anions form RTILs; to make OIPCs, cations substituted by relatively short alkyl chains are normally used, which elevates the melting point to above room temperature and can lower the energy required for rotational disorder of the cation. Thus, for example, the

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majority of research into pyrrolidinium-based salts has focused previously on cations with one methyl substituent and either methyl or ethyl as the second substituent, i.e. the \( \text{[C}_{n}\text{mpyr}]^+ \) cations where \( n = 1 \) or 2. For example, \( \text{[C}_{2}\text{mpyr}][\text{FSI}] \) is a plastic crystal with two solid-solid phase transitions, at \(-72 \, ^\circ\text{C}\) and \(-22 \, ^\circ\text{C}\), and a melt at 203 \, ^\circ\text{C}.\textsuperscript{14} This OIPC has recently been demonstrated to be a very promising solid-state electrolyte for lithium batteries, achieving good stability and cycling performance.\textsuperscript{24, 25}

As an alternative to the methyl-substituted pyrrolidinium salt, it is proposed that increased ion symmetry through use of two ethyl substituents could lead to increased crystal packing efficiency (thus higher melting points) while at the same time enabling rotational disorder of the cation. Both of these effects are predicted to encourage the formation of rotationally disordered OIPCs and hence our interest in the lesser-used \( \text{[C}_{2}\text{epyr}] \) cation. Here we have investigated the synthesis of highly conductive ILs and OIPCs combining the \( \text{[C}_{2}\text{epyr}]^+ \) cation with a range of different anions. These salts were prepared by anion metathesis of \( \text{[C}_{2}\text{epyr}]\text{Br} \) with the respective lithium, potassium or silver salts of the anion. The \( \text{[C}_{2}\text{epyr}]\text{Cl} \) salt\textsuperscript{26} was first synthesized in 1944, and later \( \text{[C}_{2}\text{epyr}]\text{Br} \textsuperscript{27, 28} \) and \( \text{[C}_{2}\text{epyr}] \textsuperscript{29, 30} \) were reported. There are some prior reports on the use of this cation for synthesis of salts with more charge diffuse anions, as summarised below, but without any thorough investigation of the physical and thermal properties. Synthesis of the \( \text{[C}_{2}\text{epyr}]\text{BF}_4 \) salt by anion exchange of the bromide salt in the presence of hydrogen peroxide and tetrafluoroboric acid was previously reported, plus the electrochemical characterisation of this salt in a solution of propylene carbonate.\textsuperscript{31} The \( \text{[C}_{2}\text{epyr}]\text{(FHF}_{2})\text{F} \) salt has been shown to exhibit two solid-solid transitions before melting at 358K, indicative of plastic crystal behaviour.\textsuperscript{27} \( \text{[C}_{2}\text{epyr}]\text{[NTf}_2 \) has also been synthesised by microwave irradiation of equimolar quantities of diethylamine and 1,4-dibromobutane in the presence of \( \text{K}_2\text{CO}_3 \) at 120 \, ^\circ\text{C}, followed by anion exchange with Li\text{NTf}_2. The characterisation reported was the melting point and decomposition temperatures, at 92-94 \, ^\circ\text{C} \text{ and 317 \, ^\circ\text{C}, respectively.}\textsuperscript{32}

Here we report the thermal behaviour of salts based on the Figure 2. Differential scanning calorimetry (DSC) traces for the \( \text{[C}_{2}\text{epyr}] \) salts (a) RTILs, and (b) OIPCs. Y-axis scaled for comparison.

\( \text{[C}_{2}\text{epyr}] \) cation with anions \( \text{[DCA]}^+, \text{[NTf}_2]^+, \text{[FSI]}^+, \text{[PF}_6]^-, \text{[BF}_4]^-, \text{and [FTFSI]}^- \). These anions were chosen in order to utilise the predicted benefits of the relatively small and symmetrical cation, with respect to forming rotationally disordered OIPCs or low-viscosity ILs, and to probe the influence of different anions on the thermal and physical properties of the new salts.

