NOVEL HYDROPHOBIC IONIC LIQUIDS BASED ON QUATERNARY AMMONIUM AND PERFLUOROALKYLTRIFLUOROBORATE

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ABSTRACT

A novel class of low-melting, hydrophobic ionic liquids based on relatively small aliphatic quaternary ammonium cations ([R1R2R3NR]+, wherein R1, R2, R3 = CH3 or C2H5, R = n-C3H7, n-C4H9, CH2CH2OCH3) and perfluoroalkyltrifluoroborate anions ([RfBF3]~, Rf = CF3, C2F5, n-C3F7, n-C4F9) have been prepared and characterized. The important physicochemical and electrochemical properties of these salts including melting point, glass transition, viscosity, ionic conductivity, and electrochemical stability, have been determined and comparatively studied with those of the corresponding [BF4]~ and [(CF3SO2)2N]~ based ones. The influence of the structure variation in the quaternary ammonium cation and perfluoroalkyltrifluoroborate ([RfBF3]~) anion on the above physicochemical properties is discussed. Most of these salts are liquids at 25 °C and exhibit low viscosities (58–210 cP at 25 °C) and moderate conductivities (1.1–3.8 mS cm⁻¹). The electrochemical windows of these salts are much larger than those of the corresponding 1,3-dialkylimidazolium salts. Additionally, a number of the salts with [RfBF3]~ show plastic crystal behavior.

INTRODUCTION

Currently the basic understanding and applications of ILs are largely governed by imidazolium systems, because the ILs based on the imidazolium cations, especially 1,3-dialkylimidazolium cations, have been empirically demonstrated to afford low viscosities and high conductivities, which are the key requirements for ILs as new reaction media or electrolytes to replace the conventional ones (1,2). However, these ILs cannot be used as electrolytes for high-energy electrochemical devices, such as 4-V class Li batteries (i.e. Li metal or carbon used as anode material), because of the electrochemical instability of the 1,3-dialkylimidazolium cations (i.e. the cathodic limit is ca. 1 V vs Li+/Li which excludes the use of Li metal or carbon as anode) (3). Compared with the 1,3-dialkylimidazolium cations, saturated quaternary ammoniums are more resistant against oxidation and reduction, thereby their ILs with electrochemically stable anions, such as bis(trifluoromethanesulfonyl)imide [(CF3SO2)2N]~ (TFSI⁻), have much larger electrochemical windows than the corresponding 1,3-dialkylimidazolium ones (4-6). Recent studies have further shown that the ILs based on the QA and robust anions, such as TFSI⁻, have enough electrochemical stability to support them as possible safety
electrolytes (nonvolatile and nonflammable) for high-energy devices, such as Li batteries (7,8).

Besides a large electrochemical window, high ionic conductivity and fast ion mobility (including the doped ions such as Li$^+$ for Li batteries) are the additional requirements for ILs as supporting electrolytes in high-energy devices. This means that the viscosity of ILs must be as low as possible and the anion involved in the ILs must have weakly coordinating ability in order to depress ion pairing. Therefore, the QA cation involved should be small, since large ones have been identified to result in high viscosities (9-11). To date, although a large number of QA salts with a wide variety of anions have been reported (4-21), very few of them appear to satisfy above requirements. This is mainly due to lack of the anions, which not only have chemical and electrochemical stability but also can form low-melting and low-viscous ILs with relatively small QA cations (total C atoms ≤ 10). For instance, several known electrochemically stable anions tend to form either high-melting (e.g. > 100 °C for high symmetry [BF$_4^-$], [PF$_6^-$], and [AsF$_6^-$] (14,15)) or very high-viscous (e.g. > 300 cP for [BF$_4^-$] (17), and >1300 cP at 25 °C for large and rigid bis(oxalato)borate [BOB]$^-$ (18)) salts with small QA cations, while those that can form low-melting and low-viscous ILs with small QA cations (e.g. trifluoro-N-(trifluoromethylsulfonyl)acetamide [(CF$_3$SO$_2$)(CF$_3$CO)N]$^-$ (6,19)) suffer from electrochemical instability. Until recently, the development of stable, low-melting and low-viscous QA salts has been almost limited to the anion TFSI$^-$ (4-11,21), because this fluoroanion not only possesses chemical and electrochemical stability (4-9) but also combines low symmetry, high flexibility, and weakly coordinating nature, all of which are beneficial to reducing the cohesive forces of the salts, thus lowering the melting point and viscosity. To further explore and extend the potential applications of the QA-based ILs in electrochemical devices, new robust anions that can form low-melting and low-viscous ILs with small QA cations are certainly needed.

Very recently, we found that a new class of chemically and electrochemically stable and weakly coordinating fluoroanions, namely perfluoroalkyltrifluoroborates ([R$_f$BF$_3^-$]) (R$_f$ = CF$_3$, C$_2$F$_5$, n-C$_3$F$_7$, n-C$_4$F$_9$) (22,23), can form low-melting and low-viscous ILs even with large 1,3-dialkylimidazolium cations (< 77 cP at 25 °C) (24-26) and relatively small aliphatic QA cations (58-86 cP at 25 °C) (27). More importantly, they are more resistant toward hydrolysis than the [BF$_4^-$] because of their hydrophobicity (24-26). Encouraged by these results, we herein report the systematic synthesis and characterization of a series of new hydrophobic and low-melting salts based on relatively small aliphatic QA cations ([R$^1$R$^2$R$^3$NR]$^+$, wherein R$^1$, R$^2$, R$^3$ = CH$_3$ or C$_2$H$_5$, R = n-C$_3$H$_7$, n-C$_4$H$_9$, CH$_2$CH$_2$OCH$_3$) and perfluoroalkyltrifluoroborate anions ([R$_f$BF$_3^-$], R$_f$ = CF$_3$, C$_2$F$_5$, n-C$_3$F$_7$, n-C$_4$F$_9$). Most of them are liquids at 25 °C, and exhibit low viscosities, moderate conductivities, and good electrochemical stability. For comparison, the corresponding QA salts with two representative anions, [BF$_4^-$] and TFSI$^-$, were also synthesized and characterized.
EXPERIMENTAL

Materials

Potassium perfluoroalkyltrifluoroborate \( \text{K}[\text{R}_3\text{BF}_3] \) (\( \text{R}_3 = \text{CF}_3, \text{C}_2\text{F}_5, \text{n-C}_3\text{F}_7, \text{n-C}_4\text{F}_9 \)). These compounds were prepared and purified according to the reported procedures (22,23).

