Brønsted Acidic Ionic Liquids and Their Zwitterions: Synthesis, Characterization and pK_a Determination

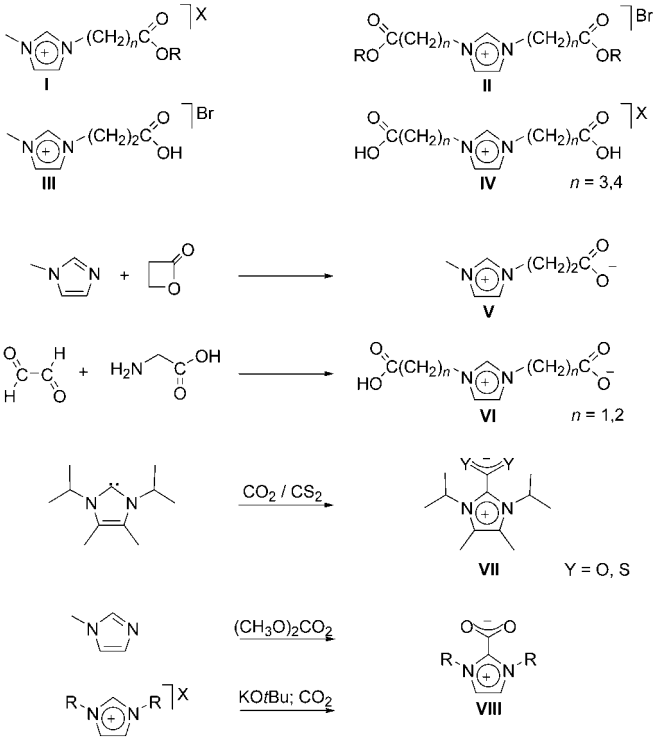
Zhaofu Fei, Dongbin Zhao, Tilmann J. Geldbach, Rosario Scopelliti, and Paul J. Dyson*[a]

Abstract: Imidazolium chlorides with one or two carboxylic acid substituent groups, 1-methyl-3-alkylcarboxylic acid imidazolium chloride, [Me{$(CH_2)_n$COOH}im]Cl ($n=1$, 3), and 1,3-dialkylcarboxylic acid imidazolium chloride, [{$(CH_2)_n$COOH}$_2$im]Cl ($n=1$, 3), have been synthesized via their corresponding acid esters. Deprotonation of the carboxylic acid functionalized imidazolium chlorides with triethylamine affords the corresponding zwitterions [Me{$(CH_2)_n$COO}im] ($n=1$, 3) and [{$(CH_2)_n$COOH}{$(CH_2)_n$COO}im] ($n=1$, 3). Subsequent reaction of the zwitterions with strong acids gives the new imidazolium salts [Me{$(CH_2)_n$COOH}im]X ($n=1$, 3; X = BF_4, CF_3SO_3) and [{$(CH_2)_n$COOH}$_2$im]X ($n=1$, 3; X = BF_4, CF_3SO_3), which exhibit melting points as low as −61 °C. The solid-state structures of two of the carboxylic acid functionalized imidazolium salts have been determined by single-crystal X-ray diffraction analysis. Extensive hydrogen bonding is present between the chloride and the imidazolium, with eight Cl···H interactions below 3 Å. The pK_a values of all the salts, determined by potentiometric titration, lie between 1.33 and 4.59 at 25 °C.

Keywords: acidity · carboxylic acids · imidazolium salts · structure elucidation · zwitterions

Introduction

Room-temperature ionic liquids continue to attract considerable interest as alternative reaction media.[1] Low-melting ionic liquids based on imidazolium cations are the most intensively investigated among those available, and a variety of functional groups have been attached in order to modify their physical and chemical properties, including, among others,[2] amines,[3,4] amides,[4] ethers and alcohols,[5] phosphines,[6] and fluorous side chains.[7] High-melting imidazolium salts with acidic groups have been known for many years, but only recently were the first room-temperature sulfonic acid functionalized ionic liquids prepared by Davis and co-workers, who employed them as both solvent and catalyst in esterification reactions.[8] Various imidazolium cations with carboxylic ester or acid groups are known; a selection is shown in Scheme 1. Cations with carboxylic ester groups (**I**) have been prepared by quarternization of 1-methyl imidazole with chloroalkylcarboxylic acid esters.[9,10] Related imidazolium salts functionalized with 1,3-dicarboxylic esters (**II**) were obtained from reaction of imidazole potassium salt with two equivalents of bromoalkylcarboxylic acid esters.[11]



Scheme 1. Some of the known imidazolium salts containing carboxylic ester and acid groups, and their corresponding zwitterions.

[a] Dr. Z. Fei, D. Zhao, Dr. T. J. Geldbach, R. Scopelliti, Prof. P. J. Dyson
Institut des Sciences et Ingénierie Chimiques
Ecole Polytechnique Fédérale de Lausanne
EPFL-BCH, 1015 Lausanne (Switzerland)
E-mail: paul.dyson@epfl.ch

DOI: 10.1002/chem.200400145

Imidazolium salts containing carboxylic acid groups (**III**) have been used as precursors for benzimidazolate zwitterions[12] and type **IV** salts appear in the patent literature as materials for the pharmaceutical industry.[13] Several examples of zwitterions based on the 1,3-imidazole skeleton are known. Compound **V** was prepared from the reaction of 1-methylimidazole with β-propiolactone,[14] and zwitterions of type **VI** were first observed as products in the glucose–glycine Maillard reaction,[15] but have subsequently been prepared by the condensation of glyoxal with glycine.[16] The solid-state structure of **VI** ($n=1$) determined by single-crystal X-ray diffraction reveals the presence of CH_2COO^- and CH_2COOH units.[17] These groups are connected by strong intermolecular O···H–O hydrogen bonding with O···O = 2.463 Å, possibly contributing to the high melting (decomposition) point of 290 °C. Furthermore, addition of CO_2 or CS_2 to 1,3-dialkylimidazolium-2-ylidenes affords 2-imidazolium zwitterions (**VII**),[18] and the condensation reaction between 1-methylimidazole and dimethyl carbonate leads to similar compounds (**VIII**).[19] The latter undergo an extensive chemistry and, in particular, can be transformed into "halogen-free" ionic liquids under controlled protonation.[20] The zwitterion **VIII** is also accessible by deprotonation of imidazolium salts under an atmosphere of CO_2.[21]

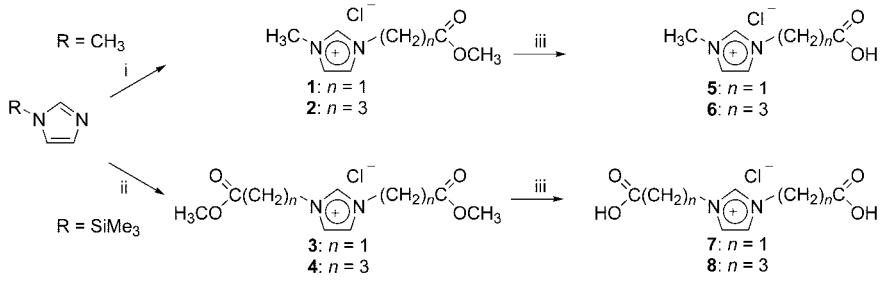
Since one of the most important applications of ionic liquids is as reaction media for clean catalysis,[1] we were interested in developing a series of low-melting imidazolium salts incorporating COOH groups. So far, however, all known examples of imidazolium salts bearing carboxylic acid groups have high melting points and therefore have had no application as reaction media. Furthermore, many of them have been prepared in a rather special manner that is not applicable to obtaining a wider range of products. We describe here the synthesis and characterization of a series of ionic liquids with carboxylic acid functionalities, with melting points as low as −61 °C. They have been derived in almost quantitative yield from their corresponding zwitterions in a way which effectively eliminates any chloride contamination.

