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Ionic Liquids

Tunable Aryl Alkyl Ionic Liquids with Weakly Coordinating Tetrakis((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)borate [B(hfip)$_4$] Anions

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Abstract: Weakly coordinating borate or aluminate anions have recently been shown to yield interesting properties of the resulting ionic liquids (ILs). The same is true for large phenyl-substituted imidazolium cations, which can be tuned by the choice, position, or number of substituents on the aromatic ring. We were therefore interested to combine these aryl alkyl imidazolium cations with the weakly coordinating tetrakis((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)borate [B(hfip)$_4$]$^-$ anions to study the physical properties and viscosities of these ionic liquids. Despite the large size and high molecular weight of these readily available ILs, they are liquid at room temperature and show remarkably low glass transition points and relatively high decomposition temperatures.

Introduction

Ionic liquids (ILs) are of interest for many different applications as they combine various interesting physical properties. These conductive salts, with melting points below 100 °C (by definition), contain only organic cations together with organic or inorganic anions. ILs with even lower melting points (below 25 °C) are called room temperature ionic liquids (RTILs).[1] The individually sought after properties of ILs such as thermal stability, nonvolatility, melting point, acidity, or viscosity vary depending on the combination of anions and cations used. ILs have, for example, been used as solvents in organic synthesis or catalysis,[1,2] for the extraction of metals,[3] as electrolytes in batteries,[4] as additives in dye-sensitized cells,[5] to stabilize nanoparticles[6] or even for the dissolution of cellulose.[7] Because of the large number of possible ILs, tools are under development to predict some of the properties/physical data so as to find ILs suitable for specific applications.[8]

In the last few years a new generation of imidazolium-based ionic liquids, called TAAILs (tunable alkyl aryl ionic liquids),[9] has been developed, which can be distinguished from the standard ionic liquids by the (substituted) phenyl ring at the N-1 nitrogen atom of the imidazolium heterocycle. Depending on the type, number, and position of substituent(s) at the phenyl ring (and the length of the alkyl chain at the N-3 nitrogen atom of the imidazolium heterocycle), we can change the electronic properties of the resulting ionic liquids through additional mesomeric and steric effects, which can easily be seen from the melting points.[9,10] By changing the core of the new ionic liquids from imidazolium to triazolium, it was demonstrated that not only the phenyl ring plays an important role.[11]

It is widely known that the anions have a strong influence on the properties of ionic liquids.[1,12] Exchanging the bromide for the bis(trifluoromethylsulfonyl)imide ([NTf$_2$]$^-$) counterion (cf.: m.p. [Ph$_{Mes}$C$_3$Im]Br: 205 °C vs. [Ph$_{Mes}$C$_3$Im]NTf$_2$: 27 °C) led to a significant temperature drop of almost 180 °C for this new kind of ILs.[9a] The asymmetric [NTf$_2$]$^-$ anion generally shows a much weaker coordination to the cation in comparison to the halides and has more available conformations and thus leads to lower melting points.[8c,13] Therefore, we were interested in other weakly coordinating counterions and started to investigate their physical properties and to look for new suitable applications for the TAAILs. Currently under investigation are the extraction behavior of the 1-aryl 3-alkyl imidazolium NTf$_2$ ILs as well as the synthesis of new nanoparticles near room temperature.[14]

During the last decade, it was found through crystal-structure determinations that the previously so-called "noncoordinating anions", such as tetrafluoroborate [BF$_4$]$^-$, hexafluorophosphate [PF$_6$]$^-$, or tetrahaloaluminate [Al(Hal)$_4$]$^-$ do coordinate and therefore larger and even more weakly coordinating new anions were synthesized.[15] This led to the development of various new anions, for example the tetrakis((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)aluminate [Al(hfip)$_4$]$^-$ anion, which is known to stabilize reactive cations.[16] Recent reports from the Krossing group on their new anions[12,15a,17] raised the question whether the combination of new cations with new anions will lead to ILs with specific, interesting properties. As the AlR$_4^-$

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anions turned out to be very moisture sensitive,[17a] we focused on the newer fluorinated tetrakis((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)borate $[B(hfip)_4]^-$ anions. In this paper we present the results of the new ionic liquids with 1-aryl 3-alkyl imidazolium cations and the weakly coordinating $[B(hfip)_4]^-$ anion as shown in Figure 1.