Quaternary ammonium bromide salts. These compounds were synthesized by reaction of trialkylamines with an equivalent of appropriate alkyl bromide in anhydrous acetone in an autoclave. A typical reaction is as follows.

\( \text{N}, \text{N}-\text{Diethyl-N-methyl-N-(n-propyl)ammonium bromide (N}_{1233}\text{Br}} \). This compound was prepared in 0.30-mol scale in a 300-mL autoclave by reaction of 1-bromopropane (37.0 g, 0.30 mol) with a little excess of ethyldimethylamine (27.0 g, 0.31 mol) in anhydrous acetone at 100 °C and ca. 6 MPa for 12 h. The cooled, red suspension was then poured into diethyl ether (150 mL). After filtration, the obtained solid was washed with diethyl ether (2 × 25 mL), and recrystallized twice from acetone to afford the \( \text{N}_{1233}\text{Br} \) (50 g, yield 80%) as a white solid. The other quaternary ammonium bromide salts were similarly prepared.

Aqueous solutions of perfluoroalkyltrifluoroborate acid \( \text{H}[\text{R}_3\text{BF}_3] \). The aq. \( \text{H}[\text{R}_3\text{BF}_3] \) was prepared by passing the corresponding \( \text{K}[\text{R}_3\text{BF}_3] \) (\( \text{R}_3 = \text{CF}_3, \text{C}_2\text{F}_5, \text{n-C}_3\text{F}_7, \text{n-C}_4\text{F}_9 \)) through a column filled in acidic ion-exchange resin as described in the literature (22). The concentration of the aq. \( \text{H}[\text{R}_3\text{BF}_3] \) determined by acid–base titration was ca. 0.2 mol dm\(^{-3}\). The resultant solution was collected in a PFA bottle, and stored in a refrigerator until required.

Aqueous solutions of quaternary ammonium hydroxide (\( \text{[QA]}\text{[OH]} \)). The same procedure was followed for aq. \( \text{H}[\text{R}_3\text{BF}_3] \) as described above, except that the basic anion-exchange resin and the corresponding quaternary ammonium bromide (\( \text{[QA]}\text{Br} \)) were used. The concentration of the aq. \( \text{[QA]}\text{[OH]} \) was ca. 0.2 mol dm\(^{-3}\). The solution was collected in a plastic bottle, and stored in a refrigerator until required.

Quaternary ammonium salts with perfluoroalkyltrifluoroborate (\( \text{[QA]}[\text{R}_3\text{BF}_3] \)). The salts \( \text{[QA]}[\text{R}_3\text{BF}_3] \) were prepared in 30-mmol scale as follows. The aq. \( \text{[QA]}\text{[OH]} \) was neutralized with equimolar aq. \( \text{H}[\text{R}_3\text{BF}_3] \) (\( \text{R}_3 = \text{CF}_3, \text{C}_2\text{F}_5, \text{n-C}_3\text{F}_7, \text{n-C}_4\text{F}_9 \)) in a PFA flask until pH was ca. 6–7. After concentrated to ca. 15 mL at 40 °C by evaporation under reduced pressure, the liquid salt precipitated in the bottom was separated directly, washed with deionized water (5 mL) and toluene (10 mL) in turn, and dried at 70 °C for 24 h under vacuum (0.03 Torr) to afford a colorless or pale yellow liquid (water content < 50 ppm). For the solid salt, it was collected by filtration, dried under vacuum, and recrystallized from 2-butanol to afford the white product.

Quaternary ammonium salts with tetrafluoroborate (\( \text{[QA]}[\text{BF}_4] \)). The salts \( \text{[QA]}[\text{BF}_4] \) were prepared in a 50-mmol scale as follows. The aq. \( \text{[QA]}\text{[OH]} \) was neutralized with equimolar aq. \( \text{H}[\text{BF}_4] \) in a PFA flask until pH was about 6–7. The solution was evaporated at 30–40 °C under reduced pressure to give a viscous liquid or solid. For the viscous liquid, it was dried at 40 °C for 48 h at room temperature under vacuum (0.03
Torr), then dissolved in anhydrous acetone (60 mL), filtered through a PTFE membrane filter (0.2 μm). The collected solution was evaporated and dried at 80 °C for 48 h under vacuum (0.03 Torr), yielding a pale yellow or colorless liquid (water content: ca. 400–600 ppm). For the solid product, recrystallization from 2-butanol/methanol gave the white solid.

Quaternary ammonium salts with bis(trifluoromethanesulfonyl)imide ([QA][TFSI]). The same procedure was followed for the [QA][R₂BF₃] as described above, except using the commercial H[TFSI] instead of aq. H[R₂BF₃].

Measurements

Water content. Water content in the liquid salts was detected by Karl-Fischer titration (Mitsubishi Chem., model CA-07).

Impurity analysis. The amounts of residual halide and potassium ions in the liquid salts were approximately estimated by a fluorescence X-ray spectrometer (JEOL, model JSX-3201).

Phase transition analysis. The calorimetric measurements were performed with a differential scanning calorimeter (Perkin Elmer Pyris 1 DSC equipped with a liquid nitrogen cryostatic cooling) in the temperature range -150 °C to a predetermined temperature. An average sample weight of 5–10 mg was sealed in an aluminum pan, and then heated and cooled at 10 °C min⁻¹ under a flow of helium. The glass transition temperature (T_g, onset of the heat capacity change), crystallization temperature (T_c, onset of the exothermic peak), solid-solid transition temperature (T_s, onset of the endothermic peak), and melting point (T_m, onset of the endothermic peak) were taken on heating in the second heating-cooling cycle.

Viscosity. The viscosity was examined using a spindle viscometer with a thermostatic water bath (Brookfield, model DV-III+, cone spindle: CP-52) at 25 °C.

Specific conductivity. The ionic conductivity (κ) of the neat liquid salts was measured by a conductivity meter (Radiometer Analytical, model CDM230) in a sealed conductivity cell at 25 °C.

