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## COMMUNICATION

# New ionic liquids from azepane and 3-methylpiperidine exhibiting wide electrochemical windows<sup>†</sup>

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New ionic liquids based on azepanium and 3methylpiperidinium cations have been synthesised; they exhibit moderate viscosities and remarkably wide electrochemical windows, thereby showing promise, *inter alia*, as electrolytes and battery materials, and as synthetic media.

The initial development of ionic liquids was closely linked to their application as electrolytes,<sup>1,2</sup> given the set of favourable properties for electrochemistry often exhibited by them, such as inherent ionic conductivity, non-flammability, negligible volatility and wide potential windows.<sup>3</sup> These desirable characteristics show real promise to overcome major safety issues related to energy devices, mostly lithium batteries, supercapacitors and fuel cells.<sup>4-8</sup>

Over the past three decades, continuous improvements have been made bringing to the scene water and air stable ionic liquids showing conductivities on a par with those of conventional organic solvent-supporting electrolyte systems.<sup>4,6,9</sup> Furthermore, the range of electrochemically robust cations and anions has been extended in recent years, allowing the preparation of new ionic liquids with enhanced applicability. In this regard, perfluorinated anions (e.g. bis{(trifluoromethyl)sulfonyl}amide (bistriflamide; [NTf2],9,10 trifluorotris(pentafluoroethyl)phosphate10 and trifluoromethanesulfonate (triflate; [OTf]-)9 created a breakthrough concerning anodic stability. Related investigations showed that ionic liquids containing tetraalkylammonium cations, either cyclic<sup>11</sup> or acyclic,<sup>12</sup> can surpass the performance of imidazolium ones, further extending the cathodic operational limits. In particular, 1,1-dialkylpyrrolidinium and 1,1-dialkylpiperidinium cations are the basis of ionic liquids showing greater promise. Sakaebe and Matsumoto reported the use of bistriflamide salts of these cations in lithium ion batteries, concluding that 1,1-dialkylpiperidinium cations are the best candidates in terms of Coulombic efficiency.<sup>13</sup> Recently,

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Teramoto *et al.* have reported the use of acyclic ammonium or piperidinium ionic liquids in commercial lithium batteries manufactured by Pionics Co., Ltd., with the safety advantage of proven self-extinguishing properties on exposure to open flames.<sup>8</sup>

Here, we report the syntheses and the physical and electrochemical properties of two new families of ionic liquids, based on 1-alkyl-1-methylazepanium<sup>‡</sup> or 1-alkyl-1,3dimethylpiperidinium cations, which had been previously noted in a very recent patent application from INVISTA.<sup>14</sup> Such compounds are derived from the parent alicyclic amines azepane (azp)<sup>15</sup> and 3-methylpiperidine (m<sub>β</sub>pip), respectively, which are in turn obtained in industrial processes related to polyamide production.<sup>16</sup> As will be shown, these cyclic secondary amines can serve as starting materials for the generation of room temperature ionic liquids with the promise of wider electrochemical windows and liquid temperature ranges. Their physical properties are compared to those of previously reported 1-alkyl-1-methylpyrrolidinium ([Rmpyrr]<sup>+</sup>) and 1-alkyl-1-methylpiperidinium ([Rmpip]<sup>+</sup>) ionic liquids.

### **Results and discussion**

The structures of the cations and anions of the newly prepared cyclic ammonium ionic liquids are depicted in Schemes 1 and 2. The 1-alkyl-1-methylazepanium and 1-alkyl-1,3-dimethylpiperidinium cations are abbreviated as  $[Rmazp]^+$  and  $[Rmm_{\beta}pip]^+$  respectively. The abbreviations  $[C_4mazp]^+$  or



Scheme 1 Syntheses of ionic liquids derived from azepane.

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Scheme 2 Syntheses of ionic liquids derived from 3-methylpiperidine.

 $[C_4 mm_\beta pip]^+$  and  $[C_6 mazp]^+$  or  $[C_6 mm_\beta pip]^+$  thus represent the 1-butyl and 1-hexyl cations, respectively. For the ether derived side chain the abbreviation MeOC<sub>2</sub> represents MeOCH<sub>2</sub>CH<sub>2</sub>.

