

## Ionic Liquids

## Tunable Aryl Alkyl Ionic Liquids (TAAILs): The Next Generation of Ionic Liquids\*\*

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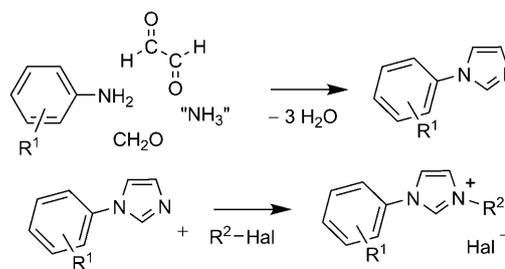
During the last 15 years ionic liquids have been shown to be very promising “green” solvents with several advantages compared to traditional organic solvents.<sup>[1]</sup> Most notably, their nonvolatility, high thermal stability, and extraordinary solvent properties make them important solvents for the chemical industry.<sup>[2]</sup> Ionic liquids (ILs) are salts which contain only organic cations and organic or inorganic anions, resulting in a melting point below 100 °C or even at room temperature (RTILs, room-temperature ionic liquids). Organic cations such as imidazolium, pyridinium, ammonium, and phosphonium ions can be combined with a variety of anions, for example, halides, PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, or (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>, which leads to a large number of possible combinations. Therefore, many of their physicochemical properties have previously been tuned by changing the anion or the substitution on the quaternary nitrogen or phosphorous center, but to date only alkyl substituents were used to modify the properties of the resulting ionic liquids.<sup>[3]</sup> The last generation, the task-specific ionic liquids,<sup>[4]</sup> still suffers from the disadvantage that the currently known motives really do not allow for a wide range of modifications to tune the properties of the ionic liquids. Only in the field of liquid crystal research has a publication recently reported the beneficial effect of aryl and biphenyl groups on the mesomorphic properties of ionic liquid crystals.<sup>[5]</sup>

Imidazolium salts are currently the most prominent class of ionic liquids, usually carrying sp<sup>3</sup>-hybridized carbon atoms as substituents at both nitrogen atoms of the heterocycle. As described herein, the combination of sp<sup>3</sup> alkyl and sp<sup>2</sup> aryl substituents at those nitrogen atoms of the imidazolium core, however, allows a far greater variation of the ionic liquid characteristics than imagined compared to the current systems. For the first time not only σ-based but also π-system-based electronic effects can be used to tune the properties. We observed a strong influence of the type (electron-withdrawing vs. donating) and number of substitu-

ents as well as of their position at the aromatic ring. The new cations can be combined with many previously used anions; this study compares the effects of Br<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, and (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>.<sup>[6]</sup>

We study imidazolium-based compounds as precursors for the synthesis of N-heterocyclic carbene (NHC) metal complexes;<sup>[7]</sup> NHCs are a very prominent class of ligands in homogeneous catalysis.<sup>[8]</sup> They are generally more stable than phosphane ligands and have been described as predominantly σ donors with negligible π character. But for substituted aromatic systems we found a large substituent effect on the chemical shifts of the imidazolium core in the corresponding NMR spectra and started to investigate the contribution of electron-withdrawing and -donating substituents.<sup>[9]</sup> We also realized that current imidazolium-based ionic liquids usually carry alkyl groups on the two nitrogen atoms, which do not allow electronic communication between the +I substituents and the core. Nowadays, changes are mainly restricted to the anionic part of the ILs. Introduction of a real electronic variation by (+/-) M effects would be a large step forward towards the development of new tunable ILs.

Owing to the aromatic rings and the possibility to introduce electronic and steric effects through substituents at the ring (Scheme 1, R<sup>1</sup>) we have additional possibilities to



**Scheme 1.** Two-step synthesis of aryl alkyl ionic liquids (TAAILs).

tune the system. Tunable aryl alkyl ionic liquids (TAAILs) are not restricted to van der Waals interactions; they also allow π-π interactions, which will be important for applications in the separation of compounds as well as for the stabilization of catalytically active metals. TAAILs can be synthesized by a two-step, atom-economical synthesis. First an aniline derivative, glyoxal, formaldehyde, and an ammonia source are converted into an aryl imidazole in a one-pot synthesis;<sup>[10]</sup> subsequent nucleophilic substitution leads to the imidazolium salt (Scheme 1).<sup>[11]</sup>

