A new family of ionic liquids based on *N*,*N*-dialkyl-3-azabicyclo[3.2.2]nonanium cations: organic plastic crystal behaviour and highly reversible lithium metal electrodeposition†

Thomas Rüther,* Junhua Huang and Anthony F. Hollenkamp

Received (in Cambridge, UK) 27th June 2007, Accepted 28th September 2007
First published as an Advance Article on the web 17th October 2007
DOI: 10.1039/b709772g

A new family of ionic liquids based on *N*,*N*-dialkyl-3-azabicyclo[3.2.2]nonanium cations exhibits wide electrochemical windows, excellent lithium deposition-stripping behaviour and plastic crystal properties and therefore these cation structures, which are extensions from pyrrolidinium- and piperidinium-based cations, complement a set of related structures for a systematic study on the physicochemical properties of ionic liquids.

The introduction by Zaworotko[1] and Carlin[2] of air and water stable ionic liquids (ILs), which by definition are composed entirely of ions and exist in the liquid state below 373 K, has made a significant impact on chemical research. Further, they have proven their merits by being employed in an increasing number of applications.[3] One key area is the development of advanced electrolyte materials in electronic applications,[4] where IL materials are attractive since they are non-volatile and can, depending on their structure, exhibit sufficiently high conductivities and wide electrochemical windows. This makes them particularly interesting for use in rechargeable lithium batteries where the use of a metallic lithium anode (as opposed to a lithium intercalation electrode) has a significant advantage in specific energy over contemporary lithium-ion devices.

However, the situation of such ionic liquid based electrolyte materials is certainly not ideal because the relationship between the chemical structure of the IL components and their physicochemical behaviour is not well understood. Although key parameters such as conductivity and ion transport have been approached with different models such as variation of the chemical nature of the cations and anions,[4d,5] fast ion transport in organic plastic crystals,[6] anion trapping,[7] liquid crystals[8] and zwitterionic[9] or Lewis base salt dissociators,[10] there is to date no comprehensive set of complementary cation structures available for a systematic study of structural influences. Thus more examples of architecturally related cations are needed to extend the understanding of the relationship between chemical structure and key physicochemical properties of liquid and solid state ionic materials.

Against this background our work is concerned with (i) the ongoing study of new electrolyte materials for energy storage devices and (ii) investigating the influence of new structural moieties on electrolyte characteristics. Here we report for the first time the synthesis and physicochemical investigation of four examples of a new family of ILs based on the 3-azabicyclo[3.2.2]nonane unit[11] (3-ABN) as the cationic component and bis(trifluoromethanesulfonyl)amide (Tf_2N^-) as the common anion. The new entities make a logical extension to a set of structurally related cations which however differ in topology as illustrated in Fig. 1.‡ The physicochemical investigation of the members reveals new examples of organic plastic crystal behaviour (OPCB) and the suitability of these materials for lithium metal electrodeposition due to their wide electrochemical window is demonstrated. The following acronyms are used: *N*-methyl-*N*-alkylpyrrolidinium (P1*n*), *N*-methyl-*N*-alkylpiperidinium (PP1*n*) and 3-ABN1*n* of this series, where *n* denotes the length of each alkyl chain.

These ionic liquids are synthesised in high quality and good overall yield from sublimed 3-azabicyclo[3.2.2]nonane as the starting material in a 3 step procedure (see Scheme 1). The *N*-alkyl-ABN derivatives **2a–d** were initially prepared in ethanol or acetonitrile but better yields were achieved in ionic liquids. Details of the latter method will be reported in a separate paper. The subsequent steps were carried out according to typical procedures reported in the literature. All compounds were obtained as colourless or pale yellow solids or liquids and were characterised by ^{1}H, ^{13}C, ^{19}F NMR and ESI-MS as well as microanalysis in most cases. The water content was determined by Karl Fischer titration and residual Li and halide content from the ion exchange reaction was determined by ICP-MS and IC methods respectively. Details are given in the ESI.†

