ORGANOBORATES AS POTENTIAL ANIONS FOR NOVEL IONIC LIQUIDS

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ABSTRACT

We have been preparing ionic liquids with non-symmetrical organoborates as anions. Two appropriately chosen tetraalkylcycloborate anions have been synthesised and further reacted in order to obtain a new class of ionic liquids with some very interesting characteristics.

INTRODUCTION

Ionic liquids exhibit some interesting properties, such as low melting point (below 100°C), negligible vapour pressure, high electrical conductivity, wide electrochemical window, tolerance to strong acids, and excellent thermal and chemical stability. Room-temperature ionic liquids have attracted growing interest as solvents for organic synthesis.1 For instance, room-temperature ionic liquids usually consist of nitrogen-containing organic cations, most commonly N,N'-dialkylimidazolium and N-alkylpyridinium, and weakly coordinating inorganic anions (AlCl4, BF4, CF3SO3, etc.).

Over the past few years, there has been an increasing interest in the synthesis of novel task specific ionic liquids, using different and unusual counter-anions, such as aminoacids for chiral synthesis,2 carborane cages as highly non-coordinative anions,3 and sweeteners.4

Recently, we have developed a new synthetic method for the synthesis of cyclo- or spiro-tetraalkylborates.5 This involves a boron-centred cyclisation reaction via formation of Grignard reagents.

Our present work is focusing on exploiting organoborates as novel counter-anions for a new class of ionic liquids. Firstly, we are interested in the synthesis of ionic liquids free from labile fluoride, being one of the most important developments for their application as ‘green’ solvents. Furthermore, we are interested in investigating how the
shape and the symmetry of the ions can influence the melting point of the salts. Therefore, the use of tetraalkylcycloborates appeared to us as a potential and remarkable breakthrough in the development of new ionic liquids. For instance, tetraalkylborates have only B–C bonds, which show higher stability compared to the more labile B–F bond of the extensively used tetrafluoroborate anions. More interestingly, the use of tetraalkylcycloborates opens up the possibility to 'design' the anion in the same fashion as we can 'design' the cationic counterpart.

Tetraalkylborates have been extensively studied in the past for the preparation of organic and organometallic compounds and as analytical reagents. Room temperature tetraalkylborate molten salts were first reported by Damico. The chemistry and the application of tetraalkylborate molten salts have been further investigated by Ford and al. Nevertheless, the chemistry of the tetraalkylborate based ionic liquids remains largely unexplored. This is basically due to the high viscosity of the ionic liquids which bear normal alkyl chains at the boron centre. The present work, introducing non-symmetrical cycloborates as anions, shows promising and highly potential results in order to obtain improve versatility and application of ionic liquids.

EXPERIMENTAL DETAILS

All manipulations of air-sensitive materials were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified and dried over Na and stored over molecular sieve under an inert atmosphere of nitrogen. All the starting materials are commercially available and were used as received without further purification.

$^1$H, $^{11}$B and $^{13}$C NMR spectra were recorded either on a JEOL-EX 270 spectrometer ($^1$H: 269.72 MHz; $^{11}$B: 86.54 MHz; $^{13}$C: 67.93 MHz), Chemical shifts for $^1$H and $^{13}$C NMR spectra are referenced to internal solvent resonances and are reported relative to tetramethylsilane ($^1$H, $^{13}$C). Chemical shifts for $^{11}$B NMR spectra are referenced to trifluoroborate diethyletherate as an external standard.

Synthesis of the anions

Synthesis of lithium(B,B-buty1methyl-9-boratabicyclo[3.3.1]nonane), (1). A 250 ml two neck round bottom flask was equipped with a magnetic stirring bar and reflux condenser leading to an oil bubbler. The apparatus was dried and filled with nitrogen. A previously prepared solution of 9-BBN (dimer, 5 g, 20.49 mmol) in THF (100 ml) was filtered and placed in the round bottom flask. 1-butene was bubbled thought the stirred solution for few hours, till the $^{11}$B NMR of the solution showed only one peak at 82.7 ppm (with complete absence of the 9-BBN peak at 26 ppm). The resulting solution was filtered and dried in vacuo to eliminate the unreacted 4-butene, yielding a colourless oil of B-buty1-9-borobicyclo[3.3.1]nonane.