The general synthetic approach for the preparation of these ionic liquids is relatively straightforward (see Schemes 1 and 2). In both cases, the key step is the initial alkylation of the azacycle.<sup>17</sup> To minimise the formation of the dialkylated products, azepane and 3-methylpiperidine were treated with the desired alkylating agent (RBr, where R = butyl, hexyl, MeOCH<sub>2</sub>CH<sub>2</sub>) in methanol at 0 °C in the presence of potassium carbonate. In all cases, the corresponding cyclic tertiary amines were obtained in 65-75% yield after distillation, and characterised by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and mass spectrometry. The related ionic liquids [Rmazp][NTf<sub>2</sub>] and [Rmm<sub>8</sub>pip][NTf<sub>2</sub>] were prepared in almost quantitative yield by treating the corresponding cyclic tertiary amines with iodomethane (this is illustrated with iodomethane, but other alkylating agents can be used with ease), and subsequent metathesis of the resultant iodide salts with Li[NTf<sub>2</sub>] in aqueous solution (Schemes 1 and 2). These materials were obtained as pale yellow liquids in all cases. The salts with trifluoroethanoate or triflate anions were obtained by direct methylation of the tertiary amines with methyl trifluoroethanoate or methyl triflate, respectively, as low melting point solids and, in some cases, as liquids (Table 1).

In the case of  $[C_4 mazp][CF_3CO_2]$ , suitable crystals for X-ray diffraction were grown by slow evaporation from a saturated solution in ethanol under a dry dinitrogen atmosphere.§ By detailed examination of the crystal packing, it was observed that each cation is coordinated by four anions. The closest cationanion contacts are established between carboxylate oxygen atoms in the anions and hydrogen atoms in the  $\alpha$  or  $\beta$  positions from the nitrogen atom in the cation (see, for example, Fig. 1). The mean  $O \cdots H$  distance, averaged over all  $O \cdots HC$  in the structure, is 2.51(8) Å, considerably shorter than the sum of the van der Waals radii (2.70 Å).18 This indicates the presence of significant hydrogen bonding in this structure, a phenomenon which has only recently achieved universal recognition.<sup>19</sup> This is as anticipated, as the hydrogen bond is between a cationic CH moiety and an anionic oxygen functionality. To the best of our knowledge, this is the first reported example of a crystal structure for any salt containing a 1,1-dialkylazepanium cation.

The physicochemical properties of the newly synthesised ionic liquids, compared to their piperidinium and pyrrolidinium analogues, are summarised in Table 1. All the new ionic

**Table 1** Physical properties of [A]X (where  $X = [NTf_2]$ , [CF<sub>3</sub>CO<sub>2</sub>] or [OTf]) and related piperidinium and pyrrolidinium salts

[A] <sup>+</sup>	$T_{\rm g}/^{\circ}{ m C}^a$	$T_{\rm m}/^{\circ}{\rm C}^a$	$\eta/cP^b$	ho/g cm <sup>-3b</sup>	$\sigma/\mu s \ cm^{-1b}$
$\mathbf{X}^{-} = [\mathbf{N}\mathbf{T}\mathbf{f}_2]^{-}$					
[C₄mazp] <sup>+</sup>	-69		315	1.3661	560
[C <sub>6</sub> mazp] <sup>+</sup>	-68		358	1.3148	331
[MeOC <sub>2</sub> mazp] <sup>+</sup>	-79		160	1.4156	1117
[C₄mpip] <sup>+</sup>	$-77^{c}$		182 <sup>c</sup>	1.3786 <sup>c</sup>	1100 <sup>c</sup>
[MeOC <sub>2</sub> mpip] <sup>+</sup>	$-82^{c}$		102 <sup>c</sup>	1.4355 <sup>c</sup>	2000 <sup>c</sup>
$[C_4 mm_\beta pip]^+$	-69		315	1.3475	550
[C <sub>6</sub> mm <sub>B</sub> pip] <sup>+</sup>	-70		392	1.2982	318
[MeOC <sub>2</sub> mm <sub>6</sub> pip] <sup>+</sup>	-70		136	1.3980	1192
[C <sub>4</sub> mpyrr] <sup>+</sup>	$-89^{c}$	-19 <sup>c</sup>	76 <sup>c</sup>	1.3931 <sup>c</sup>	2600 <sup>c</sup>
[MeOC <sub>2</sub> mpyrr] <sup>+</sup>	-91°		53°	1.4539°	3700 <sup>c</sup>
$\overline{\mathbf{X}^{-} = [\mathbf{CF}_3\mathbf{CO}_2]^{-}}$					
[C₄mazp] <sup>+</sup>		74			
[C₄mazp] <sup>+</sup>		45			
[MeOC <sub>2</sub> mazp] <sup>+</sup>	-74		577	1.2197	408
[C <sub>4</sub> mm <sub>8</sub> pip] <sup>+</sup>		58			
[C₄mm₀pip] <sup>+</sup>		41			
$[MeOC_2mm_\beta pip]^+$	-61		453	1.1966	370
X- = [OTf]-					
[C mazn]+		55			
$[C_4 mazp]^+$		08			
[MaOC mazn <sup>1+</sup>	67	20	708	1 2020	228
[C mm nin] <sup>+</sup>	-07	01	190	1.2929	320
$[C_4 \text{mm}_\beta \text{pip}]^*$		84 82			
$[C_6 \text{mm}_\beta \text{pip}]^{\dagger}$	(0	82	(5)	1 2712	240
$[WeOC_2 mm_B pip]^T$	-60		034	1.2/13	340

