

# Synthesis and physico-chemical properties of ionic liquids containing tetrakis(perfluorophenyl)borate, tetraphenylborate and trifluorophenylborate anions.

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## Abstract

Synthesis and some physico-chemical properties are reported for six new hydrophobic ionic liquids containing tetrakis(perfluorophenyl)borate, tetraphenylborate or trifluorophenylborate anions and imidazolium or pyridinium cations.

## Introduction

Room-temperature ionic liquids (RTILs) provide a new class of solvents composed only of ions. They are molten salts with melting points below 100 °C. Typical ionic liquids contain large organic cations, such as ammonium, imidazolium, pyridinium or pyrrolidinium cations, and halogen, fluorinated or organic anions.<sup>1-5</sup>

Ionic liquids are often called “green” solvents, i.e. environmental-friendly solvents, as compared to classical organic solvents, because, at normal temperatures, ionic liquids have essentially zero vapor pressure, and because they have high thermal stability (typically above 250 °C).

For extraction of offensive metallic cations from water, we require highly hydrophobic ionic liquids, that have very low solubility in water. Water-immiscible ionic liquids used previously for metal-ion extraction from water exhibit solubilities in water that are too high to be applied to industrial extraction processes. Here we report the synthesis of six new, hydrophobic ionic liquids.

Because the hydrophobicity of an ionic liquid containing a 1-alkyl-3-alkylimidazolium cation is mostly due to the hydrophobic nature of the anion<sup>1-3</sup>, tetrakis(perfluorophenyl)borate (BArF<sub>20</sub>) and tetraphenylborate anions are used here. Because the melting point of an ionic liquid depends on the length of the alkyl chain appended to the imidazolium cation, we use 1-methyl-3-octylimidazolium and 1-butyl-3-octylimidazolium cations. To investigate the influence of the cation on melting point and solubility in water of ionic liquids containing borate anions, we also used 1-octyl-4-methylpyridinium cation.

Ionic liquids containing tetrafluoroborate anions (BF<sub>4</sub><sup>-</sup>) are known to be liquid at room temperature.<sup>2</sup> They are also reported to be immiscible in water with cations such as 1-methyl-3-octylimidazolium.<sup>2</sup> We report here the synthesis of two ionic liquids containing trifluorophenylborate anion, an anion whose structure is hybrid between those of tetrafluoroborate and tetraphenylborate anions. Due to the nature of the anion, the properties of these ionic liquids are expected to be between those of ionic liquids containing tetrafluoroborate anions and tetraphenylborate anions.

Previous work<sup>8,9</sup> described the synthesis of 1-methyl-3-butylimidazolium tetraphenylborate and 1-methyl-3-butylimidazolium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (BArF<sub>24</sub>).

We report here the synthesis of six new ionic liquids: 1-methyl-3-octylimidazolium tetrakis(fluorophenyl)borate, 1-methyl-3-octylimidazolium tetraphenylborate, 1-butyl-3-octylimidazolium tetraphenylborate, 1-octyl-4-methylpyridinium tetraphenylborate, 1-methyl-3-octylimidazolium trifluorophenylborate and 1-octyl-4-methylpyridinium trifluorophenylborate. To our best knowledge, we are the first to report the synthesis and selected properties of ionic liquids containing 1-butyl-3-octylimidazolium cations or trifluorophenylborate anions.

For 1-butyl-3-octylimidazolium tetraphenylborate, 1-butyl-3-octylimidazolium bromide was synthesized first. Then, a two-step metathesis procedure was carried out to obtain 1-butyl-3-octylimidazolium tetraphenylborate. For ionic liquids containing 1-octyl-4-methylpyridinium cations, 1-octyl-4-methylpyridinium bromide was synthesized first. Then a two-step metathesis procedure was carried out to obtain the desired ionic liquids. All other ionic liquids were synthesized using a two-step metathesis.

Purity of the ionic liquids has been confirmed by NMR and elemental analysis.