NMR data for B-buty1-9-borobicyclo[3.3.1]nonane.
\(^1\)H NMR (THF-d\(_8\)): \(\delta = 0.92\) (t, \(\text{j} = 7.15\) Hz, 3H, \(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), 1.20-1.94 (br, m, 20H). \(^13\)C NMR (THF-d\(_8\)): \(\delta = 14.44\) (\(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), 24.15 ([\(\text{CH}_2\)\(_2\)\(_2\)(\(\text{CH}_2\)\(_4\))(\(\text{CH}\)\(_2\))]\(\text{B}-\text{butyl}\)), 26.81 (\(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), 27.61 (\(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), 28.34 (b, \(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), 31.71 (b, [\(\text{CH}_2\)\(_2\)(\(\text{CH}_2\)\(_4\))(\(\text{CH}\)\(_2\))]\(\text{B}-\text{butyl}\)), 33.92 ([\(\text{CH}_2\)\(_2\)(\(\text{CH}_2\)\(_4\))(\(\text{CH}\)\(_2\))]\(\text{B}-\text{butyl}\)). \(^7\)B NMR (THF-d\(_8\)): \(\delta = 82.7\) ppm.

A solution 1.6 M of \(\text{CH}_3\text{Li}\) (25.6 ml, 40.96 mmol) in diethyl ether was added dropwise at room temperature to the previously prepared 9-boro(butyl)bicyclo[3.3.1]nonane, which was re-dissolved in THF (100 ml). The resulting solution was allowed to stir overnight and thereafter filtered and dried \textit{in vacuo}. The resulting cloudy liquid was analysed via NMR spectroscopy and found to contain 1 equivalent of THF.

NMR data for I.

\(^1\)H NMR (THF-d\(_8\)): \(\delta = -0.71\) (m, 3H, \(\text{R}_2\text{B}^-(\text{butyl})(\text{CH}_3)\)), 0.03 (br, m, 4H, [\(\text{CH}_2\)\(_2\)\(_2\)(\(\text{CH}_2\)\(_4\))(\(\text{CH}\)\(_2\))]\(\text{B}^-(\text{butyl})(\text{CH}_3)\)), 0.78 (t, \(\text{j} = 8.51\) Hz, 3H, \(\text{R}_2\text{B}^-(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)\)), 1.00-2.04 (m, 20H), 3.61 (m, 4H, \(\text{O}(\text{CH}_2\)\(_2\)(\(\text{CH}_2\)\(_2\))). \(^7\)B NMR (THF-d\(_8\)): \(\delta = -19.6\).

Synthesis of lithium\((B,B\text{-pentyI)methyl-9-boratabicyclo[3.3.1]nonane}\). (2). A 250 ml two neck round bottom flask was equipped with a magnetic stirring bar and reflux condenser leading to an oil bubbler. The apparatus was dried and filled with nitrogen. A previously prepared solution of 9-BBN (dimer, 5 g, 20.49 mmol) in THF (100 ml) was filtered and placed in the round bottom flask. To this stirred solution 5-pentene (2.90 g, 41.34 mmol) was added dropwise at room temperature and stirred overnight. The resulting colourless solution was filtered and dried \textit{in vacuo} yielding \(B\text{-pentyI-9-borobicyclo[3.3.1]nonane}\) as a colourless oil.

NMR data for \(B\text{-pentyI-9-borobicyclo[3.3.1]nonane}\).