<sup>*a*</sup> Glass transition temperatures  $(T_g)$  and melting points  $(T_m)$  were recorded during the second heating cycles in the DSC traces recorded at 5 °C min<sup>-1</sup>. <sup>*b*</sup> Density, viscosity and conductivity were measured at 25 °C for neat ionic liquids. <sup>*c*</sup> From reference 20



Fig. 1 A view of an ion pair in the crystal structure of  $[C_4 mazp][CF_3CO_2]$ . Dotted red lines indicate hydrogen bonding. Distances (Å) are shown in black. White = hydrogen; grey = carbon; blue = nitrogen; red = oxygen and green = fluorine.

liquids containing 1-alkyl-1-methylazepanium or 1-alkyl-1,3dimethylpiperidinium are either liquid at room temperature or have a melting point below 100 °C. All ionic liquids with the  $[NTf_2]^-$  anion are liquids with glass transition temperatures below -68 °C. As for the salts with  $[CF_3CO_2]^-$  or  $[OTf]^-$  anions, it can be seen in Table 1 that the replacement of the 1-alkyl group in the cation with a chain containing an ether linkage results in a noticeable reduction of the melting temperatures. For example,  $[C_4mazp][CF_3CO_2]$  exhibits a melting point above room temperature ( $T_m = 74$  °C), while the etherated analogue [MeOC<sub>2</sub>mazp][CF<sub>3</sub>CO<sub>2</sub>] is liquid at room temperature ( $T_g = -74$  °C), despite the fact the chain length is four in both cases. In other words, substituting a methylene group by an oxygen atom changes the liquid range by 148 °C. A similar effect has been previously observed for piperidinium and pyrrolidinium ionic liquids<sup>20</sup>

The densities for the new azepanium and 3-methylpiperidinium ionic liquids, measured at 25 °C, lie in the range 1.30 to 1.42 g cm<sup>-3</sup> for the bistriflamide salts and the individual values are listed in Table 1. These data are compared to those of previously reported bistriflamide analogues of piperidinium and pyrrolidinium in Fig. 2.20 In every case where analogous ionic liquids containing either butyl or methoxyethyl as side chain on the cation are compared, higher densities are observed for the latter, as in the case of [C4mazp][NTf2] and [MeOC2mazp][NTf2] (1.3661 and 1.4156 g cm<sup>-3</sup>, respectively). This effect is represented by solid blue lines in Fig. 2. The effect of the different sizes of the rings in each cation also has a noticeable effect upon the densities, as represented by the green dashed lines in Fig. 2; the smaller the ring, the higher the density. Finally, comparing the two isomers 1-methylazepanium and 1,3-dimethylpiperidinium reveals a decrease in density, as represented by the red dashed line in Fig. 2.



Fig. 2 Densities (25 °C) for ionic liquids with the  $[NTf_2]^-$  anion, and the relationship between them, for the cations derived from 3-methylpiperidine (triangles), azepane (diamonds), piperidine (squares) and pyrrolidine (circles).