Results and Discussion

As the reaction of imidazole with halo acids may lead to considerable protonation at the nitrogen atom instead of alkylation, a different approach was sought to obtain carboxylic acid functionalized imidazolium cations. Reaction of methyl chloroacetate and methyl chlorobutyrate with 1-methylimidazole affords **1** and **2**, respectively, in high yield (Scheme 2). The bis-substituted compounds **3** and **4** are obtained from the addition of two equivalents of halo acid to trimethylsilyl imidazole.[22] As the next reaction step takes place in aqueous solution, the very hygroscopic nature of all the ester compounds does not cause any problems. Heating **1**–**4** to reflux in aqueous hydrochloric acid affords **5**–**8** in quantitative yield. Hence, carboxylic acid esters, synthesized by the commonly used quarternization method,[23] represent ideal precursors for the preparation of the desired carboxylic acid functionalized imidazolium salts.

The NMR spectra of the new compounds are by and large as expected (see Experimental Section). The carboxylate carbon atom is sensitive to the proximity of the positive charge and is shifted by $\delta \approx 7$ ppm to higher frequency on increasing the aliphatic chain length, that is, from $\delta =$ 172.7 ppm in **7** to $\delta = 179.7$ ppm in **8**. The positive-ion electrospray ionization mass spectra (ESI-MS) of **1**–**8** show the cation as the most abundant peak, although aggregates corresponding to oligomers $[(\text{cation})+(\text{cation}-\text{H})_n]^+$ ($n=0$–5) are present when the spectra are recorded at high concentrations. For example, the positive-ion ESI-MS of **8** diluted in water to 250 ppm shows a single peak at $m/z = 241$ corresponding to the intact 1,3-dibutylcarboxylic acid imidazolium cation. In a 500 ppm solution but otherwise under identical conditions, in addition to the peak at $m/z = 241$, a peak of low relative intensity is observed at $m/z = 481$ corresponding to $[(\text{cation})+(\text{cation}-\text{H})]^+$. At a higher concentration, approximately 1000 ppm, a third peak at $m/z = 721$ is also observed and can be assigned to the trimer $[(\text{cation})+(\text{cation}-\text{H})_2]^+$. Similarly, a tetramer at $m/z = 961$ and a pentamer at $m/z = 1201$ are observed as the concentration is increased further. All of the new salts show oligomers in which a proton is lost as a new cation is attached; this rules out aggregation due to hydrogen bonding. Presumably the carboxylate group forms an ionic interaction with the neighboring imidazolium cation. The aggregates are different in nature from those usually detected by mass spectrometry for unfunctionalized ionic liquids. There, peaks for ionic liquids other than those for the molecular cation are usually composed of cation–anion aggregates of general formula $[(\text{cation})_{n+1}+(\text{anion})_n]^+$, and these are also highly concentration-dependent.[24]

Crystals of **6** and **8** suitable for X-ray diffraction were obtained from water–acetonitrile mixtures at 0 °C. The cations are depicted in Figure 1 and a selection of bond lengths and angles of the cations in **6** and **8** are given in Table 1. From comparison of the new structures with those of unfunctionalized alkylimidazolium salts, the presence of the carboxylic acid group and the bonding within the imidazolium ring do



Scheme 2. Synthetic route to the imidazolium salts **1**–**8**. Reagents and conditions: i) 1 equiv $Cl(CH_2)_nCOOCH_3$, RT, 1 h for **1**; 60 °C, 24 h for **2**; ii) 2 equiv $Cl(CH_2)_nCOOCH_3$, 60 °C, 24 h; iii) 37 % aqueous HCl solution, 100 °C, 2 h.

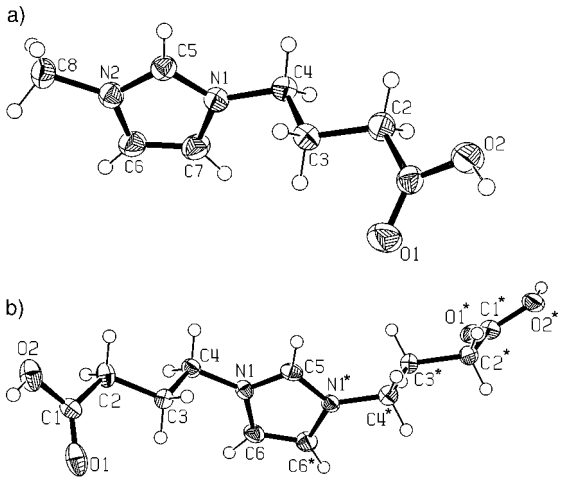


Figure 1. Top: ORTEP plot of the cation **6**; ellipsoids drawn at the 50% probability level. Bottom: ORTEP plot of the cation **8**; ellipsoids drawn at the 50% probability level; the starred atoms are obtained by the symmetry operation $-x+1, -y, z$.

Table 1. Selected bond lengths [Å] and angles [°] of **6** and **8**.

	6	**8**
C1–O1	1.206(4)	1.202(4)
C1–O2	1.318(4)	1.330(4)
C1–C2	1.505(4)	1.505(5)
C5–N1	1.337(4)	1.337(4)
C5–N2	1.328(4)	1.337(4)
C6–C7	1.347(5)	1.349(7)
N1–C7	1.373(4)	1.390(4)
N2–C6	1.377(4)	1.390(4)
O2···Cl1	3.019(4)	3.001(4)
O1-C1-O2	123.9(3)	123.7(3)
C5-N1-C7	108.1(3)	108.5(3)
C5-N2-C6	108.0(3)	108.5(3)