## Experimental

### Synthesis

*1-methyl-3-octylimidazolium tetrakis(fluorophenyl)borate*: 1.4 g of [OMIm]<sup>+</sup>[Cl]<sup>-</sup> (6.0 · 10<sup>-3</sup> mol) from Solvent Innovation, 98 % purity, used as received, were mixed for 10 h with 5.0 g of KBarF<sub>20</sub> (7.0 · 10<sup>-3</sup> mol) from Boulder Scientific, used as received, in 150 mL of acetonitrile. After filtering and removal of the acetonitrile by rotary evaporation, the resulting white powder was washed with methylene chloride and put in a freezer for 24 h. After filtering, methylene chloride was removed by rotary evaporation and the product was set under vacuum for 4 h. The resulting light-yellow white powder was then purified by silica-gel chromatography, to yield 4.0 g of [OMIm]<sup>+</sup>[BarF<sub>20</sub>]<sup>-</sup> (4.5 · 10<sup>-3</sup> mol) as a white powder (yield: 76 %).  $\delta_{\text{H}}(400 \text{ MHz}, \text{CDCl}_3, \text{SiMe}_4)$  7.984 (1H, s, N-CH-N), 7.222-7.199 (2H, d, N-(CH)<sub>2</sub>-N), 4.077-4.040 (2H, t, CH<sub>2</sub>), 3.860 (3H, s, N-CH<sub>3</sub>), 1.812 (2H, t, CH<sub>2</sub>), 1.275-1.216 (10H, m, C<sub>5</sub>H<sub>10</sub>), 0.859-0.825 (3H, t, CH<sub>3</sub>).  $\delta_{\text{F}}(400 \text{ MHz}, \text{CDCl}_3, \text{CdCl}_2)$  -132.99 (1F, FluoroPh-F<sub>p</sub>), -163.07, -163.13, -163.18 (2F, t, FluoroPh-F<sub>m</sub>), -167.51, -167.55, -167.60 (2F, t, FluoroPh-F<sub>o</sub>). (Found: C, 49.44; H, 2.58; N, 3.16. Calc. for C<sub>36</sub> H<sub>23</sub> N<sub>2</sub> B F<sub>20</sub>: C, 49.45; H, 2.65; N, 3.20).

*1-methyl-3-octylimidazolium tetraphenylborate*: 1.36 g of [OMIM]<sup>+</sup>[Cl]<sup>-</sup> (5.8 · 10<sup>-3</sup> mol) were mixed for 10 h with 3.22 g of sodium tetraphenylborate (8.8 · 10<sup>-3</sup> mol), from Sigma Aldrich, 98 % purity, used as received, in 150 mL of acetonitrile. After filtering and removal of the acetonitrile by rotary evaporation, the resulting white powder was washed with methylene chloride and put in a freezer for 24 h. After filtering, methylene chloride was removed by rotary evaporation and the product was set under vacuum for 4 h. 2.4 g of [OMIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> (4.6 · 10<sup>-3</sup> mol) was recovered as a white powder (yield: 80 %).  $\delta_{\text{H}}(400 \text{ MHz}, \text{CDCl}_3, \text{SiMe}_4)$  7.804-7.787 (8H, m, Ph-H<sub>o</sub>), 6.994-6.957 (8H, t, Ph-H<sub>m</sub>), 6.798- 6.762 (4H, t, Ph-H<sub>p</sub>), 6.446 (1H, s, N-CH), 6.357 (1H, s, N-CH), 5.665 (1H, s, N-CH-N), 3.434-3.396 (2H, t, CH<sub>2</sub>), 3.110 (3H, s, N-CH<sub>3</sub>), 1.241 (2H, m, CH<sub>2</sub>), 1.140-1.054(10H, m, C<sub>5</sub>H<sub>10</sub>), 0.886-0.852 (3H, m, oct-CH<sub>3</sub>). (Found: C, 83.92; H, 8.16; N, 5.11. Calc. for C<sub>36</sub> H<sub>43</sub> N<sub>2</sub> B: C, 84.03; H, 8.42; N, 5.44).