Results and discussion

Thermal properties

The \( N,N\text{-diethylpyrrolidinium} \) salts were synthesized in good yield by the direct reaction of \( N\text{-ethylpyrrolidine} \) with ethylbromide, as shown in Figure 1. The thermal behaviour of the synthesized salts, analysed by differential scanning calorimetry (DSC), is shown in Figure 2 and Table 1. There is a clear dependence of thermal behaviour on the nature of the
anion with, for example, melting points ranging from below
lower melting analogue; this is consistent with the relatively

room temperature to over 100 °C. Two new RTILs have been
formed through use of the symmetrical cation: [C₆epy][FFTSI]
shows two solid-solid phase transitions at low temperature
before melting at 8 °C, and [C₆epy][DCA] melts at 9 °C.
A number of the salts show multiple solid-solid phase
transitions, indicative of plastic crystal behaviour, by
convention the highest temperature phase is denoted as phase
I, with lower temperature phases denoted as phase II, III and
so on. Such multiple solid phases are understood to arise from
motions of both the cation and anion, which become
increasingly more complex as the temperature is increased.
Both [C₆epy][BF₄] and [C₆epy][PF₆] show one solid-solid
phase transition (phase II to phase I), at 53 °C and -54 °C
respectively, before a combined melt/decomposition (as
evidenced by discoulouration of the samples after the DSC
analysis) at around 300 °C. Fewer solid-solid phase transitions
are observed in the new ethyl salts than in the methyl
analogues [C₅mpyr][BF₄] and [C₅mpyr][PF₆]. While this may
be consistent with reduced degrees of freedom of the more
symmetrical cation, the OIPC phase behaviour reflects the
combined motions of both types of ions and thus the
rotational and translation motion of the anion must also be
taken into consideration when understanding the OIPC phase
behaviour. This makes isolating the effect of changing the
anion or cation very complex. For example, the
tetraalkylammonium and phosphonium BF₄ and PF₆ salts
characterised by Matsumoto et. al. shows no single anion
trend across the range of different cations. The same is true
for comparison of [C₅mpyr][BF₄] and [PF₆] salts, where n = 1-3.
Further analysis of the [C₆epy] salts, with techniques such as
solid state NMR and x-ray diffraction, will be used to
further understand the complex molecular motions within the
different materials.
For the use of OIPCs as solid-state electrolytes it is most
advantageous to have the material in phase I over the
temperature range of application as this is the most
conductive phase. This is the case for the PF₆ and BF₄ salts
reported here. However, the relatively high melting
temperature is not ideal as it suggests less disorder in the
material at ambient temperature than might be present in a
low conductivity of these materials, as discussed below.
More advantageous thermal behaviour is displayed by the
[C₆epy][NTf₂] and [C₆epy][FSI] salts. The [C₆epy][NTf₂]
exhibits three solid-solid phase transitions, which is beneficial
for increasing the disorder of the salt, before melting at 98 °C.
An interesting feature of this salt is the unusual plateau region
immediately following the first solid-solid phase transition,
 provisionally labelled phase III. We have recently observed
a similar feature in a phosphonium OIPC with the FSI- anion
(triethyl(methyl)phosphonium bis(fluorosulfonylimide). As
here, the feature appeared immediately after a solid-solid
phase transition, and spanned between -55 to -30 °C. This
feature was assigned to a second-order displacive phase
transition, attributed to the FSI anion undergoing progressive
transformation from a less energetically favourable trans
orientation to cis and assisted by cooperative motion of the
cation. The NTf₂ anion can also exist in a number of different
conformers. For example, the DSC trace of [C₆epy][NTf₂]
shows multiple solid-solid transitions, including one that
appears to be second order, and thus it is proposed that the
unusual feature in the DSC trace of [C₆epy][NTf₂] is again
primarily the result of conversion between the two conformers
of the anion. Work is underway to analyse further this low
temperature feature.
Of the new OIPCs reported here, the [C₆epy][FSI] salt displays
what appears to be the most ideal thermal behaviour for
practical application. It has a large low-temperature solid-solid
phase transition, at -35 °C, and melts at 131 °C; above the
temperature range of most applications but arguably low
enough to ensure that the material is relatively disordered at
ambient temperature. This significant disorder in phase I is
consistent with the high conductivity, discussed further below.
This salt also has the lowest entropy of melt of the series, at
only 9 J K⁻¹ mol⁻¹. A low entropy of fusion of < 20 J K⁻¹ mol⁻¹ is
consistent with Timmermans’ criterion for plastic crystal
behaviour for molecular plastic crystals, although for OIPCs
plasticity has been observed even with higher entropies of melt.7
Comparison of the melting points of the new [C₆epy] salts
with those of the methyl-substituted analogues reported