A range of aniline derivatives with a variety of different substituents R<sup>1</sup> and even systems with multiple substituents

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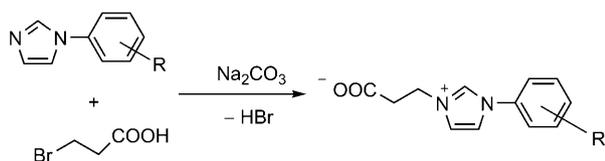
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$R^1$ , electron-withdrawing as well as -donating, are commercially available. The synthesis shown in Scheme 1 is only one of several possible ways to construct the imidazole core; many others are known.<sup>[12]</sup>

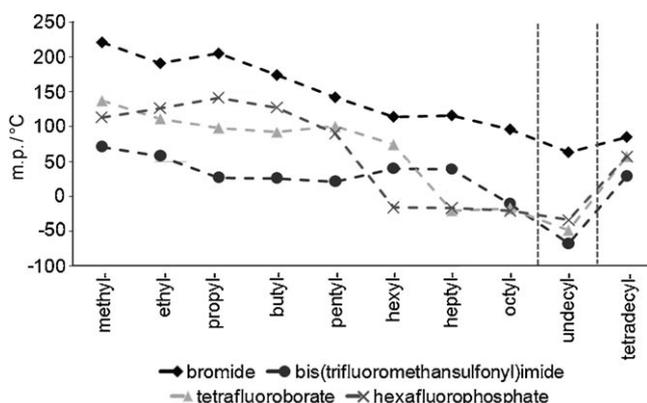
Introducing functional groups in the alkyl part of ionic liquids to form TSILs was the major improvement of the last generation of ionic liquids. The alkyl part of the new generation TAAILs (Scheme 1,  $R^2$ ) can be functionalized in a similar way, as we could show for different functional groups such as OH, COOH, and  $SO_3H$  (Scheme 2). Details are given in the Supporting Information.



**Scheme 2.** Example of the introduction of functional groups.

Our new TAAILs are superior to the currently known systems in many respects. For example, their surprising behavior allows us to pinpoint the desired melting point. The new cations can be combined with many anions known to date ( $BF_4^-$ ,<sup>[13]</sup>  $PF_6^-$ ,<sup>[13]</sup>  $N(SO_2CF_3)_2^-$ ,<sup>[14]</sup> halides, ...), and by blocking the 2-position of the imidazolium core the stability of the ionic liquid might be additionally improved. Figure 1 shows a comparison of the melting points in dependence on the chain length of the linear aliphatic substituents for four different counterions. The aromatic part in this example is the 2,4,6-trimethylphenyl (mesityl) group. It is interesting to note that the melting point difference resulting from an anion exchange (e.g.  $Br^-$  vs.  $(CF_3SO_2)_2N^-$ ,  $R^2 = 1$ -propyl) can be as big as  $160^\circ C$ , whereas for the known dialkyl systems such as 1-(1-butyl)-3-methylimidazolium (bmim), the reported difference for the same anion exchange is only  $75^\circ C$ .<sup>[2]</sup>

It becomes quite obvious that especially the bromide salts show an almost linear dependency of the melting point on the aliphatic chain length from one to eight carbon atoms



**Figure 1.** Dependence of the melting point [ $^\circ C$ ] of 1-alkyl-3-(2,4,6-trimethylphenyl)imidazolium salts on the counterion  $X^-$  ( $X = (Br, BF_4, PF_6, (CF_3SO_2)_2N)$ ) and on the alkyl chain length ( $C_1$ – $C_8$ ,  $C_{11}$ ,  $C_{14}$ ).

(Figure 1,  $\blacklozenge$ ), and that not all combinations fulfill the general ionic liquid criterion of a melting point below  $100^\circ C$ . However, starting with a chain length of more than five carbon atoms, the  $BF_4^-$ ,  $PF_6^-$ , and  $(CF_3SO_2)_2N^-$  salts fulfill this criterion, and most of the  $(CF_3SO_2)_2N^-$  salts are even RTILs.