\(^1\)H NMR (THF-d\(_8\)): \(\delta = 0.90\) (t, \(\text{j} = 6.80\) Hz, 3H, \(\text{R}_2\text{B}(\text{CH}_2\text{CH}_2\text{CH}_3)\)), 1.20-1.94 (br, m, 22H). \(^13\)C NMR (THF-d\(_8\)): \(\delta = 11.46\) (\(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), 20.46 (\(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), 21.17 ([\(\text{CH}_2\)\(_2\)(\(\text{CH}_2\)\(_4\))(\(\text{CH}\)\(_2\))]\(\text{B}-\text{pentyI}\)), 22.05 (\(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), 25.30 (b, \(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), 28.43 (b, [\(\text{CH}_2\)\(_2\)(\(\text{CH}_2\)\(_4\))(\(\text{CH}\)\(_2\))]\(\text{B}-\text{pentyI}\)), 30.98 ([\(\text{CH}_2\)\(_2\)(\(\text{CH}_2\)\(_4\))(\(\text{CH}\)\(_2\))]\(\text{B}-\text{pentyI}\)), 33.26 (\(\text{R}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)). \(^7\)B NMR (THF-d\(_8\)): \(\delta = 79.9\).

A solution 1.6 M of \(\text{CH}_3\text{Li}\) (25.6 ml, 40.96 mmol) in diethyl ether was added dropwise at room temperature to the previously prepared 9-boro(butyl)bicyclo[3.3.1]nonane, which was re-dissolved in THF (100 ml). The resulting solution was allowed to stir overnight and thereafter filtered and dried \textit{in vacuo}. The resulting cloudy liquid was analysed via NMR spectroscopy and found to contain 1 equivalent of THF.
NMR data for 2.

\(^1\)H NMR (THF-d$_8$): \(\delta = -0.73\) (m, 3H, R$_2$B'(butyl)(CH$_3$)), -0.03 (br, m, 4H, [(CH$_2$)$_2$(CH$_2$)$_4$(CH)$_3$]B'(CH$_2$CH$_2$CH$_2$CH$_2$)(CH$_3$)), 0.78 (t, \(^3\)J = 6.92 Hz, 3H, R$_2$B'(CH$_2$CH$_2$CH$_2$H$_2$)(CH$_3$)), 0.98-2.04 (m, 22H), 3.61 (m, 4H, O(CH$_2$)$_2$(CH$_2$)$_2$).

\(^1\)B NMR (THF-d$_8$): \(\delta = -19.6\).

Synthesis of ionic liquids

**Synthesis of [bmim][bm-9-BBN], (3).** To a flask containing a stirred solution of [bmim][Cl] (0.65 g, 3.72 mmol) in CH$_2$Cl$_2$ (100 cm$^3$) under N$_2$ was added a solution of Li[bm-9-BBN]-THF (0.99 g, 3.73 mmol). The mixture was stirred for 24 h under N$_2$ and the white precipitate of LiCl allowed to settle. Cannula filtration and subsequent rinsing of the LiCl residue with CH$_2$Cl$_2$ (2 \times 50 cm$^3$) gave a slight yellow liquid, which was further diluted with CH$_2$Cl$_2$ (100 cm$^3$) and washed with aliquots of water (3 \times 20 ml) until halide free, as indicated by the ES-MS. The liquid was dried *in vacuo* for 3 h at 60 °C to afford [bmim][bm-9-BBN].

NMR data for 3.