Electrochemical stability. Linear sweep voltammetry (LSV) was performed using an automatic polarization system (ALS model 600) in an argon-filled glove box (O₂ and water < 5 ppm), by using a 5 mL beaker-type three-electrode cell equipped with a glassy carbon electrode (surface area: 7.85 × 10⁻³ cm²), a Pt wire counter electrode, and an I₃⁻/I⁻ reference electrode consisting of Pt wire/0.015 mol dm⁻³ I₂ + 0.060 mol dm⁻³ [(n-C₃H₇)₄N]⁺ in [C₂mim][TFSI] ([C₂mim]⁺ = 1-ethyl-3-methylimidazolium). The potential was referred to ferrocene (Fc)/ferrocenium (Fc⁺) redox couple in each salt. The data for each salt were collected in the first cathodic and anodic scan at 25 °C.
RESULTS AND DISCUSSION

Synthesis and characterization. In the present study, 36 quaternary ammonium (QA) salts, comprising the relative small QA cations [R1R2R3NR]+ (R1, R2, R3 = CH3 or C2H5, R = n-C3H7, n-C4H9, CH2CH2OCH3) with the fluoroanions [RfBF3]- (Rf = CF3, C2F5, n-C3F7, n-C4F9), [BF4]- and TFSI-, were synthesized according to Scheme 1 (27, 28). The QA salts prepared are presented in Table 1. For convenience, a notation for the QA cations is developed (see Scheme 1), viz., using an “N” to denote the QA cations, wherein each number in the subscript denotes the number of carbons in each alkyl substituent and the subscript, “102”, denotes methoxyethyl (CH3OCH2CH2) substituent.

\[
\begin{align*}
\text{R}^1\text{R}^2\text{R}^3\text{N} & \quad \text{RBr} \quad [\text{R}^1\text{R}^2\text{R}^3\text{NR}]\text{Br} \\
\quad \text{anion exchange} \quad \text{aq.} [\text{R}^1\text{R}^2\text{R}^3\text{NR}]\text{[OH]} \\
\quad \text{aq. H[A]} \quad [\text{R}^1\text{R}^2\text{R}^3\text{NR}][\text{A}] \\
\left([\text{A}^-] = \text{[CF3BF3]}^-, \text{[C2F5BF3]}^-, \text{[n-C3F7BF3]}^-, \text{[n-C4F9BF3]}^-, \text{[BF4]}^-, \text{[(CF3SO2)2N]}^+\right)
\end{align*}
\]

Scheme 1

ILs are usually prepared by using halide salts as a source of the cation component. In this case, it is very difficult to avoid halide impurities in the resulting ILs. It is well-known that the presence of halide impurities in the resultant ILs significantly alters the physicochemical properties of the ILs (29). To depress halide contamination, the new salts [R1R2R3NR][RfBF3] in the present study were prepared via a modified route by neutralization of aqueous solutions of [R1R2R3NR][OH] with aqueous solutions of H[RfBF3] as shown in Scheme 1. The aq. [R1R2R3NR][OH] were produced via anion exchange of the corresponding [R1R2R3NR]Br salts, which were synthesized by reaction of trialkylamines with an equivalent of appropriate alkyl bromide in anhydrous acetone in an autoclave, with the exception of the Nnuc^Br that was directly prepared at room temperature. The aq. H[RfBF3] was prepared by cation exchange of the corresponding K[RfBF3] (22,23). The [BF4]- and TFSI- based salts were similarly prepared except for using aq. H[BF4] and aq. H[TFSI] instead of aq. H[RfBF3].

All the salts prepared (Table 1) by this modified method were revealed to contain less than 30 ppm of Br- and K+ ions, as estimated by fluorescence X-ray method. In addition, the [RfBF3]- and TFSI- based salts are immiscible with water to some extent,
and this allows these salts to be separated directly from water phase. The final yields of the salts prepared were over a range from moderate to high (66–92%). In the $[R_{f}BF_{3}]^{-}$ series, increasing the length of the perfluoroalkyl (Rf) chain in the $[R_{f}BF_{3}]^{-}$ generally resulted in an increase in yield as expected by the increased hydrophobicity.

The newly prepared salts in Table 1 were characterized by $^1H$, $^{19}F$ and $^{11}B$ NMR, FAB-MS and elemental analysis (27,28). All the characterization data are consistent with the expected compositions and structures. The water content in the $[R_{f}BF_{3}]^{-}$ and TFSI$^{-}$-based salts was less than 50 ppm after drying at 70 °C and 0.02 Torr for 24 h because of their hydrophobicity, whereas the $[BF_{4}]^{-}$-based ones are miscible with water and still contained an appreciable amount of water (ca. 400–600 ppm) even after rigorously drying at 80 °C and 0.02 Torr for 48 h.

The phase transitions of these prepared salts were determined by differential scanning calorimetry (DSC). For the salts that are liquids at 25 °C, the physicochemical properties including dynamic viscosity ($\eta$), ionic conductivity ($\kappa$), and electrochemical stability, were also determined. The influence of the structure variation in the cation and anion on the above properties will be further detailed in the following sections.

Phase transition. The solid-liquid phase transitions of these QA salts were investigated using differential scanning calorimetry (DSC). The data for glass transition temperature ($T_g$), crystallization temperature ($T_c$), solid-solid transition ($T_{s-s}$), and melting point ($T_m$), if appropriate, are collected in Table 1. In general, four types of phase transition behavior were observed for these QA salts on heating. The typical DSC traces for these four types of behavior are exemplified in Figure 1.

The first type of behavior is characterized by the salts having single melting transition (Figure 1a, entries 5, 6, 9, 21, 25, 26, 27, 30, and 33 in Table 1). The second type of behavior is represented by a number of salts which exhibited one or multiple solid-solid transitions ($T_{s-s}$s) before melting (Figures 1b and c, entries 1, 2, 3, 4, 7, 8, 13, 14, 15, 18, 19, 20, 24, and 31 in Table 1). As can be seen in Table 1, most of the $[R_{f}BF_{3}]^{-}$-based salts show this behavior; however, such behavior was not observed among the $[BF_{4}]^{-}$-based ones. The unique property associated with this behavior will be further detailed below. The third type of behavior is represented by the salts which only exhibited glass transitions at a very low temperature in the range −95 to −113 °C without melting (Figure 1d, entries 11, 16, 17, 23, 34, and 35 in Table 1). The fourth type of behavior was observed in the remainder salts (entries 10, 12, 22, 28, 29, 32, and 36 in Table 1). A typical DSC trace for this behavior is shown in Figure 1e. On heating, these salts showed a glass transition ($T_g$) at a very low temperature (from −95 to −117 °C) to form a supercooled liquid, which then crystallized ($T_c$, observed as an exothermic peak) at a relatively high temperature, followed by a melting transition ($T_m$) as the temperature further increased.

