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# Alkali Metal Salts with Designable Aryltrifluoroborate Anions

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ABSTRACT: Aryltrifluoroborate ( $[ArBF_3]^{-}$ ) has a designable basic anion structure. Various  $[ArBF_3]^{-}$ -based anions were synthesized to create novel alkali metal salts using a simple and safe preparation process. Nearly forty novel alkali metal salts were successfully obtained, and their physicochemical characteristics, particularly their thermal properties, were elucidated. These salts have lower melting points than simple inorganic alkali halide salts, such as KCl or LiCl, due to the weaker interactions between the alkali metal cations and the  $[ArBF_3]^{-}$  anions and the anions' larger entropy. Moreover, interestingly, potassium cations were electrochemically reduced in the potassium (*meta*-ethoxyphenyl)trifluoroborate (K[*m*-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>]) molten salt at 433 K. These findings contribute substantially to furthering molten salt chemistry, ionic liquid (IL) chemistry, and electrochemistry.

# INTRODUCTION

Anhydrous liquid alkali metal salts are known as molten salts and have unique features, such as negligible vapor pressure, incombustibility, a wide electrochemical window, and relatively high ionic conductivity.<sup>1</sup> Molten salts are very important non-aqueous solvents and have been employed in various fields, e.g., smelting, fuel cells, and chemical production.<sup>2-5</sup> However, most molten salt systems must be handled under high-temperature conditions to remain in the liquid state, unlike other common solvents. This requirement is often considered a disadvantage. Thus, by applying several approaches to decrease the handling temperature, a number of low-temperature molten salt systems have been reported in the last decade.<sup>6-11</sup> Typical approaches are adding other salt(s) to the original salt, resulting in, for example, LiCl-KCl binary systems<sup>6,8-12</sup> and NaCl-KCl-CsCl ternary systems,<sup>7,13–17</sup> and designing ionic species with lower surface charge densities, delocalized charges, and various molecular motions, thereby decreasing the lattice energy by increasing the interionic distance and entropy.<sup>18</sup> The latter approach is commonly used to obtain ionic liquids (ILs). One example well-known is 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonvl)amide  $([C_4 mim][Tf_2N])$ , which is synthesized using 1-butyl-3-methylimidazolium chloride  $([C_4 mim]Cl)$ (melting point: 342 K)<sup>19</sup> and potassium bis(trifluoromethanesulfonyl)amide (K[Tf<sub>2</sub>N]) (melting point: 472 K).<sup>6</sup> However, few articles on the design and synthesis of alkali metal cation-based low-temperature molten salt systems with polyatomic anions are available<sup>6-11</sup> because introducing target substituent(s) to a polyatomic anion is typically difficult because of the simple basic structure.

In this study, to design and synthesize novel polyatomic anions, we focused on aryltrifluoroborate anions ( $[ArBF_3]^-$ ), which can be easily and safely prepared on a large scale using commercially available reagents.<sup>20</sup> The basic chemical structure is depicted in Figure 1. These anions are elaborated by replacing one fluorine of tetrafluoroborate ( $BF_4^-$ ) with an aromatic group. The trifluoroborate group substantially decreases the negative charge on the aromatic ring. Because of the

characteristics of the anion structure, these salts are expected to be molten salts with relatively low melting temperatures. Nearly forty alkali metal salts with different  $[ArBF_3]^-$  anionic species were successfully produced. The aim of this study was to elucidate the thermal and electrochemical properties, such as the electrochemical window, of the resulting salts.

# EXPERIMENTAL SECTION

Aryltrifluoroborate alkali metal salts (M[ArBF<sub>3</sub>] (M: K or Cs)) were synthesized using appropriate arylboronic acids (ArB(OH)<sub>2</sub>) (Wako Pure Chemical Co. (Japan), Tokyo Chemical Co. (Japan), and others), alkali metal fluorides (MF (M: K or Cs)) (Wako Pure Chemical Co.), and L-tartaric acid (Wako Pure Chemical Co.), according to the following protocol (Scheme 1).<sup>20</sup> An alkali metal fluoride aqueous solution (4 equiv., 2 mL) containing the target cationic species was added to a solution of arylboronic acid (5 mmol) in acetonitrile (20 mL), and the mixture was stirred for 5 min at ambient temperature. L-Tartaric acid (2.05 equiv.) dissolved in tetrahydrofuran (THF) (10 mL) was slowly added to the mixture, and then, a white by-product precipitated immediately. The reaction mixture was agitated for 1 hour at ambient temperature and filtered to remove the precipitate. The resultant filtrate was concentrated *in vacuo*, and the crude alkali metal salt was obtained as a solid. The crude product was purified by recrystallization to give a pure aryltrifluoroborate alkali metal salt. The obtained salt was dried at 353 K under vacuum for 4 hours. The final product was confirmed by nuclear magnetic resonance (NMR), mass spectrometry, and elemental analysis.