The decomposition temperatures mainly depend on the anion, and are for some of the TAAILs they are significantly higher than for most currently known dialkyl imidazolium-based ionic liquids. It is interesting to note that mesityl alkyl imidazolium salts with the  $(CF_3SO_2)_2N^-$  counterion decompose at about  $440^\circ C$ , independent of the length of the alkyl chain. According to thermogravimetric analysis (TGA, see the Supporting Information), the TAAILs contain only small amounts of water after the workup. Concerning the miscibility with other solvents and their solubility in other polar or nonpolar solvents, the properties strongly depend on the individual system (substituents, chain lengths, counterion).

The general concept is not restricted to imidazolium compounds, and we see similar behavior in the case of benzimidazolium- as well as 1,2,3- and 1,2,4-triazolium-based ionic liquids, which will be reported in the near future.<sup>[15]</sup>

We could obtain solid-state structures of some of the TAAILs with higher melting points, and all compounds have been characterized by  $^1H$  and  $^{13}C$  NMR spectroscopy as well as by elemental analysis; some were also characterized by differential scanning calorimetry (DSC) and TGA measurements. The NMR spectra do not show a large dependence on the counterion or chain length. Comparing the chemical shifts in the NMR spectra of the imidazolium and phenyl rings of mesityl bromide TAAILs, we observed only very small differences (0.1–0.2 ppm) for different lengths of the alkyl chain (1–14 carbon atoms). Examples are the  $^{13}C$  signal of the C1 carbon atom of the mesityl substituent next to the imidazolium nitrogen, observed at  $(131.2 \pm 0.1)$  ppm, or the imidazolium NCN carbon atom at  $(137.1 \pm 0.2)$  ppm. Typical signals in the  $^1H$  NMR spectrum (in  $[D_6]DMSO$ ) are those of the hydrogen atoms at the aromatic ring, observed at  $(7.19 \pm 0.02)$  ppm, and the hydrogen atom at the C2 position of the imidazolium ring at  $(9.50 \pm 0.05)$  ppm, which indicate that the length of the alkyl chain has almost no electronic influence on the imidazolium core. But it does show a strong influence on the melting points of the new TAAILs!

Not only the variation of the chain length and of the counterions leads to strong effects. It was also interesting to evaluate the electronic influence of a substituent in the *para*-position of the aromatic ring. We therefore synthesized substituted imidazoles with various aromatic substituents with *para*- $R^1$  groups, which was possible in good yields. Owing to the large number of possible combinations, we restricted the comparison to one short (1-propyl), two medium (1-hexyl, 1-heptyl), and one long alkyl chain (1-tetradecyl). The results clearly show an influence of electron-withdrawing and -donating substituents on the melting points. Electron-withdrawing groups ( $NO_2$ , halogens) tend to lead to higher melting points than electron-donating (Me, OMe, OEt) substituents in the *para*-position of the phenyl ring at the imidazole. After exchanging the bromide counterion for a non-coordinating anion, similar trends can be observed as

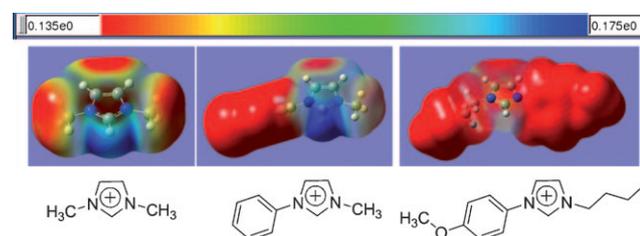
described above for the mesityl system. The melting points drop in a way similar to that shown in Figure 1.<sup>[9]</sup>

By means of high-level density functional theory calculations<sup>[16]</sup> (B3LYP/6-311 + G(d,p)), we further compared the charge distribution in the cationic part of the well-known dialkyl ionic liquids to the new generation of ionic liquids (TAAILs). The chain length on the alkyl side was kept constant (CH<sub>3</sub>) while we compared 4-methoxyphenyl, 4-nitrophenyl, 4-bromophenyl, 4-chlorophenyl, and phenyl to a methyl (mmim) and a 1-butyl substituent (bmim). The charge distribution is given in Table 1. All systems carry a