The melting entropies ($\Delta S_m$'s) of the salts prepared are also presented in Table 1. Timmermans (30) reported that plastic crystal phases in simple molecular compounds typically have $\Delta S_m$'s < 20 J K$^{-1}$ mol$^{-1}$. Recently, MacFarlane (21) and coworkers reported that it is more appropriate to modify this criterion to ca. 40 J K$^{-1}$ mol$^{-1}$ when a relative large and flexible anion (e.g. TFSI$^{-}$) exists in the ionic compound. This new
criterion appears to be applicable to the \([R_f BF_3]^-\)-based salts (\(R_f = CF_3, C_2F_5, n-C_3F_7, n-C_4F_9\)), as these new anions containing a perfluoroalkyl (\(R_f\)) chain may have higher degrees of freedom than those with simple symmetry (e.g., \([BF_4]^-\) (15) and \([PF_6]^-\) (16)), and the salts with the former anions therefore may afford higher residual entropies of melting than those with the latter ones. Thus, it seems reasonable that many of the \([R_f BF_3]^-\)-based salts, which show solid-solid transitions with \(\Delta S_m^e < 40\) J K\(^{-1}\) mol\(^{-1}\) (Table 1), are exhibiting varying extents of plastic crystal behavior. It is of current interest to explore conductive organic plastic crystals as all-solid-state electrolyte for high-energy devices such as Li batteries (31,32), and our future work will therefore investigate the conductivity properties of these salts and the mixtures with their corresponding lithium salts. Among the salts to be investigated, the \(N\)\(_{1223}\)[CF\(_3\)BF\(_3\)] (entry 1) and \(N\)\(_{1223}\)[C\(_2\)F\(_5\)BF\(_3\)] (entry 7) may be the particularly interesting ones, which enter a plastic crystal phase at a low temperature (ca. –40 °C for 1 and ca. –21 °C for 7) and exists in this phase up to a high temperature (95 °C for 1 and 54 °C for 7) before melting.

The plastic crystal phase within these temperature regions is very suitable for practical application, because the electrolytes in many electrochemical devices are required to operate in ambient temperature region (from –40 to 80 °C).

**Melting point.** It was reported that the melting point (\(T_m\)) of a compound is determined by the strength of its crystal lattice, which in turn is controlled by three main factors: intermolecular forces, molecular symmetry, and the conformational degrees of the freedom of a molecule (33). For aliphatic QA salts, the influence of structure variation in the cation and anion on the \(T_m\) has been investigated previously (9-11,14-16,19-21). Generally, low symmetry and relatively large ion size for the cation, and low symmetry and effective charge distribution in the anion favor to destabilize packing efficiency of the crystal lattice of the QA salts, thus decreasing the strength of the crystal lattice which in turn lowers the \(T_m\). Additionally, introducing an alkylether to the QA cation also tends to depress the \(T_m\) in some cases (4-6,12,13,17,18).

On the base of above known knowledge, we therefore tried to prepare low-melting QA salts by using the QA cations with relatively low symmetry and/or having an alkylether substituent as shown in Scheme 1. Indeed, low \(T_m\)s were achieved for most salts in our study (Table 1). With the exceptions of \(N\)\(_{1223}\)[BF\(_4\)] and \(N\)\(_{1224}\)[BF\(_2\)], all the salts prepared have a \(T_m\) of < 100 °C, 23 are liquids at room temperature, most of the liquids are those containing an alkylether (CH\(_3\)OCH\(_2\)CH\(_2\)) substituent in the cation.

Figure 2 shows the observed \(T_m\)s of these salts. As a general trend, for each anion, the salts with higher symmetry cations show a higher \(T_m\) than those with lower symmetry cations. For example, the \([N\)\(_{2222}\)]\(^+\)-based salts with \([R_f BF_3]^-\) (\(R_f = C_2F_5, n-C_3F_7, n-C_4F_9\)) decompose directly at a high temperature (278–290 °C) on heating instead of melting (22); however, replacing the \([N\)\(_{2222}\)]\(^+\) of these salts with lower symmetry but equal formula weight \([N\)\(_{1223}\)]\(^+\) brings the \(T_m\) down to the low-melting range 54–97 °C. This is also true for the TFSI-based salts, e.g. \(N\)\(_{2222}\)[TFSI] (105–109 °C) (9,10) vs \(N\)\(_{1222}\)[TFSI] (14 °C). Likewise, the salts with lower symmetry \([N\)\(_{112,102}\)]\(^+\) and \([N\)\(_{222,102}\)]\(^+\) (containing three different substituents) generally exhibit a lower \(T_m\) than the corresponding salts with higher symmetry \([N\)\(_{111,102}\)]\(^+\) and \([N\)\(_{222,102}\)]\(^+\) (containing two different substituents).
Table 1. Phase transition properties of various salts prepared

