Three novel anions based on pentafluorophenyl amine combined with two new synthetic strategies for the synthesis of highly lipophilic ionic liquids[†]‡

Thomas Linder and Jörg Sundermeyer*

Received (in Cambridge, UK) 24th December 2008, Accepted 10th March 2009 First published as an Advance Article on the web 1st April 2009 DOI: 10.1039/b823153b

The three new fluorinated anions BPFPA, PFTFSI, and PFNFSI for highly hydrophobic, hydrolytically stable ionic liquids are introduced, together with a strategy allowing a combinatorial approach for the synthesis of imidazolium and phosphonium based ionic liquids of these relatives of bistriflylimide (BTFSI).

Highly hydrophobic, non-hygroscopic and water immiscible ILs are promising candidates for two-phase (water–IL) catalysis or as solvents for lithium electrolytes in electrochemical devices.^{1,2} Most known hydrophobic ILs consist of imidazolium or phosphonium cations in combination with anions such as tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) and, in particular BTFSI, which is more stable with respect to hydrolysis. In a simplified model, the strong electron withdrawing properties of the fluorine atoms give rise to delocalization of the negative anion charge, and as a consequence low coulombic interactions between anion and cation, and by that means low lattice energies and melting points.

For ILs used in electrochemical devices synthetic procedures have to be provided that guarantee the absence of any oxidizable anion impurities, such as chloride, bromide or iodide. Unfortunately the most common procedure for IL synthesis, ion metathesis, has the disadvantage of ending up in halide exchange equilibria that have to be shifted more or less to one side. Direct synthesis of ILs from volatile anion and cation precursors that are easily purified *via* distillation is a highly competitive alternative, realized for example in the direct synthesis of imidazolium triflates *via* methylation of *N*-alkylimidazoles by methyl triflate or in the deprotonation of Brønsted acids by *N*-heterocyclic carbenes reported by Seddon *et al.*³ and a patent by BASF AG.⁴

Here we describe the favourable combination of two innovations in IL design and synthesis: introduction of three new fluorinated anions related to the prominent parent BTFSI *via* stepwise substitution of alkylsulfonyl groups by electronwithdrawing pentafluorophenyl groups and the use of two types of uncommon volatile zwitterionic and strongly basic cation precursors as synthons for IL synthesis, namely 2-alkyl-

Fachbereich Chemie der Philipps-Universität Marburg,

idene-imidazolines⁵ (also known as N,N-ketenediacetals or ene-1,1-diamines) and trialkyl phosphonium ylides, next to N-heterocyclic carbenes.

On the anion precursor side bis(2,3,4,5,6-pentafluorophenyl)amine $HN(C_6F_5)_2$ is easily synthesized on a large scale from the cheap starting materials LiNH₂ and C₆F₆.⁶ We developed a better synthesis for the known acid N-(2,3,4,5,6-pentafluorophenyl)-N-trifluoromethylsulfonamide $HN(C_6F_5)SO_2CF_3$ and its new derivative N-(2,3,4,5,6-pentafluorophenyl)-N-nonafluorobutylsulfonamide $HN(C_6F_5)SO_2C_4F_9$ (Scheme 1).[‡] On the cation precursor side, we developed a method to deprotonate 1,2-dimethyl-3-alkyl imidazolium salts by strong bases such as NaNH₂, KH or KO-tert-Bu and to purify the so unknown asymmetrically substituted air-sensitive far 1-methyl-2-methylidene-3-alkylimidazolines (alkyl = ethyl, *n*-butyl, *n*-octyl) by distillation. Furthermore the vlide *n*-Bu₃P-CH₂⁸ is easily synthesized from technically available and cheap Bu₃P, distilled and stored as an air-sensitive liquid on a large scale. In a combinatorial approach combining three bases with three acids in an inert solvent (hexane or ether) nine new ILs formed almost quantitatively. Their melting or glass temperatures as well as decomposition temperatures were determined by DSC/TGA (Scheme 2).