Differential scanning calorimetry (DSC) was conducted using a Bruker DSC3100SA. The sample was sealed in an aluminum pan with an aluminum top. The sealed pan was heated and cooled at a rate of 5 K min<sup>-1</sup>. The glass-transition temperature and melting point were obtained from the DSC curve of the second heating process. These values were estimated by the tangential intersection

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method near the temperature at which a phase transformation occurred. Thermogravimetric (TG) analysis was performed using a Bruker TG-DTA2000SA. The sample was placed on an aluminum pan, and the pan was heated from room temperature to 773 K at a rate of 5 K min<sup>-1</sup> under flowing dry nitrogen gas. The thermal degradation temperature was determined as the 5 wt% loss point of the TG curve. These two instruments were controlled with a Bruker MTC1000SA workstation utilizing the Bruker WS003 software. All specimens for these measurements were prepared in an argon gas-filled glove box (Vacuum Atmospheres Co., Omni-Lab, O<sub>2</sub> and H<sub>2</sub>O < 1 ppm).

Electrochemical measurements were conducted using an IVIUM Technologies CompactStat portable electrochemical analyzer. All electrochemical experiments were performed in a three-electrode cell. The working electrode was a platinum disk ( $\phi$  1.6 mm), which was polished with an alumina suspension ( $\phi$  0.06 µm) before use. Platinum wire (diameters of 0.5 mm) was used as the counter electrode. Platinum and silver wires (diameters of 1.0 mm) were employed for the quasi-reference electrode. The measurement was conducted at 433 K or 453 K in an argon gas-filled glove box to prevent any contamination. When a potassium electrodeposition experiment was performed, a tin plate (5 mm × 5 mm) was used as the working electrode. The electrodeposition was conducted at 433 K in an argon gas-filled glove box. The electrodeposits were observed by a Hitachi S-3400N scanning electron microscope (SEM) system. The composition was determined by an EDAX Octane Prime energy-dispersive X-ray spectroscopy (EDX) instrument mounted on the SEM system. The crystal structure of the electrodeposit was identified by a Rigaku Ultima IV X-ray diffractometer (XRD) with Cu K $\alpha$  radiation. This measurement was performed in the 2 $\theta/\theta$  scan mode with a scan rate of 1 degree min<sup>-1</sup>.

The Gaussian 09 program<sup>21</sup> was used for the *ab initio* molecular orbital calculations. The basis sets implemented in the Gaussian program were used. Electron correlation was accounted for by the second-order Mølloer-Plesset perturbation (MP2) method.<sup>22,23</sup> The geometries of complexes were

fully optimized at the HF/6-311G(d,p) level. The intermolecular interaction energies ( $E_{int}$ ) were calculated at the MP2/6-311G(d,p) level by supermolecule method. Our previous calculations of the [C<sub>2</sub>mim][BF<sub>4</sub>] and Li[Tf<sub>2</sub>N] complexes<sup>24,25</sup> show that the basis set effects on the calculated interaction energies of the complexes are very small, if basis sets including polarization functions are used, and that the effects of electron correlation beyond MP2 are negligible. Therefore, we calculated the interaction energies of the complexes at the MP2/6-311G(d,p) level in this work. The basis set superposition error (BSSE)<sup>26</sup> was corrected for all the interaction energy calculations using the counterpoise method.<sup>27</sup> The stabilization energy by the formation of complex from isolated ions ( $E_{form}$ ) was calculated as the sum of the  $E_{int}$  and the deformation energy ( $E_{def}$ ), which is the increase of energy of aryltrifluoroborate anion by deformation of the geometry associated with the complex formation.<sup>24,28</sup> The  $E_{def}$  was calculated at the MP2/6-311G(d,p) level.