![Table 1: Thermal data of the pyrrolidinium salts determined by DSC. (FTFSI), (FSI), (DCA) and (NTf₂); transitions taken from second heating cycle; (BF₄) and (PF₆); transitions taken from first heating cycle to avoid any contamination of the sample through decomposition. *Sample decomposed before clear melting point. Onset temperatures are reported for all transitions. Melting points were also confirmed using visual melting point apparatus.](image)

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<td>ΔS / J K⁻¹ mol⁻¹ ± 10%</td>
<td>T / °C ± 1</td>
<td>ΔS / J K⁻¹ mol⁻¹ ± 10%</td>
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<tr>
<td>[C₆epy][FTFSI]</td>
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<td>-69</td>
<td>13</td>
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<tr>
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<td>13</td>
<td>-45</td>
<td>2</td>
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<tr>
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<td>33</td>
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previously highlights the complexity of factors that dictate this property. The melting point of [C₂epy]
DCA is higher than that of [C₂mpy][DCA] (9 °C and -10 °C respectively), and similarly the melting point of [C₂epy][NTf₂] is a little higher than that of

<table>
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<th>Eₐ / kJ mol⁻¹</th>
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<td>[C₂epy][DCA]</td>
<td>1.8 × 10⁻¹</td>
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<tr>
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<td>8.5 × 10⁻¹</td>
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<tr>
<td>[C₂epy][FSI]</td>
<td>1.9 × 10⁻¹</td>
<td>-</td>
</tr>
<tr>
<td>[C₂epy][PF₆]</td>
<td>3.6 × 10⁻¹</td>
<td>-</td>
</tr>
<tr>
<td>[C₂epy][BF₄]</td>
<td>1.7 × 10⁻¹</td>
<td>-</td>
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Table 2: Conductivity and activation energies (Eₐ) for the new [C₂epy] salts, and the viscosity for the two RTILs, at 30 °C.

[C₂mpy][NTf₂] (98 °C and 91 °C, respectively). However, moving to the ethyl substituent in the FSI family produces a surprising reduction in melting point: from 205 °C to 131 °C. This shows that it is not just the symmetry of the cation that affects the melting point – in addition, changes to the anion symmetry (such as possible differences in the relative populations of the different conformers), and different crystal packing of the anion conformer(s) with the new cation, may impact the melting temperature.

Transport properties

The conductivity of an electrolyte is a key parameter that determines its suitability for electrochemical applications, and achieving suitable transport properties is an ongoing challenge for solid-state electrolytes. The conductivities of OIPCs vary significantly, depending on the nature of the cation and anion that dictate the thermal and transport properties; both the cation and anion may be mobile and contribute to the total ionic conductivity. To allow their use in Li batteries, these materials are doped with Li salts, typically with the same anion as the OIPC, and this can give rise to orders of magnitude improvements in conductivity. Here, we compare the properties of neat salts to allow assessment of the effect of different anions on the transport of the pure OIPCs. However, it is important to note that to enable their practical application the OIPCs would be doped with target ions, thereby further increasing the conductivity.

The ionic conductivities of the new [C₂epy]⁺ salts, over a range of temperatures, are shown in Figure 3a and the activation energies for conduction given in Table 2. The solid-state conductivity is affected by both the nature of the anion and the thermal behaviour, with the highest conductivity observed in phase I (the phase prior to melting). The most conductive of the new solid salts is [C₂epy][FSI], at 1.9 × 10⁻⁵ S cm⁻¹ at 30 °C, which also displays the lowest activation energy. This is among the highest OIPC conductivity found to-date and higher than the previously reported [C₂mpy][FSI] (1.23 × 10⁻⁶ S cm⁻¹ at 25 °C). For the new solid salts, the conductivity is dominated by the Li⁺ diffusion, for all temperatures.