One of the fundamental properties required for evaluating the applicability of ionic liquids as electrolytes is a low viscosity, since the electrolytes in many electrochemical devices are required to operate in ambient temperature ranges. It is now well established that the viscosity of ionic liquids amongst other physicochemical properties can be dramatically affected by a slight modification of their cations. Table 1 shows the dynamic viscosites for the different ionic liquids at 25 °C. For ionic liquids with the [NTf<sub>2</sub>]<sup>-</sup> anion, introduction of an ether bond in the side chain of the cation reduces the viscosity is reduced from 315 cP for [C<sub>4</sub>mazp][NTf<sub>2</sub>] to 160 cP for [MeOC<sub>2</sub>mazp][NTf<sub>2</sub>] by simply replacing the butyl group in the cation with MeOCH<sub>2</sub>CH<sub>2</sub>. The different cation cores are also compared in Fig. 3, showing that viscosities decrease in the order [Rmazp]<sup>+</sup>  $\approx$  [Rmm<sub>p</sub>pip]<sup>+</sup>



Fig. 3 Viscosities (25 °C) for ionic liquids with  $[NTf_2]^-$  anion derived from 3-methylpiperidine (triangles), azepane (diamonds), piperidine (squares) and pyrrolidine (circles).

> [Rmpip]<sup>+</sup> > [Rmpyrr]<sup>+</sup>. These results show that an expansion in the cation core size from 5-membered through to 7-membered rings leads to a progressive increase in viscosity. A similar effect is observed with the introduction of asymmetry *via* a methyl substituent in the case of the piperidinium based ionic liquids. For example, the viscosity is increased from 182 cP for [C<sub>4</sub>mpip][NTf<sub>2</sub>] to 315 cP for [C<sub>4</sub>mm<sub>β</sub>pip][NTf<sub>2</sub>].

The different structural features in the cations also have a noticeable effect on the conductivities of the ionic liquids based on the [NTf<sub>2</sub>]<sup>-</sup> anion (Table 1 and Fig. 4). The introduction of an ether linkage to the side chain of the cation leads to an increase in ionic conductivity and a corresponding decrease in viscosity. In addition, a decrease in the ring size of the cation induces an increase in conductivity in the order [Rmazp]<sup>+</sup>  $\approx$  [Rmm<sub>β</sub>pip]<sup>+</sup> < [Rmpip]<sup>+</sup> < [Rmpyrr]<sup>+</sup>, which reflects the decreasing viscosities. For example, the conductivity at 25 °C is reduced from 1100 µS cm<sup>-1</sup> for [C<sub>4</sub>mpip][NTf<sub>2</sub>]<sup>20</sup> to 560 for [C<sub>4</sub>mazp][NTf<sub>2</sub>].



Fig. 4 Conductivities (25 °C) for ionic liquids with  $[NTf_2]^-$  anion derived from 3-methylpiperidine (triangles), azepane (diamonds), piperidine (squares) and pyrrolidine (circles).

The utility of a liquid for electrochemical applications is frequently reflected in the width of the electrochemical window, combined with low viscosity, and hence high diffusivity. For conventional solvents, this window is less than 3 V,<sup>4,21,22</sup> whereas for the ionic liquids presented here, values in the range 5.0 to 6.5 V were obtained. The lowest value in this range (see Fig. 5 and Table 2) is over 0.5 V larger than for the analogous

Table 2	Electrochemical	windows $(\Delta E)$	specifying cath	nodic $(E_c)$ and
anodic li	mits $(E_a)$ of [A]X	(where $X = [N]$	Tf <sub>2</sub> ], [CF <sub>3</sub> CO <sub>2</sub> ]	or [OTf]) and
related p	yrrolidinium salts	3		

$[A]^{+}$	$\Delta E/\mathrm{V}^a$	$E_{\rm c}/{ m V}^a$	$E_{\rm a}/{ m V}^{a}$
$\overline{X^- = [NTf_2]^-}$			
[C <sub>4</sub> mazp] <sup>+</sup>	6.50	-3.25	3.25
[C <sub>6</sub> mazp] <sup>+</sup>	6.25	-3.25	3.00
[MeOC <sub>2</sub> mazp] <sup>+</sup>	5.50	-2.75	2.75
$[C_4 mm_\beta pip]^+$	6.25	-3.00	3.25
$[C_6 mm_8 pip]^+$	6.00	-3.00	3.00
[MeOC <sub>2</sub> mm <sub>B</sub> pip] <sup>+</sup>	6.00	-3.00	3.00
[C₄mpyrr] <sup>+</sup>	5.50	-2.75	2.75
[MeOC <sub>2</sub> mpyrr] <sup>+</sup>	5.50	-3.00	2.50
$\overline{\mathbf{X}^{-} = [\mathbf{CF}_3\mathbf{CO}_2]^{-}}$			
[MeOC <sub>2</sub> mazp] <sup>+</sup>	5.00	-3.00	2.00
$[MeOC_2mm_\beta pip]^+$	5.25	-3.00	2.25
$\overline{X^- = [OTf]^-}$			
[MeOC <sub>2</sub> mazp] <sup>+</sup>	5.50 <sup>b</sup>	-2.75 <sup>b</sup>	2.75 <sup>b</sup>
[MeOC <sub>2</sub> mm <sub>β</sub> pip] <sup>+</sup>	5.50 <sup>b</sup>	$-3.00^{b}$	2.50 <sup>b</sup>