#### **RESULTS AND DISCUSSION**

Thermal Behavior of Aryltrifluoroborate Alkali Metal Salts. A large number of aryltrifluoroborate alkali metal salts were prepared according to Scheme 1, and their thermal properties were examined by DSC and TG analyses. The melting point  $(T_m)$  and thermal degradation temperature  $(T_d)$  of M[ArBF<sub>3</sub>] (M: K or Cs) with different substituents are given in Tables 1-4. Non-substitutive potassium phenyltrifluoroborate (K[PhBF<sub>3</sub>]), which the simplest is aryltrifluoroborate potassium salt, had a melting point of 568 K (Table 1). The aromatic potassium salts with substituents, R, at the *meta* position of the phenyl group, K[m-RC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>], showed lower melting points than the non-substitutive K[PhBF<sub>3</sub>], except for the *tert*-butyl group, bromomethyl and carbamoyl group. Specifically, potassium (meta-ethoxyphenyl)trifluoroborate group, (K[m-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>]) with an ethoxy group at the *meta* position on the aromatic ring melted at 390 K; thus, introducing the ethoxy group substantially decreased the melting point. As shown in Table 5,

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this value was considerably lower than those of other common potassium salts,<sup>6, 29–32</sup> likely because of the obtained salts' increased interionic distances and entropies. From these data, we can also discuss the effects of the substituents in a little more detail. For example, there is an obvious difference between the melting points of K[*m*-OMeC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] and K[*m*-OCF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>]. The OCF<sub>3</sub> group works as a strong electron withdrawing group because of the electronegativity of the three fluorine atoms. The charge density of the anion consequently decreases by the OCF<sub>3</sub> group compared to OMe group without the fluorine atom. The resulting weak ionic interaction between the K<sup>+</sup> and the [*m*-OCF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>]<sup>-</sup> would cause the lower melting point. As described later, quantum chemical calculations support this idea.

A similar approach was also applied to Cs salt preparation. The thermal properties of the Cs salts are summarized in Table 2. Cesium phenyltrifluoroborate (Cs[PhBF<sub>3</sub>]) exhibited a melting point of 445 K, lower than that of its potassium counterpart. The same was true for other Cs salts with the following substituents at the *meta* position: CF<sub>3</sub>, F, OCF<sub>3</sub>, and O<sup>n</sup>Pr. The larger ionic radius of the cesium ion compared to that of the potassium ion is commonly believed to decrease the Cs salt's lattice energy.<sup>6,8,10,11</sup> In contrast, the  $T_m$  of Cs salts with a methylthio or ethoxy group clearly increased compared to those of potassium salts with the same anions. These Cs salts should have a favorable ion packing structure. A similar exception regarding the melting temperatures derived from the differences in the cation and anion radii in inorganic alkali metal halides has been reported.<sup>33,34</sup> The thermal properties of the *ortho*-substituted potassium aryltrifluoroborate (K[*o*-RC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>]) are summarized in Table 3. Most salts showed only a thermal degradation temperature without a melting point. Furthermore, for those salts, it was much higher than those of the *meta*-substituted ones. To determine the underlying reason, we carried out quantum chemical calculations for evaluating the interactions of K<sup>+</sup> with substituted phenyltrifuluoroborate anions. The optimized structures of the ion pairs of K<sup>+</sup> and *meta*- and *ortho*-substituted phenyltrifuluoroborate anions are depicted in Fig. 2.