Figure 3: a) Conductivity of the [C₂epy] RTILs and OIPCs, and b) Walden Plot for the two RTILs, including comparison with three previously reported pyrrolidinium DCA salts.

It is also notably more conductive than the new [C₂epy][NTf₂] salt (Table 1). This is consistent with the higher entropy of fusion of the latter (Table 1), which indicates that the material is more ordered in phase I. Thus, the [C₂epy][FSI] appears to be very promising as a new electrolyte material.

When OIPCs are heated they undergo one or more solid-solid phase transitions, which are often correlated with a step-increase in conductivity as a result of the onset of additional rotational and/or translational motions. The new [C₂epy][BF₄] displays such behaviour, with a significant increase in conductivity at the phase II I transition at around 55 °C, and also a significant decrease in the activation energy of the conduction of the new solid [C₂epy][BF₄]. The conductivity of [C₂epy][BF₄] becomes higher than that of [C₂mpy][NTf₂] after the phase II I transition. As for the thermal behaviour, the effect on solid-state conductivity of changing from a methyl to an ethyl group on the cation is not predictable. For the NTf₂ and BF₄ salts, the
ambient temperature conductivity of the ethyl analogue is lower than the methyl analogue (the latter of which are ca. 10⁻⁸ and 10⁻⁷ S cm⁻¹ respectively). However, as noted above, use of the ethyl-substituted cation with the FSI anion results in significant enhancement in conductivity. The ionic conductivities of the new RTILs [C₆epy][DCA] and [C₆epy][FTFSI], over a range of temperatures, are shown in Figure 3a and the viscosity is given in Table 2. The [C₆epy][DCA] has a lower viscosity than [C₆epy][FTFSI], and both are relatively low compared to many other ionic liquids with larger or less charge-diffuse anions. Low viscosities have also been reported for other DCA-based RTILs, such as with the [C₆mpyr] [47, 48] and [C₆hympyr][DCA].[49] The ionic conductivity of [C₆epy][DCA] is higher than [C₆epy][FTFSI], attributed to the lower viscosity that results from the small, charge-diffuse anion, and also to less ion pairing in the former as shown by the Walden plot. The Walden rule correlates molar conductivity (log Λ) to viscosity (log η⁻¹), and standard KCI can be used as a reference (i.e. as an ideal salt with completely dissociated ions), shown in Figure 3b and equation 1.

\[
C = A \eta^\alpha
\]

Where C is Walden product, Λ is molar conductivity in S cm² mol⁻¹, η is viscosity in Pa s and α is the slope of the line.[44, 45] For ionic liquids, the Walden plot (Figure 3b) can be used to correlate molar conductivity with fluidity and thus study the “ionicity” - the extent of ion aggregation - of ionic liquids.[46, 47] Both of the new RTILs lie below the standard KCl line and both show increasing deviation from the ideal line as the temperature increases – this is most evident in the [C₆epy][DCA] salt. This effect, consistent with prior studies on other ILs,[46, 47] indicates an increase in ion aggregation with temperature. For comparison, the position of similar DCA salts on the Walden plot is also shown, derived using data from the literature. [C₆epy][DCA] (at 30 °C) and N-allyl-N-methylpyrrolidinium dicyanamide ([C₆hympyr][DCA] (at 25 °C) appear at similar positions on the Walden plot. In contrast, the position of [C₆epy][DCA] (at 30 °C) suggests more ion paring than in [C₆mpyr][DCA] or [C₆mpyr][DCA] (at 20 °C). Consistent with the lower conductivity, the [C₆epy][FTFSI] salt appears to be less dissociated than the DCA as it lies further from the ideal line. Nevertheless, for both of the new [C₆epy] RTILs the viscosity is sufficiently low and the conductivity sufficiently high to indicate their promise as solvents or electrolytes for a range of applications.