*1-butyl-3-octylimidazolium bromide*: We synthesized this bromide ionic liquid as a preliminary step toward synthesizing 1-butyl-3-octylimidazolium tetraphenylborate. 6 g of 1-butyl-imidazole (4.8 · 10<sup>-3</sup> mol) were mixed for 10 h with 10.22 g of sodium tetraphenylborate (8.8 · 10<sup>-3</sup> mol) in 150 mL of acetonitrile. After filtering and removal of the acetonitrile by rotary evaporation, the resulting white powder was washed with methylene chloride and put in a freezer for 24 h. After filtering, methylene chloride was removed by rotary evaporation and the product was set under vacuum for 4 h. 13.6 g of [OBIM]<sup>+</sup>[Br]<sup>-</sup> (4.3 · 10<sup>-3</sup> mol) was recovered as a light yellow liquid (yield: 90 %).

*1-butyl-3-octylimidazolium tetraphenylborate*: 3.01 g of [OBIM]<sup>+</sup>[Br]<sup>-</sup> (9.4 · 10<sup>-3</sup> mol) were mixed for 10 h with 4.03 g of sodium tetraphenylborate (11.75 · 10<sup>-3</sup> mol) in 150 mL of acetonitrile. After filtering and removal of the acetonitrile by rotary evaporation, the resulting white powder was washed with methylene chloride and put in a freezer for 24 h. After filtering, methylene chloride was removed by rotary evaporation and the product was set under vacuum for 4 h. 4.7 g of [OBIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> (8.4 · 10<sup>-3</sup> mol) was recovered as a white-yellowish solid (yield: 89 %).  $\delta_{\text{H}}(400 \text{ MHz}, \text{CDCl}_3, \text{SiMe}_4)$  7.481 (8H, s, Ph-H<sub>o</sub>), 6.976-6.940 (8H, t, Ph-H<sub>m</sub>), 6.807- 6.771 (4H, t, Ph-H<sub>p</sub>), 5.972 (2H, s, N-(CH)<sub>2</sub>-N), 4.765 (1H, s, N-CH-N), 3.110-3.072 (4H, t, but-C<sub>2</sub>H<sub>4</sub>), 1.353-1.260 (12H, m, oct-C<sub>6</sub>H<sub>12</sub>), 1.140-1.054(4H, m, but-C<sub>2</sub>H<sub>4</sub>), 0.895-0.844 (6H, m, oct-CH<sub>3</sub>,but-CH<sub>3</sub>). (Found: C, 83.92; H, 9.16; N, 4.81. Calc. for C<sub>39</sub> H<sub>49</sub> N<sub>2</sub> B: C, 84.15; H, 8.87; N, 5.04).

*1-octyl-4-methylpyridinium tetraphenylborate*: 1.78 g of [MOPYR]<sup>+</sup>[Br]<sup>-</sup> (6.2 · 10<sup>-3</sup> mol) were mixed for 10 h with 3.28 g of sodium tetraphenylborate (9.6 · 10<sup>-3</sup> mol) in 50 mL of acetonitrile. After filtering and removal of the acetonitrile by rotary evaporation, the resulting white powder was washed with methylene chloride and put in a freezer for 24 h. After filtering, methylene chloride was removed by rotary evaporation and the product was set under vacuum for 24 h. 3.11 g of [MOPYR]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> (5.9 · 10<sup>-3</sup> mol) was recovered as a white-yellowish solid (yield: 89 %).  $\delta_{\text{H}}(400 \text{ MHz}, \text{CDCl}_3, \text{SiMe}_4)$  7.487 (8H, s, Ph-H<sub>o</sub>), 6.927-6.878 (8H, t, Ph-H<sub>m</sub>), 6.745- 6.698 (4H, t, Ph-H<sub>p</sub>), 6.282, 6.261 (2H, d, CH-N-CH<sub>pyr</sub>), 5.721, 5.700 (2H, d, 2CH<sub>pyr</sub>), 2.963-2.912 (2H, t, N-CH<sub>2</sub>), 2.144 (3H, s, CH<sub>3</sub>), 1.310-1.051 (10H, m, C<sub>5</sub>H<sub>10</sub>), 0.961-0.848 (5H, m, CH<sub>2</sub>-CH<sub>3</sub>). (Found: C, 87.04; H, 8.68; N, 2.73. Calc. for C<sub>38</sub> H<sub>44</sub> N B: C, 86.84; H, 8.44; N, 2.66).