Whereas the K<sup>+</sup> has contact with three fluorine atoms of –BF<sub>3</sub> in all the ion pairs of *meta*-substituted phenyltrifuluoroborates, in all the ion pairs of *ortho*-substituted ones, the K<sup>+</sup> has contact with two fluorine atoms of -BF<sub>3</sub> and one negatively charged atom in the substituent. The stabilization energies by the formation of the complexes from isolated species ( $E_{\text{form}}$ ) calculated for the ion pairs and the difference between the  $E_{\text{form}}$  for the ion pair of *meta*-substituted phenyltrifuluoroborate and that for the ion pair of *ortho*-substituted phenyltrifuluoroborate ( $\Delta E$ ) are given in Fig. 2. For example, the  $E_{\text{form}}$  calculated for the optimized structure of K[m-OMeC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] (-456.7 kJ·mol<sup>-1</sup>) was 34.4 kJ·mol<sup>-1</sup> smaller (less negative) than that for the K[o-OMeC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] (-491.1 kJ·mol<sup>-1</sup>). The  $E_{\text{form}}$ calculated for the ion pair of *meta*-substituted phenyltrifuluoroborates is always smaller than that for the ion pair of corresponding *ortho*-substituted phenyltrifuluoroborates. These calculations show that the dissociation of the ion pair of *meta*-substituted phenyltrifuluoroborate can occur more easily than the dissociation of the ion pair of corresponding *ortho*-substituted phenyltrifuluoroborates.<sup>35,36</sup> The computational results suggest that the K<sup>+</sup> salts with *meta*-substituted phenyltrifuluoroborates have lower melting temperatures compared with the salts of corresponding ortho-substituted 

 phenyltrifuluoroborates owing to weaker attraction between the cation and anion. In addition to the aforementioned salts, the K<sup>+</sup> salts with three disubstituted phenyltrifluoroborate anions and two other aryltrifuluoroborate anions were also synthesized (Table 4). These salts had no melting point except for a potassium 1-naphthyltrifluoroborate (K[1-NaphBF<sub>3</sub>]). The thermal degradation temperatures of alkali salts with aryltrifluoroborate anions prepared in this study scatter over wide temperature ranges from 404 to 611 K. Different thermal stability of the substituents in aryltrifluoroborate anions would be the major source of the difference of the thermal degradation temperatures. **Electrochemical Analyses.** As shown in Tables 1-4, K[*m*-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] had the lowest melting point, i.e., 390 K, among the studied salts. Cyclic voltammograms recorded using a Pt disk electrode in the

 $K[m-OEtC_6H_4BF_3]$  molten salt are shown in Fig. 3. The electrochemical window was determined based on the anodic and cathodic limiting potentials at which the current densities reached the current density of  $\pm 0.3$  mA cm<sup>-2</sup> in a forward scan. The current increment initiated at ca. 1.36 V (vs. quasi-Pt wire reference electrode) and ca. 0.71 V (vs. quasi-Ag wire reference electrode) in the anodic region (blue line) was attributable to the decomposition of the  $[m-OEtC_6H_4BF_3]^-$  anion. In the cathodic region (red line), the negative limiting potential was ca. -2.48 V (vs. Pt wire) and ca. -3.13 V (vs. Ag wire) Hence, the electrochemical window was 3.84 V at 453 K. This range is comparable to those of typical alkali metal molten salt systems, such as LiCl-KCl (3.8 V).<sup>37-39</sup> Therefore, this K[m-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] molten salt has great promise as a low-temperature molten salt. Further electrochemical analyses were conducted to elucidate the unknown electrochemical redox reactions observed at the negative limiting potential. As shown in Fig. 3, a small oxidation peak appeared at -2.3 V (vs. Pt wire) in the reverse scan of the cathodic region. We speculated that the oxidation wave was related to the dissolution of metal potassium deposited in the potential range of  $-2.4 \sim -2.5$  V (vs. Pt wire). However, the coulombic efficiency of the redox reaction estimated based on the cyclic voltammogram was only 4 %. Given metallic potassium's low melting point (337 K), it is highly likely that the metal potassium electrodeposited on the electrode floats or precipitated in the  $K[m-OEtC_6H_4BF_3]$  molten salt at 453 K soon after deposition. These processes would lead to the observed significantly low coulombic efficiency. In fact, we could not identify any deposits on the Pt electrode after electrolysis at the limiting potential. We collected more accurate information on the relevant electrochemical reaction via two approaches: double-step chronoamperometry using short potential step times and alloying with a tin electrode that can readily form a K-Sn binary alloy.<sup>40</sup> Figure 4 shows the double-step chronoamperograms recorded using a Pt disk electrode in the  $K[m-OEtC_6H_4BF_3]$  molten salt at 433 K. Based on these chronoamperograms, we can discuss the kinetic complications involved in the electrode reaction. When a certain type of ionic species is

oxidized or reduced ideally on the electrode surface during double-step chronoamperometry, the kinetic complications are determined by the following equation:<sup>41</sup>