The thermal stability of this set of ILs is mainly dependent on the nature of the anion. Whereas BPFPA derived ILs show a mass loss at temperatures between 170 °C and 190 °C, triflyl and nonaflyl derivatives with PFTFSI and PFNFSI anions exhibit higher thermal stabilities of up to 290 °C. Some of them, namely [BMIM][PFTFSI], [BMIM][PFNFSI], [BMMIM][PFNFSI], [Bu₃PMe][PFTFSI] and [Bu₃PMe][PFNFSI], are liquids at room temperature (RTIL). It is worth mentioning that, on the cation side, 2-H substituted imidazolium salts are in general less stable towards thermal decomposition or the formation of carbene complexes when used as solvents for metal catalysts⁹ than the 2-alkyl imidazolium and tetraalkyl



Scheme 1 Preparation of the anion precursors.

Hans-Meerwein-Str., 35032 Marburg, Germany.

E-mail: jsu@staff.uni-marburg.de; Fax: +49 6421 28-25711; Tel: +49 6421 28-25693

[†] Dedicated to Professor Helmut Werner on the occasion of his 75th birthday.

[‡] Electronic supplementary information (ESI) available: Experimental details. CCDC 715077–715078. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b823153b



Scheme 2 General procedure for the synthesis of the ILs ($X^- = Cl^-$, Br^- or I^- ; HA = BPFPA-H, PFTFSI-H or PFNFSI-H).

phosphonium based counterparts, accessible by the general strategy reported here.

The most powerful method for studying specific anioncation interactions is single crystal XRD analysis. Interestingly, independent of the cation, all PFTFSI and PFNFSI salts reveal good solubility in Et₂O whereas BPFPA salts show limited solubility in Et₂O, which served as the solvent for growing single crystals of [BMMIM][BPFPA]. In order to directly compare this 1-methyl-2-methyl-3-butylimidazolium with a 1-methyl-3-butylimidazolium salt with the same anion, [BMIM][BPFPA] was crystallized; however the crystals were



Fig. 1 ORTEP-plot of the molecular structure of [BMMIM][BPFPA]. Thermal ellipsoids are shown for a probability of 30%.



Fig. 2 ORTEP-plot of the molecular structure of [*iPiPIM*][BPFPA]. Thermal ellipsoids are shown for a probability of 30%.

not of X-ray quality. Therefore a 1,3-diisopropyl-2*H*-imidazolium salt [*iPiPIM*][BPFPA] was chosen as reference for specific anion–cation interactions. The results of the XRD analyses are shown in Fig. 1 and 2 and Table 1. In both structures all proton positions could be localized and were refined isotropically.

[BMMIM][BPFPA] consists of a quasi naked bis(pentafluorophenyl)amide anion packed into the lattice of imidazolium cations. As the imidazole ring is substituted by a methyl group at the 2-position (C13), the closest contact of the amide nitrogen atom N1 to the most acidic CH bond of the cation is defined by N1–H2 248(2) pm or N1–C14 336.4(2) pm, whereas the shortest distance to the 2-H imidazolium cation of [*iPiPIM*][BPFPA] is defined by N1–H1 220(2) pm or N1–C13 312.2(3) pm. In both lattice structures there are

