

# Synthesis and characterization of rare and highly hydrolysis-resistant boronium (+3) cations

*Margaret E. Crowley,<sup>a</sup> Christopher D. Stachurski,<sup>b\*</sup> James H. Davis, Jr.,<sup>\*a</sup> Paul C. Trulove,<sup>b</sup> David P. Durkin,<sup>b</sup> Andrzej Wierzbicki,<sup>a</sup> E. Alan Salter,<sup>a</sup> Matthias Zeller,<sup>c</sup> Richard A. O'Brien,<sup>a</sup> and Gabriel A. Merchant<sup>a</sup>*

<sup>a</sup>Department of Chemistry, University of South Alabama, Mobile, Alabama 36688 USA

<sup>b</sup>Department of Chemistry, U. S. Naval Academy, Annapolis, Maryland 21402 USA

<sup>c</sup>Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 USA

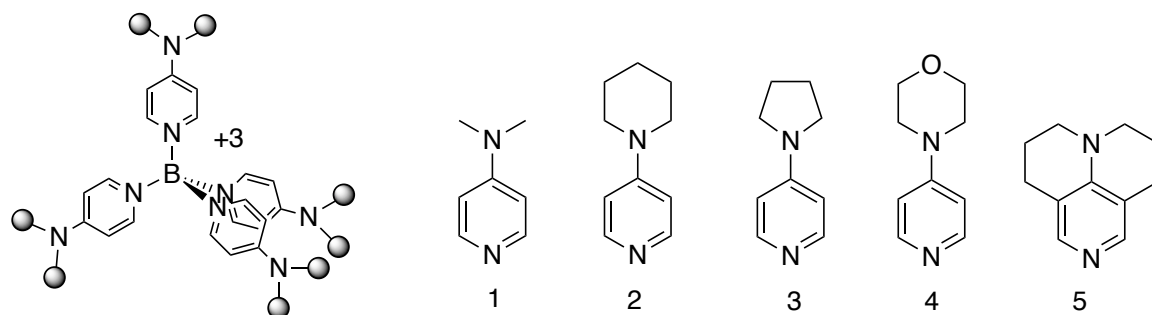
**ABSTRACT** Boronium (+3) cations,  $L_4B^{3+}$ , are rare and scarcely studied. But, thanks to their rigid tetrahedral shape and high cationic charge they may be promising tectons for creating hybrid organic-inorganic solids, especially since a single cation can serve as a nucleating center around which three anions can be assembled. However, the few boronium (+3) cations which have been reported are generally water-sensitive, a factor which is a potential impediment to the former endeavor (as is the case with many perovskite photovoltaics). Herein we report the synthesis and characterization (X-ray, NMR, DSC, TGA, CV) of multiple boronium (+3) salts, all of which are highly water stable across the 1-14 pH range. And, as a preliminary investigation of the template-tecton hypothesis, the BETI [bis(pentafluoroethanesulfonyl)imide] salt of a representative cation was prepared. Significantly, the crystals of the latter were determined by X-ray crystallography to feature continuous, fluorine-rich veins.

## INTRODUCTION

Boronium (+3) ions are very rare and their chemistry is woefully under-explored. They, like their boronium (+1) and (+2) counterparts, consist of a central boron atom in a tetrahedral

ligand field. However, unlike the (+1) and (+2) ions, all four ligands/substituents in the (+3) ion are neutral, N-donor Lewis bases; the latter are almost always pyridine or a simple alkyl pyridine variant thereof. They are particularly interesting for several reasons. First, they fill a gap in the fundamental chemistry of coordination complexes; to our knowledge, there are no tetrahedral, +3 complexes of a transition-metal or main-group element supported only by neutral ligands. Second, the parent  $\text{Py}_4\text{B}^{3+}$  (Py = pyridine) ion is evocative of the tetraphenylphosphonium ion,  $\text{Ph}_4\text{P}^+$ , which is invaluable for forming easily crystallizable salts of anions of interest.<sup>1</sup> Further, the latter cation has seen widespread use as a probe ion in studies of mitochondrial membrane potentials.<sup>2</sup> Finally, the combination of large size, tetrahedral geometry, structural rigidity, and high charge on these boronium ions offers considerable yet unexplored potential for use in engineering hybrid organic-inorganic crystalline solids, provided issues with their hydrolytic instability can be overcome.<sup>3</sup> The latter concern is non-trivial, a current case-in-point being the water sensitivity of many perovskites being investigated as solar cell materials.<sup>4</sup>