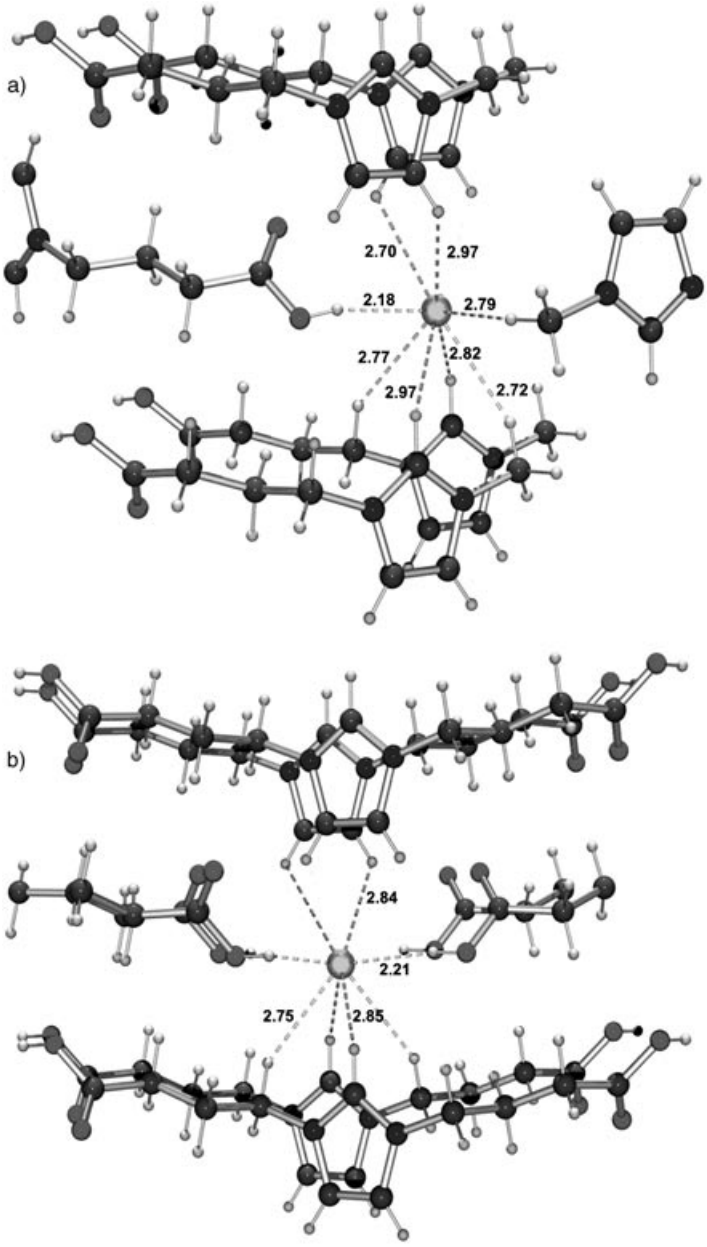


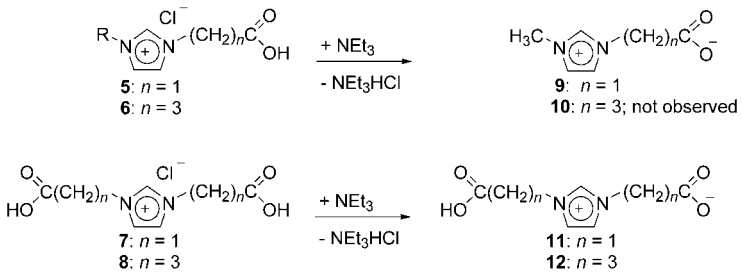
Figure 2. Top: Ball and stick representation of the hydrogen-bonding interactions between the cation and chloride in **6**. Bottom: Ball and stick representation of the hydrogen-bonding interactions between the cation and the chloride in **8**.

not appear to influence each other significantly. Bond lengths and angles are basically identical, within experimental error, with those reported previously.[25] The bond lengths within the imidazolium ring, ranging between 1.328(4) and 1.390(4) Å, are in agreement with the presence of conjugated double bonds. Even in zwitterionic structures, for example, **VIII** in Scheme 1, these bond lengths remain essentially unchanged.[19]

More interesting is the presence of a strong hydrogen-bonding network in both compounds; Figure 2 shows the interaction of the chloride ion in **6** and **8** with proximate hydrogen atoms, all being closer than 3 Å. Such hydrogen bonding is well known from other imidazolium chloride structures,[17,19,25] but it is especially pronounced in **6** and **8**, in which there are eight contacts close (<3 Å) to the chloride stemming from six different cations. The strongest interactions arise from the OH protons, with O–H···Cl distances and angles of 2.18 Å and 167.0° (**6**) and 2.21 Å and 169.1° (**8**), respectively. In **8**, this leads to formation of infinite, one-dimensional chains of the cation and anion. In addition, all the hydrogen atoms belonging to the imidazolium ring are involved in hydrogen bonding to different chloride anions, together with the axial protons at C4 and, in case of **6**, two protons at C8.

The carboxylic acid functionalized imidazolium salts **5**–**8** are Brønsted acids, and treatment with a mild base such as triethylamine is sufficient to afford the corresponding zwitterions **9**, **11**, and **12**, within 24 h in essentially quantitative yield (Scheme 3) (stronger bases could result in a Hofmann-type elimination).[26]

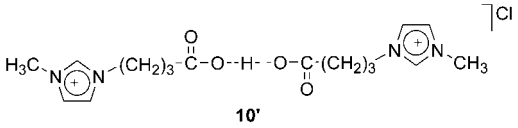
Compound **11** has been prepared previously, though in an entirely different manner; see **VI** ($n=1$) in Scheme 1. As the resulting compounds are insoluble in nonprotic solvents, the NEt_3·HCl formed can be easily removed by washing the residue with dichloromethane. Further recrystallization of



Scheme 3. Synthesis of zwitterions **9**, **11**, and **12**.

the products from water–acetone at room temperature afforded the products in pure, chloride-free form. Absence of chloride impurities was established in the first instance by a negative test reaction with aqueous $AgNO_3$ and then by ESI-MS.

In contrast to the chemistry of **5**, **7**, and **8**, reaction of **6** with triethylamine does not afford the desired zwitterion **10**; this might be a reflection of the significantly weaker acidity of **6** than **5** (vide infra). Reaction of the isolated product with $AgNO_3$ provides a positive test for the presence of chloride. In the mass spectrum, the signal at $m/z = 169$ for the single acid unit is the most intense peak, but a dimeric cation at $m/z = 337$ is also observed. Crystals suitable for X-ray diffraction were obtained from water–acetonitrile, but because of the presence of a disordered water molecule the structure could not be solved unambiguously. On the basis of the available data, we tentatively propose structure **10′**, in which one proton is shared by two imidazolium molecules, as the reaction product; this is also in accordance with the elemental analysis.



In D_2O the ^1H and ^{13}C NMR spectra undergo only minor changes on conversion of the acids to the zwitterion derivatives. However, the IR spectra of **9**–**12** clearly differ from those of the starting materials. The chloride salts **5**–**8** contain weak/medium absorptions in the range 2400–2800 cm^{-1}, which have been assigned to C–H···Cl vibrations. In the zwitterions these vibrational bands are no longer observed, providing further evidence that chloride is no longer present (Figure 3). Although a chloride anion is still present in **10′**, its interaction with the cation appears to have changed considerably, according to IR spectroscopy, as most of the bands in the 2400–2800 cm^{-1} region mentioned above have disappeared.

Treatment of **11** and **12** with excess triethylamine at room temperature does not lead to further deprotonation. However, careful titration of **12** with stronger inorganic bases, such as NaOH or KOH (the pH of the reaction mixture must not exceed 7.0), results in solutions that exhibit peaks at $m/z =$ 263 and 279 in the ESI-MS spectrum, suggesting the formation of the sodium and potassium salts **13** and **14**, respectively (Scheme 4).

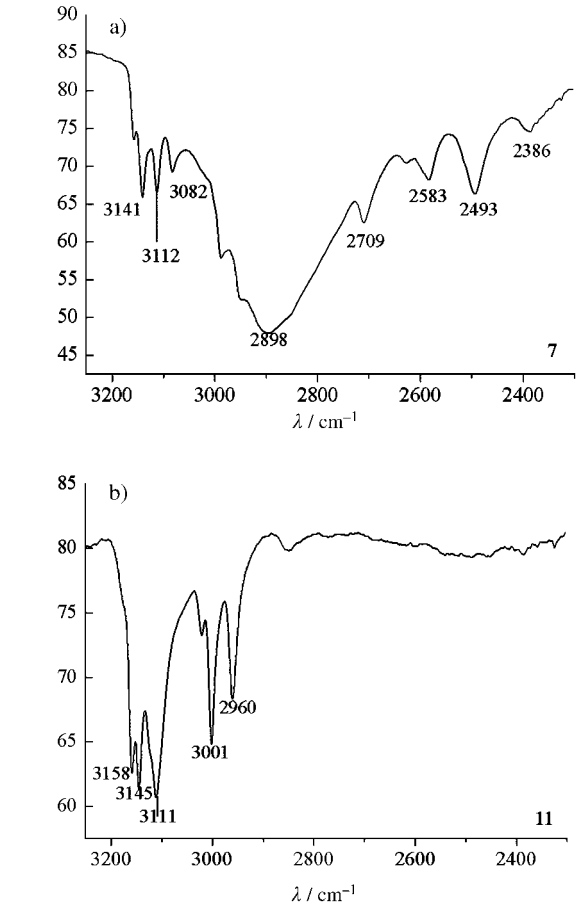
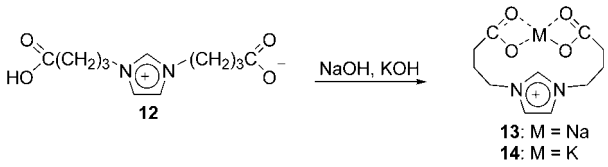
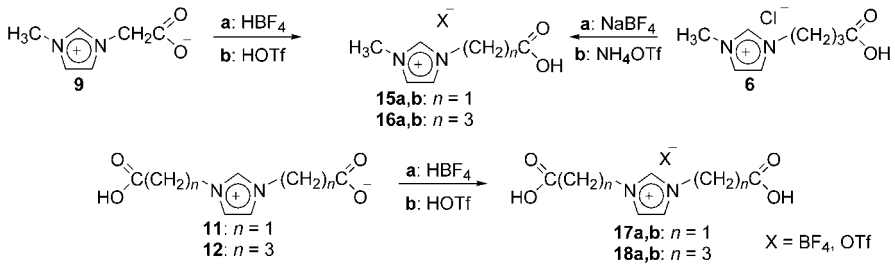


Figure 3. IR spectra of the imidazolium chloride **7** (top) and its corresponding zwitterions **11** (bottom).