**Experimental**

**Materials and methods**

N-Ethylpyrrolidine (97%, Sigma Aldrich, Australia), bromoethane (98%, Sigma Aldrich, Australia), lithium bis(trifluoromethanesulfonyl)imide (>99.9%, Solvay, Canada), potassium bis(fluorosulfonyl)imide (>99.9%, Suzhuo Fluolyte Co, China), silver tetrafluoroborate (99%, Oakwood, USA), lithium (fluorosulfonyl)trifluoromethanesulfonylimide (99%, PROVISO CS, Czech Republic), potassium hexafluorophosphate (≥ 99%, Sigma Aldrich, Australia), sodium dicyanamide (≥ 99%, Sigma Aldrich, Australia) and silver nitrate (≥ 99%, Sigma Aldrich, Australia) were used without further purification.

The structures, abbreviations and synthetic route is shown in Figure 1. The synthesis was predominantly performed using a nitrogen Schlenk line. Milli-Q water was used in all the syntheses. ¹H, ¹³C and ¹⁹F NMR spectra were collected on Bruker Avance III instrument operating at 400 MHz, 100 MHz and 375 MHz respectively, in CD₃OD by referencing the solvent peak. Mass spectrometry was performed on an Agilent 1200 series HPLC system. All samples were dried for at least 72 hours on a Schlenk line. All samples were sent to The Campbell Microanalytical Laboratory, New Zealand for elemental analysis. Bromide, silver and potassium contents were determined by an Iodone U-Ag or Br selective electrode, or Hanna potassium selective electrode, respectively, after calibration with 10 and 100 ppm solutions of the respective ion. Water contents were measured using a Metrohm 831 Karl-Fisher Coulometer. Quantitation of Lithium was carried out using an inductively coupled plasma-mass spectrometer (ICP-MS; NexION 350X, PerkinElmer, USA). The internal standards Sc (200 ppb) and Rh (20 ppb) in 1% aqua regia were used for correction of matrix effects. The internal standard solution was mixed prior to the nebulizer using a T-piece in a 1:1 ratio. Calibration standards for lithium (Perkin Elmer, Lithium standard 1000 ppm in 2% HNO₃) were prepared at 0.1, 1, 10, 50, 100 and 500 ppb with 2% HNO₃ in each. The mass spectrometer was operated in kinetic energy discrimination mode (KED) with 50 ms dwell times, 20 sweeps, one reading and three replicates. The plasma source conditions were: nebulizer gas flow 1.02 L.min⁻¹, auxiliary gas flow 1.2 L.min⁻¹, plasma gas flow 15 L.min⁻¹, ICP RF power 1500 W. Data analysis was carried out using Syngistix (PerkinElmer) software. Signal responses were normalized to the scandium internal standard.

Viscosity (2.5 mm tube) and density were measured on a dual Lova 2000 M/ME from 20 to 90 °C. Before performing DSC, the melting points were determined visually using a Gallenkamp melting point apparatus. DSC was measured on a Mettler Toledo DSC STAR®e with a scan rate of 10 °C/min for both the heating and cooling cycles. Three heating and cooling cycles were performed, using a sample size of 4-10 mg in an aluminium pan under inert atmosphere. The temperature ranges used were from -173 K, up to 333 K for DCA and FTFSI salts, 423 K for TFSI and FSI salts, and 573K for the BF₄ and PF₆ salts. The data reported is from the second heating run unless otherwise specified. The cooling traces are shown in the supporting information. Before measurement the heat flow and temperature was calibrated using cyclohexane.

The ionic conductivity was measured by electrochemical impedance spectroscopy using Solartron Modulab (Solartron Analytical, Ametek). The solid samples were pressed into a pellet with 13 mm diameter. The pellet was placed between two stainless steel electrodes (with spacer) in a dry barrel cell in an inert atmosphere. The thickness of the pellet was
measured both before and after measurement. In the case of [Crypy][FSI] the sample was manually pressed between two stainless steel plates, without additional applied pressure, as this material was very soft. The conductivities were measured from 30 to 80 °C with a temperature setting time of 40 minutes, frequency range from 1 MHz to 0.1 Hz with an amplitude of 100 mV. For liquid samples the conductivities were measured using a dip cell with platinum electrodes, with a temperature range from 30 to 90 °C. The cell constant was measured using 1mM KCl solution at 30 °C. The conductivity of the samples were determined from the real axis intercept in the Nyquist plot of the impedance data. The activation energies were calculated using fits to the Arrhenius equation, which gave linear relationships between ln ø and 1/T.

