

# Physicochemical Characterization of $MF_m^-$ -Based Ammonium Ionic Liquids

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**S** Supporting Information

**ABSTRACT:** A series of ammonium-based ionic liquids (ILs), which share a homologous series of cations  $(CH_3CH_2)_3N^+(C_nH_{2n+1})$  with n = 2, 4, 6, 8 and the anions with either  $BF_4^-$ ,  $PF_6^-$ , or  $SbF_6^-$ , was synthesized. Their structures were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, ESI-MS, and elemental analysis. Meanwhile, the content of impurity (e.g., water and bromide ions) was also determined using Karl Fischer titrator and ion chromatography. The thermal properties of the ILs were determined by TGA and DSC.



Five of the investigated ILs have been shown to have a low melting point (< 100 °C): N,N,N,N-tetraethylammonium tetrafluoroborate,  $[N_{2222}]BF_4$ , N,N,N,N-tetraethylammonium hexafluorophosphate,  $[N_{2222}]PF_6$ , N,N,N-triethylhexylammonium tetrafluoroborate,  $[N_{2226}]BF_4$ , N,N,N-triethyloctylammonium hexafluorophosphate,  $[N_{2228}]PF_6$  and N,N,N-triethyloctylammonium h

# INTRODUCTION

In the past few years, a great effort has been devoted to the study of ionic liquids (ILs) due to their peculiar chemical—physical properties such as negligible vapor pressure, high ion conductivity, and high thermal stability.<sup>1–3</sup> The most important driving force of the booming research on ILs, typically including those based on imidazolium, pyrrolidinium, ammonium, phosphonium, guanidinium, and pyridinium, is their potential in substituting for volatile organic solvents in chemical synthesis.<sup>4,5</sup>

Recently, ILs integrated with functionalities for specific purposes have been reviewed as promoters in various chemical reactions.<sup>6–14</sup> Notwithstanding having many successful efforts about ILs as reaction media, catalysts, and promoters, they currently have not been widely applied in any applications.<sup>13,15</sup> To reach a better understanding of how to tune the properties of ILs to meet industry requirements, knowledge about the origins of these fundamental properties of ILs have begun to be reported among researchers. But the investigated ILs were majorly focused on the imidazolium cation. Among the imidazolium and quaternary ammonium ILs, the basic difference in the properties is that the former has a labile proton which limits its use in organic reactions compounds.<sup>16</sup> In 1997, MacFarlane<sup>17</sup> began to prepare a series of quaternary ammonium ILs (more than 16) with  $\mathrm{NTf}_2^{\,-}$  anion and then applied them in the field of electrochemistry. Since then, the ILs based on the quaternary ammonium and robust anions, such as  $NTf_2^{-}$ ,  $^{-}C(CN)_3$ , and

 $BF_4^-$ , have been supported as adequate electrolytes for highenergy devices owing to their sufficient electrochemical stability compared with the imidazolium-based ILs. Recently, a significant number of articles have been published on other topics about ammonium ILs, such as CO<sub>2</sub> capture, <sup>18</sup> surfactants, <sup>19</sup> lubricant,<sup>20</sup> acid catalysts, and solvent.<sup>21,22</sup> However, there is little knowledge in which both the cation and the anion of ammonium ILs have been systematically varied.<sup>23,24</sup> From fundamental and industrial points of veiw, reliable and accurate data of ILs are the key for the development of certain and economical process designs.<sup>25</sup>

In this study, a variety of ammonium ILs which share a homologous series of cations  $(CH_3CH_2)_3N^+(C_nH_{2n+1})$  with n = 2, 4, 6, 8 and the anions with either  $BF_4^-$ ,  $PF_6^-$ , or  $SbF_6^-$  (Figure 1) were synthesized and characterized. The physicochemical properties including decomposition temperature  $(T_d)$ , phase transition temperatures  $(T_m)$  and  $T_{s-s}$ ), density  $(\rho)$ , and solubility in different solvents have been investigated, focusing on the properties that depend on the change in the alkyl chain length of cation and the anion nature, to know the relationships between structure and property. Nowadays, many organic reactions are performed in the presence of liquid acid coupled with ILs as catalyst.<sup>26</sup> So the refractive indexes  $(n_D)$  of binary mixtures of the presented ILs with trifluoromethanesulfonic acid at different

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**Figure 1.** General structure of ammonium ILs ([ $(CH_3CH_2)_3N^+(C_nH_{2n+1})$ ][ $MF_m$ ]); *n* is the number of carbon atoms in the side alky chain, *m* is the number of fluorine atoms of anion; M is the metal or nonmetal coordinated with fluorine.

Entry	Ionic Liquid	Acronym	Cation	Anion
I1 <sup>a</sup>	N,N,N,N-Tetraethylammonium Tetrafluoroborate	[N <sub>2222</sub> ]BF <sub>4</sub>	N	F B F
2	N,N,N,N-Tetraethylammonium Hexafluorophosphate	[N <sub>2222</sub> ]PF <sub>6</sub>	,	
3	N,N,N,N-Tetraethylammonium Hexafluoroantimonate	[N <sub>2222</sub> ]SbF <sub>6</sub>		
4	N,N,N-Triethylbutylammonium Tetrafluoroborate	[N <sub>2224</sub> ]BF <sub>4</sub>		F B B F F
5	N,N,N-Triethylbutylammonium Hexafluorophosphate	[N <sub>2224</sub> ]PF <sub>6</sub>		
6	N,N,N-Triethylbutylammonium Hexafluoroantimonate	[N <sub>2224</sub> ]SbF <sub>6</sub>		
7	N,N,N-Triethylhexylammonium Tetrafluoroborate	[N <sub>2226</sub> ]BF <sub>4</sub>		F B G
8	N,N,N-Triethylhexylammonium Hexafluorophosphate	[N <sub>2226</sub> ]PF <sub>6</sub>		
9	N,N,N-Triethylhexylammonium Hexafluoroantimonate	[N <sub>2226</sub> ]SbF <sub>6</sub>		
10	N,N,N-Triethyloctylammonium Tetrafluoroborate	[N <sub>2228</sub> ]BF <sub>4</sub>		F B
11	N,N,N-Triethyloctylammonium Hexafluorophosphate	[N <sub>2228</sub> ]PF <sub>6</sub>		FM <sup>O</sup> F <sup>MO</sup> F <sup>MO</sup>
12	N,N,N-Triethyloctylammonium Hexafluoroantimonate	[N <sub>2228</sub> ]SbF <sub>6</sub>		

<sup>a</sup>Representation of ionic liquids obtained from market.

mass fraction (w, w = mass of ionic liquid/(mass of ionic liquid + mass of acid)) were measured and intended to obtain some information about interaction behavior.