Scheme 4. Possible formation of **13** and **14**.

Addition of the strong acid HBF_4 or HO_3SCF_3 to the zwitterions **9**, **11**, and **12** affords the new carboxylic acid functionalized imidazolium salts **15**, **17**, and **18**, respectively (Scheme 5). Because the zwitterion **10** could not be obtained from reaction of **6** with triethylamine, **16a** and **16b** were prepared by the anion exchange reaction with $NaBF_4$ or $AgSO_3CF_3$ from **6**. Imidazolium salts with BF_4^- or $SO_3CF_3^-$ as anions are usually synthesized by reaction of the corresponding halide with $NaBF_4$[27] or $NH_4SO_3CF_3$;[28] or alternatively, for $SO_3CF_3^-$, direct reaction of alkyltriflate with alkylimidazole.[29] This route via the zwitterions provides two main advantages. First, the reaction is fast and no solvent is required. Secondly, use of theoretically chloride-free zwitterions makes possible the efficient removal of chloride



Scheme 5. Pathway to the carboxylic acids **15**–**18**.

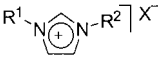
sources, such as NaCl, which can be detrimental in certain applications.[30]

The nature of both the anion and the cation strongly influences the melting point of potential ionic liquids; systematic studies have been undertaken, for example, for imidazolium and tetraalkylammonium salts.[31] These demonstrate that factors such as size, symmetry, and charge distribution play an important role. For unfunctionalized 1-alkyl-3-methylimidazolium salts, some trends have evolved: for the anion, the melting points decrease roughly in the order $Cl \gg PF_6 > BF_4 = Tf_2N = OTf$; for the cation, melting points decrease with increasing alkyl chain length up to C_6–C_8, then increase again. Whether the presence of polar functional groups has a strong effect on the melting point is hard to predict.

Exchanging the hard chloride anion in **5**–**8** for soft, non- or weakly coordinating anions such as BF_4 or OTf, which exert a more diffuse charge distribution, leads to a significant decrease in the melting point (up to $\Delta T = 232\,^{\circ}C$). This is mainly because the hydrogen-bond network between the chloride and imidazolium cation is broken (vide supra). Those salts with short alkyl chains, namely **15** and **17**, have melting/decomposition points above room temperature, ranging between 68 °C and 210 °C, whereas an increase in the chain length leads to a further marked decrease in the melting point. Compounds **16** and **18** are viscous liquids and melt at surprisingly low temperatures, −59 °C to −61 °C. The flexibility of the side arms and the strength of the acid are presumably related to the melting point of the salt, which is discussed further below.

Determination of pK_a: Many chemical transformations are sensitive to the presence of protons. Therefore, knowledge of the pK_a value, especially of the liquid salts **17** and **18**, is important in order to decide about their possible application as reaction media. The acidic strength of carboxylic acids has been subjected to extensive experimental[32] and theoretical[33,34] studies. Imidazolium salts with carboxylic acid groups can be regarded as nonclassical acids due to the presence of the positively charged imidazolium ring and of a counter anion. The pK_a values of the carboxylic acid groups of compounds **5**–**12** and **15**–**18** (Table 2) have been determined by titration with KOH (see Experimental Section). As one might expect, the dicarboxylic acid with the shortest alkyl chain, **7**, is the strongest acid in the series (pK_a = 1.33), its acidity being comparable with the first deprotonation step in oxalic acid.[35] The other acids **5**, **15a**/**15b**, and **17a**/**17b** with $-CH_2COOH$ groups all have a lower first pK_a value (1.40–2.03) than the corresponding halogen-substituted acetic acids (XCH_2COOH, X = F, Cl, Br, I, 2.66–3.13),[32,35] implying that the positively charged imidazolium ring is more strongly electron withdrawing than the halides.

Table 2. pK_a values of carboxylic acids at 25 °C.



	R^1	R^2	X^-	pK_a
5	CH_3	CH_2COOH	Cl	1.90
15a	CH_3	CH_2COOH	BF_4	2.00
15b	CH_3	CH_2COOH	SO_3CF_3	2.03
6	CH_3	$(CH_2)_3COOH$	Cl	3.83
16a	CH_3	$(CH_2)_3COOH$	BF_4	3.95
16b	CH_3	$(CH_2)_3COOH$	SO_3CF_3	4.11
7	CH_2COOH	CH_2COOH	Cl	1.33
17a	CH_2COOH	CH_2COOH	BF_4	1.40
17b	CH_2COOH	CH_2COOH	SO_3CF_3	1.44
8	$(CH_2)_3COOH$	$(CH_2)_3COOH$	Cl	3.46
18a	$(CH_2)_3COOH$	$(CH_2)_3COOH$	BF_4	3.60
18b	$(CH_2)_3COOH$	$(CH_2)_3COOH$	SO_3CF_3	3.65
10′	–	–	–	4.59
11	CH_2COOH	CH_2COO^-	–	2.92
12	$(CH_2)_3COOH$	$(CH_2)_3COO^-$	–	4.47

As is known from aliphatic carboxylic acids, increasing the alkyl chain length leads to a decrease in acidity. Accordingly, for **6**, **16a**/**16b**, **8**, and **18a**/**18b**, the first pK_a ranges between 3.46 and 4.11. Thus, the presence of the positive charge on the imidazolium ring has only a minor effect on the acidity once the aliphatic spacer is sufficiently long. The pK_a values of the zwitterionic acids **11** and **12** correspond approximately to the pK_{a2} of the corresponding binary carboxylic acids **7** and **8** without considering any counterion effects. We believe that the latter are a reflection of the different hydrogen-bonding capabilities of the anions. In general, the stronger acids have higher melting points than the weaker acids, and although this can be attributed to increased hydrogen-bonding interactions, the various types of bonds and forces present in an ionic liquid that contribute toward determining the melting point are very complex, so a simple relationship between acidity and melting point cannot be found.

Conclusion

In summary, a versatile and virtually chloride-free route to ionic liquids bearing carboxylic acid functionalities has been established. Depending on the counterion and alkyl chain length, melting points significantly below 0 °C can be observed; the acidity of these novel compounds lies between those of oxalic acid and acetic acid. The route to the zwitter-

ions using triethylamine is straightforward and can be generalized to synthesize other Brønsted acid functionalized imidazolium salts. Controlled acidification of the zwitterions leads to "halide-free" imidazolium salts. Many of the carboxylic acids and zwitterions have melting points below 100 °C; several are liquid at room temperature, and thus can be classified as ionic liquids. Strong Brønsted acidic ionic liquids have been used as reagents/reaction media in organic syntheses[8] and very mildly acidic ionic liquids have been successfully applied as solvents in, for example, ruthenium-catalyzed metathesis reactions.[36] Solid Brønsted acids based on mercury have also been used as reagents in non-Brønsted acidic ionic liquids for which exclusion of water is essential,[37] and the imidazolium salts described herein could probably find many applications as nonaqueous acids, used either neat or dissolved in other ionic liquids. They are also considerably more environmentally benign than many of the alternatives in current use.