**Synthetic procedures**

**N,N-Diethylpyrrolidinum bromide, [Crypy][Br]**

[Crypy][Br] was synthesised following a previously reported procedure.27 N-Ethylpyrrolidine (6.71 g, 68 mmol) was added to 50 mL of dry *iso*-propanol and then ethylbromide (15 mL, 102 mmol) was added dropwise to the above stirred solution. The solution was heated at 45 °C for 24 hours under inert atmosphere, during which time the reaction mixture turned yellow. The reaction was then cooled to room temperature and n-hexane (50 mL) added dropwise until the solid white product separated to start. The solution was then left in freezer for 2 hours and the supernatant decanted. The solid product was washed with n-hexane twice, followed by drying in vacuo to get a white solid of [Crypy][Br] (12.92 g, 92 %).1H NMR (400 MHz, CD2OD): δ 1.41 (tt, *J*HH = 7.2 Hz, *J*HH = 2.0 Hz, NCH2CH3, 6H). 2.20 (m, CH2CH3, 4H), 3.42 (q, *J*HH = 7.2 Hz, NCH2CH3, 4H), 3.50 (m, CH2NCH2, 4H) ppm.13C NMR (100 MHz, CD2OD): 7.52 (CH3), 21.54 (CH2), 54 (NCH2CH3), 61.71 (CH2NCH2) ppm. ES+ m/z 128.1 ([C4H9N]+), ES- m/z 80.9 (Br). Anal. Calculated for C6H13SN,Br,O2.23; C, 45.18; H, 8.77; N, 6.58. Found: C, 45.27; H, 8.78; N, 6.46.

**N,N-Diethylpyrrolidinum (fluorosulfonyl)trifluoromethanesulfonil)limide, [Crypy][FTS][FSI]**

[Crypy][Br] (1.971 g, 9.5 mmol) was dissolved in 10 mL of water and lithium (fluorosulfonyl)trifluoromethanesulfonil)limide (2.261 g, 9.6 mmol) dissolved in 10 mL of water. Upon mixing the above solutions, the mixture clouded and the mixture was left stirring for an hour at room temperature. The aqeous mixture was then extracted with CH2Cl2 (3 x 50 mL). The combined organic layers were then washed twice with water (100 mL) and dried in vacuo to obtain the product as a colourless oil of [Crypy][FTS][FSI] (2.63 g, 77%).1H NMR (400 MHz, CD2OD): 1.36 (tt, *J*HH = 7.2, 2.0 Hz, 6H, NCH2CH3), 2.20 (m, 4H, NCH2CH3), 3.38 (q, *J*HH = 7.2 Hz, 4H, CH2NCH2), 3.52 (m, 4H, NCH2CH3) ppm.13C NMR (100 MHz, CD2OD): 7.45 (CH2CH3), 21.42 (NCH2CH3), 54.11 (NCH2CH3), 61.60 (CH2NCH2) ppm.19F NMR (376.5 MHz, CD2OD): -79.85 (CF3), 54.94 (F) ppm. ES+ m/z 129.1 ([C6H13N]+), ES- m/z 229.7 ([FTS][FSI]). Anal. Calculated for C6H13N,F2OS2C; C, 30.17; H, 5.06; N, 7.82; S, 17.89. Found: C, 30.46; H, 4.91; N, 7.81; S, 17.59. Bromide content (ISE) 88 ppm. Water content 300 ppm.