In 1970 Bohl and Galloway isolated the parent  $\text{Py}_4\text{B}^{3+}$  ion as an iodide salt which they reported to be exquisitely sensitive to water, decomposing rapidly upon addition to an aqueous solution of  $\text{KPF}_6$  in an attempt at anion exchange; the sole published characterization data for it consists of elemental analysis (C, H, N, and I).<sup>5</sup> Contemporaneously, Ryschkewitsch and co-workers found that a related cation bearing four 4-methylpyridine ligands was more stable, albeit on a pH dependent basis. This cation was stable for ~1 week in water at pH = 1, moderately stable for 24 h at pH = 7, decomposed in ~1 h at pH = 11 and in ~1 min at pH = 13.6. The increase in stability was attributed to the 4-alkyl group increasing electron density at the pyridyl nitrogen. Against this background, we were interested in trying to further – hopefully by a large degree – improve the aqueous stability of boronium (+3) ions so that their chemistry might be more extensively developed. It was our hypothesis that doing so might be accomplished by using as ligands the powerful nucleophilic donor DMAP (4-dimethylamino pyridine) and variants thereof (Figure 1).<sup>7</sup>



**Figure 1.** Left: Generic structure of  $\text{Py}_4\text{B}^{3+}$  cations. Right: Structures of the 4-(alkyl)amino pyridine ligands used in the present study.

## EXPERIMENTAL

### Representative synthesis

In a well-ventilated fume hood, a 500 mL, two-neck round bottomed flask was charged with a magnetic stirbar and 200 mL of reagent grade chlorobenzene. It was then fitted with a heating mantle and an air-cooled condenser which was loosely plugged at the top with a Kimwipe. 4-N,N-dimethylamino pyridine (DMAP; 15.6 g, 0.128 mol) was added through the side neck, and the resulting pale ivory solution brought to reflux. Through the side neck were then added, portion-wise, 10.0 g of solid  $\text{Me}_2\text{SBBR}_3$  (note: fumes in air). Upon mixing there was vigorous off-gassing of the dimethylsulfide as the boron reagent dissolved. Once all the latter had been added, the side neck was stoppered and reflux continued for 12 h, during which time the orange-yellow solution faded in color and a voluminous quantity of white solid separated. The suspension was vacuum filtered while still hot (Caution! Chlorobenzene  $T_b = 132\text{ }^\circ\text{C}$ ). The collected white, granular solid was then washed successively with fresh chlorobenzene, toluene, and (after cooling to room temperature) diethyl ether. Yield of  $\mathbf{1}\cdot\text{3Br}$ : 21.2g (89.6%). The product was used without further purification in the subsequent anion exchange step.

A 500 mL Erlenmeyer flask was charged with 200 mL of hot water and a magnetic stirbar. While stirring, 15.0 g (0.020 mol) of the preceding bromide salt was added. It dissolved quickly, producing a colorless solution. Separately, 20.0 g (0.062 mol) of  $\text{KTf}_2\text{N}$  [potassium bis(trifluoromethanesulfonyl)imide] was likewise dissolved in hot water, and the resulting solution slowly added to that of the bromide salt. Upon mixing, a copious amount of white solid precipitated. Stirring was continued for an hour after which time the product  $[\mathbf{1}\cdot(\text{Tf}_2\text{N})_3]$  was

separated by vacuum filtration, washed with water, and dried in vacuo (25.7 g, 96%). The corresponding [1·(BETI)<sub>3</sub>] salt was prepared in the same fashion (and with similar results) using LiBETI in place of KTF<sub>2</sub>N. The foregoing procedures were used for the preparation of boronium (+3) salts of cations **2-5** as well, with similar results. However, the scale of the synthesis of salts of cation **5** was much smaller (2 g scale) due to the expense of the pyridine used (9-azajulolidene).