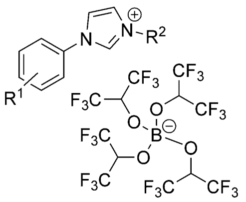


Figure 1. General structure of the investigated borate ILs.

Results and Discussion

Synthesis

The imidazolium salts with borate $[B(hfip)_4]^-$ anions were prepared using the sodium borate $Na[B(hfip)_4]$,[17a] as reported by Krossing et al. For comparison, the corresponding ILs with one of the most commonly used anions, $[NTf_2]^-$, were also synthesized.

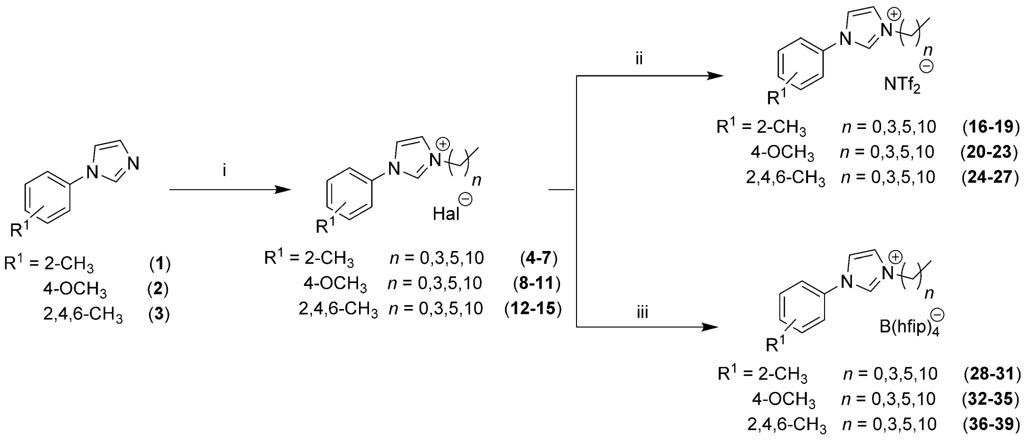
For the cationic part, we chose phenyl alkyl imidazolium cations with various alkyl chain lengths (short, medium, long) and with substituents in different positions on the aryl ring, leading to a total of 24 new compounds (Scheme 1). The electron-donating substituents like 2-methyl (2-Me), 4-methoxy (4-OMe) and mesityl (2,4,6-Me, Mes) have a significant influence on the electronic properties of the aryl ring. The inductive effect of the methyl group in the 2-position is very different compared to the mesomeric effect of the methoxy substituent, which interacts via the π-system. The mesityl group allows us to additionally consider the steric influence, as the rings are orthogonal to each other according to solid-state structures.[18]

The one-pot synthesis starting from the commercially available anilines led to the imidazoles **1**–**3**[9a] and only two more reaction steps were needed to synthesize the different TAAILs **16**–**39** (Scheme 1). First, a nucleophilic substitution reaction with different alkyl halides led to the imidazolium salts **4**–**15** by dissolving the imidazoles **1**–**3** in THF, addition of the alkyl halides, and heating in a pressure tube from room temperature to 80 °C for several days.[9a] A significant difference in the reaction rates could be observed, with 1-aryl 3-methyl imidazolium halide salts already forming at room temperature. Aryl imidazolium salts with longer alkyl chain lengths needed higher temperatures to form. For the purification of the materials, it was necessary to use different techniques. For some halide salts, column chromatography was used, and in other cases, the solid salts could be washed with immiscible solvents to remove impurities, providing yields between 56–98 %.

By anion metathesis, ionic liquids with $[NTf_2]^-$ **16**–**27** and $[B(hfip)_4]^-$ **28**–**39** counterions (Scheme 1) were synthesized. No influence of the halide salt used (bromide or iodide) in the anion exchange reaction could be observed. For the ILs with an $[NTf_2]^-$ anion,[9a] the imidazolium halide salts **4**–**15** were dissolved in methanol and $Li[NTf_2]$ in water was added, immediately forming a two-phase system. After stirring the mixture at room temperature for 12 h, the organic IL-containing phase was extracted and washed with water. The solvent was removed, and yields of over 90 % could be obtained. ILs containing the $[B(hfip)_4]^-$ counterion **28**–**39** were synthesized by dissolving the aryl imidazolium halide salts **4**–**15** in dichloromethane, adding equimolar amounts of $Na[B(hfip)_4]$*DME (DME. 1,2-dimethoxyethane), and stirring the solution at room temperature for 24 h. After the reaction was complete, the precipitate was filtered off and a clear filtrate could be obtained. The solvent was removed and the ILs were isolated in yields between 81–97 %.