**N,N-Diethylpyrrolidinum dicyanamide, [Crypy][DCA]**

Silver dicyanamide was synthesised as follows: Sodium dicyanamide (5.721 g, 64 mmol) and silver nitrate (10.922 g, 64 mmol) were dissolved separately in 50 mL of water. The above solutions were combined and stirred at room temperature for 3 hours in the dark. The white precipitate was isolated by filtration and washed twice with chilled water before being dried under vacuum. [Crypy][Br] (5.356 g, 26 mmol) and freshly prepared AgDCA (11.734 g, 64 mmol) were added to water (55 mL) and the resulting mixture was stirred at room temperature overnight in the dark. The reaction mixture was then filtered under vacuum and the filtrate was refrigerated for 3 hours. Solid AgBr was removed by filtration, followed by centrifugation at 15000 rpm at 0°C for 10 minutes and the filtration through a 0.2 μm syringe filter. The resulting filtrate was dried in vacuo to obtain [Crypy][DCA] (4.331 g, 88%).1H NMR (400 MHz, CD2OD): 1.36 (tt, *J*HH = 7.2, 2.0 Hz, 6H, CH2CH3), 2.20 (m, 4H, NCH2CH3), 3.39 (q, *J*HH = 7.2 Hz, 4H, CH2NCH2), 3.53 (m, 4H, NCH2CH3) ppm;13C NMR (100 MHz, CD2OD): 7.46 (CH2CH3), 21.43 (NCH2CH3), 54.10 (NCH2CH3), 61.62 (CH2NCH2) ppm. ES+ m/z 129.2 ([C6H13N]+), ES- m/z 65.9 (DCA). Anal. Calculated for C6H15N2O4S; C, 54.28; H, 9.57; N, 25.32. Found: C, 54.8; H, 9.7; N, 25.8. Bromide content (ISE) is 378 ppm. Silver (ICP-MS) 23 ppm. Water content less than 300 ppm.

**N,N-Diethylpyrrolidinum bis(trifluoromethanesulfonyl)limide, [Crypy][NTF2]**

[Crypy][Br] (1.251 g, 6 mmol) was dissolved in 10 mL of water. Lithium bis(trifluoromethanesulfonyl)limide (1.773 g, 6.2 mmol) was separately dissolved in 10 mL of water. Upon mixing the above solutions, a white precipitate formed instantly. CH2Cl2 (20 mL) was added and the solution was left to stir for one hour at room temperature. The organic layer was washed with water (4 x 20 mL). The organic layer was removed in vacuo for 24 hours at 50 °C to get a white solid of [Crypy][NTF2] (1.85 g, 77%).1H NMR (400 MHz, CD2OD): δ 1.36 (tt, *J*HH = 7.2, 2.0 Hz, 6H, NCH2CH3, 6H), 2.21 (m, CH2CH3, 4H), 3.42 (q, *J*HH = 7.2 Hz, NCH2CH3, 4H), 3.53 (m, CH2NCH2, 4H) ppm.13C NMR (100 MHz, CD2OD): 7.44 (CH3), 21.42 (CH2), 54.17 (NCH2CH3), 61.60 (CH2NCH2), 119.20 (CF3, *J*HH = 320 Hz).19F NMR (375 MHz, CD2OD): -80.68 (CF3) ppm. ES+ m/z 128.1 ([NC6H13N]+), ES- m/z 279.9 (NTF2). Anal. Calculated for C6H12N2F4O3S2; C, 29.41; H, 4.44; N, 6.86; S, 15.71. Found: C, 29.62; H, 4.42; N, 6.76; S, 15.72. Bromide content (ISE) 12 ppm. Lithium (ICP-MS) < 1 ppm.