\(^1\)H NMR (THF-d$_8$): \(\delta = -0.65\) (m, 3H, R$_2$B'(butyl)(CH$_3$)), 0.06 (br, m, 4H, [(CH$_2$)$_2$(CH)$_3$]B'(CH$_2$CH$_2$CH$_2$CH$_2$)(CH$_3$)), 0.81 (t, \(^3\)J = 7.16 Hz, 3H, R$_2$B'(CH$_2$CH$_2$CH$_2$CH$_2$)(CH$_3$)), 0.95 (t, \(^3\)J = 7.42 Hz, 3H, N(CH$_2$)$_3$CH$_3$), 1.01-1.42 (m, 12H), 1.62-2.05 (m, 8H), 3.93 (s, 3H, NCH$_3$), 4.22 (t, 2H, NCH$_2$(CH$_2$)$_2$CH$_3$), 7.58 (m, 2H, NC(CH$_2$N)), 8.98 (s, 1H, NCN). \(^1\)B NMR (THF-d$_8$): \(\delta = -19.6\). m/z (FAB$^+$) 139 ([bmim]$^+$, 100); m/z (FAB$^-$) 193 ([bm-9-BBN]$^-$, 100).

**Synthesis of [bmpy][pm-9-BBN], (4).** To a flask containing a stirred solution of [bmpy][Cl] (2.10 g, 11.82 mmol) in CH$_2$Cl$_2$ (100 cm$^3$) under N$_2$ was added a solution of Li[pm-9-BBN]-THF (3.30 g, 11.81 mmol). The mixture was stirred for 24 h under N$_2$ and the white precipitate of LiCl allowed to settle. Cannula filtration and subsequent rinsing of the LiCl residue with CH$_2$Cl$_2$ (2 \times 50 cm$^3$) gave a slight yellow liquid, which was further diluted with CH$_2$Cl$_2$ (100 cm$^3$) and washed with aliquots of water (3 \times 20 ml) until halide free, as indicated by the ES-MS. The liquid was dried *in vacuo* for 3 h at 60 °C to afford [bmpy][pm-9-BBN].

NMR data for 4.

\(^1\)H NMR (THF-d$_8$): \(\delta = -0.63\) (m, 3H, R$_2$B'(butyl)(CH$_3$)), 0.07 (br, m, 4H, [(CH)$_2$(CH$_2$)$_4$(CH)$_3$]B'(CH$_2$CH$_2$CH$_2$CH$_2$)(CH$_3$)), 0.82 (t, \(^3\)J = 6.90 Hz, 3H, R$_2$B'(CH$_2$CH$_2$CH$_2$CH$_2$)(CH$_3$)), 0.98 (t, \(^3\)J = 7.28 Hz, 3H, N(CH$_2$)$_3$CH$_3$), 1.01-1.49 (m, 12H), 1.65-1.84 (m, 4H), 1.97 (m, 4H), 2.21 (m, 4H), 3.05 (s, 3H, NCH$_3$), 3.32 (m, 2H, NCH$_2$(CH$_2$$_2$CH$_3$), 3.51 (m, 4H, O(CH$_2$)$_2$(CH$_2$)$_2$). \(^1\)B NMR (THF-d$_8$): \(\delta = -19.6\). m/z (FAB$^+$) 142 ([bmpy]$^+$, 100); m/z (FAB$^-$) 207 ([pm-9-BBN]$^-$, 100).
RESULTS AND DISCUSSION

Designing ionic liquids is one of the most interesting and useful properties of those novel materials.\textsuperscript{10} The design of ionic liquid has been achieved so far, by modifying the alkyl chains and the their substituents on certain position of the cations (\textit{e.g.} \(N,N'\)-dialkylimidazolium, \(N,N\)-dialklylpyridinium, \(N\)-alkylpyridinium, \textit{etc.}). By simply varying the alkyl chain of the cation or by introducing functionalities in the latter alkyl chain, it is possible to fine tune the chemical and physical properties of ionic liquids. On the other hand, the anions of the ionic liquids have so far not been used in this way. This is basically due to the fact that they are usually inorganic non-coordinating anions (\textit{e.g.} \(\text{AlCl}_4\), \(\text{BF}_4\), \(\text{CF}_3\text{SO}_3\)), which are not suitable for any designing purpose, and are purchased in their final form.