# EXPERIMENTAL SECTION

**Material and Apparatus.** All the chemicals and solvents mentioned in this study were used as received unless otherwise noted. *N*-Butyl bromide ( $\geq$  98.0 %), *N*-hexyl bromide ( $\geq$  98.0

%), *N*-octyl bromide ( $\geq$  99.0 %) and triethylamine ( $\geq$  99.0 %) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ammonium fluoroborate (NH<sub>4</sub>BF<sub>4</sub>,  $\geq$  98.5 %), potassium hexafluorophosphate (KPF<sub>6</sub>,  $\geq$  98 %), and sodium hexafluoroantimonate (NaSbF<sub>6</sub>,  $\geq$  98 %) were received from Alfa Aesar. *N*,*N*,*N*,*N*-Tetraethylammonium bromide and *N*,*N*,*N*,*N*-tetraethylammonium tetrafluoroborate with 99 % purity were obtained from Shanghai Chengjie Chemical Co., Ltd., China and

dried under high vacuum for 24 h prior to use. Trifluoromethanesulfonic acid (TFSA, > 99.9 % in purity) was used as received from 718th Research Institute of China Ship Building Industry Corporation.

<sup>1</sup>H and <sup>13</sup>C NMR spectrum were measured using a JEOL ECA 600 spectrometer (25 °C). Electrospray ionization mass spectra (ESI-MS) was recorded on a micrOTOF-Q II spectrometer. C, H, and N contents (wt %) were determined using a Vario EL cube elemental analyzer (EA).

**Preparation of Triethylalkylammonium Bromides.** Triethylalkylammonium bromides were prepared by the alkylation of triethylamine with the corresponding alkyl bromides (*N*-butyl bromide, *N*-hexyl bromide, *N*-octyl bromide) using previously published methods.<sup>27</sup> The triethylalkylammonium bromides were dried under high vacuum for 48 h prior to further use. FT-IR data for the triethylalkylammonium bromides are provided in the Supporting Information.

*N*,*N*,*N*-Triethylbutylammonium Bromide [N<sub>2224</sub>]Br. The yield was 94.9 %, white powder; mp, 173.26 °C. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 3.28–3.25 (m, 6H), 3.10–3.07 (m, 2H), 1.46–1.44 (m, 2H), 1.24–1.18 (m, 2H), 1.15 (t, *J* = 7.56 Hz, 9H), 0.76 (t, *J* = 7.56 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 57.30, 53.48, 23.86, 19.68, 13.57, 8.04. Elemental analysis for CHN, analysis (% calculated): C 49.64 (50.42), H 10.03 (10.16), N 5.95 (5.88). ESI-MS *m*/*z* (%): 158.1891 [N<sub>2224</sub>]<sup>+</sup> (C<sub>10</sub>H<sub>24</sub>N<sup>+</sup> requires 158.1909, 100).

*N*,*N*,*N*-Triethylhexylammonium Bromide [N<sub>2226</sub>]Br. The yield was 81.6 %, white solid; mp, 104.57 °C. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 3.42–3.37 (m, 6H), 3.19–3.16 (m, 2H), 1.59–1.55 (m, 2H), 1.33 (t, *J* = 7.56 Hz, 4H), 1.27 (t, *J* = 7.56 Hz, 9H), 1.23–1.28 (m, 2H), 0.77 (t, *J* = 6.90 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 57.59, 53.58, 31.20, 26.10, 22.39, 22.05, 13.86, 8.14. Elemental analysis for CHN, analysis (% calculated): C 53.47 (54.13), H 10.36 (10.60), N 5.33 (5.26). ESI-MS *m*/*z* (%): 186.2221 [N<sub>2226</sub>]<sup>+</sup> (C<sub>12</sub>H<sub>28</sub>N<sup>+</sup> requires 186.2222, 100).

*N*,*N*,*N*-Triethyloctylammonium Bromide [N<sub>2228</sub>]Br. The yield was 65.4 %, white sheet solid; mp, 113.92 °C. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 3.73−3.69 (m, 6H), 3.53−3.50 (m, 2H), 1.72−1.67 (m, 2H), 1.39 (t, *J* = 6.84 Hz, 8H), 1.31−1.26 (m, 2H), 1.24 (t, *J* = 6.90 Hz, 9H), 0.88 (t, *J* = 6.90 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 57.56, 53.58, 31.66, 29.15, 29.08, 26.50, 22.60, 22.13, 14.10, 8.17. Elemental analysis for CHN, analysis (% calculated): C 56.05 (57.13), H 10.35 (10.96), N 5.05 (4.76). ESI-MS *m*/*z* (%): 214.2521 [N<sub>2228</sub>]<sup>+</sup> (C<sub>14</sub>H<sub>32</sub>N<sup>+</sup> requires 214.2535, 100).

**Synthesis of MF\_m^- Based Ammonium Ionic Liquids.** The  $MF_m^-$ -based ammonium ILs were synthesized via rapid anion metathesis reactions between the triethylalkylammonium bromides and the corresponding nonmetallic salt ( $NH_4BF_4$ ) or metallic salts ( $KPF_6$  and  $NaSbF_6$ ). The nomenclature, acronyms, and chemical structures of these ILs were listed in Table 1. All the ILs samples were dried under high vacuum for 48 h and stored in a desiccator prior to the measurements. The synthesis details and FT-IR data of these ILs are supplied in the Supporting Information.

*N*,*N*,*N*.**Tetraethylammonium Hexafluorophosphate** [N<sub>2222</sub>]**PF**<sub>6</sub>. The yield was 75.8 %, white powder. <sup>1</sup>H NMR (600 Hz, DMSO-d<sub>6</sub>, TMS):  $\delta$  (ppm) 3.21–3.18 (m, 8H), 1.16 (t, *J* = 2.10, 12H). <sup>13</sup>C NMR (600 Hz, DMSO-d<sub>6</sub>, TMS):  $\delta$  (ppm) 51.87, 7.57. ESI-MS *m*/*z* (%): 130.1536 [N<sub>2222</sub>]<sup>+</sup> (C<sub>8</sub>H<sub>20</sub>N<sup>+</sup> requires 130.1596, 100); 144.9670 [PF<sub>6</sub>]<sup>-</sup> (PF<sub>6</sub><sup>-</sup> requires 144.9642, 100). *N*,*N*,*N*.**Tetraethylammonium Hexafluoroantimonate** [N<sub>2222</sub>]**SbF**<sub>6</sub>. The yield was 70.2 %, white powder. <sup>1</sup>H NMR (600 Hz, DMSO-d<sub>6</sub>, TMS): δ (ppm) 3.21−3.18 (m, 8H), 1.16 (t, *J* = 2.10, 12H). <sup>13</sup>C NMR (600 Hz, DMSO-d<sub>6</sub>, TMS): δ (ppm) 51.90, 7.55. ESI-MS *m*/*z* (%): 130.1564 [N<sub>2222</sub>]<sup>+</sup> (C<sub>8</sub>H<sub>20</sub>N<sup>+</sup> requires 130.1596, 100); 234.8980 [SbF<sub>6</sub>]<sup>−</sup> (SbF<sub>6</sub><sup>−</sup> requires 234.8942, 100).