Thermal behavior

After synthesis and basic characterization, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) curves as well as temperature-dependent viscosities of the ILs were measured. The results are shown in Table 1, together with the data of known ILs for comparison.



Scheme 1. Synthesis of the reported ionic liquids: i) alkyl halide, THF, RT–80 °C, 2–5 d; ii) $Li[NTf_2]$, $MeOH/H_2O/DCM$, RT, 12 h; iii) $Na[B(hfip)_4]$*DME, DCM, RT, 24 h.

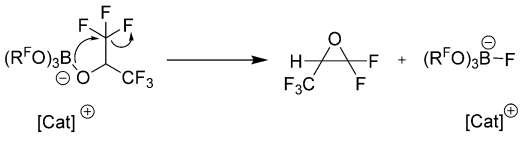
Table 1. Overview of collected physicochemical data of the synthesized ILs. R^1, R^2 and anions are defined according to Figure 1. V_m^+ = molecular volume of the cation, T_m = melting temperature, T_{gh} = glass transition temperature upon heating, T_{gc} = glass transition temperature upon cooling, T_d = decomposition temperature, η = viscosity. Volumes of $[B(hfip)_4]^-$ and $[NTf_2]^-$ are 0.559 and 0.233 nm^3, respectively.[8a]

IL acronym	R^2	R^1	Anion	V_m^+ [nm^3]	T_m [°C]	T_{gh} [°C]	T_{gc} [°C]	T_d [°C]	η (25 °C) [mPa -s]
28	Me ($n=0$)	2-Me	$[B(hfip)_4]^-$	0.228	no thermal effects measured			205	400
32	Me	4-MeO	$[B(hfip)_4]^-$	0.238	no thermal effects measured			210	–
36	Me	Mes	$[B(hfip)_4]^-$	0.277		−53	–	198/221	140[a]
16	Me	2-Me	$[NTf_2]^-$	0.228		−54	−60	431	401
20	Me	4-MeO	$[NTf_2]^-$	0.238		−48	−50	427	445
24	Me	Mes	$[NTf_2]^-$	0.277	71[9a]	–	–	–	–
29	*n*Bu ($n=3$)	2-Me	$[B(hfip)_4]^-$	0.291		−60	–	179	213
33	*n*Bu	4-MeO	$[B(hfip)_4]^-$	0.310	−79[b]	−55	–	188/368	308
37	*n*Bu	Mes	$[B(hfip)_4]^-$	0.349		−53	–	192	456
17	*n*Bu	2-Me	$[NTf_2]^-$	0.291		−64	–	402	242
21	*n*Bu	4-MeO	$[NTf_2]^-$	0.310		−53	−56	396	328
25	*n*Bu	Mes	$[NTf_2]^-$	0.349	26[9a]	–	–	–	–
30	*n*Hex ($n=5$)	2-Me	$[B(hfip)_4]^-$	0.347		−62	–	192	204
34	*n*Hex	4-MeO	$[B(hfip)_4]^-$	0.357		−56	−67	199/382	276
38	*n*Hex	Mes	$[B(hfip)_4]^-$	0.396		−56	–	192	403
18	*n*Hex	2-Me	$[NTf_2]^-$	0.347	no thermal effects measured			400	143
22	*n*Hex	4-MeO	$[NTf_2]^-$	0.357		−54	−60	206/424	411
26	*n*Hex	Mes	$[NTf_2]^-$	0.396	40[9a]	–	–	–	–
31	*n*Undec ($n=10$)	2-Me	$[B(hfip)_4]^-$	0.467		−55	−76	192/372	253
35	*n*Udec	4-MeO	$[B(hfip)_4]^-$	0.476		−62	–	188/368	296
39	*n*Undec	Mes	$[B(hfip)_4]^-$	0.518		−57	−59	206/385	378
19	*n*Undec	2-Me	$[NTf_2]^-$	0.467		−55	−72	411	404
23	*n*Undec	4-MeO	$[NTf_2]^-$	0.476		−60	–	411	448
27	*n*Undec	Mes	$[NTf_2]^-$	0.518	32[9a]	–	–	–	–

[a] Measured at 50 °C. [b] Crystallization temperature.