Table 1 Crystallographic data

[BMMIM][BPFPA]	
Empirical formula	$C_{21}H_{17}F_{10}N_3$
Formula weight	501.38
Crystal system	Triclinic
Unit cell dimensions	
$a = 9.8625(11) \text{ Å}_{a}$	$\alpha = 81.843(13)^{\circ}$
b = 10.3192(12) Å	$\beta = 80.651(13)^{\circ}$
c = 10.8965(12) Å	$\gamma = 75.228(13)^{\circ}$
Volume	$1052.2(2) \text{ Å}^3$
Temperature	193(2) K
Space group	$P\overline{1}$
Z	2
Reflections collected	10 424
Independent reflections	3839 [R(int) = 0.0573]
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0345, WR2 = 0.0943
R indices (all data)	R1 = 0.0433, WR2 = 0.0984
CCDC no.	715077
[IPTPINI][BPFPA]	CHEN
	$C_{21}\Pi_{17}\Gamma_{10}N_3$
Formula weight	SUI.38 Manaalinia
Unit call dimensions	Wonoenne
a = 14.1670(16) Å	$ = 00^{\circ}$
a = 14.1070(10) A b = 11.0200(10) Å	$\alpha = 90$ $\rho = 01.0680(10)^{\circ}$
b = 11.0290(10) A a = 12.6160(14) Å	p = 91.0080(10)
c = 13.0100(14) A	$\gamma = 90$ 2127 1(4) Å ³
Temperature	2127.1(4) A 103(2) K
Space group	$C^{2/c}$
7	4
Reflections collected	10 551
Independent reflections	2269 [R(int) = 0.0338]
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0355 wR2 = 0.0969
R indices (all data)	R1 = 0.0507, WR2 = 0.1020
CCDC no.	715078

	λ_{max}/nm (Reichardt)	$E_{\rm T}{}^{\rm N}$	$\lambda_{\rm max}/{\rm nm}$ (Spange 1)	β	$\lambda_{\rm max}/{\rm nm}$ (Spange 2)	π^*	α
[BMIM][NTf ₂]	—	0.644	585.5	0.42	630.0	0.92	0.64
[BMIM][PFTFSI]	560.8	0.626	602.0	0.52	629.5	0.91	0.61
[BMIM][PFNFSI]	557.5	0.635	597.0	0.49	626.0	0.86	0.67

Table 2 Absorption maxima and polarity parameters of the novel [BMIM]-ILs

additional long anion cation contacts via very weak F-HC hydrogen bridges.[‡] The amide anion of [*i*P*i*PIM][BPFPA] reveals crystallographically imposed C_2 symmetry. The N1-C1 distance 136.3(2) pm well between the ideal C-C single and double bond length and the C1–N1–C1' angle of $121.7(2)^{\circ}$ are indicators of an sp² character of the amide nitrogen atom and a perfect charge delocalisation into the C₆F₅ rings. In the non-fluorinated diphenylamide [Ph3PEt][NPh2] contact ion pair, N-C bond distances of 138.0(5) pm, 136.5(3) pm and an angle of 121.5(3)° was found.¹⁰ In this BPFPA salt accumulation of negative charge at the para fluorine ring atoms is also indicated by a shift of $\delta_{\rm F}$ (D₃CCN) values from -166.53 ppm (free acid) to -187.19 ppm ([BMIM][BPFPA]) upon deprotonation. However, perfect conjugation within the anion is hampered by steric factors. The interplanar angle of both pentafluorophenyl rings is 57.7°.

To evaluate the hydrophobic nature of ILs containing the new perfluorinated anions the maximum water uptake of the RTILs [BMIM][PFTFSI] and [BMIM][PFNFSI] was examined using the Karl-Fischer titration method. Probes of both ILs were equilibrated with deionized water and stirred at room temperature for five hours. After phase separation the water content of the IL phase was determined. [BMIM][PFTFSI] exhibits a maximum water uptake of 2.7 mass% and [BMIM][PFNFSI] an uptake of 2.8 mass%. These values are slightly higher than the reported values for the RTIL [BMIM][BTFSI] (2.0 mass%) and lie in the same range as the value observed for the IL [BMIM][PF6] (2.7 mass%).¹¹

Furthermore the polarity displays a significant characteristic for the hydrophobic nature of a liquid. To achieve comparable values for the novel ILs UV/VIS spectra with a set of solvatochromic dyes were recorded. Reichardt's betaine dye provides the normalized polarity solvent scale values $E_T^{N,12}$ and the two dyes recently developed by Spange allowed a direct determination of the Kamlet–Taft parameters β (a measure of anion H-bond acceptor ability) and π^* (a measure of polarizability).¹³ Structures of the dyes are depicted in the ESI.[‡] The last parameter α (a measure of the cation H-bond donator ability) can be calculated according to an equation developed by Marcus.¹⁴ The obtained absorption maxima and the resulting parameters are summarized in Table 2.