*1-octyl-4-methylpyridinium trifluorophenylborate*: 2.02 g of [MOPYR]<sup>+</sup>[Br]<sup>-</sup> (7.3 · 10<sup>-3</sup> mol) were mixed for 10 h with 2.0 g of potassium trifluorophenylborate (10.9 · 10<sup>-3</sup> mol) in 100 mL of acetonitrile. After filtering and removal of the acetonitrile by rotary evaporation, the resulting white powder was washed with methylene chloride and put in a freezer for 24 h. After filtering, methylene chloride was removed by rotary evaporation and the product was set under vacuum for 24 h. 2.14 g of [MOPYR]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> (6.1 · 10<sup>-3</sup> mol) was recovered as a white-yellowish solid (yield: 84 %).  $\delta_{\text{H}}(400 \text{ MHz}, \text{CDCl}_3, \text{SiMe}_4)$  8.262, 8.246 (2H, d, N-CH<sub>2</sub>), 7.507, 7.491 (2H, d, CH-N-CH<sub>pyr</sub>), 7.414-7.399 (2H, d, Ph-H<sub>m</sub>), 7.141-7.054 (3H, m, Ph-H), 4.154-4.117 (2H, t, CH-B-CH), 2.415 (3H, s, CH<sub>3</sub>-C<sub>pyr</sub>), 1.698-1.623 (2H, m, CH<sub>2</sub>), 1.240-1.105 (10H, m, C<sub>5</sub>H<sub>10</sub>), 0.849-0.815 (3H, t, oct-CH<sub>3</sub>). (Found: C, 68.07; H, 8.49; N, 3.93. Calc. for C<sub>20</sub> H<sub>29</sub> N F<sub>3</sub> B: C, 68.38; H, 8.32; N, 3.99).

*1-methyl-3-octylimidazolium trifluorophenylborate*: 2.61 g of [OMIM]<sup>+</sup>[Cl]<sup>-</sup> (11.3 · 10<sup>-3</sup> mol) were mixed for 10 h with 2.5 g of potassium trifluorophenylborate (13.6 · 10<sup>-3</sup> mol), from Sigma Aldrich, 98 % purity, used as received, in 100 mL of acetonitrile. After filtering and

removal of the acetonitrile by rotary evaporation, the resulting white powder was washed with methylene chloride and put in a freezer for 24 h. After filtering, methylene chloride was removed by rotary evaporation and the product was set under vacuum for 4 h. 3.3 g of [OMIM]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> (9.8·10<sup>-3</sup> mol) was recovered as a light-yellow viscous liquid (yield: 88 %).  $\delta_{\text{H}}(400 \text{ MHz, CDCl}_3, \text{SiMe}_4)$  8.604 (1H, s, N-CH-N), 7.522, 7.505 (2H, d, N-CH-N), 7.18-7.071 (4H, m, Ph-H), 7.001-6.997 (1H, t, Ph-H<sub>p</sub>), 3.870-3.833 (2H, t, N-CH<sub>2</sub>), 3.676 (3H, s, N-CH<sub>3</sub>), 1.769-1.621 (2H, m, CH<sub>2</sub>), 1.266-1.214 (10H, m, C<sub>3</sub>H<sub>10</sub>), 0.871-0.836 (3H, t, oct-CH<sub>3</sub>). (Found: C, 63.19; H, 8.51; N, 8.41. Calc. for C<sub>18</sub> H<sub>28</sub> N<sub>2</sub> F<sub>3</sub> B: C, 63.54; H, 8.30; N, 8.23).

### Melting points and thermal stability

All ionic liquids containing tetraphenylborate or BArF<sub>20</sub> are solid at room temperature. Their melting points were determined using a Perkin-Elmer differential scanning calorimeter, DSC 7. Melting points are shown in Table 1. Temperatures are given ± 1 °C.