<sup>*a*</sup> Recorded by cyclic voltammetry *vs.* Ag/Ag<sup>+</sup> using glassy carbon working of 3 mm diameter and Pt coil counter electrodes. <sup>*b*</sup> Recorded for 0.1 M solutions in ethanenitrile because of the high viscosity of the neat liquids.



**Fig. 5** Cyclic voltammograms  $(25 \,^{\circ}\text{C})$  of (a) neat [MeOC<sub>2</sub>mazp][NTf<sub>2</sub>] (blue), and (b) [C<sub>4</sub>mim][NTf<sub>2</sub>] (red) on glassy carbon electrodes *vs.* Ag/Ag<sup>+</sup> at 100 mV s<sup>-1</sup>.

 $[C_4 mim][NTf_2]$  ( $[C_4 mim]^+ = 1$ -butyl-3-methylimidazolium),<sup>9</sup> which has been extensively studied for device applications. For the largest value of electrochemical window ( $[C_4 mazp][NTf_2]$ ), there is almost a 2 V advantage over the conventionally studied  $[C_4 mim][NTf_2]$ . This is because the aromatic imidazolium core is much more readily reduced than the azepane system, which contains no vacant  $\pi^*$  orbitals. It has to be noted that the  $[NTf_2]^-$  anion can be cleaved at potentials within the reported windows, albeit in low current processes.<sup>23</sup> Nevertheless, the bulk oxidation and reduction processes are well represented by the potential limits shown in Table 2. In the data reported here, the cations based on azepanium have clear advantages in terms of electrochemical stability over those based on piperidinium or pyrrolidinium (see Table 2),<sup>11</sup> but all are superior to systems based on heterocyclic aromatic cations.<sup>7</sup>

Finally, some of the newly synthesised salts were also used as solvents for chemical reactions such as the Heck coupling, which is known to proceed well in other ionic liquids.<sup>24</sup> These new ionic liquids compare well with those already published in the literature. In a further example, the *O*-ethanoylation of glucose with ethanoic anhydride in  $[C_4mm_\beta pip][N(CN)_2]$  gave a yield of 87%, essentially identical to that reported in the literature.<sup>25</sup>

### Conclusions

We have synthesised two new families of ionic liquids from the readily available starting materials, azepane and 3methylpiperidine, by reaction with a range of standard alkylating reagents. Salts with the bistriflamide anion are liquid in all cases, whereas salts with the trifluoroethanoate or triflate anions are low melting solids when the cation core is substituted with alkyl chains, but liquids when the core is substituted with alkoxyalkyl chains. Examining these two series revealed systematic changes in density, viscosity and conductivity, which correlated strongly with alicyclic ring size, chain length and the degree of oxygen substitution in the chain, thus allowing them to be optimised by design to produce ionic liquids for specific electrochemical and/or solvent applications. The current evidence suggests that the azepanium-based ionic liquids are superior for battery applications to the more conventionally used pyrrolidinium systems.

#### Notes and references

<sup>‡</sup> Alternative names for azepane include hexamethyleneimine (HMI), hexahydro-1H-azepine, perhydroazepine or azacycloheptane.<sup>15</sup> § Crystal data for [C<sub>4</sub>mazp][CF<sub>3</sub>CO<sub>2</sub>]: C<sub>13</sub>H<sub>24</sub>F<sub>3</sub>NO<sub>2</sub>, T = 293(2) K, orthorombic, Pbna, a = 12.2840(2), b = 13.2290(2), c = 18.3910(3) Å, V = 2988.63(8) Å<sup>3</sup>, Z = 8,  $D_c = 1.259$  mg m<sup>-3</sup>, reflections collected/unique 31969/2619 ( $R_{int} = 0.0964$ ),  $\mu = 0.108$  mm<sup>-1</sup>, S = 1.062,  $R_1 = 0.0789$  ( $I > 2\sigma$ ), w $R_2 = 0.2428$  (all data). CCDC reference number 792935.

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