Our approach to the synthesis of novel ionic liquids is both innovative and challenging since for the first time introduces the concept of designing the ionic liquids by modifying the alkyl moieties on the anion. This may result in an implementation of our understanding of how to change chemical and physical properties of ionic liquids and their performances.

The synthesis of suitable tetraalkylborate based ionic liquids has been conceived baring in mind the following requirements:
- easy and versatile synthetic pathways,
- synthesis from commercial available reagents,
- stability and low reactivity of the target material,
- making the anion non symmetric in order to lower the melting points.

Synthesis of non-symmetrical tetraalkycycloborates has been achieved, as shown in Scheme 1, by reacting the commercially available 9-BBN (9-borobicyclo[3.3.1]-nonane) with a slight excess of an alkene in order to afford quantitatively the trialkylborane species, which has been characterised by \(^1\text{H}, \text{\textit{^11}B, and } \text{\textit{^13}C NMR spectroscopy. The previous compound has been further reacted with CH\textsubscript{3}Li in THF, to quaternarise the boron centre. This allows us to obtain the lithium salt of the desired tetraalkylborate.

\[
\begin{align*}
\text{1/2} & \quad \text{H}_2\text{BH} \quad \text{n} \\
\quad & \quad \Downarrow \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad 📜
us to investigate how the alkyl chain length will influence both the melting point and the physical and chemical stability of the proposed novel ionic liquids. The starting material has been chosen to be the 9-borobicyclo[3.3.1]nonane, 9-BBN, which is commercially available and one of the most useful and exploited boron reagents.\textsuperscript{11} Subsequently, the further used reagents are common terminal alkenes and methyl-lithium.

Previously reported tetraalkylborate based ionic liquids, such as triethyl-n-hexylammonium triethyl-n-hexilborate (N\textsubscript{2}B\textsubscript{2}),\textsuperscript{12} were prepared simply adding one long alkyl chain to both the boron and the nitrogen centre. The resulting salts show melting points usually between room temperature and 100°C. The limitation in exploiting those ionic liquids has proven to be their high viscosities,\textsuperscript{13} which it might derive from strong ion dipole, ion induced dipole and dispersion forces. In this work, reporting the use of tetraalkylcycloborates, we suggest that some of those interactions that make the \textit{n}-alkylborates might be reduced.

We prepared two tetraalkylcycloborates as lithium salts. For instance, the lithium-(\textit{B},\textit{B}-butylmethyl-9-boratabicyclo[3.3.1]nonane), Li[bm-9-BBN], (1) and lithium-(\textit{B},\textit{B}-pentylmethyl-9-boratabicyclo[3.3.1]nonane), Li[pm-9BBN], (2) have been prepared following the previously discussed synthetic pathway (Scheme 1).

Salt metathesis reaction in DCM of the organoborate lithium salts with suitable chloride salts, such as 1-butyl-3-methylimidazolium chloride (Scheme 2) of 1-butyl-1-methylpyrrolidinium chloride (Scheme 3), after precipitation of the insoluble LiCl, afford the isolation of [bmim][bm-9-BBN] (3) and [bmpy][pm-9-BBN] (4), respectively.

\textbf{Scheme 2. Synthesis of [bmim][bm-9-BBN].}

\textbf{Scheme 3. Synthesis of [bmpy][pm-9-BBN].}
The resulting salts (3) and (4) are liquid at room temperature. They show some reactivity towards air, but high stability in degassed water, in which they are immiscible. Therefore, they are easily purified from any chloride content with a few washes. Unfortunately, detailed viscosity measurements are still under study. Nevertheless, we can already report their viscosities to be comparable to some of the most commonly used ionic liquids (e.g. Bmim BF₄).

CONCLUSIONS

We presented the use of tetraalkylcycloborates as innovative anions for ionic liquids. The synthesis and characterisation of non-symmetrical cycloborates has been developed and two novel ionic liquids have been produced. This work may open up the wider use of borates as anions for ionic liquids and for other applications.

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