Thermal stabilities of ionic liquids studied have been determined using a Perkin-Elmer thermo-gravimetric analyzer, TGA 7. Decomposition temperature onsets for the six ionic liquids studied here are reported in Table 1. Temperatures are given ± 5 °C.

### Solubility in water

Mass fraction solubilities *w* of ionic liquids in water were obtained by recording the UV spectra (Beckman DU640) of an aqueous phase in equilibrium with the ionic liquid. The intensity of the absorption of ionic liquids containing [OMIM]<sup>+</sup> cations was recorded at 211 nm; this wavelength corresponds to the wavelength of maximum absorption for the N-methylimidazole group. For an ionic liquid containing [MOPYR]<sup>+</sup> cations, the intensity of absorption was recorded at 254 nm, corresponding to the wavelength of maximum absorption of 4-methylpyridine.

Dilute aqueous solutions containing known mass fractions of ionic liquid (between 0.001 and 0.02 %) were used for calibration. An aqueous solution saturated with ionic liquid was prepared and diluted 100 times. Table 1 shows the mass fraction solubilities of ionic liquids in water. Mass fraction solubilities are given ± 0.01 %.

## Results and discussion

### Melting points

Three of the six molten salts have melting points above 100 °C. Ionic liquids containing BArF<sub>20</sub> anion exhibit melting points higher than those for ionic liquids containing tetraphenylborate anion.

As expected<sup>2</sup>, the melting points of ionic liquids decrease with the length of the alkyl chain on the cation. Previously<sup>8</sup>, 126 °C was reported for the melting point of [BMIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup>. The melting point for [OMIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> here is 107 °C. Further increase of the alkyl chain, as for [OBIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup>, gives a melting point of 69 °C.

The melting point of [OMIM]<sup>+</sup>[BArF<sub>20</sub>]<sup>-</sup> is higher than the one for [BMIM]<sup>+</sup>[BArF<sub>24</sub>]<sup>-</sup> (109 °C<sup>9</sup>), despite the longer alkyl chain in the case of [OMIM]<sup>+</sup>[BArF<sub>20</sub>]<sup>-</sup>. Since [BArF<sub>24</sub>]<sup>-</sup> is less spherical and symmetric than [BArF<sub>20</sub>]<sup>-</sup>, our measurements are in agreement with general observations<sup>2,5</sup> that ionic liquids with asymmetric anions exhibit lower melting points than those with symmetric or spherical anions.

Ionic liquids containing trifluorophenylborate anion exhibit low melting points. [OMIM]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> exhibit a melting point at 37.5 °C. [MOPYR]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> does not exhibit any melting point. Instead, a single glass-transition point is observed at -76 °C. This result is surprising since ionic liquids based on pyridinium cations usually exhibit melting points higher than those based on imidazolium cations.<sup>10,11</sup>

### Thermal stability

[OMIM]<sup>+</sup> [BArF<sub>20</sub>]<sup>-</sup> is the most thermally stable ionic liquid of this study, showing high thermal stability with decomposition onset at 300 °C.

Ionic liquids containing [OMIM]<sup>+</sup> cations are stable up to 300 °C.<sup>2,3</sup> It is somehow surprising to observe the low stability of [OMIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> and [OMIM]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> studied here. Considering that ionic liquids containing trifluorophenylborate are slightly more stable than those containing tetraphenyl borate anions, and that [OMIM]<sup>+</sup>[BArF<sub>20</sub>]<sup>-</sup> has a high thermal stability, the low stability of [OMIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> and [OMIM]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> is obviously due to the nature of the anion.

[OBIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> is more stable than [OMIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup>, with a decomposition onset at 225 °C, close to the one at 210 °C for [OBIM]<sup>+</sup>[Br]<sup>-</sup>. [OBIM]<sup>+</sup>[Br]<sup>-</sup> has been observed to undergo some decomposition after a few weeks: color changes from light yellow to brown. A small decomposition onset was also observed at 80 °C (<2 % IL decomposed at that temperature), which could be due to bromooctane residue.