| Entry | Salts | \(T_x^{[a]}\) [°C] | \(T_c^{[b]}\) [°C] | \(T_{ss}^{[c]}\) [°C] | \(T_m^{[d]}(\Delta S_m^{[e]})\) [°C] (J/mol*K^{-1}) |
|-------|-------|----------------------|----------------------|----------------------|--------------------------------------------------|
| 1     | \(\text{N}_{122}[\text{CF}_3\text{BF}_3]\) | -40, -30, -21         | 95 (7.4)              |                      |                                                  |
| 2     | \(\text{N}_{124}[\text{CF}_3\text{BF}_3]\) | -40                   | -3 (9.5)              |                      |                                                  |
| 3     | \(\text{N}_{11.12}[\text{CF}_3\text{BF}_3]\) | 51                    | 77 (33.3)             |                      |                                                  |
| 4     | \(\text{N}_{12.12}[\text{CF}_3\text{BF}_3]\) | -7                    | 8 (28.8)              |                      |                                                  |
| 5     | \(\text{N}_{12.12}[\text{CF}_3\text{BF}_3]\) | -22                   | 22 (29.9)             |                      |                                                  |
| 6     | \(\text{N}_{11.12}[\text{CF}_3\text{BF}_3]\) | 10                    | (60.7)                |                      |                                                  |
| 7     | \(\text{N}_{122}[\text{C}_2\text{F}_5\text{BF}_3]\) | -67, -40              | 54 (29.3)             |                      |                                                  |
| 8     | \(\text{N}_{122}[\text{C}_2\text{F}_5\text{BF}_3]\) | -49                   | 15 (32.7)             |                      |                                                  |
| 9     | \(\text{N}_{111.12}[\text{C}_2\text{F}_5\text{BF}_3]\) | 30                    | (38.4)                |                      |                                                  |
| 10    | \(\text{N}_{11.12}[\text{C}_2\text{F}_5\text{BF}_3]\) | -117                  | -76, -65              | -33 (57.9)           |                                                  |
| 11    | \(\text{N}_{11.12}[\text{C}_2\text{F}_5\text{BF}_3]\) | -113                  |                      |                      |                                                  |
| 12    | \(\text{N}_{122.102}[\text{C}_2\text{F}_5\text{BF}_3]\) | -98                   | -63, -51              | 3 (88.4)             |                                                  |
| 13    | \(\text{N}_{122}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -53, 25               | 57 (15.7)             |                      |                                                  |
| 14    | \(\text{N}_{122}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -58                   | 50 (41.1)             |                      |                                                  |
| 15    | \(\text{N}_{111.12}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -86                   | 23 (45.9)             |                      |                                                  |
| 16    | \(\text{N}_{11.12}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -113                  |                      |                      |                                                  |
| 17    | \(\text{N}_{12.12}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -112                  |                      |                      |                                                  |
| 18    | \(\text{N}_{122}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -33                   | 6 (30.7)              |                      |                                                  |
| 19    | \(\text{N}_{122}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | 12, 24                | 54 (17.9)             |                      |                                                  |
| 20    | \(\text{N}_{122}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -76, 3                | 60 (29.6)             |                      |                                                  |
| 21    | \(\text{N}_{111.12}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | 50                    | (54.4)                |                      |                                                  |
| 22    | \(\text{N}_{11.12}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -110                  | -56                   | -28 (60.2)           |                                                  |
| 23    | \(\text{N}_{12.12}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -108                  |                      |                      |                                                  |
| 24    | \(\text{N}_{122}[\text{n-C}_3\text{F}_7\text{BF}_3]\) | -11                   | 11 (26.1)             |                      |                                                  |
| 25    | \(\text{N}_{122}[\text{BF}_4]\) |                      | 186 (13.6)            |                      |                                                  |
| 26    | \(\text{N}_{124}[\text{BF}_4]\) |                      | 165 (20.6)            |                      |                                                  |
| 27    | \(\text{N}_{111.12}[\text{BF}_4]\) |                      | 54 (45.8)             |                      |                                                  |
| 28    | \(\text{N}_{11.12}[\text{BF}_4]\) | -97                   | 4 (55.0)              |                      |                                                  |
| 29    | \(\text{N}_{122.102}[\text{BF}_4]\) | -95                   | 8 (61.0)              |                      |                                                  |
| 30    | \(\text{N}_{122}[\text{BF}_4]\) |                      | 56 (57.0)             |                      |                                                  |
| 31    | \(\text{N}_{122}[\text{TFSI}]\) |                      | -21, -2               | 14 (15.8)            |                                                  |
| 32    | \(\text{N}_{124}[\text{TFSI}]\) | -93                   | 9 (87.6)              |                      |                                                  |
| 33    | \(\text{N}_{111.12}[\text{TFSI}]\) |                      | 37 (85.6)             |                      |                                                  |
| 34    | \(\text{N}_{11.12}[\text{TFSI}]\) | -96                   |                      |                      |                                                  |
| 35    | \(\text{N}_{122.102}[\text{TFSI}]\) | -95                   |                      |                      |                                                  |
| 36    | \(\text{N}_{122}[\text{TFSI}]\) | -82                   | 20 (81.3)             |                      |                                                  |

[a] Glass transition temperature; [b] crystallization temperature; [c] solid-solid transition temperature; [d] melting point; [e] entropy of melting (\(\Delta S_m = \Delta H_m/T_m\), where \(\Delta H_m\) is melting enthalpy at \(T_m\) (K)).
Figure 1. DSC traces; inset is an enlarged trace for (e) $\text{Ni}_{12}\text{[C}_2\text{F}_5\text{BF}_3]$ around $T_g$.

Figure 2. Melting point of various salts.

Exchanging the $[\text{Ni}_{1223}]^+$ of the salts for a larger $[\text{Ni}_{1224}]^+$ generally further decreased the $T_m$'s (e.g. entry 1 vs 2, 7 vs 8, 13 vs 14, 25 vs 26, 31 vs 32 in Table 1). Likewise, for the same cation, all the salts with lower symmetry $[\text{R}_7\text{BF}_3]^-$ and TFSI$^-$ exhibit a lower $T_m$ than those with higher symmetry $[\text{BF}_4]^-$.

Another notable effect on the $T_m$ of the aliphatic QA salt is to introduce a methoxyethyl (CH$_3$OCH$_2$CH$_3$) group to the QA cation, which was also observed in literatures (12,13,17,18). However, the reasons for this effect are not well understood. To gain an insight into the influence of the alkylether chain on the $T_m$ of the aliphatic QA salt, we therefore carried out a comparative study by comparing the $T_m$'s of the $[\text{Ni}_{1224}]^+$-based...
salts with those of the [N\textsubscript{122,102}]\textsuperscript{+}-based ones. As shown in Figure 2, for all the [N\textsubscript{122,102}]\textsuperscript{+}-based salts, replacing the n-butyl group in the [Ni\textsubscript{12,02}]\textsuperscript{+} with an isoelectronic methoxyethyl (CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{2}) group, resulted in a significant decrease in \(T_m\) in all cases. For example, N\textsubscript{122,102}[BF\textsubscript{4}] (8 °C) vs N\textsubscript{122,102}[CF\textsubscript{3}BF\textsubscript{3}] (22 °C) vs N\textsubscript{122,102}[CF\textsubscript{3}BF\textsubscript{3}] (−3 °C), and only \(T_g\) (−95 to −113 °C) for the [N\textsubscript{122,102}]\textsuperscript{+} salts with [R\textsubscript{f}BF\textsubscript{3}] (R\textsubscript{f} = C\textsubscript{2}F\textsubscript{5}, n-C\textsubscript{3}F\textsubscript{7}, n-C\textsubscript{4}F\textsubscript{9}, entries 11, 17, and 23) and TFSI\textsuperscript{−} (entry 35). In addition, the salts with the cations [N\textsubscript{i11,102}]\textsuperscript{+}, [N\textsubscript{i12,102}]\textsuperscript{+}, and [N\textsubscript{22,102}]\textsuperscript{+} also show low \(T_m\). Moreover, low-melting events have also been observed in the QA salts containing other alkylether groups such as methoxyethyl (CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{2}), ethoxymethyl (CH\textsubscript{3}CH\textsubscript{2}OCH\textsubscript{2}), ethoxyethyl (CH\textsubscript{3}CH\textsubscript{2}OCH\textsubscript{2}CH\textsubscript{2} group (4-6,12,13,17,18). Given that the alkyl ether group is more flexible but more polar than its isoelectronic alkyl group and the flexibility tends to lower the \(T_m\) while the polarity has an opposite effect, a tentative explanation for the lower \(T_m\) s for the QA salts having an alkylether group is that the better flexibility of the alkylether group might prevails over its polarity and plays a determinant role in determining the \(T_m\).