All ILs proved to be stable under the applied conditions in TGA experiments (heating rate: 10 K min^{-1}, N_2 atmosphere) up to temperatures between 179 and 431 °C. In the case of six salts, at least two degradation steps were observed, whereas all other ILs showed a single degradation process, in which a mass loss of typically 80–90 % occurred. The presence of both the methoxy residues and $[B(hfip)_4]^-$ anions seems particularly inclined to induce two-step degradation events, with the first decomposition step leading to a mass loss of approximately 48 %, and the second event causing a mass loss between 10–35 %. Hence, the first mass loss may be assigned to the evolution of three equivalents of the volatile epoxide as exemplarily shown for the first step in Scheme 2. This would amount to a mass loss of 44–49 %, depending on the total molar mass of the respective IL.

Analogous decomposition products have already been detected in mass spectrometry experiments of $[Al(OR^F)_4]^-$ anions and are also likely to form under thermal stress.[13b,19] Apart from this effect, no clear correlation could be found between the structure of the cation and the stability of the respective IL. A comparison of $[B(hfip)_4]^-$ and $[NTf_2]^-$ ILs, however, showed a generally higher thermal stability of the $[NTf_2]^-$ ILs, which typically lie 200 °C above those of the $[B(hfip)_4]^-$ ILs. Additionally, the $[NTf_2]^-$ ILs show similar thermal stabilities compared to common ILs such as $[C_4MIm][NTf_2]$ ($T_d = 314–422$ °C)[20] or $[C_4MIm][BF_4]$ ($T_d = 361$ °C).[20c] Interestingly, borate ILs with nonfunctionalized imidazolium cations,[17a] or their corresponding aluminate analogues,[13b,19] possess decomposition temperatures that are rather lower than the ILs reported here.



Scheme 2. Epoxide-generating decomposition of the $[B(hfip)_4]^-$ anion. [Cat] = cation. Note that this reaction was only drawn in a unimolecular fashion for the sake of clarity, but is likely to rather occur in a bi- or trimolecular way.

Altogether, the new ILs are sufficiently stable for most applications, although no long-term TGA measurements have yet been performed. As is known from literature data,[21] results of long-term measurements are of course more relevant for most applications and can differ severely from short-term experiments.

Subsequent DSC measurements yielded typical results for ionic liquids, that is, the tendency to form glasses instead of true crystal lattices and broad hystereses of up to 17 °C. Accordingly, second-order transitions are the dominant pattern seen in DSC thermograms. Furthermore, most of the ILs remained liquid even at temperatures well below 0 °C, independent of the anion. Especially in the case of $[B(hfip)_4]^-$ ILs, this behavior is remarkable, as only one RTIL comprising of this borate anion has been reported so far.[17a] Hence, the functionalization of imidazolium cations indeed has a tremendously beneficial effect on the overall properties.

Viscosity measurements

Viscosities were measured between 20 and 80 °C in the liquid range of the ILs, and were fitted afterwards with a Vogel–Fulcher–Tammann (VFT) approach [Equation (1)]. Graphic representations of the data are given in Figures 2 and 3 and VFT parameters are shown in Table 2. Data points of the measurements are given in the Supporting Information. In the case of **32**, no viscosity data could be collected due to its high melting point. Furthermore, the measurement of **28** proved difficult, as a homogeneous melt was only obtained after heating to 80 °C for 10 min. Hence, in contrast to the other ILs, data for this IL were recorded during cooling and should be considered with caution due to possible hysteresis effects. For the VFT equation for the description of temperature-dependent viscosities η, see below:

$$\eta = \eta_0 \cdot \exp\left(\frac{B}{T - T_0}\right) \qquad (1)$$

in which η_0 = viscosity at infinite temperature, B = constant, T_0 = Vogel temperature.