*N*,*N*,*N*-Triethylbutylammonium Tetrafluoroborate [N<sub>2224</sub>]BF<sub>4</sub>. The yield was 65.83 %, white powder. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 3.32–3.28 (m, 6H), 3.15–3.12 (m, 2H), 1.65–1.62 (m, 2H), 1.45–1.37 (m, 2H), 1.32 (t, *J* = 1.92 Hz, 9H), 0.99 (t, *J* = 7.56 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 56.91, 52.93, 23.58, 19.69, 13.62, 7.45. ESI-MS *m*/*z* (%): 158.1829 [N<sub>2224</sub>]<sup>+</sup> (C<sub>10</sub>H<sub>24</sub>N<sup>+</sup> requires 158.1909, 100).

*N*,*N*,*N*-Triethylbutylammonium Hexafluorophosphate [N<sub>2224</sub>]PF<sub>6</sub>. The yield was 65.7 %, white powder. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 3.28–3.24 (m, 6H), 3.10–3.08 (m, 2H), 1.62–1.54 (m, 2H), 1.43–1.40 (m, 2H), 1.31 (t, *J* = 6.84 Hz, 9H), 0.99 (t, *J* = 7.56 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 57.07, 53.32, 23.92, 19.94, 14.01, 7.96. ESI-MS m/z (%): 158.1866 [N<sub>2224</sub>]<sup>+</sup> (C<sub>10</sub>H<sub>24</sub>N<sup>+</sup> requires 158.1909, 100); 144.9682 [PF<sub>6</sub>]<sup>-</sup> (PF<sub>6</sub><sup>-</sup> requires 144.9642, 100).

*N*,*N*,*N*-Triethylbutylammonium Hexafluoroantimonate [N<sub>2224</sub>]SbF<sub>6</sub>. The yield was 81.3 %, white powder. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 3.29–3.26 (m, 6H), 3.11–3.08 (m, 2H), 1.55–1.43 (m, 2H), 1.35–1.1.32 (m, 2H), 1.28 (t, *J* = 4.86 Hz, 9H), 1.01 (t, *J* = 7.56 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 56.93, 52.88, 23.27, 19.50, 13.30, 7.03. ESI-MS *m*/*z* (%): 158.1877 [N<sub>2224</sub>]<sup>+</sup> (C<sub>10</sub>H<sub>24</sub>N<sup>+</sup> requires 158.1909, 100); 234.8994 [SbF<sub>6</sub>]<sup>-</sup> (SbF<sub>6</sub><sup>-</sup> requires 234.8942, 100).

*N*,*N*,*N*-Triethylhexylammonium Tetrafluoroborate [N<sub>2226</sub>]BF<sub>4</sub>. The yield was 74.2 %, white solid. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 3.32–3.29 (m, 6H), 3.14–3.11 (m, 2H), 1.66–1.62 (m, 2H), 1.39–1.33 (m, 2H), 1.32 (t, *J* = 5.52 Hz, 9H), 1.22 (t, *J* = 7.56 Hz, 4H), 0.89 (t, *J* = 6.84 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 57.14, 52.95, 31.20, 26.01, 22.45, 21.68, 13.94, 7.47. ESI-MS *m*/*z* (%): 186.2118 [N<sub>2226</sub>]<sup>+</sup> (C<sub>12</sub>H<sub>28</sub>N<sup>+</sup> requires 186.2222, 100).

*N*,*N*,*N*-Triethylhexylammonium Hexafluorophosphate [ $N_{2226}$ ]PF<sub>6</sub>. The yield was 60.5 %, white powder. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 3.28–3.24 (m, 6H), 3.09–3.07 (m, 2H), 1.63–1.60 (m, 2H), 1.38–1.34 (m, 2H), 1.32 (t, *J* = 7.56 Hz, 9H), 1.29 (t, *J* = 7.56 Hz, 4H), 0.89 (t, *J* = 6.90 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 57.21, 52.98, 31.14, 25.95, 22.44, 21.60, 13.93, 7.35. ESI-MS *m*/*z* (%): 186.2114 [ $N_{2226}$ ]<sup>+</sup> ( $C_{12}H_{28}N^+$  requires 186.2222, 100); 144.9667 [PF<sub>6</sub>]<sup>-</sup> (PF<sub>6</sub><sup>-</sup> requires 144.9658, 100).

*N*,*N*,*N*-Triethylhexylammonium Hexafluoroantimonate [N<sub>2226</sub>]SbF<sub>6</sub>. The yield was 81.2 %, white powder. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 3.26−3.22(m, 6H), 3.15−3.98 (m, 2H), 1.63−1.56 (m, 2H), 1.34−1.32 (m, 2H), 1.28 (t, *J* = 7.56 Hz, 9H), 1.26 (t, *J* = 7.08 Hz, 4H), 0.88 (t, *J* = 6.90 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 57.22, 52.94, 30.97, 25.80, 22.33, 21.41, 13.79, 7.12. ESI-MS *m*/*z* (%): 186.2191 [N<sub>2226</sub>]<sup>+</sup> (C<sub>12</sub>H<sub>28</sub>N<sup>+</sup> requires 186.2222, 100); 234.9009 [SbF<sub>6</sub>]<sup>−</sup> (SbF<sub>6</sub><sup>−</sup> requires 234.8942, 100).

*N*,*N*,*N*-Triethyloctylammonium Tetrafluoroborate [ $N_{2228}$ ]BF<sub>4</sub>. The yield was 82.8 %, white powder. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 3.32–3.29 (m, 6H), 3.13–3.10 (m, 2H), 1.63–1.61 (m, 2H), 1.33 (t, *J* = 6.84 Hz, 8H), 1.31 (t, *J* = 7.56 Hz, 9H), 1.28–1.23 (m, 2H), 0.88 (t, *J* = 6.84 Hz, 3H).



<sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 57.11, 52.93, 31.69, 29.10, 26.36, 22.64, 21.74, 14.13, 7.47. ESI-MS m/z (%): 214.2406 [N<sub>2228</sub>]<sup>+</sup> (C<sub>14</sub>H<sub>32</sub>N<sup>+</sup> requires 214.2535, 100).