**Glass transition.** Figure 3 shows the glass transition temperature \((T_g)\) of the salts in Table 1. It seems that the \(T_g\) s of these QA salts are mainly governed by the strength of ion interactions, ion size, and flexibility and polarizability of the anion. As seen in Figure 3, the \(T_g\) s of the salts with large [R\textsubscript{f}BF\textsubscript{3}] (−117 to −98 °C, R\textsubscript{f} = C\textsubscript{2}F\textsubscript{5}, n-C\textsubscript{3}F\textsubscript{7}, n-C\textsubscript{4}F\textsubscript{9}) are all lower than those with the small [BF\textsubscript{4}] (−97 °C for 28 and −95 °C for 29) or the large but a bit polarizable TFSI\textsuperscript{−} (−82 to −96 °C), and much lower than those with the large nonfluorinated and more rigid and polarizable [BOB]\textsuperscript{−} (it comprises two rigid five-member rings and each of them contains two carbonyl (C=O) groups, \(T_g\) −36 to −44 °C) (18).

For the same cation, the \(T_g\) regularly increases in the order [C\textsubscript{2}F\textsubscript{5}BF\textsubscript{3}] < [n-C\textsubscript{3}F\textsubscript{7}BF\textsubscript{3}] < [n-C\textsubscript{4}F\textsubscript{9}BF\textsubscript{3}] < [BF\textsubscript{4}] ≈ TFSI\textsuperscript{−} < [BOB]. Similar trend was also observed in the related imidazolium salts (24,25). This trend strongly suggests that (1) replacing the [BF\textsubscript{4}] with a larger [R\textsubscript{f}BF\textsubscript{3}] weakens the electrostatic interactions (including possible hydrogen-bonding) between the cation and anion in the salt which in turn decreases the \(T_g\); (2) the decrease of the electrostatic interactions dominates over the increase of van der Waals interactions in the [R\textsubscript{f}BF\textsubscript{3}]\textsuperscript{−}-based salts (R\textsubscript{f} = C\textsubscript{2}F\textsubscript{5}, n-C\textsubscript{3}F\textsubscript{7}, n-C\textsubscript{4}F\textsubscript{9}) because of the extremely low polarizability of fluorine atom, and (3) the ion interactions in the salts with the small [BF\textsubscript{4}] is more determined by the electrostatic interactions than by van der Waals interactions, while those in the [R\textsubscript{f}BF\textsubscript{3}]\textsuperscript{−}-based salts (R\textsubscript{f} = C\textsubscript{2}F\textsubscript{5}, n-C\textsubscript{3}F\textsubscript{7}, n-C\textsubscript{4}F\textsubscript{9}) are more under the control of van der Waals interactions than of the electrostatic interactions as the \(T_g\) increased with the [R\textsubscript{f}BF\textsubscript{3}]\textsuperscript{−} size increased.

On the other hand, one may note that the TFSI\textsuperscript{−}-based salts show a bit higher \(T_g\)\'s than the corresponding [BF\textsubscript{4}]\textsuperscript{−}-based ones, and much higher \(T_g\)\'s than the corresponding [R\textsubscript{f}BF\textsubscript{3}]\textsuperscript{−}-based ones (Figure 3 and Table 1), though the TFSI\textsuperscript{−} has much better flexibility and charge distribution than the [BF\textsubscript{4}]\textsuperscript{−} and would be expected to give lower \(T_g\)\'s for the corresponding salts. This result may be attributed to the facts that (1) the size of the TFSI\textsuperscript{−} is much larger than that of the [BF\textsubscript{4}]\textsuperscript{−}, and (2) the partially fluorinated TFSI\textsuperscript{−} (it contains two sulfonyl (-SO\textsubscript{2}-) groups) is more polarizable than the perfluorinated [BF\textsubscript{4}]\textsuperscript{−} and highly perfluorinated [R\textsubscript{f}BF\textsubscript{3}]\textsuperscript{−}, both of which significantly trade off the flexibility and charge distribution of the TFSI\textsuperscript{−} and tend to increase the attractive forces (i.e. van der Waals interactions) in the TFSI\textsuperscript{−}-based salts, thus raising the \(T_g\). Moreover, comparing the
$T_g$ of the nonfluorinated [BOB]$^-$-based salts with that of the perfluorinated [n-$C_4F_9BF_3$]$^-$-based ones (the size of the [n-$C_4F_9BF_3$]$^-$ should be larger than that of the [BOB]$^-$ viz. [B(C$_2$O$_4$)$_2$]$^-$) more clearly manifests the significant impact of rigidity and polarizability of the anion, e.g. N$_{112,102}$[BOB] (−36 °C) (18) vs N$_{112,102}$[n-$C_4F_9BF_3$] (−110 °C).

For the same anion, the $T_g$'s of all the salts increased as the cation size increased, as expected by the increased van der Waals interactions. Because the glass transition temperature ($T_g$) is a qualitative signature of ion mobility in ILs and low $T_g$'s are a sign of high ion mobility (9,17,18), the lower $T_g$'s for the [R$_4$BF$_3$]$^-$-based salts than for the [BF$_4$]$^-$-based ones may partly explain why the former exhibit lower viscosities than the latter (see below).

![Figure 3. Glass transition temperature of various ionic liquids.](image)

![Figure 4. Viscosity of various liquid salts at 25 °C.](image)
Viscosity. The viscosity of the QA salts is essentially determined by the strength of ion interactions (mainly including the electrostatic and van der Waals interactions), ion size, and polarizability and flexibility of the anion. Figure 4 shows the viscosities ($\eta$) of the liquid salts based on the $[RFBF_3]^-$ ($R_F = C_2F_5, n-C_3F_7, n-C_4F_9$), $[BF_4]^-$ and $[TFSI]^-$ at 25 °C. The viscosities of the $[RFBF_3]^-$ and $[TFSI]^-$-based ILs are in the range 58–210 cP, all of which are significantly lower by > 100 cP than those of the $[BF_4]^-$-based ones (335 cP for 28 and 426 cP for 29 at 25 °C), and much lower than those of the QA salts with the nonfluorinated $[BOB]^-$ (> 1300 cP at 25 °C (18)).