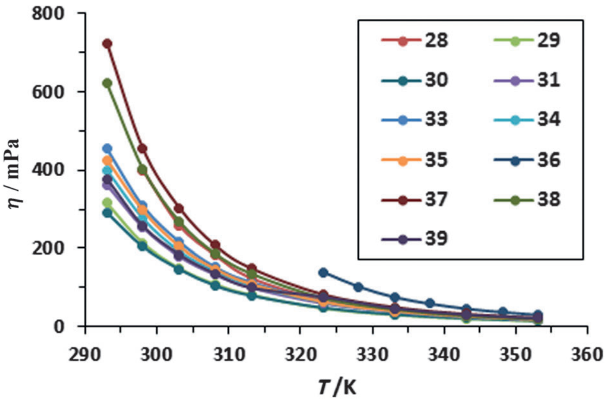


Figure 2. Temperature-dependent viscosities of the investigated $[B(hfip)_4]^-$ ILs.

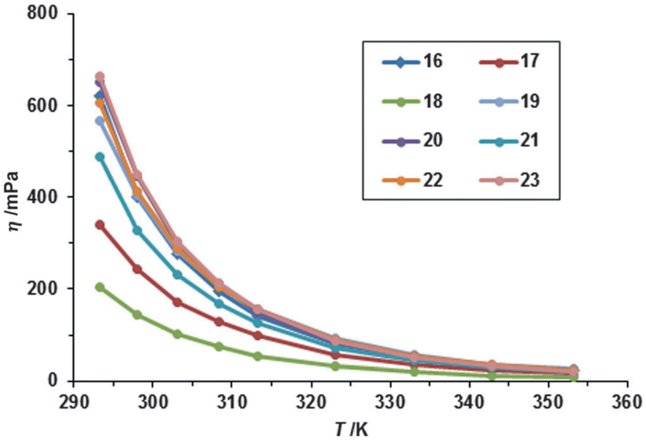


Figure 3. Temperature-dependent viscosities of the investigated $[NTf_2]^-$ ILs.

Table 2. Parameters of the VFT fits according to Equation (1).

IL	η_0 [mPa-s]	B [K]	T_0 [K]
28	0.0419*	960*	193[a]
32	–	–	–
36	0.1981	634	226
16	0.1119	838	196
20	0.0286	1171	177
29	0.0830	832	192
33	0.0228	1207	171
37	0.1672	721	207
17	0.0091	1556	145
21	0.0496	1064	177
30	0.0655	923	183
34	0.0448	1073	175
38	0.0276	1121	181
18	0.0015	1861	135
22	0.0403	1153	173
31	0.0448	1077	173
35	0.0194	1282	165
39	0.0428	1063	181
19	0.0206	1395	157
23	0.0013	2167	129

[a] This sample could only be measured during cooling (cf. Supporting Information).

Room-temperature viscosities of both $[B(hfip)_4]^-$ and $[NTf_2]^-$ ILs lie roughly between 100 and 500 mPa-s, and thus are quite high compared to common, low-viscous ILs such as $[C_2MIm][NTf_2]$ or $[C_2MIm][N(CN)_2]$.[17c,22] However, their viscosities are similar to those of other borate ILs with nonfunctionalized cations.[17a] The Vogel temperatures lie within ranges that are typical for most ILs, whereas the η_0 values are generally approximately one order of magnitude lower than in common $[NTf_2]^-$ ILs.[23]

No clear general trends in viscosity with respect to the choice of the cation can be drawn from the data. Molecular volumes of the cations were calculated using the COSMO model[8b] and are given in Table 1. The volumes cover a range from 0.228 to 0.518 nm^3, and hence may be compared to common 1-*n*-alkyl-3-methyl imidazolium ions from $[C_5MIm]^+$ (0.220 nm^3) to $[C_{10}MIm]^+$ (0.331 nm^3) or to ammonium cations from $[N_{2225}]^+$ (0.268 nm^3) to $[N_{1888}]^+$ (0.604 nm^3). In the case of R^1 = 4-OMe or Mes, viscosities seem to decrease with increasing chain length, but only when combined with the borate anion. If R^1 = 2-Me, viscosities reach a minimum at R^2 = Hex.

Within the TAAILs with similar alkyl residues, the ordering of the viscosities always follows 2-Me < 4-OMe < 2,4,6-Me ($[B(hfip)_4]$-ILs) or 2-Me < 4-OMe ($[NTf_2]$-ILs). Although differences are small, this consistently observed trend may be attributed to a combination of steric and electronic effects: Thus, the π-donating nature of the 4-OMe residue suggests that the rotation around the bond of the aryl residue to the imidazolium nitrogen atom is somewhat restricted, so that in addition to the very slightly increased size, the conformational freedom is also more restricted in the 4-OMe case. In contrast, the steric demand of the 2-Me or 2,4,6-Me substitution now decouples the π-systems of the arene and imidazolium moiety, allowing for the adoption of at least two conformers by rotation around the N-arene bond, which for the less-restricted 2-Me case appears to lead to more favorable properties than for the larger and more restricted mesityl case.