All new ionic liquids were studied by TGA and DSC analysis. Results are summarised along with other physicochemical data in Table 1. The TGA traces for each of the new compounds reveal a remarkable thermal stability with decomposition not setting in until around 400 °C. The melting points were determined by DSC and it is important to note that the first three members melt 12 to 25 °C lower than their pyrrolidinium counterparts.[5e] The relationship is reversed for the butyl derivatives; while the melting point in the P1*n* series continues to decline, **4d** is a solid at room temperature, however displaying a great tendency for supercooling, which is indicative of a slow nucleation mechanism.§ The lower melting points of **4a–c** are most likely a result of the extra ring which reduces the cation–anion interactions, possibly due to steric effects. The melting point of PP13 (+8.7 °C) of the piperidinium series[5c] is between that of the P1*n* and the 3-ABN1*n* series whereas PP14 melts at −25 °C.[12]

Importantly, the DSC traces of **4a,b** (Fig. 2) display a multitude of features. For the quenched material **4b**, up to three distinct endothermic solid–solid phase transitions are observed over a

---

CSIRO Energy Technology, P.O. Box 312, Clayton South, VIC 3169, Australia. E-mail: Thomas.Ruether@csiro.au; Fax: +61 3 9545 8500; Tel: 9545 8597

† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b709772g

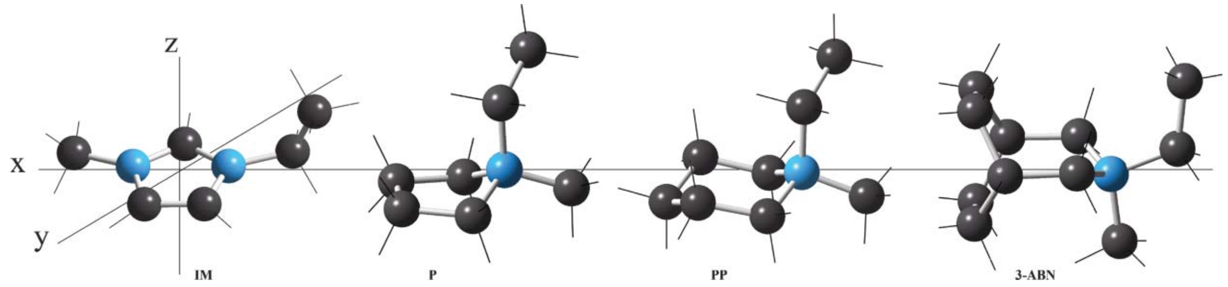
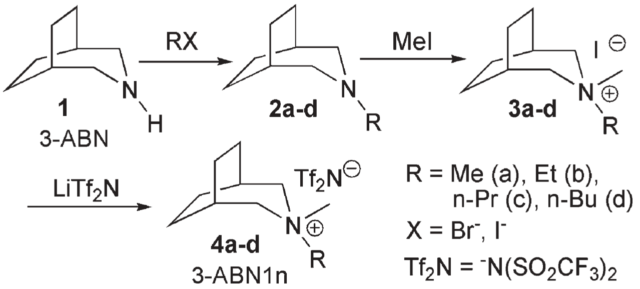


Fig. 1 Topological comparison of related N-heterocyclic cation structures imidazole (IM), pyrrolidinium (P), piperidinium (PP) and 3-azabicyclo[3.2.2] nonane (3-ABN); the images were produced through the use of Gaussview 3.0. The structures were optimised with the *ab-initio* simulations program Gaussian 03 using B3LYP/6-311++G**. The choice of axes is arbitrary and they do not depict moments of inertia or centres of masses.



Scheme 1 Synthesis of new ILs **4a–d**.