### NMR spectroscopy

All NMR spectra – <sup>1</sup>H (500 MHz), <sup>13</sup>C (125 MHz), and <sup>10</sup>B (54 MHz) – were collected using a JEOL JNM-ECA series, 500 MHz FT-NMR spectrometer. For compounds **1-2**, the <sup>1</sup>H spectra are reported in ppm referenced to the D<sub>2</sub>O solvent (δ 4.79). For compounds **3-5**, the <sup>1</sup>H and <sup>13</sup>C spectra are reported referenced to methanol-d<sub>4</sub> (δ 4.87 and δ 49.0, respectively). After subsequent ion exchange of compounds **1-5** to the bis(trifluoromethanesulfonyl)imide anion, all were found to be soluble in acetone. NMR analysis of the same three nuclei was performed in acetone-d<sub>6</sub> referenced at δ 2.05 for <sup>1</sup>H and δ 206.26 for <sup>13</sup>C. With the addition of the fluorinated anion, <sup>19</sup>F (471 MHz) spectra were also acquired.

### Thermal gravimetric analysis

Thermal stability of the Tf<sub>2</sub>N<sup>-</sup> salts of trications **1-5** were evaluated using thermal gravimetric analysis (TGA) (TA Instruments TGA 5500). Samples were loaded into platinum pans and heated under nitrogen from 20-800 °C at a heating rate of 10 °C min<sup>-1</sup>. The decomposition temperature (*T*<sub>5</sub>) was taken as the point at which 5 wt% of the initial sample mass was lost.

### Differential scanning calorimetry

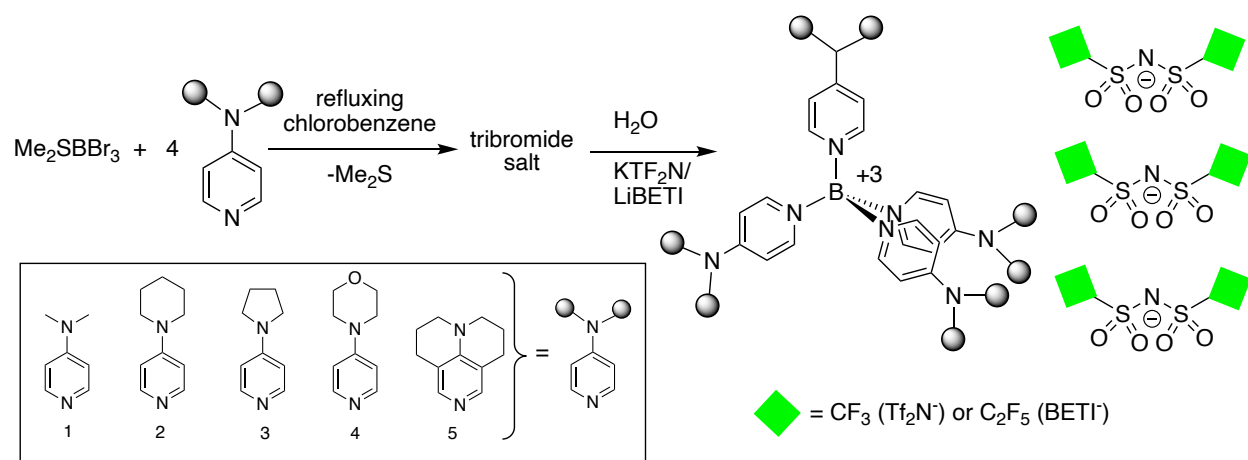
Thermal phase transitions were measured using differential scanning calorimetry (DSC) (TA Instruments Q2000) equipped with liquid nitrogen cooling. Samples were sealed in hermetic aluminum pans under nitrogen and cycled from room temperature (RT) to -150 °C, then 350 °C at 10 °C min<sup>-1</sup> under a helium purge at a flow rate of 25 mL min<sup>-1</sup>.