The lower viscosities for the $[RFBF_3]^-$ and $[TFSI]^-$-based ILs than for the $[BF_4]^-$-based ones may be explained by the decreased ion interactions and increased ion mobility due to better charge distribution, lower symmetry and lower polarizability for the $[RFBF_3]^-$ and better charge distribution, larger flexibility, and lower symmetry for the $[TFSI]^-$, respectively. Notwithstanding that the $[BOB]^-$ is among the most weakly coordinating anions (34), the extremely high viscosities were observed for all the $[BOB]^-$-based salts (18), which is essentially attributed to high rigidity (comprising two five-member rings) and somewhat polarizability (containing four carbonyl (C=O) groups) and large size of the $[BOB]^-$ as discussed in $T_g$. The first factor reduces the flexibility and the latter two increase van der Waals interactions in the salts, all of which in turn increase the viscosity significantly. These impressive examples based on the $[BOB]^-$ and its derivatives clearly indicate that an anion with high rigidity and polarizability and large size is not suitable for forming low-viscous ILs despite its weakly coordinating ability (18).

In the family of the fluoroborate ($[RFBF_3]^-$ and $[BF_4]^-$) ILs, for a given cation, the viscosities show the increasing order $[C_2F_5BF_3]^-$ < $[n-C_3F_7BF_3]^-$ < $[CF_3BF_3]^-$ < $[n-C_4F_9BF_3]^-$ << $[BF_4]^-$ with the exception of the $N_{122.102}[CF_3BF_3]$. It is very interesting to note that this order in viscosity is exactly consistent with that in $T_g$ (i.e. the lower the $T_g$, the more fluid the ILs), with the exception of the salts containing the $[CF_3BF_3]^-$ (no $T_g$ observed). These results further suggest that the ion interactions in the salts with relative large $[RFBF_3]^-$ ($R_F = C_2F_5, n-C_3F_7, n-C_4F_9)$ are essentially determined by van der Waals interactions, and a very large anion in this class (e.g. $[n-C_4F_9BF_3]^-$) is therefore unsuitable for forming low-viscous ILs despite its good charge distribution and extremely low polarizability. The most unexpected is that the salts with the smaller $[CF_3BF_3]^-$ show a higher viscosity than those with the larger $[RFBF_3]^-$ ($R_F = C_2F_5, n-C_3F_7$). It appears that (1) the ion interactions in the former is stronger than those in the latter and are still under the influence of the electrostatic interactions due to the small size of the $[CF_3BF_3]^-$, as in the case of the $[BF_4]^-$-based salts; and (2) the $[RFBF_3]^-$ with a longer $R_F$ group ($R_F = C_2F_5, n-C_3F_7$) have more degrees of freedom than the $[CF_3BF_3]^-$.

The lowest viscosities for the $[C_2F_5BF_3]^-$-based salts are essentially attributed to good charge distribution and medium size for the $[C_2F_5BF_3]^-$.

As shown in Figure 4, for the same cation, the viscosity values of the $[TFSI]^-$-based salts are nearly equivalent to those of the most fluid $[C_2F_5BF_3]^-$-based ones (e.g. $N_{112.102}[TFSI]$ (60 cP) vs $N_{122.102}[C_2F_5BF_3]$ (58 cP) and $N_{122.102}[TFSI]$ (69 cP) vs $N_{122.102}[C_2F_5BF_3]$ (68 cP)), although the $[TFSI]^-$ has a larger size than the $[C_2F_5BF_3]^-$.
seems that better flexibility and charge delocalization of the [TFSI] plays a dominant role over its size and polarizability in determining the viscosity. All above results indicate that the viscosities of the QA salts are strongly dependent on the type of anion present. Therefore, in the search of more low-viscous QA salts, new stable anions, especially fluoroanions with relatively low symmetry, high flexibility and good charge distribution, are expected to be discovered and investigated in future.

The structure variation in the cation also influences the viscosity. For the same anion, the viscosities of the QA salts containing a methoxyethyl (CH₃OCH₂CH₂) group are generally lower than those of the tetraalkylammonium salts (e.g. entries 9, 10, 11, 12 vs 8). This may be due to the flexibility of the methoxyethyl group in the QA cation, which results in an increase in the ion mobility, as the Zₚ's of the former salts are lower than that of the latter one (Figure 3). In the family of the QA salts containing a methoxyethyl group, the viscosity increased as the cation size increased in the order [Ni12.102]+, [Ni11.102]+ < [Ni12.102]+ < [Ni22.102]+, as expected by the increase of van der Waals interaction. This trend suggests that, to further reduce the viscosity of the QA salts, the cation involved should be smaller, at least not larger, than those used in this study.

It should be noted that the viscosities of all the QA salts in the present study are all remarkably higher than those of the related 1,3-dialkylimidazolium ones with similar formula weight (24,25). For example, the viscosity of the Ni12.102[CF₃BF₃] (Mₜ 269) is 97 cP at 25 °C, which is ca. 1.3 times greater than that of the 1-methyl-2-methoxyethylimidazolium salt with [CF₃BF₃] (43 cP at 25 °C, Mₜ 278) (24,25). It seems that the almost-flat shape and good charge distribution of the imidazolium ring plays a critical role in lowering the viscosity. This may explain why the five-member cyclic QA cations, N-alkyl-N-methylpyrrolidinium, are preferred to the acyclic QA cations to form ILs in recent studies (8,21). The reason is that the former cations show a quasi-flat shape to some extent and can form more fluid ILs than acyclic QA cations containing the same number of carbon atom, e.g. Pi13[TFSI] (Pi13 = N-methyl-N-propylpyrrolidinium, 63 cP at 25 °C) vs Ni124[TFSI] (110 cP at 25 °C) (10). Therefore, it seems reasonable that the [RfBF₃] could form low-viscous ILs with the pyrrolidinium cations.