Table 3. Crystallographic data for compounds **6** and **8**.

	6	**8**
formula	$C_8H_{13}ClN_2O_2$	$C_{11}H_{17}ClN_2O_4$
M	204.65	276.72
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12$
a [Å^{-1}]	7.728(6)	18.479(6)
b [Å^{-1}]	4.5947(10)	4.5176(5)
c [Å^{-1}]	27.824(10)	7.753(4)
α [°]	90	90
β [°]	97.61(5)	90
γ [°]	90	90
V [Å^{-3}]	979.3(9)	647.2(4)
Z	4	2
ρ_{calcd} [Mg m^{-3}]	1.388	1.420
T [K]	140	140
θ range [°]	3.23–25.02	3.43–24.99
μ [mm^{-1}]	0.360	0.304
reflections measured	5358	4090
unique reflections [$I>2\sigma(I)$]	1653 ($R_{int}=0.0353$)	1125 ($R_{int}=0.0600$)
final $R1$, $wR2[I>2\sigma(I)]$	0.0461, 0.1134	0.0521, 0.1350

Experimental Section

General: The methyl ester of 4-chlorobutyric acid, 1-methylimidazole, and 1-trimethylsilylimidazole were purchased from Acros. HBF_4, CF_3SO_3H, $NaBF_4$, and $AgCF_3SO_3$ were purchased from Aldrich and were used as received without further purification. IR spectra were recorded on a Perkin–Elmer FT-IR 2000 system. NMR spectra were measured in D_2O on a Bruker DMX 400, with $SiMe_4$ as external standard, at 20 °C. The ESI-MS of samples diluted with water were recorded on a ThermoFinnigan LCQ -Deca XP Plus quadrupole ion-trap instrument.[38] Samples were infused directly into the source at 5 μL min^{-1} by using a syringe pump (spray voltage 5 kV; capillary temperature 100 °C). Melting points of all the liquid compounds were measured by differential scanning calorimetry with a SETARAM DSC 131 instrument. Elemental analysis was carried out at the EPFL.

For pK_a determinations in triplicate, a stock solution (0.01 mol L^{-1}) of the complex was prepared in degassed water. The solution was then titrated with aqueous KOH solution (0.100 mol L^{-1}). The pH of the solution was measured using a calibrated glass electrode on a Metrohm 780 pH meter at 295.0(±0.10) K. The pK_a for each compound was calculated by the procedure described by Albert and Serjeant.[39]

Crystallography: Data collection for the X-ray structure determinations was performed on a mar345 IPDS diffractometer system with graphite-monochromated $Mo_{K\alpha}$ (0.71070 Å) radiation and a low-temperature device ($T=140(2)$ K). Colorless crystals of **6** and **8** suitable for X-ray diffraction were obtained from a water–acetonitrile mixture at 0 °C. Data reduction was performed by CrysAlis RED (Oxford Diffraction, 68 Milton Park, Abingdon OX144RX, UK). Structure solution and refinement were performed on PCs by means of the SHELX97[40] software package, and graphical representations of the structures were made with ORTEP32.[41] Structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F^2). An empirical absorption correction (DELABS)[42] was applied for **6**. All atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model, although they can all be located from a Fourier difference density map.

Relevant crystallographic data, and data collection and refinement details, are compiled in Table 3. CCDC-231134 and CCDC-231135 contain the crystallographic data (excluding structure factors) for the structures reported in this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Synthesis of 1 and 2: Under an inert atmosphere of dry nitrogen a mixture of 1-methylimidazole (0.010 mol) and $ClCH_2COOCH_3$ (0.010 mol) was stirred at RT for 1 h, during which time the reaction mixture turned to a solid. The solid was washed with diethyl ether (3×30 mL) and dried under vacuum for 24 h to give **1**. Compound **2** was obtained similarly by refluxing a mixture of 1-methylimidazole (0.010 mol) and $ClCH_2CH_2CH_2COOCH_3$ (0.010 mol) at 60 °C for 24 h and following the same purification procedure; an oil was obtained.

Data for 1: Yield: >99 %; m.p. 240 °C (decomp); ^{1}H NMR: $\delta=8.80$ (s, 1H), 7.50 (s, 1H), 7.48 (s, 1H), 5.18 (s, 2H), 3.94 (s, 3H), 3.83 ppm (s, 3H); ^{13}C NMR: $\delta=171.7$, 140.5, 126.6, 126.5, 56.6, 52.8, 39.0 ppm; IR: $\tilde{\nu}=3144$, 3098, 3002, 2961, 2932, 2841, 1752, 1567, 1426, 1368, 1215, 1175 cm^{-1}; ESI-MS: 155 $[M-Cl]^+$; elemental analysis calcd (%) for $C_7H_{11}ClN_2O_2$: C 44.10, H 5.82, N 14.70; found: C 44.21, H 5.91, N 14.75.

Data for 2: Yield: 97 %; yellowish oil; ^{1}H NMR: $\delta=8.77$ (s, 1H), 7.45 (s, 1H), 7.40 (s, 1H), 4.17 (t, ^3J(H,H) = 7.1 Hz, 2H), 3.80 (s, 3H), 3.60 (s, 3H), 2.38 (t, ^3J(H,H) = 7.1 Hz, 2H), 2.08 ppm (m, 2H); ^{13}C NMR: $\delta=$ 177.7, 139.0, 126.6, 125.2, 55.3, 51.5, 38.5, 33.2, 27.7 ppm; IR: $\tilde{\nu}=3107$, 2956, 1728, 1560, 1438, 1365, 1170 cm^{-1}; ESI-MS: 183 $[M-Cl]^+$; elemental analysis calcd (%) for $C_9H_{15}ClN_2O_2$: C 49.43, H 6.91, N 12.81; found: C 49.51, H 6.98, N 12.80.

Synthesis of 3 and 4: In a typical procedure, a mixture of trimethylsilylimidazole (0.010 mol) and $ClCH_2COOCH_3$ (0.020 mol) for **1** ($ClCH_2CH_2CH_2COOCH_3$ for **2**) was refluxed at 60 °C for 24 h under an inert atmosphere of dry nitrogen. The reaction mixture was washed with diethyl ether (3×30 mL) and dried under vacuum for 24 h.

Data for 3: Yield: 99 %; m.p. 230 °C (decomp); ^{1}H NMR: $\delta=8.90$ (s, 1H), 7.51 (s, 2H), 5.33 (s, 4H), 3.75 ppm (s, 6H); ^{13}C NMR: $\delta=171.4$, 141.4, 126.5, 56.5, 52.9 ppm; IR: $\tilde{\nu}=3074$, 2959, 2921, 2598, 1743, 1560, 1439, 1223 cm^{-1}; ESI-MS: 213 $[M-Cl]^+$; elemental analysis calcd (%) for $C_9H_{13}ClN_2O_4$: C 43.47, H 5.27, N 11.27; found: C 43.53, H 5.34, N 11.35.

Data for 4: Yield: 95 %; off-white oil; ^{1}H NMR: $\delta=8.80$ (s, 1H), 7.49 (s, 2H), 4.20 (t, ^3J(H,H) = 6.8 Hz, 4H), 3.60 (s, 6H), 2.41 (t, ^3J(H,H) = 6.8 Hz, 4H), 2.14 ppm (m, 4H); ^{13}C NMR: $\delta=178.4$, 138.6, 125.5, 55.3, 51.7, 33.2, 27.6 ppm; IR: $\tilde{\nu}=3150$, 2953, 1730, 1564, 1439, 1369, 1170 cm^{-1}; ESI-MS: 269 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{13}H_{21}ClN_2O_4$: C 51.23, H 6.95, N 9.19; found: C 51.36, H 7.02, N 9.13.