$$-\frac{i_{\rm r}}{i_{\rm f}} = 1 - \left(1 - \frac{\tau}{t_{\rm r}}\right)^{\frac{1}{2}} \tag{1}$$

where  $i_{\rm f}$  is the forward current in the first potential step,  $i_{\rm r}$  is the reversal current in the second potential step,  $t_r$  is the time at any current in the second potential step, and  $\tau$  is the retention time of the first potential step. Figure 5a depicts an ideal current response in double-step chronoamperometry when the first step is the cathodic reaction. The data shown in Fig. 4 were converted into  $-i_r/i_f$  and  $t_r/\tau$ by eq. 1 and are presented graphically in Fig. 5b. The solid line in the figure represents an ideal line calculated using this equation. At a longer step time, i.e., 0.05 s, a large deviation from the ideal line occurred. Conversely, the plots were very similar to the ideal line when a shorter time step of 0.01 s was used. Therefore, the electrode reaction proceeded reversibly at only very short reduction potential step times. Direct evidence of potassium electrodeposition was obtained by constant potential electrolysis at -2.6 V (vs. Pt wire) for 3600 s on a Pt electrode. No deposits were identified. However, when a tin plate with metallic luster was used as the working electrode (Fig. 6a), the surface became covered with a dark gray deposit under the same electrolysis conditions (Fig. 6b). SEM images of the electrode surface before and after electrolysis are shown in Fig. 6c and d, respectively. The original tin electrode had a smooth surface, but after electrolysis, the surface exhibited a dramatic change, becoming rough with many cracks.<sup>42-44</sup> The tin electrode was characterized by XRD, and the results obtained before and after electrolysis are shown in Fig. 7. The specimen after electrolysis had a unique XRD pattern. In addition to that of metallic tin, the pattern for the K<sub>4</sub>Sn<sub>23</sub> binary alloy was also evident; thus, K-Sn binary alloy was formed on the Sn electrode

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surface. The K-Sn alloy probably formed immediately after K(I) reduction on the Sn electrode. EDX analysis of the specimen indicated that the major components were potassium and tin. Based on these results, the redox reaction observed at the negative limiting potential in the K[m-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] molten salt was identified as the electrode reaction for K(I), which is in agreement with the results of the few papers available that address metal potassium deposition in ILs and organic solvents.<sup>45–47</sup>

#### CONCLUDING REMARKS

Nearly forty aryltrifluoroborate alkali metal salts with various substituents were designed and successfully obtained via a simple and safe preparation process. We revealed that the choice of substituents and their positions strongly affected the thermal properties of the resulting salts. The alkali metal salts clearly had lower melting points than common inorganic alkali halides, e.g., LiCl, KCl, and KF. We prepared a structure-designed potassium aryltrifluoroborate, K[*m*-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>], i.e., a low-temperature molten salt, for the electrodeposition of metal potassium. Our results and the preparation process for the M[ArBF<sub>3</sub>] (M: K or Cs) salts reported in this article will be useful for scientists and engineers in the fields of molten salts, ILs, and electrochemical technology.

# ASSOCIATED CONTENT

# **Supporting Information**

Additional experimental data. 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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**Table 1.** Thermal properties of the synthesized  $K[ArBF_3]$  salts with a substituent at the *meta* position





<sup>*a*</sup>Melting point. <sup>*b*</sup>Thermal degradation temperature at 5 wt% loss. <sup>*c*</sup>Decomposition before melting.

**Table 2.** Thermal properties of the synthesized Cs[ArBF<sub>3</sub>] salts with a substituent at the *meta* position

Es Cs	F₃ R	
$\sim_{R}$ (Abbreviations for substituents)	$T_{\rm m}{}^a$ / K	$T_{d}^{b} / K$
∼н	445	566
CF₃	403	549
F	409	611
$\sim_{O}$ -CF <sub>3</sub> (-OCF <sub>3</sub> )	398	534
S <sup>−CH</sup> <sub>3</sub> (-SMe)	413	565
O CH <sub>3</sub> (-OEt)	433	572
$\sim CH_3$ (-O <sup>n</sup> Pr)	409	567

<sup>*a*</sup>Melting point. <sup>*b*</sup>Thermal degradation temperature at 5 wt% loss.