For both [BPh<sub>4</sub>]<sup>-</sup> and [BF<sub>3</sub>Ph]<sup>-</sup> anions, ionic liquids containing [OMIM]<sup>+</sup> appear to be less stable than those containing [MOPYR]<sup>+</sup> cations, revealing that pyridinium cations with borate anions yield more stable ionic liquids than their imidazolium homologues.

Thermal stabilities of [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> and 1-octyl-3-methylpyridinium tetrafluoroborate have previously been reported<sup>2, 11</sup>. Both ionic liquids had higher thermal stabilities than their tetraphenylborate or trifluorophenylborate homologues, but were less stable than [OMIM]<sup>+</sup>[BArF<sub>20</sub>]<sup>-</sup>. For a specific cation, the thermal stability of ionic liquids containing fluoroborate or phenylborate anions appears to follow the level of fluorination of borate anions:

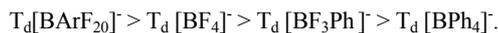


Figure 2 shows the thermal stabilities of three of the six ionic liquids reported here.

### Solubility in water

Table 1 shows the solubilities of ionic liquids in water. Due to the very low solubility in water for ionic liquids containing tetraphenylborate or BArF<sub>20</sub> anions, we could not obtain UV-Vis spectra for aqueous solutions saturated with ionic liquid. Therefore, mass fraction solubilities at ambient conditions were observed visually by adding 3 mg of an ionic liquid to various amounts of water. This experiment terminated after 1 liter of water was added. In all cases, after 24 h, white crystals could be observed at the bottom of the flask. The solubilities of these ionic liquids were determined below 3 ppm.

Solubilities in water of the two ionic liquids containing BF<sub>3</sub>Ph<sup>-</sup> anions are fairly low. Values of 0.51 % and 0.39 % for the solubilities in water of [OMIM]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> and [MOPYR]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> were obtained. As expected, these values are higher than those of ionic liquids containing tetraphenylborate anions, but lower than those of ionic liquids containing tetrafluoroborate anions, (1.62 % and 1.58 % for the solubilities in water of [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> and [MOPYR]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>, respectively).

We also studied the solubilities of 1-methyl-3-octylimidazolium tetraphenylborate, 1-butyl-3-octylimidazolium tetraphenylborate and 1-methyl-3-octylimidazolium tetrakis(fluorophenyl)borate in low-melting ionic liquids. Near room temperature, they are soluble in 1-methyl-3-ethylimidazolium ethylsulfate, in 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide, and in 1-methyl-3-butylimidazolium tetrafluoroborate.

### Conclusion

Six ionic liquids containing tetrakis(fluorophenyl)borate, tetraphenylborate or trifluorophenylborate anions, and 1-methyl-3-octylimidazolium, 1-butyl-3-octylimidazolium or 1-butyl-4-methylpyridinium cations have been synthesized. The melting points of these ionic liquids are high. Ionic liquids containing tetraphenylborate anion exhibit a lower melting point than those for ionic liquids containing the BArF<sub>20</sub> anion. The lower melting point probably follows from the lower molecular weight of the tetraphenylborate anion as compared to that of the BArF<sub>20</sub> anion.

Increasing the length of the alkyl chain appended to the imidazolium cation from 1-methyl-3-octylimidazolium to 1-butyl-3-octylimidazolium slightly reduces the melting points of ionic liquids when tetraphenylborate is the anion.

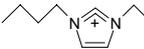
As expected, solubility in water for ILs containing trifluorophenylborate are lower than for those containing tetrafluoroborate anions, and higher than for those containing tetraphenylborate anions. As for melting points, [OMIM]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> exhibits a melting point at 37.5°C, lower than those for ILs containing tetraphenylborate anions, and higher than those for ILs containing tetrafluoroborate anions.