**N,N-Diethylpyrrolidinum bis(fluorosulfonyl)limide, [Crypy][FSI]**

[Crypy][Br] (1.87 g, 9 mmol) was dissolved in 10 mL of water, and potassium bis(fluorosulfonyl)limide (1.725 g, 9.3 mmol) was separately dissolved in 10 mL of water. Upon mixing the above solutions, a white precipitate formed instantly. After the addition of CH2Cl2 (20 mL) the solution was
left stirring for an hour at room temperature. The organic layer was then washed with water (4 x 20 mL). The organic layer was dried in vacuo for 24 hours at 50 °C to get a white sticky solid of [C_2epyr][FSL] (1.8 g, 65%).^3 1H NMR (400 MHz, CD_2OD): δ 1.36 (tt, J_H,H = 7.2 Hz, J_H,N = 2 Hz, NCH_2CH_2H), 2.22 (m, CH_2CH_2), 3.44 (q, J_H,N = 7.2 Hz, NCH_2CH_2H), 3.57 (m, CH_2CH_2H), 4.02 ppm. 13C NMR (100 MHz, CD_2OD): 7.50 (CH_3), 21.42 (CH_2), 54.17 (NCH_2CH_2), 61.62 (NCH_2CH_2). ^3F NMR (375 MHz, CD_2OD): 50.42 (F ppm).

N,N-Diethylpyrrolidinium hexafluorophosphate, [C_2epyr][PF_6] To synthesise silver hexafluorophosphate, potassium hexafluorophosphate (3.643 g, 20 mmol) was dissolved in CH_3CN (10 mL) and silver nitrate (3.36 g, 20 mmol) was dissolved in CH_3CN (10 mL). Upon mixing the above solutions, a yellow precipitate formed instantly and the solution was left to stir at room temperature under an inert atmosphere for 2 hours in the dark. The solution was then filtered and the solvent was removed in vacuo at 50 °C to get a white solid of AgPF_6 (2.84 g, 96%). ^19F NMR (375 MHz, CD_2OD): -74.84 (d, J_F,F = 692 Hz) ppm. ES' m/z 108.8 [Ag]^{3+}, ES' m/z 144.9 (PF_6)^{-1}. Analyzed for C_2H_3N,F_2O,P,Ag; P, 9.38: Ag, 32.71. Found: P, 9:2; Ag, 33.0.

[C_2epyr]Br (2.265 g, 11 mmol) and AgPF_6 (3.59 g, 11 mmol) were added to a pre-dried flask. After the addition of dry acetonitrile (30 mL) via syringe, the solution was stirred under an inert atmosphere (N_2) for an hour in the dark. The solution was filtered, followed by centrifugation for 15 min (4000 rpm at 4 °C). The solution was then filtered through a syringe filter (0.22 μm, PTFE). The organic solvent was removed in vacuo to obtain a white powder of [C_2epyr][BF_4] (3.490 g, 84% yield). ^1H NMR (400 MHz, CD_2OD): 1.36 (tt, J_H,H = 7.2, 1.9 Hz, 6H, CH_2CH_2), 2.20 (m, 4H, NCH_2CH_2), 3.38 (q, J_H,N = 7.2 Hz, 4H, CH_2CH_2), 3.52 (m, 4H, NCH_2CH_2) ppm; ^13C NMR (100 MHz, CD_2OD): 7.44 (CH_2CH_2), 21.40 (NCH_2CH_2), 54.10 (NCH_2CH_2), 61.57 (NCH_2CH_2) ppm; ^19F NMR (376.5 MHz, CD_2OD): -154.49 ppm; ES' m/z 129.1 (C_8H_15N){^3}_2, ES' m/z 87 (BF_4)^{-1}. Analyzed for C_2H_3N,F_2O,P,B; C, 44.64: H, 8.43: N, 6.50. Found: C, 44.64: H, 8.68: N, 6.54. Bromide content (ISE) 11 ppm. Silver content (ISE) 199 ppm.

Conclusions
The N,N-diethylpyrrolidinium cation has been used to synthesise two new room temperature ionic liquids and four organic ionic plastic crystals. Both of the RTILs, [C_2epyr][DCA] and [C_2epyr][FSL], exhibit low viscosities. The organic ionic plastic crystals, utilising anions [NTf_2]^{-}, [FSL], [BF_4]^{-} or [PF_6]^{-}, display a variety of interesting thermal and transport behaviour. Of these materials, the [C_2epyr][FSL] is particularly promising as a new solid-state electrolyte as it displays among the highest ionic conductivity to-date for OIPCs, at 1.9 x 10^{-5} S cm^{-1} at 30 °C.

Conflicts of interest
There are no conflicts to declare.

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Notes and references
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