Conductivity. It seems that the ionic conductivities of these QA salts are mainly governed by their viscosities and formula weight. Figure 5 shows the specific conductivities (κ) of the liquid salts based on the [RfBF₃] (Rf = CF₃, C₂F₅, n-C₃F₇, n-C₄F₉), [BF₄] and [TFSI] at 25 °C. For a given anion, the conductivity values decreased in the order [Ni12.102]+ > [Ni11.102]+ > Ni123, [Ni22.102]+ > [Ni224]+ with the exception of the Ni122.102[CF₃BF₃], as expected by the increased viscosity (Figure 4), and formula weight because the number of the ion carriers per unit volume generally decreased with increasing formula weight. For a given cation, the conductivity decreased in the order [C₂F₅BF₃]+ > TFSI+, [n-C₃F₇BF₃]+, [CF₃BF₃]+ > [n-C₄F₉BF₃]+ ≈ [BF₄]+. This trend strongly indicates that an anion, which has a large formula weight (e.g. TFSI+, [n-C₄F₉BF₃]+) or results in high viscosity (e.g. [BF₄]+, [CF₃BF₃]+), is unfavorable for producing highly conductive ILs. Among these QA salts, the Ni124[CF₃BF₃] (10) exhibits the highest conductivity (3.8 mS cm⁻¹ at 25 °C) due to its lowest viscosity (58 cP at 25 °C) and relatively low formula weight.
On the other hand, all the QA salts in this study show much lower conductivities than the imidazolium salts with similar formula weight, e.g. the most conductive QA salt $N_{112.102}[C_2F_5BF_3]$ (3.8 mS cm$^{-1}$ and 57 cP at 25 °C, $M_w$ 319) vs the 1-methyl-2-methoxyethylimidazolium salt with $[C_2F_5BF_3]^-$ (25) (6.1 mS cm$^{-1}$ and 38 cP at 25 °C, $M_w$ 328). This is mainly caused by the higher viscosities for the former (57 cP at 25 °C) than for the latter (25) (38 cP at 25 °C). Therefore, one of the significant challenges in developing conductive QA salts is how to further reduce their viscosity.

Figure 5. Specific conductivity of various liquid salts at 25 °C; the data in parentheses is formula weight ($M_w$) of the cation.

Figure 6. Linear sweep voltammogram of various ionic liquids on a glassy carbon electrode (surface area: $7.85 \times 10^{-3}$ cm$^2$) in the first scan at 25 °C.
Electrochemical stability. The electrochemical stability of most QA salts in this study was investigated by linear sweep voltammetry (LSV) on a glassy carbon (GC) electrode under the same conditions. Figure 6 displays the polarization curves of seven salts, which mainly manifests the impact of the cation structure on the cathodic stability (i.e. the significant influence of having a methoxyethyl group in the QA cations and the sizes of these cations on the cathodic stability).

As shown in Figure 6, all the QA cations exhibit better cathodic stability than the \([\text{C}_2\text{mim}]^+\) in the following order: \([\text{C}_2\text{mim}]^+ < [\text{N}_{11,102}]^+ < [\text{N}_{12,102}]^+ < [\text{N}_{11,114}]^+ \approx [\text{N}_{22,102}]^+ \approx [\text{N}_{224}]^+\). This order clearly indicates that replacing the alkyl in the tetraalkylammonium cations with an isoelectronic alkylether tends to reduce the cathodic stability of the cations while increasing the sizes of trialkyl(methoxyethyl)ammonium cations tends to increase their cathodic stability. A preliminary explanation for these results is that there are somewhat electrostatic interactions occurring between the lone-pair electrons of oxygen atom of the methoxyethyl group and positive charge nitrogen atom in the cation, which likely increases the cathodic stability of the positively charged nitrogen atom through decreasing positive charge density on the nitrogen atom but reduces the cathodic stability of the methoxyethyl group due to electron density decrease on its oxygen atom. These interactions are more stronger for the smaller trialkyl(methoxyethyl)ammonium due to its higher charge density. Thus, the lower cathodic stability for the small trialkyl(methoxyethyl)ammonium cations may be due to electroreduction of the methoxyethyl group in the cation at a relative high potential, while increasing the trialkyl(methoxyethyl)ammonium size may effectively “bury” the positive charge on the nitrogen atom of the ammonium, which in turn decreases the interactions mentioned above, thus inhibiting the decomposition of the methoxyethyl group (i.e. increasing the cathodic stability of the cation). From these results, we may conclude that having an alkylether chain in the small QA cations is unfavorable for producing electrochemically stable QA salts. The distinctive cathodic stability of the tetraalkylammoniums (e.g. \([\text{N}_{1114}]^+\) and \([\text{N}_{1234}]^+\)) and large trialkyl(methoxyethyl)ammonium (e.g. \([\text{N}_{222,103}]^+\)) may favor their salts with electrochemically stable anions as promising candidates for electrolytes in high-energy devices.

For anodic stability, as shown in Figure 6, all the QA salts are obviously more resistant toward oxidation than the \([\text{C}_2\text{mim}][\text{CF}_3\text{BF}_3]\). This result suggests that the anodic stability of the former are determined by the involved anions, while that of the latter is essentially limited by the decomposition of the cation \([\text{C}_2\text{mim}]^+\). This result is in keeping our previous conclusion that both the cathodic and anodic stability of 1,3-dialkylimidazolium salts with electrochemically stable anions, such as \([\text{R}_6\text{BF}_3]^+, [\text{BF}_4]^−\) and TFSI, are limited by the cations but not by the anions (25,26). However, as seen in Figure 6, the anodic stability of these anions is hardly distinguishable and show somewhat dependence on the cations. Additionally, it should be noted that the reported better anodic stability for the inorganic fluoroanion, \([\text{BF}_4]^−\), than for the organic fluoroanion, TFSI, was not observed in this study (14,35). This may be due to the presence of relatively high amounts of water in our \([\text{BF}_4]^−\)-based salts (400–600 ppm), which reduces the anodic stability of the salts, as reported in the literature (36).
CONCLUSIONS

A novel family of low-melting, hydrophobic ionic liquids comprising small aliphatic quaternary ammoniums ([R1R2R3NR]+, wherein R1, R2, R3 = CH3 or C2H5, R = n-C3H7, n-C4H9, CH2CH2OCH3) and perfluoroalkyltrifluoroborates ([RfBF3]−, Rf = CF3, C2F5, n-C3F7, n-C4F9) has been prepared and characterized. Most of them are liquids at room temperature and exhibit much lower viscosities (58–210 cP at 25 °C) than those with [BF4]− (335–426 cP at 25 °C) due to relatively lower symmetry and better charge distribution for the [RfBF3]−. Many of them exhibit plastic crystal behavior which has a fundamental importance in all-solid-state electrolytes. More importantly, all these quaternary ammonium salts show better cathodic and anodic stability, hence larger electrochemical windows, than the corresponding 1,3-dialkylimidazolium ones. Because of these desire properties, these new salts not only enrich the existing arsenal of quaternary ammonium ionic liquids but may be also served as new media for some special organic and biocatalytic reactions and as electrolytes for high-energy devices and electrochemical processes, in which the 1,3-dialkylimidazolium salts cannot operate.

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