*N*,*N*,*N*-Triethyloctylammonium Hexafluorophosphate [N<sub>2228</sub>]PF<sub>6</sub>. The yield was 87.1 %, white solid. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 3.29–3.25 (m, 6H), 3.10–3.04 (m, 2H), 1.63–1.62 (m, 2H), 1.34 (t, *J* = 3.48 Hz, 8H), 1.29 (t, *J* = 6.90 Hz, 9H), 1.26–1.22 (m, 2H), 0.88 (t, *J* = 6.90 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS): δ (ppm) 57.16, 52.95, 31.67, 29.07, 29.04, 26.31, 22.63, 21.67, 14.12, 7.35. ESI-MS *m*/*z* (%): 214.2432 [N<sub>2228</sub>]<sup>+</sup> (C<sub>14</sub>H<sub>32</sub>N<sup>+</sup> requires 214.2535, 100); 144.9667 [PF<sub>6</sub>]<sup>-</sup> (PF<sub>6</sub><sup>-</sup> requires 144.9642, 100).

*N*,*N*,*N*-Triethyloctylammonium Hexafluoroantimonate [ $N_{2228}$ ]SbF<sub>6</sub>. The yield was 77.2 %, solid with slight yellow. <sup>1</sup>H NMR (600 Hz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 3.26–3.23 (m, 6H), 3.08–3.05 (m, 2H), 1.63–1.62 (m, 2H), 1.34 (t, *J* = 5.52 Hz, 8H), 1.30 (t, *J* = 6.84 Hz, 9H), 1.29–1.24 (m, 2H), 0.88 (t, *J* = 6.18 Hz, 3H). <sup>13</sup>C NMR (600 Hz, CDCl<sub>3</sub>, TMS):  $\delta$  (ppm) 57.28, 53.04, 31.68, 29.07, 29.03, 26.31, 22.65, 21.66, 14.14, 7.35. ESI-MS *m*/*z* (%): 214.2419 [ $N_{2228}$ ]<sup>+</sup> ( $C_{14}H_{32}$ N<sup>+</sup> requires 214.2535, 100); 234.8976 [SbF<sub>6</sub>]<sup>-</sup> (SbF<sub>6</sub><sup>-</sup> requires 234.8942, 100).

Water and Bromide Content Measurement. The water contents of the investigated ILs were determined using a coulometric Karl Fischer titrator (Mettler Toledo C20) in a drying chamber. Prior to the measurement, desired milligrams of the ILs were dissolved in redistilled acetonitrile (water content < 15 ppm). Each water content was measured by introducing a few milligrams of acetonitrile solution in the apparatus with the help of an injector. All measurements for each IL were performed in triplicate.

The bromide contents of the investigated ILs were determined using ion chromatography (IC, ICS-900 Dionex, ThermoFisher) with (4.0 × 250) mm analytical column, suppressed conductivity detection, and ThermoFisher scientific ICS-900 software version 2011. The eluent used was a 4.5 mM Na<sub>2</sub>CO<sub>3</sub> + 1.4 mM NaHCO<sub>3</sub> mixture. The bromide standard was obtained from the National Institute of Metrology (China). Prior to the measurement of bromide contents of ILs, a specification curve of the bromide standards at different concentrations was constructed. The IL samples for analysis were prepared by dissolving 0.1 g of IL in 2 mL of HPLC grade acetonitrile and then being diluted to 10 mL with ultrapure water (Watsons). About 0.01 mL of the IL solution, treated with 0.2  $\mu$ m syringe filter, was injected for each measurement. The content of bromide ion was quantified using the obtained specification curve.

**Decomposition Temperature Measurement.** The decomposition temperature was measured with a TA TGA/Q5000 thermal gravimetric analyzer (TGA) and the TA universal analysis window was used to evaluate the data. The nickel and calcium oxalate, supplied by TA, were used respectively for the temperature and weight calibrations. The samples (typically about 10 mg) were loaded into the crucible (platinum, 100  $\mu$ L) and heated at a rate of 10 °C·min<sup>-1</sup> for temperatures ranging from 50 °C to 500 °C under a flow of nitrogen (60 mL·min<sup>-1</sup>). The mass and temperature precision of TGA is ± 0.1  $\mu$ g and ± 0.1 °C, respectively.

**Phase Transition Temperature Measurement.** Measurements of phase transition temperature were performed using a Mettler-Toledo differential scanning calorimeter (DSC), model DSC1 (STAR<sup>e</sup> system), and the data was evaluated using the Mettler-Toledo STAR<sup>e</sup> software version 10.00. The temperature and heat flow were calibrated with zinc and indium reference samples (purity, 99.999 %) provided by Mettler-Toledo. The sample (typically around 4–8 mg) was placed in a 40  $\mu$ L aluminum pan with a pinhole at the top of the hermetically sealed pan. A blank aluminum pan was used as the reference. The sample inside the DSC furnace was heated from the beginning temperature (about 0 or 25 °C) to the predetermined temperature, close to the decomposition temperature of the studied compound, at a rate of 10 °C·min<sup>-1</sup> under nitrogen flow.

**Density Measurement.** Density  $(\rho)$  measurements are based on the sweeping tube method with an automatic gas displacement density analyzer (AccuPyc II 1340 Series Pycnometers, Micromeritics). The densimeter was calibrated with a standard stainless steel ball with a volume of 0.718517 cm<sup>-3</sup> provided by the supplier. The true volume of sample (typically 2/3 cm<sup>-3</sup>) in a sample chamber (1 cm<sup>-3</sup>) was determined by nitrogen sweeping (0.1 MPa) and then a density was obtained with the weight of the sample divided by its true volume. Each density measurement was replicated five times and the average values are reported for the densities and standard deviations. The density of ILs was experimentally measured at T = 20  $^{\circ}$ C. The analyzer was validated by measuring the density of the common ILs, including [BMim]Cl, [BMim]Br, [EMim]Cl, and  $[BMMim]PF_{6}$ , which were in good agreement with the reported values. Details were shown in the Supporting Information.

**Refractive Index Measurement.** The refractive indexes  $n_D$  were measured with an Abbe refractometer (2W, Shanghai Tian Zhu Optical Instrument Co., Ltd.) which was calibrated using ultrapure water with a known refractive index (1.333 at 20 °C). The temperature of the samples was controlled using a laboratory thermostat with an accuracy of  $\pm$  0.05 °C. The  $n_D$  of the binary mixtures of ILs and TFSA was experimentally measured at T = 20 °C, P = 0.1 MPa.