**Table 3.** Thermal properties of the synthesized K[ArBF<sub>3</sub>] salts with a substituent at the *ortho* position

	⊕ BF <sub>3</sub> K R	
$\sim_{R}$ (Abbreviations for substituents)	$T_{\rm m}{}^a$ / K	$T_{d}^{b}$ / K
F	<i>C</i>	587
$\sim_{O}$ -CF <sub>3</sub> (-OCF <sub>3</sub> )	<i>c</i>	555
$\sim_{S}$ -CH <sub>3</sub> (-SMe)	549	564
$\sim_{O}$ -CH <sub>3</sub> (-OMe)	554	579
℃ CH <sub>3</sub> (-OEt)	<i>c</i>	565
NO <sub>2</sub>	<i>c</i>	492
$\mathcal{CH}_{CH_3}$ (-COCH <sub>3</sub> )	c	482

<sup>*a*</sup>Melting point. <sup>*b*</sup>Thermal degradation temperature at 5 wt% loss. <sup>*c*</sup>Decomposition before melting.

Potassium salts (Abbreviations for anions) $T_{\rm m}^{\ a}$ / K		
$ \overset{\bigoplus}{K} \overset{\bigoplus}{HeO} \overset{F}{F} (2\text{-}F\text{-}5\text{-}OMeC_6H_3BF_3) $	<i>c</i>	481
$ \overset{\bigoplus}{K} \overset{\bigoplus}{F_3C} \overset{Cl}{I} (2\text{-}Cl-5\text{-}CF_3C_6H_3BF_3) $	c	404
$ \overset{\bigoplus}{K} \overset{\bigoplus}{\underset{O_2N}{\overset{O_2R}{\overset{O_2H_3}{\overset{O_2H_3}{\overset{O_2H_3}{\overset{O_2H_3}{\overset{O_2H_3}}}} (3\text{-}\mathrm{CO}_2\mathrm{Me}\text{-}5\text{-}\mathrm{NO}_2\mathrm{C}_6\mathrm{H}_3\mathrm{BF}_3) $	c	495
$ \overset{\bigoplus}{\overset{H}{\overset{K}}{\overset{K}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}{\overset{K}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}}{\overset{K}{\overset{K}}{\overset{K}}{\overset{K}}{\overset{K}{\overset{K}}{\overset{K}}{\overset{K}}{\overset{K}}{\overset{K}}{\overset{K}}{\overset{K}}{\overset{K}}{\overset{K}{\overset{K}}{\overset{K}}{\overset{K}}{\overset{K}}{\overset{K}}}}}}}}}$	<i>c</i>	550
$ \overset{}{_{K}} \overset{}{_{BF_3}} (1\text{-NaphBF}_3) $	461	534

Table 4. Thermal properties of other K[ArBF<sub>3</sub>] salts

<sup>*a*</sup>Melting point. <sup>*b*</sup>Thermal degradation temperature at 5 wt% loss. <sup>*c*</sup>Decomposition before melting.

# 6

Salts	$T_{\rm m}^{\ a}$ / K	Ref.
KF	1131	30
KCl	1043	31
KBr	1006	31
KI	952	31
KBF <sub>4</sub>	803	29
KTfO	503	32
KTf <sub>2</sub> N	472	6
K[m-OEtC <sub>6</sub> H <sub>4</sub> BF <sub>3</sub> ]	390	This work

<sup>*a*</sup>Melting point.

#### **Scheme and Figure Captions**

Scheme 1. Synthesis of aryltrifluoroborate alkali metal salts.

Figure 1. Chemical structure of the aryltrifluoroborate anion ([ArBF<sub>3</sub>]<sup>-</sup>).

**Figure 2.** Optimized structures of ion pairs consisting of K<sup>+</sup> and *meta-* and *ortho-*substituted phenytrifluoroborate anions and their stabilization energies by the formation of ion pairs ( $E_{\text{form}}$ ).  $\Delta E$  (=  $E_{\text{form}(meta)} - E_{\text{form}(ortho)}$ ) is the difference between the  $E_{\text{form}}$  for the ion pair of *meta-*substituted phenytrifluoroborate anion ( $E_{\text{form}(ortho)}$ ) and the  $E_{\text{form}}$  for the ion pair of *ortho-*substituted phenytrifluoroborate anion ( $E_{\text{form}(ortho)}$ ).