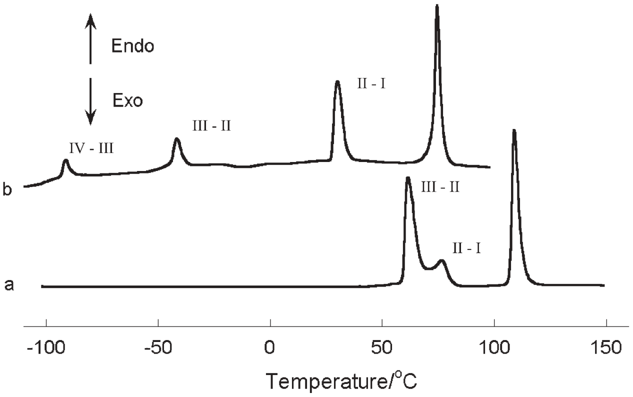


Fig. 2 Differential scanning calorimeter thermogram of **4a** (trace a) and **4b** (trace b) recorded at a heating rate of 10 °C min^{-1} after cooling from room temperature to −140 °C.

relatively wide range of temperature at −94 (IV → III), −44 (III → II)¶ and 30 °C (II → I) before final melting at 73 °C, indicating progressive transformation from a fully ordered state through a series of increasingly disordered phases. These rotator phases which are characteristic of plastic crystal behaviour are a result of dynamically disordered orientations of constituents of the salts about the molecular axis, which could also be associated with the creation of lattice vacancies in the crystal state.[13] The final entropies of fusion (ΔS_f: **4a** = 24, **4b** = 34 J mol^{-1} K^{-1}) are somewhat higher than the Timmerman's criterion ($\Delta S_f \sim$ 20 J mol^{-1} K^{-1}) for molecular plastic crystals. However, this is not uncommon for plastic crystals composed of larger cations and anions[5e,13b] as compared to simple molecular crystals. It is interesting to note that OPCB was also displayed by the parent tertiary amine (3-ABN). This property is carried through to the quaternary ammonium salt structure, even when anions are introduced into the crystal structure.[11b] Only a limited number of examples of IL-materials showing OPCB have been reported, including the earlier work on alkyl[14] and alkoxyalkyl ammonium cations,[15] the more recent pyrrolidinium systems,[5e,13b] and the most recently reported example of a bicyclic heterocycle, which however differs chemically by containing a second tertiary amine function.[10] The ABN system provides an interesting complementary example for a comparison with known OPCs.

Conductivities were determined, over a temperature range of 20 to 135 °C, for all new materials **4a–d** and for **4b** doped with 0.4 mol kg^{-1} LiTf$_2$N. In the liquid state the conductivities of the new ILs range between similar and approximately one order of magnitude less conductive when compared with the corresponding P[5e,13b] and PP[5c,12] systems. As a consequence of the bicyclic non-planar structure of the cation, the dynamic rotational and

Table 1 Properties of **4a–d**, P11–P14, PP13 and PP14

	mp/°C	ΔS_f/J mol^{-1} K^{-1}	Phase II → I/°C	Phase III → II/°C	Phase IV → III/°C	$T_{dec.}$/°C	$^a\sigma^T$/mS cm^{-1} $^{\circ C}$	ΔE/V	η^T/mPa s $^{\circ C}$
4a	105	24	76	59		407	7^{mp}	n.m.	n.m.
4b	73	34	28	−44	−94	406	4.4^{mp}	4.7	n.m.
4c	−1	52				394	0.35^{25}	6.1	209^{40}
4d	35	63				399	0.1^{35}	6.6	n.m.
P11[13b]	137	51	81	26	−41		5.6^{mp}		
P12[13b]	90	25	45	14	−87		4.4^{mp}		
P13[5e]	12	43	−18				1.4^{25}		63^{25}
P14[5e]	−18	41	−24				2.2^{25}	6.1	85^{25}
PP13[5c]	8.7						1.4^{25}	6.1	117^{25}
PP14[12]	−25					400	1.2^{25}	4.5	183^{25}

[a] Conductivities are reported for the molten state at the mp.

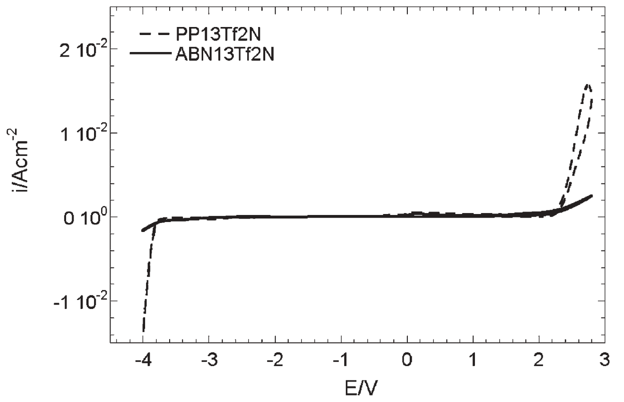


Fig. 3 Linear-sweep voltammograms of 3-ABN13Tf$_2$N and PP13Tf$_2$N obtained on a platinum working electrode; scan rate: 50 mV s^{-1}; temperature: ambient; reference electrode Ag/AgTf (10 mM in P14Tf$_2$N).