Synthesis of 5–8: In a typical procedure, a mixture of **1** (0.010 mol) and HCl (37 % H_2O solution; 0.011 mol for **5** and **6**; 0.022 mol for **7** and **8**) was refluxed for 30 min. The solvent was removed under reduced pressure and the remaining solid was washed with acetone and diethyl ether to give the product as a white powder.

Data for 5: Yield: >98 %; m.p. 204 °C; ^{1}H NMR: $\delta=8.78$ (s, 1H), 7.50 (s, 1H), 7.49 (s, 1H), 5.08 (s, 2H), 3.95 ppm (s, 3H); ^{13}C NMR: $\delta=173.3$, 140.2, 126.4, 126.3, 53.1, 38.8 ppm; IR: $\tilde{\nu}=3418$, 3119, 3097, 2988, 2579, 2490, 2401, 1715, 1580, 1570, 1439, 1400, 1209, 1197 cm^{-1}; ESI-MS: 141 $[M-Cl]^+$; elemental analysis calcd (%) for $C_6H_9ClN_2O_2$: C 40.81, H 5.14, N 15.86; found: C 40.88, H 5.19, N 15.85.

Data for 6: Yield: 95%; m.p. 105°C; ^{1}H NMR: δ=8.77 (s, 1H), 7.45 (s, 2H), 4.17 (t, ^3J(H,H)=7.1 Hz, 2H), 2.38 (t, ^3J(H,H)=7.1 Hz, 2H), 2.08 ppm (m, 2H); ^{13}C NMR: δ=179.7, 139.0, 126.6, 125.2, 51.5, 38.5, 33.2, 27.7 ppm; IR: $\tilde{\nu}$=3404, 3107, 2956, 2762, 2640, 2563, 2509, 2453, 1702, 1558, 1463, 1410, 1268, 1193, 1157, 1063 cm^{-1}; ESI-MS: 169 [M−Cl]$^+$; elemental analysis calcd (%) for $C_8H_{13}ClN_2O_2$: C 46.95, H 6.40, N 13.69; found: C 47.01, H 6.42, N 13.65.

Data for 7: Yield: 97%; m.p. 260°C (decomp); ^{1}H NMR: δ=8.84 (s, 1H), 7.47 (s, 2H), 5.06 ppm (s, 4H); ^{13}C NMR: δ=172.7, 141.1, 126.4, 52.1 ppm; IR: $\tilde{\nu}$=3141, 3112, 2898, 2583, 2493, 1730, 1565, 1404, 1163 cm^{-1}; ESI-MS: 185 [M−Cl]$^+$; elemental analysis calcd (%) for $C_7H_9ClN_2O_4$: C 38.11, H 4.11, N 12.70; found: C 38.23, H 4.14, N 12.65.

Data for 8: Yield: 96%; colorless solid; m.p. 172°C; ^{1}H NMR: δ=8.77 (s, 1H), 7.45 (s, 2H), 4.17 (t, ^3J(H,H)=7.1 Hz, 4H), 2.38 (t, ^3J(H,H)=7.1 Hz, 4H), 2.08 ppm (m, 4H); ^{13}C NMR: δ=179.7, 138.5, 125.5, 51.6, 33.2, 27.6 ppm; IR: $\tilde{\nu}$=3421, 3104, 2920, 2581, 2512, 1710, 1558, 1461, 1433, 1406, 1374, 1263, 1181, 1153, 1063 cm^{-1}; ESI-MS: 241 [M−Cl]$^+$; elemental analysis calcd (%) for $C_{11}H_{17}ClN_2O_4$: C 47.75, H 6.19, N 10.12; found C 47.81, H 6.22, N 10.05.

Synthesis of 9–12: In a typical procedure, a mixture of **5** (0.010 mol) and triethylamine (0.011 mol) in dichloromethane (20 mL) was stirred at RT for 24 h under an inert atmosphere of dry nitrogen. The solid was filtered and washed with dichloromethane (3×15 mL) to give the product.

Data for 9: Yield: 97%; colorless solid; m.p. 270°C (decomp); ^{1}H NMR: δ=8.61 (s, 1H), 7.34 (s, 1H), 7.32 (s, 1H), 4.71 (s, 2H), 3.82 ppm (s, 3H); ^{13}C NMR: δ=175.3, 139.8, 126.3, 126.1, 54.8, 38.6 ppm; IR: $\tilde{\nu}$=3186, 3148, 3096, 3061, 2994, 2953, 2866, 2242, 1692, 1624, 1567, 1376, 1310, 1294, 1188, 1119, 1034 cm^{-1}; ESI-MS: 141 [M+H]$^+$; elemental analysis calcd (%) for $C_6H_8N_2O_2$: C 51.42, H 5.75, N 19.99; found: C 51.51, H 5.81, N 20.01.

Data for 10: Yield: 98%; colorless solid; m.p. 95°C; ^{1}H NMR: δ=8.64 (s, 1H), 7.40 (s, 1H), 7.34 (s, 1H), 4.14 (t, ^3J(H,H)=7.1 Hz, 2H), 3.79 (s, 3H), 2.22 (t, ^3J(H,H)=7.1 Hz, 2H), 2.06 ppm (m, 2H); ^{13}C NMR: δ=182.0, 139.0, 126.6, 125.2, 51.7, 38.6, 35.0, 28.4 ppm; IR: $\tilde{\nu}$=3367, 3089, 3066, 2962, 2849, 1659, 1564, 1471, 1397, 1176 cm^{-1}; ESI-MS: 337 [M−Cl]$^+$; elemental analysis calcd (%) for $C_{16}H_{25}ClN_4O_4$: C 51.54, H 6.76, N 15.03; found: C 51.61, H 6.82, N 15.25.

Data for 11: Yield: 97%; colorless solid; m.p. 290°C (decomp); ^{1}H NMR: δ=8.84 (s, 1H), 7.50 (s, 2H), 4.98 ppm (s, 4H); ^{13}C NMR: δ=174.0, 140.7, 126.4, 54.2 ppm; IR: $\tilde{\nu}$=3145, 3111, 2960, 1666, 1613, 1562, 1334, 1163; ESI-MS: 185 [M+H]$^+$; elemental analysis calcd (%) for $C_7H_8N_2O_4$: C 45.66, H 4.38, N 15.21; found: C 45.73, H 4.40, N 15.18.

Data for 12: Yield: 99%; colorless solid; m.p. 176°C; ^{1}H NMR: δ=8.72 (s, 1H), 7.40 (s, 2H), 4.12 (t, ^3J(H,H)=7.1 Hz, 4H), 2.21 (t, ^3J(H,H)=7.1 Hz, 4H), 2.01 ppm (m, 4H); ^{13}C NMR: δ=181.9, 138.4, 125.4, 51.8, 34.9, 28.3 ppm; IR: $\tilde{\nu}$=3386, 3100, 2953, 1708, 1558, 1409, 1176, 1020 cm^{-1}; ESI-MS: 241 [M+H]$^+$; elemental analysis calcd (%) for $C_{11}H_{16}N_2O_4$: C 54.99, H 6.71, N 11.66; found: C 55.06, H 6.76, N 11.65.