Figure 3. Cyclic voltammograms recorded at a Pt disk electrode in (—) the cathodic region and (—) the anodic region in the K[m-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] low-temperature molten salt at 453 K. The scan rate was 10 mV s<sup>-1</sup>.

**Figure 4.** Double-step chronoamperograms recorded at a Pt disk electrode in the K[*m*-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] low-temperature molten salt at 433 K with a potential step of -2.6 V (*vs.* Pt wire) followed by 0 V (*vs.* Pt wire). The potential step times were (—) 0.01 s and (—) 0.05 s.

**Figure 5.** (a) Ideal current response in typical double-step chronoamperometry.  $i_f$  is the forward current in the first potential step,  $i_r$  is the reversal current in the second potential step,  $t_f$  is the time at any current in the first potential step, and  $\tau$  is the potential step time for the first potential step. (b) –  $i_r/i_f vs. t_r/\tau$  plot derived from the chronoamperograms shown in Fig. 4. The potential step times were ( $\bigcirc$ ) 0.05 s and ( $\bullet$ ) 0.01 s. The solid line in the figure represents the ideal line calculated using eq. 1.

**Figure 6.** Optical microscope and SEM images of the tin electrode (a and c) before and (b and d) after electrolysis at -2.6 V (*vs.* Pt wire) in the K[*m*-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] low-temperature molten salt at 433 K. The SEM images are shown in (c) and (d).

**Figure 7.** XRD patterns (Cu-K $\alpha$ ) of the tin electrode before and after electrolysis at -2.6 V (*vs.* Pt wire) in the K[*m*-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] low-temperature molten salt at 433 K. As references, the diffraction patterns of  $\beta$ -Sn (JCPDS-ICDD, file 00-004-0673) and K<sub>4</sub>Sn<sub>23</sub> (JCPDS-ICDD, file 03-065-3351) are also shown.





Scheme 1. Synthesis of aryltrifluoroborate alkali metal salts.



Figure 1. Chemical structure of the aryltrifluoroborate anion ([ArBF<sub>3</sub>]<sup>-</sup>).





**Figure 2.** Optimized structures of ion pairs consisting of K<sup>+</sup> and *meta-* and *ortho-*substituted phenytrifluoroborate anions and their stabilization energies by the formation of ion pairs ( $E_{\text{form}}$ ).  $\Delta E$  (=  $E_{\text{form}(meta)} - E_{\text{form}(ortho)}$ ) is the difference between the  $E_{\text{form}}$  for the ion pair of *meta-*substituted phenytrifluoroborate anion ( $E_{\text{form}(ortho)}$ ) and the  $E_{\text{form}}$  for the ion pair of *ortho-*substituted phenytrifluoroborate anion ( $E_{\text{form}(ortho)}$ ).



**Figure 3.** Cyclic voltammograms recorded at a Pt disk electrode in (—) the cathodic region and (—) the anodic region in the K[*m*-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] low-temperature molten salt at 453 K. The scan rate was  $10 \text{ mV s}^{-1}$ .





**Figure 4.** Double-step chronoamperograms recorded at a Pt disk electrode in the K[*m*-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] low-temperature molten salt at 433 K with a potential step of -2.6 V (*vs.* Pt wire) followed by 0 V (*vs.* Pt wire). The potential step times were (—) 0.01 s and (—) 0.05 s.



**Figure 5.** (a) Ideal current response in typical double-step chronoamperometry. *i*<sub>f</sub> is the forward current in the first potential step, *i*<sub>r</sub> is the reversal current in the second potential step, *t*<sub>f</sub> is the time at any current in the first potential step, and  $\tau$  is the potential step time for the first potential step. (b) –  $i_r/i_f vs. t_r/\tau$  plot derived from the chronoamperograms shown in Fig. 4. The potential step times were ( $\bigcirc$ ) 0.05 s and ( $\bigcirc$ ) 0.01 s. The solid line in the figure represents the ideal line calculated using eq. 1.

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**Figure 6.** Optical microscope and SEM images of the tin electrode (a and c) before and (b and d) after electrolysis at -2.6 V (*vs.* Pt wire) in the K[*m*-OEtC<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>] low-temperature molten salt at 433 K. The SEM images are shown in (c) and (d).







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