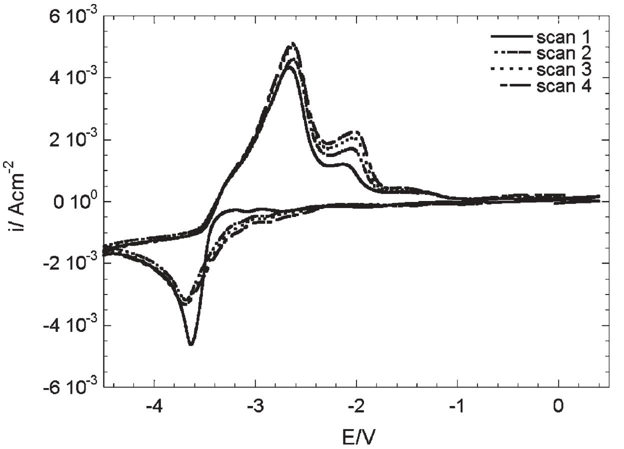


Fig. 4 Cyclic voltammograms of 3-ABN12Tf$_2$N containing 0.4 mol kg^{-1} LiTf$_2$N obtained on a Pt electrode; scan rate: 50 mV s^{-1}; reference electrode Ag/AgTf (10 mM in P14Tf$_2$N); temperature: 80–90 °C.

translational motion of the ring system is more restricted than in the related but more planar pyrrolidinium and piperidinium systems. This correlation, which is reflected in the higher viscosities of the non-planar heterocycles *vs.* the planar imidazolium systems, was noted earlier by MacFarlane *et al.*[5e] The viscosity of **4c**, which is a liquid at room temperature, was found to be 209 mPa s at 40 °C.

Interestingly, the OPC material **4b**, when mixed with LiTf$_2$N (0.4 mol kg^{-1}), showed significant solid state conductivity of $\sim 6 \times 10^{-6}$ S cm^{-1}at 35 °C.[6]

The electrochemistry of the new salts was investigated at temperatures above their melting point on a platinum electrode and a Ag/AgTf (10 mM in P14Tf$_2$N) reference electrode arrangement developed by our group.[16] All compounds have wide electrochemical windows, similar to those of the P1*n* and PP1*n* systems (Fig. 3). This is in contrast to the recently reported hetero-bicyclic compound exhibiting an electrochemical window of 4 V.[10] Importantly, the cathodic stability extends beyond the reduction potential of lithium and the feasibility of reversible electrodeposition of lithium in these salts was demonstrated for **4b** + 0.4 mol kg^{-1} LiTf$_2$N on a platinum and copper electrode respectively. The plating and stripping peaks characteristic of the redox reaction of Li$^+$ could be observed (Fig. 4) and the coulombic efficiencies were estimated to be approximately 83%.

In conclusion, we have developed a new family of very stable ionic liquids based on the 3-azabicyclo[3.2.2]nonane ring structure which makes a logical contribution to a set of existing cation structures. A study of physicochemical properties and a comparison with related structures have revealed organic plastic crystal phases, wide electrochemical windows and highly reversible lithium metal electrodeposition. These properties will allow ABN1*n*Tf$_2$N–LiTf$_2$N mixtures to be used in rechargeable lithium-metal batteries, and also offer the prospect of a solid electrolyte equivalent through harnessing one of the OPC phases.

Notes and references

‡ We thank James Beavis and Dr Rob Rees for the computational work.

§ We note that the P15 salt of the pyrrolidinium series is a solid at 25 °C.

¶ This phase transition is observed when **4b** is isolated from water.