Protonation of zwitterions: On a 0.01 mol scale, addition of HBF_4/HSO_3CF_3 to **9** (1:1 molar ratio) at RT under an inert atmosphere of dry nitrogen gave **15a**/**15b**; similarly **17a**/**17b** and **18a**/**18b** were obtained by adding HBF_4/HSO_3CF_3 to the zwitterions **11** and **12**. In all cases, the solid salts became oils after addition of HBF_4/HSO_3CF_3; **15a**/**15b** and **17a**/**17b** changed back to solid again after two days at RT. The acids **16a**/**16b** were obtained by anion exchange from **6** and $NaBF_4$/$AgSO_3CF_3$ according to the literature method.[27,28]

Data for 15a: Yield: 98%; colorless solid; m.p. 138°C; ^{1}H NMR: δ=8.66 (s, 1H), 7.37 (s, 1H), 7.36 (s, 1H), 5.00 (s, 2H), 3.81 ppm (s, 3H); ^{13}C NMR: δ=173.2, 140.2, 126.4, 126.3, 53.0, 38.7 ppm; IR: $\tilde{\nu}$=3132, 3106, 2970, 2901, 1723, 1628, 1570, 1420, 1365, 1242, 1163, 1150 cm^{-1}; ESI-MS: 141 [cation]$^+$; elemental analysis calcd (%) for $C_6H_9BF_4N_2O_2$: C 31.61, H 3.98, N 12.29; found: C 31.71, H 4.01, N 12.32.

Data for 15b: Yield: 99%; colorless solid; m.p. 68°C; ^{1}H NMR: δ=8.65 (s, 1H), 7.38 (s, 1H), 7.37 (s, 1H), 5.00 (s, 2H), 3.82 ppm (s, 3H); ^{13}C NMR: δ=173.0, 140.2, 126.3, 120.9–124.1 (m, CF_3), 52.8, 38.7 ppm; IR: $\tilde{\nu}$=3306, 3171, 2987, 2901, 1751, 1579, 1403, 1173, 1034 cm^{-1}; ESI-MS: 141 [cation]$^+$; elemental analysis calcd (%) for $C_7H_9F_3N_2O_5S$: C 28.97, H 3.13, N 9.65; found: C 29.01, H 3.16, N 9.62.

Data for 16a: Yield: >99%; colorless liquid; m.p. −58°C; ^{1}H NMR: δ=8.63 (s, 1H), 7.42 (s, 1H), 7.37 (s, 1H), 4.19 (t, ^3J(H,H)=7.1 Hz, 2H), 3.82 (s, 3H), 2.38 (t, ^3J(H,H)=7.1 Hz, 2H), 2.11 ppm (m, 2H); ^{13}C NMR: δ=179.7, 139.0, 126.7, 125.2, 51.4, 38.6, 33.1, 27.7 ppm; IR: $\tilde{\nu}$=3161, 3120, 2947, 1734, 1576, 1421, 1168, 1055 cm^{-1}; ESI-MS: 169 [cation]$^+$; elemental analysis calcd (%) for $C_8H_{13}BF_4N_2O_2$: C 37.53, H 5.12, N 10.94; found: C 37.61, H 5.17, N 10.99.

Data for 16b: Yield: 99%; colorless liquid; m.p. −61°C; ^{1}H NMR: δ=8.63 (s, 1H), 7.40 (s, 1H), 7.35 (s, 1H), 4.16 (t, ^3J(H,H)=7.1 Hz, 2H), 3.80 (s, 3H), 2.37 (t, ^3J(H,H)=7.1 Hz, 2H), 2.07 ppm (m, 2H); ^{13}C NMR: δ=179.7, 139.0 126.6, 125.2, 120.9–124.1 (m, CF_3), 51.4, 38.6, 33.10, 27.6 ppm; IR: $\tilde{\nu}$=3484, 3156, 3117, 2962, 1722, 1575, 1416, 1249, 1224, 1157, 1027 cm^{-1}; ESI-MS: 169 [cation]$^+$; elemental analysis calcd (%) for $C_9H_{13}F_3N_2O_5S$: C 33.96, H 4.12, N 8.80; found: C 34.06, H 4.15, N 8.83.

Data for 17a: Yield: >97%; colorless solid; m.p. 210°C (decomp); ^{1}H NMR: δ=8.83 (s, 1H), 7.55 (s, 2H), 5.15 ppm (s, 4H); ^{13}C NMR: δ=172.7, 141.2, 126.5, 53.0 ppm; IR: $\tilde{\nu}$=3164, 3132, 2974, 1736, 1571, 1403, 1176, 1005 cm^{-1}; ESI-MS: 185 [cation]$^+$; elemental analysis calcd (%) for $C_7H_9BF_4N_2O_4$: C 30.91, H 3.34, N 10.30; found: C 31.03, H 3.39, N 10.25.

Data for 17b: Yield: >96%; colorless solid; m.p. 140°C (decomp); ^{1}H NMR: δ=8.71 (s, 1H), 7.33 (s, 2H), 4.92 ppm (s, 4H); ^{13}C NMR: δ=172.2, 141.1, 126.3, 120.9–124.1 (m, CF_3), 52.7 ppm; IR: $\tilde{\nu}$=3165, 2990, 1743, 1663, 1423, 1175 cm^{-1}; ESI-MS: 185 [cation]$^+$; elemental analysis calcd (%) for $C_8H_9F_3N_2O_7S$: C 28.75, H 2.71, N 8.83; found: C 28.83, H 2.79, N 8.85.

Data for 18a: Yield: >99%; colorless liquid; m.p. −57°C; ^{1}H NMR: δ=8.74 (s, 1H), 7.43 (s, 2H), 4.16 (t, ^3J(H,H)=7.1 Hz, 4H), 2.34 (t, ^3J(H,H)=7.1 Hz, 4H), 2.07 ppm (m, 4H); ^{13}C NMR: δ=179.8, 138.5, 125.5, 51.6, 33.2, 27.6 ppm; IR: $\tilde{\nu}$=3153, 2943, 1712, 1566, 1417, 1161, 1061 cm^{-1}; ESI-MS: 241 [cation]$^+$; elemental analysis calcd (%) for $C_{11}H_{17}BF_4N_2O_4$ (%): C 40.27, H 5.22, N 8.54; found: C 40.41, H 5.28, N 8.55.

Data for 18b: Yield: >99%; colorless liquid; m.p. −60°C; ^{1}H NMR: δ=8.76 (s, 1H), 7.44 (s, 2H), 4.16 (t, ^3J(H,H)=7.1 Hz, 4H), 2.36 (t, ^3J(H,H)=7.1 Hz, 4H), 2.07 ppm (m, 4H); ^{13}C NMR: δ=179.8, 138.5, 125.5, 120.9–124.1 (m, CF_3), 51.6, 33.1, 27.55 ppm; IR: $\tilde{\nu}$=3147, 1710, 1565, 1412, 1241, 1223, 1155, 1027 cm^{-1}; ESI-MS: 241 [cation]$^+$; elemental analysis calcd (%) for $C_{12}H_{17}F_3N_2O_7S$: C 36.92, H 4.39, N 7.18; found: C 37.01, H 4.43, N 7.20.

Acknowledgements

We thank the EPFL and Swiss National Science Foundation for financial support.

[1] For leading reviews see: a) K. R. Seddon, *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351; b) T. Welton, *Chem. Rev.* **1999**, *99*, 2071; c) P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 3772; d) C. M. Gordon, *Appl. Catal. A* **2001**, *222*, 101; e) H. Olivier-Bourbigou, L. Magna, *J. Mol. Catal.* **2002** *182–183*, 419; f) D. Zhao, M. Wu, Y. Kou, E. Min, *Catal. Today* **2002**, *74*, 157; g) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667.

[2] Imidazolium salts and variations leading to functionalized ionic liquids: J. H. Davis, Jr., in *Ionic Liquids in Synthesis* (Eds.: P. Wasserscheid, T. Welton), Wiley-VCH, Weinheim, **2003**, Chapter 2, p. 33.

[3] W. A. Herrmann, C. Köcher, L. J. Goossen, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 1627.

[4] K.-M. Lee, Y.-T.-Y. Lee, J. B. Lin, *J. Mater. Chem.* **2003**, *13*, 1079.