Table 2. Mass Fraction of Water  $(w_{H2O})$  and Mass Fraction of Bromide  $(w_{Br})$  for MF<sub>m</sub><sup>-</sup>-Based Ammonium Ionic Liquids

	[N <sub>2222</sub> ]		[N <sub>2224</sub> ]		[N <sub>2226</sub> ]			[N <sub>2228</sub> ]				
	BF <sub>4</sub>	PF <sub>6</sub>	SbF <sub>6</sub>	BF <sub>4</sub>	PF <sub>6</sub>	SbF <sub>6</sub>	BF <sub>4</sub>	PF <sub>6</sub>	SbF <sub>6</sub>	BF <sub>4</sub>	PF <sub>6</sub>	SbF <sub>6</sub>
$w_{\rm H2O}(10^6w)$	149	92	96	120	84	93	125	96	87	131	86	93
$w_{\rm Br}(10^6w)$	73	52	56	48	63	85	47	72	59	64	78	51

able 5. Thermar I	loperties for fo	ine Liquids					
cmpd	$T_{\rm m}/^{\circ}{\rm C}$	$T_{s-s}/^{\circ}C$	$T_d/^{\circ}C$	cmpd	$T_{\rm m}/^{\circ}{\rm C}$	$T_{s-s}/^{\circ}C$	$T_d/^{\circ}C$
$[N_{2222}]BF_4^{\ b}$	71.4		385.2	[N <sub>2226</sub> ]BF <sub>4</sub>	88.2		366.3
$[N_{2222}]PF_{6}^{c}$	77.1		367.6	[N <sub>2226</sub> ]PF <sub>6</sub>	161.6		330.2
[N <sub>2222</sub> ]SbF <sub>6</sub>			376.4	[N <sub>2226</sub> ]SbF <sub>6</sub>	174.0		362.9
[N <sub>2224</sub> ]BF <sub>4</sub>	161.9	32.7	371.3	[N <sub>2228</sub> ]BF <sub>4</sub>	101.4		361.4
[N <sub>2224</sub> ]PF <sub>6</sub>	178.9		353.2	[N <sub>2228</sub> ]PF <sub>6</sub>	88.3	38.5	249.8
[N <sub>2224</sub> ]SbF <sub>6</sub>	184.0		364.1	$[N_{2228}]SbF_6$	73.6		359.2

 ${}^{a}T_{m}$ , melting temperature (°C);  $T_{s,s}$  solid-solid transition temperature (°C);  $T_{d}$ , decomposition temperature (°C). The uncertainty in determining the melting temperature and the solid-solid transition temperature is within the range  $\pm 0.1$  °C, and the uncertainty in determining the decomposition temperature is within the range  $\pm 0.2$  °C.  ${}^{b}72$  °C  $T_{m}$  reported by ref 35.  ${}^{c}70$  °C  $T_{m}$  and 388 °C of  $T_{d}$  reported by ref 35.

#### RESULTS AND DISCUSSION

**Synthesis of lonic Liquids.** An efficient mean of generating ILs, allowing ILs to be produced by simple acid—base reactions and completely avoiding the use of halide ions, has been reported.<sup>28</sup> However, the relative limitation of this mentioned methodology is more time consumption.<sup>29</sup> Traditionally, two steps, namely quaterization and anion metathesis reactions, are still widely used during the synthesis of ILs. In this study, the  $MF_m^-$  based ammonium ILs were synthesized by a metathesis reaction between desired anion compounds and the ammonium bromide salts which were synthesized by alkylation of the corresponding tertiary amines with bromoalkanes (Scheme 1). All investigated ILs, which have been verified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, ESI-MS and FTIR as having been successful synthesized, are solid state at ambient temperature.

Water and Bromide Content. The purity of ILs is a very important issue on physical properties and the presence of impurities can be extremely detrimental to the performance of ILs.  $PF_6^-$  anion-based ILs started to decompose to release the toxic product in the presence of the traces of water at 60 °C.<sup>30</sup> Seddon et al.<sup>31</sup> have reported that the increasing content of chlorine ion to imidazolium ILs produced a nonlinear decrease of the density. Huddleston et al. also have discussed the influence of ILs.<sup>32</sup>

The water and bromide contents were determined to supply some information on the investigated ILs. The average contents given in mass fraction of impurities in the IL ( $w_{H2O}$  and  $w_{Br}$ ) are presented in Table 2. According to these measurements, the mass fraction purities of all of the ILs are determined to be more than 99.9 %. The residual water content of ILs is primarily related to the nature of the anion. For every cation studied here, ILs containing BF<sub>4</sub> hydrophilic anion exhibited the highest water contents (< 150 ppm).

**Decomposition Temperature.** Thermal decomposition behaviors of the samples were measured by TGA and the 10 % weight loss temperature was defined as the decomposition temperature  $(T_d)$ .<sup>33</sup> Their  $T_d$  and TGA traces are shown in Table 3 and Figures 2 to 4, respectively. The TGA curves of all studied ILs were similar except for  $[N_{2228}]PF_6$ . For  $[N_{2228}]PF_6$ , the weight of the sample decreased at the start temperature but decreased significantly about 250 °C. The  $T_d$  results show that the thermal stability of the ammonium-based ILs is in the



**Figure 2.** TGA traces of BF<sub>4</sub> anion-based ionic liquids:  $\bullet$ ,  $[N_{2222}]BF_4$ ;  $\blacktriangle$ ,  $[N_{2224}]BF_4$ ;  $\Delta$ ,  $[N_{2226}]BF_4$ ;  $\blacksquare$ ,  $[N_{2228}]BF_4$ .



**Figure 3.** TGA traces of PF<sub>6</sub> anion-based ionic liquids:  $\bullet$ ,  $[N_{2222}]PF_6$ ;  $\blacktriangle$ ,  $[N_{2224}]PF_6$ ;  $\Delta$ ,  $[N_{2226}]PF_6$ ;  $\blacksquare$ ,  $[N_{2228}]PF_6$ .

temperature range from 249  $^{\circ}$ C to 385  $^{\circ}$ C, depending on the structure of the cations and anions (Table 3).

Figure 5 depicts the  $T_d$  variation of the studied ILs with the cationic alkyl chain length. With the same anions, the  $T_d$  observed of the ILs decreased with increasing number of carbon atoms in the alkyl chain from  $[N_{2222}]$  to  $[N_{2228}]$ , where no noticeable change in the  $T_d$  except for PF<sub>6</sub><sup>-</sup>-based ILs could be



**Figure 4.** TGA traces of SbF<sub>6</sub> anion-based ionic liquids:  $\bullet$ ,  $[N_{2222}]$ SbF<sub>6</sub>;  $\blacktriangle$ ,  $[N_{2224}]$ SbF<sub>6</sub>;  $\Delta$ ,  $[N_{2226}]$ SbF<sub>6</sub>;  $\blacksquare$ ,  $[N_{2228}]$ SbF<sub>6</sub>.