In an earlier study, by means of a modified Marcus theory, we could show that increasing the anion diameter up to approximately 1 nm yields a minimal activation energy for the movement of ions in an IL.[17c] Therefore, $[B(hfip)_4]^-$ ILs should also exhibit very good dynamic properties. Other studies, however, showed that the short B–O bonds lead to limited rotational freedom, decreased melting entropy and worsening transport properties.[8a,d,17d] Additionally, electrostatic interactions are more pronounced, as in the case of the very similar $[Al(hfip)_4]^-$ anion. As a result, increasing the cation diameter may have a different influence on ILs with $[B(hfip)_4]^-$ anions than with $[Al(hfip)_4]^-$ ILs. With electrostatic forces not being negligible, extending the alkyl chains of the cations leads to an increased mean distance between the cations and anions and decreases viscosities. In contrast to $[Al(hfip)_4]^-$ salts, the increase in dispersive interactions appears not to overbalance this effect.

A comparison of $[NTf_2]^-$ ILs with their $[B(hfip)_4]^-$ analogues showed that in almost all cases, the $[B(hfip)_4]^-$ salts are less viscous. This is in accordance with earlier findings concerning a comparison of $[NTf_2]^-$ and $[Al(hfip)_4]^-$ ILs,[17c] and can also probably be attributed to low overall interaction potentials in the large, highly fluorinated $[B(hfip)_4]^-$ ILs. Additionally, it is known that $[B(hfip)_4]^-$ ILs are quite stable against (short-term) exposure towards water and are completely stable against oxygen at ambient temperatures.[17a,24] Therefore, even though the use of such ILs in, for instance, electrochemistry, is unlikely, the viscosity and thermal data of these functionalized ILs should enable an application in fields such as lubrication research or material processing.

Conclusion

We synthesized the first TAAILs with a $[B(hfip)_4]^-$ anion and investigated their thermal behavior and viscosities. The ILs with $[B(hfip)_4]^-$ and $[NTf_2]^-$ anions both show remarkably low glass transition temperatures around $-60\,^\circ C$ and are stable up to $200\,^\circ C$ ($[B(hfip)_4]^-$) or $400\,^\circ C$ ($[NTf_2]^-$), which represents a large window of more than 250/450 K. The viscosities of the borate ILs are generally lower than those of the respective $[NTf_2]^-$ ILs, but slightly higher in comparison to standard alkyl imidazolium $[B(hfip)_4]^-$ ILs, which is likely induced by the additional phenyl ring. Overall, the synthesized $[B(hfip)_4]^-$ ILs are stable against air and show good hydrolytic stability together with promising physical properties. Furthermore, it is very interesting to note that the melting points of these borate ILs are typically below room temperature and are generally lower than those of the traditional all-alkyl-imidazolium borate ILs. This indicates that the aromatic residue appears to have an interesting and liquefying effect on these ILs.

Acknowledgements

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Keywords: aluminate anions · borate anions · imidazolium salts · ionic liquids · TAAILs

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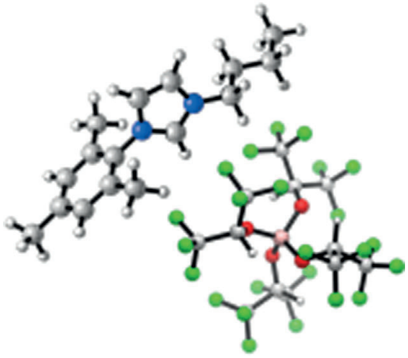
FULL PAPER

Bulky TAAILs: Combining weakly coordinating bulky tetrakis((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)borate $[B(hfip)_4]^-$ anions with aryl alkyl imidazolium cations results in tunable alkyl aryl ionic liquids (TAAILs; see figure) that show remarkably low melting points despite of their large size and high molecular weight. These TAAILs are liquid at room temperature.



Ionic Liquids

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■■ – ■■

Tunable Aryl Alkyl Ionic Liquids with Weakly Coordinating Tetrakis((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)borate $[B(hfip)_4]$ Anions