The values obtained are similar to the values obtained for the prototype of a hydrophobic IL [BMIM][BTFSI].^{12,15} The IL incorporating the PFTFSI anion possesses the lowest E_T^N value of all investigated ILs with a value of 0.626. Both our ILs tend to have a higher ability to accept hydrogen bridges, represented by the β value, compared to [BMIM][BTFSI], whereas the dipolarity/polarizability is nearly identical for all investigated RTILs. As expected the α values, representing the hydrogen-bridge-donation ability, is nearly identical for all investigated ILs since this value is mainly influenced by the cations. The lower π^* value of the PFNFSI-based compared to PFTFSI-based ILs is in accord with delocalisation of negative charge by a larger perfluoroalkyl substituent. [BMIM][PFNFSI] possesses the lowest π^* value among all known and investigated ILs.

Our results hopefully will encourage the science community to use highly basic zwitterionic cation precursors, namely 1-methyl-2-alkylidene-3-alkylimidazolines, tetraalkylphosphonium ylides, next to *N*-heterocyclic carbenes as synthons for highly efficient IL syntheses and in combinatorial approach. We also hope that the three new fluorinated anions BPFPA, PFTFSI, and PFNFSI related to the most prominent parent BTFSI will provide some impulse for further investigations with respect to their use in highly hydrophobic, water immiscible and hydrolytically stable ILs or their use as electrolyte anions such as in lithium salts.

This work was supported by the Deutsche Forschungsgemeinschaft, Priority Program 1191, Ionic Liquids.

Notes and references

- Ionic Liquids in Synthesis, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Weinheim, Germany, 2003; *Electrochemical Aspects* of Ionic Liquids, ed. H. Ohno, Wiley-Interscience, New York, 2005.
- 2 T. Frömling, M. Kunze, M. Schönhoff, J. Sundermeyer and B. Roling, J. Phys. Chem. B, 2008, 112, 12985–12990.
- 3 M. J. Earle and K. R. Seddon, WO 01/77081 A1, 2001.
- 4 M. Maase and K. Massonne, DE 103 33 239 A1, 2005.
- 5 T. Linder and J. Sundermeyer, WO 2007/131498 A2; Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser and R. Boese, J. Chem. Soc., Chem. Commun., 1993, 1136–1137; A. Fürstner, M. Alcarazo, R. Goddard and C. W. Lehmann, Angew. Chem., Int. Ed., 2008, 47, 3210–3214.
- 6 R. Koppang, Acta Chem. Scand., 1971, 25, 3067-3071.
- 7 R. D. Trepka, J. K. Harrington, J. W. McConville, K. T. McGurran, A. Mendel, D. R. Pauly, J. E. Robertson and J. T. Waddington, J. Agric. Food Chem., 1974, 22, 1111–1119.
- 8 R. Köster, D. Simić and M. A. Grassberger, *Liebigs Ann. Chem.*, 1970, **739**, 211–219.
- 9 L. Xu, W. Chen and J. Xiao, Organometallics, 2000, 19, 1123–1127.
- 10 M. G. Davidson and S. Lamb, Polyhedron, 1997, 16, 4393-4395.
- 11 J. Jaquemin, P. Husson, A. A. H. Padua and V. Majer, *Green Chem.*, 2006, 8, 172–180.
- 12 C. Reichardt, Chem. Soc. Rev., 1992, 147–153; C. Reichardt, Pure Appl. Chem., 2004, 76, 1903–1919.
- 13 A. Oehlke, K. Hofmann and S. Spange, New J. Chem., 2006, 30, 533–536.
- 14 Y. Marcus, Chem. Soc. Rev., 1993, 22, 409-416.
- 15 R. Lungwitz and S. Spange, New J. Chem., 2008, 32, 392-394.