**Figure 5.** Decomposition temperature variation with the cation alkyl chain length of ammonium ionic liquid:  $\Box$ , BF<sub>4</sub><sup>-</sup>; O, PF<sub>6</sub><sup>-</sup>;  $\Delta$ , SbF<sub>6</sub><sup>-</sup>.

seen. Joshi and Anderson<sup>34</sup> also observed that the thermal stability of ILs was mainly determined by the anion nature of the ILs and little affected by the alkyl chain length of the cation. Figure 6 shows the effect of the anion types of the ILs with fixed cations on their  $T_d$ . For the fixed cations, the  $T_d$  observed of the ILs with the SbF<sub>6</sub> anion was in the middle, lower than that of the ILs with the BF<sub>4</sub> anion and higher than that of the ILs with the



**Figure 6.** Decomposition temperature variation with the anion of ammonium ionic liquid:  $\Box$ ,  $[N_{2222}]^+$ ;  $\blacksquare$ ,  $[N_{2224}]^+$ ;  $\Delta$ ,  $[N_{2226}]^+$ ; O,  $[N_{2228}]^+$ .

 $PF_6$  anion. This was consistent with the finding in the literature which showed that a comparative higher thermal stability of  $BF_4^-$ -based ILs occurred than that of  $PF_6^-$ -based ILs.<sup>35</sup>

**Phase Transition Temperature.** The phase-transition temperatures were investigated as the inflection point of change in the DSC trace (Figures 7 to 9) and the values were tabulated in



Figure 7. DSC scan for  $BF_4$  anion-based ionic liquid: (a)  $[N_{2222}]BF_4$ ; (b)  $[N_{2224}]BF_4$ ; (c)  $[N_{2226}]BF_4$ ; (d)  $[N_{2228}]BF_4$ .



**Figure 8.** DSC scan for PF<sub>6</sub> anion-based ionic liquids: (a)  $[N_{2222}]PF_{6i}$ (b)  $[N_{2224}]PF_{6i}$  (c)  $[N_{2226}]PF_{6i}$  (d)  $[N_{2228}]PF_{6}$ .



**Figure 9.** DSC scan for SbF<sub>6</sub> anion-based ionic liquids: (a)  $[N_{2222}]$ SbF<sub>6</sub>; (b)  $[N_{2224}]$ SbF<sub>6</sub>; (c)  $[N_{2226}]$ SbF<sub>6</sub>; (d)  $[N_{2228}]$ SbF<sub>6</sub>.

ionic liquid	$ ho/( extrm{g}\cdot extrm{cm}^{-3})$	σ	ionic liquid	$ ho/( extrm{g}\cdot extrm{cm}^{-3})$	σ
$[N_{2222}]BF_4$	1.2204	0.0007	[N <sub>2226</sub> ]BF <sub>4</sub>	1.0935	0.0003
[N <sub>2222</sub> ]PF <sub>6</sub>	1.4395	0.0005	[N <sub>2226</sub> ]PF <sub>6</sub>	1.3513	0.0005
[N <sub>2222</sub> ]SbF <sub>6</sub>	1.7152	0.0008	[N <sub>2226</sub> ]SbF <sub>6</sub>	1.4882	0.0012
[N <sub>2224</sub> ]BF <sub>4</sub>	1.1397	0.0003	[N <sub>2228</sub> ]BF <sub>4</sub>	1.0653	0.0017
[N <sub>2224</sub> ]PF <sub>6</sub>	1.3662	0.0005	[N <sub>2228</sub> ]PF <sub>6</sub>	1.1902	0.0005
[N <sub>2224</sub> ]SbF <sub>6</sub>	1.6402	0.0011	[N <sub>2228</sub> ]SbF <sub>6</sub>	1.4389	0.0011

Tab	le 4. I	Experimental	l Density o	of Ionic Liq	uids at Tem	perature T = 20	°C and	Pressure	$p = 0.1 \text{ MPa}^{\prime\prime}$
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 ${}^{a}\rho$  is the density of ionic liquid, and  $\sigma$  is the standard deviation. Standard uncertainties *u* are u(T) = 0.1 °C, u(p) = 0.01 MPa, and the combined expanded uncertainty  $U_c$  is  $U_c(\rho) = 0.008$  g·cm<sup>-3</sup> (0.95 level of confidence). The phase for each investigated IL was solid at the experimental conditions, and the details were given in the section describing the synthesis of ILs.

Table 3. In this table, the melting temperature  $(T_m)$  and the solid—solid transition temperature  $(T_{s-s})$  were taken as the onset of the transition of an endothermic peak on heating curve. The glass-transition temperature  $(T_g)$ , defined as the midpoint of an endothermic peak on heating from the amorphous glass state to a liquid state, was not found in the DSC traces of all investigated ILs.

It is well-known that thermal properties of ILs depend on the structure of the cation and anion.<sup>36</sup> Illustrative DSC thermograms in Figures 7 to 9 were all obtained on heating. Two distinctive endothermic peaks on heating, which indicated that a single  $T_{s-s}$  transition was shown before the melting point, were observed in  $[N_{2224}]BF_4$  and  $[N_{2228}]PF_6$  DSC curves of Figure 7 and Figure 8, respectively. In addition, no heat capacity change was shown for the  $[N_{2222}]SbF_6$  compound. Other ILs except the aforementioned three compounds only exhibited a big broad endothermic peak corresponding to the  $T_{m}$ , where the coincidence of  $T_{s-s}$  with  $T_m$  was observed.

The melting points of ILs depend largely on the specific anions. Chiappe et al.<sup>37</sup> and Ohno et al.<sup>38</sup> made systematic studies of the influence of the anion nature on the melting point. In this study, when the nature of anion was changed with a fixed cationic structure ranging from  $\left[N_{2222}\right]$  to  $\left[N_{2226}\right]$  , the variation order in temperature dependence of  $T_{\rm m}$  was [cation]BF<sub>4</sub> <  $[cation]PF_6 < [cation]SbF_6$ . On the contrary, when the cationic alkyl chain length was eight carbon atoms, the  $T_{\rm m}$  began to decrease ( $[N_{2228}]BF_4 > [N_{2228}]PF_6 > [N_{2228}]SbF_6$ ). In comparison to anions, cations also have a remarkable impact on the melting temperature of the investigated ILs. The present observations, which followed the order  $[N_{2224}]PF_6 > [N_{2226}]PF_6$ >  $[N_{2228}]PF_6$  and  $[N_{2224}]SbF_6$  >  $[N_{2226}]SbF_6$  >  $[N_{2228}]SbF_{67}$ were in agreement with the finding that the presence of the electron donating alkyl substituent on the ammonium cation led to ILs with lower melting temperatures.<sup>39</sup> So we assumed that the studied phase transition temperatures reflected the strength of the interaction between the cation headgroup and the anion.

**Density.** The density values are reported in Table 4 together with the standard deviations ( $\sigma$ ). The effects of the alkyl chain length of the cation and the anion on the density have been investigated and shown as Figure 10 and Figure 11, respectively.