### Electrochemistry

All electrochemical experiments were conducted in a nitrogen filled glovebox to control for ambient water exposure (<1 ppm H<sub>2</sub>O). Samples were prepared in acetonitrile to predetermined

concentrations (25- and 35-mM solutions of the  $\text{Tf}_2\text{N}^-$  salts of trications **2** and **3** (respectively) and 50 mM concentrations for the remaining salts). A standard solution of 50 mM tetrabutylammonium hexafluorophosphate in acetonitrile was used to establish a baseline behavior. Cyclic voltammetry (CV) was performed using a Biologic SP-200 potentiostat. All samples were analyzed in a standard three-electrode cell comprised of a glassy carbon working electrode (EDAQ, surface area =  $7.8 \times 10^{-3} \text{ cm}^2$ ), a platinum mesh counter electrode, and a silver wire serving as a quasi  $\text{Ag}/\text{Ag}^+$  reference electrode, all kept in the same compartment and not separated by a frit or membrane. Potentials were adjusted to the  $E_{1/2}$  of the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple for each cell following analysis of the boronium salt. For all standard cyclic voltammograms, the working electrode was held at the open circuit potential ( $E_{oc}$ ) before sweeping between the switching potentials at a scan rate of  $50 \text{ mV s}^{-1}$ . Unless specified, the working electrode was polished between scans using a series of alumina slurries (6, 1,  $0.25 \mu\text{m}$ ) and cleaned with a microfiber polishing pad.

## RESULTS AND DISCUSSION



**Scheme 1.** Synthesis of  $\text{Py}_4\text{B}^{3+}$  salts.

### Synthesis of $\text{Py}_4\text{B}^{3+}$ salts (Py = DMAP and structural analogues)

Five new boronium (+3) cations were prepared (**1-5**, Scheme 1) as bromide salts. The synthetic procedure for the salts was a modification of that used by Bohl and Galloway as well as Ryschkewitsch and his co-workers for the synthesis of  $\text{L}_4\text{B}^{3+}$  cations (L = pyridinyl ligand); in short, four molar equivalents of the pyridine of interest were combined with  $\text{Me}_2\text{SBBBr}_3$  (the

Galloway and Ryschkewitsch work utilized  $\text{Me}_3\text{NBI}_3$ ) in refluxing chlorobenzene, the target boronium salt then precipitating in essentially quantitative yield. The bromide salts are all white solids. Those of cations **1**, **4**, and **5** are non-hygroscopic while those of **2** and **3** absorb atmospheric moisture. The bis(trifluoromethanesulfonyl)imide ( $\text{Tf}_2\text{N}^-$ ) salts of each of the cations were prepared by an aqueous anion exchange between the bromide salt and  $\text{KTf}_2\text{N}$ . Unlike the experience of Bohl and Galloway when attempting an anion exchange between the iodide salt of  $\text{Py}_4\text{B}^{3+}$  and  $\text{KPF}_6$ , no sensitivity to water was observed for the present cations.