[5] L. C. Branco, J. N. Rosa, J. J. Moura Ramos, C. A. M. Alfons, *Chem. Eur. J.* **2002**, *8*, 3671.

[6] a) D. J. Brauer, K. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt, P. Wasserscheid, *J. Organomet. Chem.* **2001**, *630*, 177; b) R. P. J. Bronger, M. S. Silva, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Chem. Commun.* **2002**, 3044.

[7] T. L. Merrigan, E. D. Bates, S. C. Dorman, J. H. Davis, Jr., *Chem. Commun.* **2000**, 2051.
[8] A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, J. H. Davis, Jr., *J. Am. Chem. Soc.* **2002**, *124*, 5962.
[9] N. Gathergood, P. J. Scammells, *Aust. J. Chem.* **2002**, *55*, *557*.
[10] D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741.
[11] W. A. Herrmann, L. J. Goossen, M. Spiegler, *J. Organomet. Chem.* **1997**, *547*, 357.
[12] a) E. Alcalde, M. Gisbert, L. Perez-Garcia, *Heterocycles* **1996**, *4*, 567; b) V. Barboiu, E. Streba, M. N. Holerca, C. Luca, *J. Macromol. Sci. Pure Appl. Chem.* **1995**, *A32*, 1385; c) E. Alcalde, M. Gisbert, L. Perez-Garcia, *Chem. Lett.* **1992**, *12*, 2357; d) G. M. Blackburn, H. L. H. Dodds, *J. Chem. Soc. Perkin Trans. 2*, **1974**, 377.
[13] a) T. Watanabe (Fuji Photo Film Co, Ltd., Japan), Jpn. Kokai Tokkyo Koho JKXXAF JP 2003017148 A2 20030117, **2001** [Application: JP 2001-20409020010704]; L. Goossen, M. Hendrix (Bayer AG, Germany), Eur. Pat. Appl. EPXXDW EP 1157995 A2 20011128, **2001** [Application: EP **2001**–1111720010511].
[14] G. M. Blackburn, H. L. H. Dodds, *J. Chem. Soc. Perkin Trans. 2*, **1974**, 377.
[15] a) J. Velisek, T. Davidek, J. Davidek, *Maillard Reaction in Foods and Medicine*, RSC Special Publication 223, Royal Society of Chemistry, Cambridge, **1998**, pp. 204 – 208; b) J. Velisek, T. Davidek, J. Davidek, *Lebensm.-Wiss. Technol.* **1992**, *25*, 74; c) T. Davidek, J. Velisek, J. Davidek, P. Pech, *J. Agric. Food Chem.* **1991**, *39*, 1374.
[16] J. Velisek, T. Davidek, J. Davidek, P. Trska, F. Kvasnicka, K. Velcova, *J. Food Sci.* **1989**, *54*, 1544.
[17] B. Kratochvil, J. Ondracek, J. Velisek, J. Hasek, *Acta Crystallogr. Sect. C* **1988**, *44*, 1579.
[18] a) N. Kuhn, H. Bohnen, G. Henkel, *Z. Naturforsch. Teil B* **1994**, *49*, 1473; b) N. Kuhn, E. Niquet, M. Steinmann, I. Walker, *Z. Naturforsch. Teil B* **1999**, *54*, 1181; c) L. L. Borer, J. V. Kong, E. Oram, *Acta Crystallogr. Sect. C* **1989**, *45*, 1169.
[19] J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R. D. Rogers, *Chem. Commun.* **2003**, 28.
[20] "Ionic Liquids as Green Solvents: Progress and Prospects": M. Aresta, I. Tkatchenko, I. Tommasi, *ACS Symp. Ser.* **2003**, *856*, 93.
[21] H. A. Duong, T. N. Tekavec, A. M. Arif, J. Louie, *Chem. Commun.* **2004**, 112.
[22] K. J. Harlow, A. F. Hill, T. Welton, *Synthesis* **1996**, 697.
[23] a) P. B. Hitchcock, K. R. Seddon, T. Welton, *J. Chem. Soc. Dalton Trans.* **1993**, 2639; b) P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza, J. Dupont, *Polyhedron* **1996**, *15*, 1217.
[24] P. J. Dyson, J. S. McIndoe, D. Zhao, *Chem. Commun.* **2003**, 508.
[25] a) A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y. M. Tan, T. Welton, J. A. Zora, *J. Chem. Soc. Dalton Trans.* **1995**, 3467; b) J. J. Golding, D. R. MacFarlaine, L. Spiccia, M. Forsyth, B. W. Skelton, A. H. White, *Chem. Commun.* **1998**, 1593; c) J. Fuller, R. T. Carlin, H. C. De Long, D. Haworth, *J. Chem. Soc. Chem. Commun.* **1994**, 229.
[26] A. Horváth, *Synthesis* **1995**, 1183.
[27] J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1992**, 965.
[28] J. Fuller, R. T. Carlin, *Proc. Electrochem. Soc.* **1999**, *98*, 277.
[29] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168.
[30] a) P. J. Dyson, D. J. Ellis, W. Henderson, G. Laurenczy, *Adv. Synth. Catal.* **2003**, *345*, 216; b) I. Billard, G. Moutiers, A. Labet, A. El Azzi, C. Gaillard, C. Mariet, K. Lützenkirchen, *Inorg. Chem.* **2003**, *42*, 1726.
[31] For a summary of factors influencing the melting point, see, for example: J. D. Holbrey, R. D. Rogers, in *Ionic Liquids in Synthesis* (Eds.: P. Wasserscheid, T. Welton), Wiley-VCH, Weinheim, **2003**, Chapter 3, p. 41.
[32] The pK_a values of carboxylic acids are slightly different in some textbooks, and the calculated values also differ slightly, depending on the theoretical models adopted in the calculation. pK_a values can be found in: a) J. March, *Advanced Organic Chemistry—Reactions, Mechanisms and Structure*, 4th ed., Wiley-Interscience, New York, **1992**, Chapter 8; b) R. Stewart, *The Proton: Applications to Organic Chemistry: Organic Chemistry, A Series of Monographs, Vol. 46* (Ed.: H. H. Wasserman), Academic Press, New York, **1985**.
[33] a) C. O. Silva, E. C. da Silva, M. A. Chaer Nascimento, *J. Phys. Chem. A* **2000**, *104*, 2402; b) C. O. da Silva, E. C. da Silva, M. A. Chaer Nascimento, *J. Phys. Chem. A* **1999**, *103*, 11194.
[34] G. Schürmann, M. Cossi, V. Barone, J. Tomasi, *J. Phys. Chem. A* **1998**, *102*, 6706.
[35] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 78th ed., CRC Press, Boca Raton, **1997–1998**.
[36] M. Picquet, I. Tkatchenko, I. Tommasi, P. Wasserscheid, J. Zimmermann, *Adv. Synth. Catal.* **2003**, *345*, 959.
[37] P. J. Dyson, M. C. Grossel, N. Srinivasan, T. Vine, T. Welton, D. J. Williams, A. J. White, T. Zigras, *J. Chem. Soc. Dalton Trans.* **1997**, 3465.
[38] P. J. Dyson, J. S. McIndoe, *Inorg. Chim. Acta* **2003**, *354*, 68.
[39] A. Albert, E. P. Serjeant, *The Determination of Ionization Constants: A Laboratory Manual*, 3rd ed., Chapman and Hall, New York, **1984**.
[40] G. M. Sheldrick, SHELX-97. Structure Solution and Refinement Package, University of Göttingen, Göttingen (Germany), **1997**.
[41] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[42] N. Walker, D. Stuart, *Acta Crystallogr. Sect. A* **1983**, *39*, 158.

Received: February 13, 2004
Published online: August 17, 2004