From the experimental densities for a constant anion as shown in Figure 10, the density has been found to decrease with an increase in the length of alkyl chain in the cation. In other words, a decrease in the density and an increase in the formula weight were observed with increasing number of carbon atoms in the alkyl chain. Taking  $[N_{222n}]SbF_6$  as an example, the density decreased from 1.7152 g·cm<sup>-3</sup> for  $[N_{2222}]SbF_6$  to 1.7389 g·cm<sup>-3</sup> for  $[N_{2228}]SbF_6$ . Similar trends were consistent with the reported observations in other IL tethered imidazolium, pyridinium, and phosphonium cations.<sup>40–42</sup> This could be rationalized that the



**Figure 10.** Density variation with the cation alkyl chain length of ammonium-based ionic liquids:  $\Box$ , BF<sub>4</sub><sup>-</sup>;  $\bigcirc$ , PF<sub>6</sub><sup>-</sup>;  $\triangle$ , SbF<sub>6</sub><sup>-</sup>.



**Figure 11.** Density variation with the anion of ammonium-based ionic liquid:  $\Box$ ,  $[N_{2222}]^+$ ;  $\blacksquare$ ,  $[N_{2224}]^+$ ;  $\Delta$ ,  $[N_{2226}]^+$ ; O,  $[N_{2228}]^+$ .

increasing occupied volume of the cations resulted from the increased interionic separation and the lowered packing efficiency with the elongation of the alkyl chain length, resulting in a lower overall density.<sup>43</sup>

Figure 11 shows the anion nature dependency of density for the ILs, and the density has clearly increased with an increase in the bulkiness of the anion in the order  $SbF_6^- > PF_6^- > BF_4^-$ . It can be noted that excellent agreement has been observed between our density data and the literature values by Sánchez et al.<sup>44</sup> and Zhang et al.<sup>45</sup> Taking into account the results, Fredlake et al.<sup>46</sup> have attributed the high densities of the ILs to the nature of the anions, which can occupy nearby positions around the cation. The obtained results of this study indicate that the Table 5. Experimental Refractive Index,  $n_D$ , of the System Ionic Liquids + TFSA for Different Mass Fractions *w* at Temperature T = 20 °C and Pressure p = 0.1 MPa<sup>*a*</sup>

ILs	w = 0.00	w = 0.10	w = 0.20	w = 0.30	w = 0.40	w = 0.50	w = 0.60
[N <sub>2222</sub> ]BF <sub>4</sub>	1.3292	1.3421	1.3512	1.3601	1.3656	1.3732	
[N <sub>2222</sub> ]PF <sub>6</sub>	1.3292	1.3398	1.3499	1.3602	1.3691		
[N <sub>2222</sub> ]SbF <sub>6</sub>	1.3292	1.3349	1.3408	1.3498	1.3571	1.3641	1.3678
$[N_{2224}]BF_4$	1.3292	1.3451	1.3543	1.3636	1.3698	1.3771	1.3857
[N <sub>2224</sub> ]PF <sub>6</sub>	1.3292	1.3405	1.3522	1.3632	1.3745	1.3786	1.3782
[N <sub>2224</sub> ]SbF <sub>6</sub>	1.3292	1.3382	1.3449	1.3532	1.3611	1.3693	1.3745
[N <sub>2226</sub> ]BF <sub>4</sub>	1.3292	1.3475	1.3572	1.3654	1.3728	1.3782	
[N <sub>2226</sub> ]PF <sub>6</sub>	1.3292	1.3421	1.3549	1.3667	1.3762		
[N <sub>2226</sub> ]SbF <sub>6</sub>	1.3292	1.3381	1.3462	1.3563	1.3628	1.3722	1.3809
$[N_{2228}]BF_4$	1.3292	1.3493	1.3583	1.3672	1.3745	1.3811	
[N <sub>2228</sub> ]PF <sub>6</sub>	1.3292	1.3427	1.3562	1.3681	1.3781	1.3875	
[N <sub>2228</sub> ]SbF <sub>6</sub>	1.3292	1.3381	1.3484	1.3578	1.3668	1.3760	1.3866

<sup>*a*</sup>w is the mass fraction of ionic liquid in the (ionic liquid + TFSA) systems. Standard uncertainties *u* are  $u(T) = 0.05 \, ^{\circ}\text{C}$ ,  $u(p) = 0.01 \, \text{MPa}$ , u(w) = 0.005 and the combined expanded uncertainty  $U_c$  is  $U_c(n_D) = 0.005$  (0.95 level of confidence).

densities of these ILs can be fine-tuned with judicious selection of the cation and anions.

**Refractive Index.** In the past few years, numerous papers<sup>24,47–49</sup> have been published about refractive indices of ILs. However, investigation on the refractive index of binary mixtures of ILs and acid, which maybe directly acid-catalyzed guided reactions, has been scarcely reported. In this study, the refractive indices  $(n_D)$  of the binary mixture of ILs and TFSA at different mass fraction (w, w = mass of ionic liquid/(mass of ionic liquid + mass of acid)) ranging from 0.00 to 0.60 in the temperature of 20 °C at atmospheric pressure are summarized in Table 5.

The refractive indices of the ILs studied in this work were plotted against mass fraction in Figures 12, 13, and 14. As can be



**Figure 12.** Refractive index of binary mixture of BF<sub>4</sub> anion-based ILs and acid variation with the *w*:  $\Box$ ,  $[N_{2222}]BF_4$ ;  $\blacksquare$ ,  $[N_{2224}]BF_4$ ;  $\Delta$ ,  $[N_{2226}]BF_4$ ; O,  $[N_{2228}]BF_4$ .

seen, the refractive index,  $n_{\rm D}$ , increased pseudolinearly with increasing the mass fraction of ILs over the studied w range. Furthermore, taking into account of the studied  $[N_{222n}]$  (for n = 2, 4, 6, and 8)-based ILs with a constant anion, like PF<sub>6</sub>, BF<sub>4</sub>, or SbF<sub>6</sub>, it was observed that the elongation of alkyl chain on the cation had a positive effect on the  $n_{\rm D}$  of binary mixture of TFSA and ILs with fixed w. Taking the  $[N_{222n}]$ SbF<sub>6</sub> as an example, the  $n_{\rm D}$  increased from 1.368 for the TFSA/ $[N_{2222}]$ SbF<sub>6</sub> to 1.387 for the TFSA/  $[N_{2228}]$ SbF<sub>6</sub> with w = 0.6.



**Figure 13.** Refractive index of binary mixture of PF<sub>6</sub> anion-based ILs and acid variation with the w:  $\Box$ ,  $[N_{2222}]PF_{6i} \blacksquare$ ,  $[N_{2224}]PF_{6i} \Delta$ ,  $[N_{2226}]PF_{6i}$ , O,  $[N_{2228}]PF_{6i}$ .