**Table 1:** Comparison of the charge distribution between mmim, bmim, and different TAAILs.

		N <sup>1</sup>	C <sup>2</sup>	N <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>
R <sup>1</sup> =	CH <sub>3</sub>	-0.046	0.179	-0.046	0.106	0.106
	C <sub>4</sub> H <sub>9</sub>	-0.013	-0.079	-0.110	-0.077	-0.118
	C <sub>6</sub> H <sub>5</sub>	0.017	0.058	0.337	0.202	0.084
	C <sub>6</sub> H <sub>4</sub> Cl	0.017	0.080	0.291	0.204	0.090
	C <sub>6</sub> H <sub>4</sub> Br	0.019	0.076	0.368	0.219	0.083
	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	0.005	0.106	0.332	0.224	0.093
	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	0.012	0.098	0.381	0.262	0.056

positive charge, but the charge distribution is quite different. For the previously known dialkyl cations such as 1,3-dimethylimidazolium (mmim) or 1,3-butylmethylimidazolium (bmim), the positive charge is mostly located on the alkyl groups, while the new TAAILs carry most of the charge (ca. 70 %) at the imidazolium core (Figure 2).



**Figure 2.** Different charge distributions in standard ILs and TAAILs. The numbers represent energy per charge in units of Hartree per elemental charge.

Our concept of combining aromatic and aliphatic substituents at the imidazolium core leads to a new generation of ionic liquids, TAAILs, an interesting class with promising properties. Electronic interaction between the aromatic substituent and the imidazolium core together with a great variety of possible substitution patterns on the aromatic ring allows us to tune these new ionic liquids far better than is currently possible by inductive interactions. It is also possible to modify the alkyl part of the TAAILs in the same way as it

has been done for the third generation of ILs, the TSILs. We can combine these new cations with all anions and can therefore optimize the properties of our TAAILs for different applications.

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- [10] The aniline (0.1 mol) is dissolved in MeOH (50 mL) and aqueous glyoxal (0.1 mol) is added. The mixture is stirred at room temperature (2–30 h) until a yellow precipitate forms. The suspension is diluted with MeOH (400 mL), and NH<sub>4</sub>Cl (0.2 mol) and formaldehyde solution (37%, 0.21 mol) are added. After addition of H<sub>3</sub>PO<sub>4</sub> (14 mL, 85%), the solution is heated at reflux for 5–9 h. The majority of the solvent (ca. 85%) is removed, and ice water and KOH solution are used to adjust the pH value to pH 9. The product is extracted with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic layers are dried over MgSO<sub>4</sub>, and the solvent is removed in vacuo. The product is subsequently purified by distillation or recrystallization.
- [11] A tube is filled with 1-*N*-substituted imidazole (1.0 equiv) dissolved in THF (10 mL) and haloalkane (1.1 equiv) and then sealed. The reaction mixture is heated to 80–110 °C in the sealed tube for 8–10 h. Filtration furnishes the solid precipitate, which is washed several times with THF and dried in vacuo.
- [12] T. Eicher, S. Hauptmann, H. Suschitzky, *The Chemistry of Heterocycles*, Wiley-VCH, Weinheim, **2003**.
- [13] Imidazolium bromide salt (1.0 equiv) is dissolved in H<sub>2</sub>O (or H<sub>2</sub>O/MeOH) before NH<sub>4</sub>BF<sub>4</sub> (or NH<sub>4</sub>PF<sub>6</sub>; 1.1 equiv) is added. After a short time, two phases separate. The ionic liquid is separated from the aqueous phase by extraction with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases are dried over MgSO<sub>4</sub> and filtered, and the solvent is removed in vacuo.
- [14] Imidazolium bromide salt (1.0 equiv) is dissolved in H<sub>2</sub>O or H<sub>2</sub>O/MeOH before Li<sup>+</sup>(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> (1.1 equiv) is added. After a short time two phases separate. The ionic liquid is separated from the aqueous phase by extraction with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were dried over MgSO<sub>4</sub> and filtered, and the solvent is removed in vacuo.
- [15] D. Meyer, T. Strassner, unpublished results.
- [16] All calculations were performed with Gaussian03 using the density functional/Hartree–Fock hybrid model Becke3LYP and the split valence triple- $\zeta$  (TZ) basis set 6-311++G(d,p). No symmetry or internal coordinate constraints were applied during optimizations. Details and references are given in the Supporting Information.