1 L. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1992, 965.
2 L. Fuller, R. T. Carlin, H. C. De Long and D. Haworth, *J. Chem. Soc., Chem. Commun.*, 1994, 299.
3 (*a*) *Ionic Liquids in Synthesis*, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Weinheim, Germany, 2003; (*b*) T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459; (*c*) J. Eßer, P. Wasserscheid and A. Jess, *Green Chem.*, 2004, **6**, 316; (*d*) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3773; (*e*) J. D. Holbrey and K. R. Seddon, *Clean Prod. Process*, 1999, **1**, 223.
4 (*a*) M. C. Buzzeo, R. G. Evans and R. G. Compton, *ChemPhysChem*, 2004, **5**, 1106; (*b*) S. Z. El Abedin, E. M. Mustafa, R. Hempelmann, H. Natter and F. Endres, *Electrochem. Commun.*, 2005, **7**, 1111; (*c*) P. C. Howlett, D. R. MacFarlane and A. F. Hollenkamp, *Electrochem. Solid-State Lett.*, 2004, **7**, A97–A101; (*d*) H. Sakaebe and H. Matsumoto, *Electrochem. Commun.*, 2003, **5**, 594; (*e*) P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar and M. Grätzel, *J. Am. Chem. Soc.*, 2003, **125**, 1166.
5 (*a*) T. Herzig, C. Schreinera, D. Gerhard, P. Wasserscheid and H. J. Gores, *J. Fluorine Chem.*, 2007, **128**, 612; (*b*) Z. Zhou, H. Matsumoto and K. Tatsumi, *Chem.–Eur. J.*, 2006, **12**, 2196; (*c*) H. Matsumoto, H. Sakaebe and K. Tatsumi, *J. Power Sources*, 2005, **146**, 45; (*d*) D. Gerhard, S. C. Alpaslan, H. J. Gores, M. Uerdingen and P. Wasserscheid, *Chem. Commun.*, 2005, 5080; (*e*) D. R. MacFarlane, P. Meakin, J. Sun, N. Amini and M. Forsyth, *J. Phys. Chem. B*, 1999, **103**, 4164; (*f*) J. Sun, M. Forsyth and D. R. MacFarlane, *J. Phys. Chem. B*, 1998, **102**, 8858.
6 D. R. MacFarlane, J. Huang and M. Forsyth, *Nature*, 1999, **402**, 792.
7 N. Matsumi, M. Miyake and H. Ohno, *Chem. Commun.*, 2004, 2852.
8 T. Mukai, M. Yoshio, T. Kato, M. Yoshizawa and H. Ohno, *Chem. Commun.*, 2005, 1333.
9 C. Tiyapiboonchaiya, J. M. Pringle, J. Sun, N. Byrne, P. C. Howlett, D. R. MacFarlane and M. Forsyth, *Nat. Mater.*, 2004, 3, 29.
10 M. Yoshizawa-Fujita, D. R. MacFarlane, P. C. Howlett and M. Forsyth, *Electrochem. Commun.*, 2006, **8**, 445.
11 (*a*) V. L. Brown, Jr. and T. E. Stanin, *Ind. Eng. Chem. Prod. Res. Dev.*, 1965, **4**, 40; (*b*) C. A. Wulff and E. F. Westrum, *J. Phys. Chem.*, 1964, **68**, 430.
12 F. F. C. Bazito, Y. Kawano and R. M. Torresi, *Electrochim. Acta*, 2007, **52**, 6427.
13 (*a*) J. Timmermans, *J. Phys. Chem. Solids*, 1961, **18**, 1; (*b*) A. J. Hill, J. Huang, J. Efthimiadis, P. Meakin, M. Forsyth and D. R. MacFarlane, *Solid State Ionics*, 2002, **154–155**, 119.
14 T. Shimizu, S. Tanaka, N. Onoda-Yamamuro, S. Ishimaru and R. Ikeda, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 321.
15 E. I. Cooper and C. A. Angell, *Solid State Ionics*, 1986, **18–19**, 570.
16 G. A. Snook, A. S. Best, A. G. Pandolfo and A. F. Hollenkamp, *Electrochem. Commun.*, 2006, **8**, 1405.