**Figure 14.** Refractive index of binary mixture of SbF<sub>6</sub> anion-based ILs and acid variation with the w:  $\Box$ ,  $[N_{2222}]$ SbF<sub>6</sub>;  $\blacksquare$ ,  $[N_{2224}]$ SbF<sub>6</sub>;  $\Delta$ ,  $[N_{2226}]$ SbF<sub>6</sub>; O,  $[N_{2228}]$ SbF<sub>6</sub>.

**Miscibility.** Variable solubility of ILs in organic solvents is another interesting physicochemical property to their application.<sup>50</sup> The solubility of the studied ILs in various organic solvents were then investigated at room temperature and the corresponding results are presented in Table 6.

As is known, the cation combined with  $BF_4$  anion results in hydrophilic ILs, whereas the same cation associated with  $PF_6$ 

Table 6. N	liscibility	of Ionic	Liauids in	Different	Solvents <sup><i>a</i></sup>
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entry	ILs	$H_2O$	DMSO	CHCl <sub>3</sub>	EtOAc	EtOH	Et <sub>2</sub> O	MeCN	Me <sub>2</sub> CO	$CH_2Cl_2$
1	$[N_{2222}]BF_4$	m	nm	nm	nm	nm	nm	m	pm	nm
2	[N <sub>2222</sub> ]PF <sub>6</sub>	nm	m	nm	nm	nm	nm	m	m	nm
3	[N <sub>2222</sub> ]SbF <sub>6</sub>	pm	m	nm	nm	nm	nm	m	m	m
4	$[N_{2224}]BF_4$	m	m	m	nm	m	nm	m	m	m
5	[N <sub>2224</sub> ]PF <sub>6</sub>	nm	m	pm	m	pm	nm	m	m	nm
6	[N <sub>2224</sub> ]SbF <sub>6</sub>	nm	m	m	m	pm	nm	m	m	m
7	$[N_{2226}]BF_4$	m	m	m	m	m	nm	m	m	m
8	[N <sub>2226</sub> ]PF <sub>6</sub>	nm	m	pm	m	pm	nm	m	m	pm
9	[N <sub>2226</sub> ]SbF <sub>6</sub>	nm	m	m	m	pm	nm	m	m	m
10	$[N_{2228}]BF_4$	m	m	m	m	m	nm	m	m	m
11	[N <sub>2228</sub> ]PF <sub>6</sub>	nm	m	m	m	m	nm	m	m	m
12	[N <sub>2228</sub> ]SbF <sub>6</sub>	nm	m	m	m	m	nm	m	m	m

<sup>a</sup>Determined at room temperature: m, miscible; nm, nonmiscible; pm, partially miscible. Dimethyl sulfoxide, DMSO; ethyl acetate, EtOAc; ethanol, EtOH; ethyl ether, Et<sub>2</sub>O; acetonitrile, MeCN; acetone, Me<sub>2</sub>CO.

anion produces strongly hydrophobic compounds. This conclusion that the anion nature (BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup>) determined the hydroscopicity of ILs also obtained from the Table 6. Without exception, all the investigated ILs were fully soluble in highly polar MeCN solvent and absolutely insoluble in poorly polar Et<sub>2</sub>O solvent. The polarity of the solvents studied here decrease in the order as H<sub>2</sub>O > DMSO > MeCN > Me<sub>2</sub>CO > CHCl<sub>3</sub> > EtOAc > EtOH > CH<sub>2</sub>Cl<sub>2</sub> > Et<sub>2</sub>O. On the other hand, polar solvents of DMSO and Me<sub>2</sub>CO could dissolve all of the studied ILs except [N<sub>2222</sub>]BF<sub>4</sub>. Unexpectedly, the solubility of ILs in these solvents mentioned above seemed not to be affected by the length of the alkyl chain on the cation.<sup>51</sup>

However, the solubility of these ILs fixed with the anion in other low polar solvents, such as CHCl<sub>3</sub>, EtOAc, EtOH, and CH<sub>2</sub>Cl<sub>2</sub>, changed from insoluble or partially soluble to fully soluble with elongation of the alkyl chain on the cation (Table 6, entries 1, 4, 7 and 10; 2, 5, 8 and 11; 3, 6, 9 and 12). These phenomenon helped to elucidate that the polarities of the ammonium cation containing ILs decrease with an increase in the alkyl chain length of the cation,  $^{52-54}$  thus corresponding to an increase of the solubility in low polar solvents. This conclusion was supposed that the degree of aggregation of ILs decreased with an increase in the alkyl chain length of cation, such a promoted the organic cation dispersing better in the low polar solvents. The solubility in these solvents (CHCl<sub>3</sub>, EtOAc, EtOH, and CH<sub>2</sub>Cl<sub>2</sub>) confirmed the coexistence of apolar and polar domains, arising from the alkyl chain and polar moieties, respectively.<sup>45</sup>

## CONCLUSIONS

In this work, series of  $MF_m^-$ -based ILs have been synthesized and characterized. The experimental data for the thermal temperature, density, and refractive index were discussed. Meanwhile, their miscibility of the investigated ILs in solvents also has been measured. We found a general trend in the influence of the alkyl chain length of the cation and the nature of the anion on the physicochemical properties of ILs: with the same anions, ILs containing elongation of the alkyl chain of ammonium cation exhibited lower decomposition temperature, lower density, but higher solubility in low polar solvents than those in polar solvents. When the cation tethered with ethyl, butyl, or hexyl was considered, an increase of the anion size led to a decrease on the melting point to ILs. However, when the number of carbon atoms at the alkyl chain was higher than 6, there was an inversion of melting point on the anion size sequence. The pattern in density change also observed for the ILs with the fixed cation corresponded to the anion nature; for example, the density increased with an increase in the size of anion. To the best of our knowledge, this was the first report that the refractive index of a binary mixture of IL and acid was measured at different mass fractions. The refractive index versus mass fraction pointed out the occurrence of a trend that refractive index increased pseudolinearly with increasing w values. In addition, the phenomenon of solubility of ILs in different solvents might be interpreted as the principle of "like dissolves like".

## ASSOCIATED CONTENT

#### **S** Supporting Information

Synthetic process of investigated ionic liquids; FT-IR spectrum and NMR spectrum of selected precursor and data of all synthesized precursors (Figure S1, Figure S5, Figure S6, and Table S1); FT-IR spectrum and NMR spectrum of selected ionic liquid and data of all synthesized ionic liquids (Figure S2, Figure S7, Figure S8 and Table S2). This material is available free of charge via the Internet at http://pubs.acs.org..

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#### Notes

The authors declare no competing financial interest.

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