Although the high melting points of the four ionic liquids containing tetraphenylborate or BArF<sub>20</sub> anions synthesized here make them unsuitable for extraction of metal ions from water, ionic liquids containing BArF<sub>20</sub> and tetraphenylborate anions appear to be essentially immiscible in water due to the hydrophobic nature of BArF<sub>20</sub> and tetraphenylborate anions. However, near room temperature, these ionic liquids are soluble in other ionic liquids containing imidazolium cations (such as 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide) that are also immiscible with water. Therefore, it may be possible that task-specific ionic liquids<sup>12,13</sup> where BArF<sub>20</sub> is the anion may be useful for extraction of offensive cations from water when dissolved in a low-melting, water-immiscible ionic liquid.

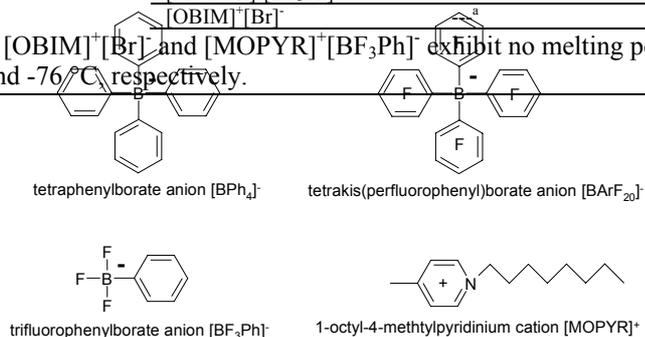
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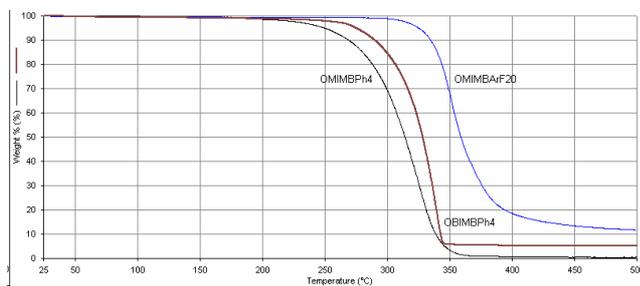
**Table 1** Melting point  $t_m$ , decomposition temperature  $t_d$  and mass fraction solubility  $w$  in water for seven ionic liquids.

	$t_m / ^\circ\text{C}$	$t_d / ^\circ\text{C}$	100 $w$
	[OMIM] <sup>+</sup> [BArF <sub>20</sub> ] <sup>-</sup> 127	300	<0.0003
	[OMIM] <sup>+</sup> [BPh <sub>4</sub> ] <sup>-</sup> 105	175	<0.0003
	[MOPYR] <sup>+</sup> [BPh <sub>4</sub> ] <sup>-</sup> 130	205	<0.0003
1-butyl-3-octylimidazolium cation [OMIM] <sup>+</sup>	[OBIM] <sup>+</sup> [BPh <sub>4</sub> ] <sup>-</sup> 69	225	<0.0003
	[OMIM] <sup>+</sup> [BF <sub>3</sub> Ph] <sup>-</sup> 37.5	180	0.51
	[MOPYR] <sup>+</sup> [BF <sub>3</sub> Ph] <sup>-</sup> --- <sup>a</sup>	230	0.49
	[OBIM] <sup>+</sup> [Br] <sup>-</sup> --- <sup>a</sup>	210	miscible

<sup>a</sup>: [OBIM]<sup>+</sup>[Br]<sup>-</sup> and [MOPYR]<sup>+</sup>[BF<sub>3</sub>Ph]<sup>-</sup> exhibit no melting points; instead, glass-transition points are observed at -59.9 °C and -76 °C, respectively.



**Fig. 1** Structures of the cations and anions studied here.



**Fig. 2** Thermal stabilities of [OMIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup>, [OBIM]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup>, and [OMIM]<sup>+</sup>[BArF<sub>20</sub>]<sup>-</sup>. The heating rates were 20 °C / min under dry-nitrogen flow. The average sample weight was 9 mg. The samples were kept in a 1-mbar vacuum for 24 h prior to measurement..