### Evaluation of water stability as a function of pH

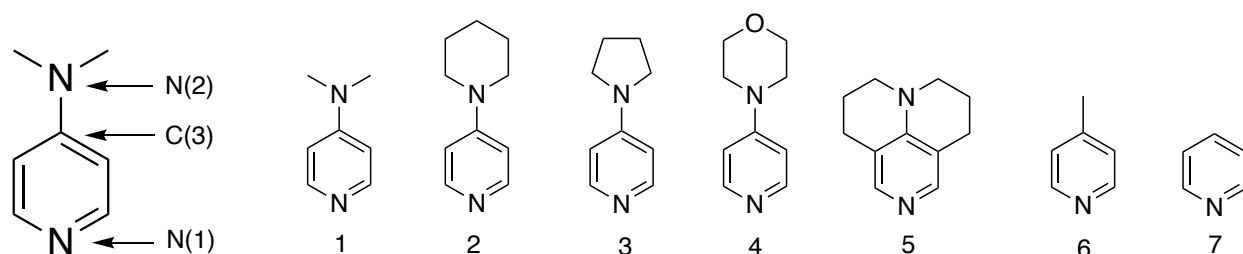
$\text{D}_2\text{O}$  solutions were prepared having pH (pD) values ranging monotonically from 7-14. The bromide salt of the parent DMAP boronium, **1**, as well as that of **2**, a representative analogue bearing a more lipophilic  $\text{R}_2\text{N}^-$  group, were dissolved in these solutions and  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{10}\text{B}$ -NMR spectra were acquired ( $T = 20^\circ\text{C}$ ) five minutes after dissolution, after one week, after two weeks, and finally after four months (spectra provided in the Supporting Information). The outcomes were clear. The spectra of DMAP cation **1** were unchanged at any of these pHs over any length of time; no evidence of decomposition or reaction was observed. Those of **2** showed no changes for any duration at pH values from 7-12. However, resonances suggestive of a very small amount of an unidentified new material(s) became evident at pHs = 13 and 14 after two weeks, but **2** remained overwhelmingly the principal component even after four months. Given the very well-known propensity for most molecular monoboron compounds to react with water to form boric acid ( $\Delta G^\circ_f = -1,093 \text{ kJ/mol}$ ), this degree of pH-independent stability for a molecular boron compound towards water is quite remarkable. Developing boronium (+3) ions insensitive to water, especially at or above pH = 7, was a key objective of the present work and one which the preceding data show was clearly achieved. Doing so was made possible by using pyridine ligands with strongly electron-donating dialkylamine groups in the ring 4-position. However, we realized that using those ligands might also potentially create a sensitivity on the part of these boroniums towards *acidic* media because of the lone electron pair on the dialkylamine groups. We note that protonation of the  $\text{Me}_2\text{N}^-$  group of an already coordinated DMAP was reported by Harman, *et al.*, when it was used as a ligand in a molybdenum complex.<sup>8</sup> Further, Forsythe and co-workers have shown that DMAP already protonated at the pyridine nitrogen can simultaneously be protonated at the  $\text{Me}_2\text{N}$  group in acidic media.<sup>9</sup> Consequently, we thought it essential to extend the pH-stability studies into the

acidic domain. Accordingly, the bromide salts of **1** and **2** were dissolved in D<sub>2</sub>O having pH (pD) values varying monotonically from 1 – 7, with <sup>1</sup>H-, <sup>13</sup>C-, and <sup>10</sup>B-NMR spectra acquired on each after five minutes, one week, two weeks, and four months. Once again, no changes were observed for either boronium at any of those pH values over any of those intervals, indicating that the cations remained stable in the acidic pH domain as well. Interestingly, the lack of any chemical shift changes suggests that no protonation at the R<sub>2</sub>N- substituents occurs in these ions, in contrast to the Harman and Forsythe cases (*vide supra*). We posit that the coordination of the present ligands to the B (+3) center is sufficiently depleting of electron density on the R<sub>2</sub>N- nitrogen atoms to render them inert to protonation. Globally, these NMR studies provide clear evidence that boronium cations **1** and **2** – and by extension, we posit, **3-5** as well – are highly resistant to hydrolysis under conditions ranging from very acidic to very basic, in sharp contrast to previous reports about (Py)<sub>4</sub>B<sup>3+</sup> (the Bohl cation) and (Pic)<sub>4</sub>B<sup>3+</sup> (Pic = picoline, 4-methylpyridine, the Ryschkewitsch cation).

### Computational analysis

To gain deeper insight into origins of the enhanced stability of cations **1-5**, their geometries were optimized and atomic natural bond order (NBO) partial charges were assigned using Gaussian 16.<sup>10</sup> All structures were optimized under *S*<sub>4</sub> symmetry using the wB97XD density functional method and the 6-31g(d) basis set, followed by evaluation of frequencies, then reoptimized using the cc-pvtz basis set. Subsequently, electrostatic potential maps were generated by Spartan'24 from single-point calculations.<sup>11</sup> Provided in Table 1 are the partial charges on B and both N atoms (where present) on each. Interestingly, the presence of a dialkylamine group in the pyridine 4-position enhances the partial negative charge on the pyridinyl nitrogen in **1-5** relative to those in cations **6** and **7**. In turn, the *p*-methyl group on cation **6** enhances the negative charge on the pyridinyl nitrogen versus that on cation **7**. But notably the **6** vs. **7** negative-charge  $\delta$  of 0.007 is dwarfed by that of 0.043 which exists between that of the average value on cations **1-5** versus cation **7**. This appears to validate our expectation that introducing an R<sub>2</sub>N- substituent in the 4-position of pyridine would result in ligands better able to stabilize the high charge on a boronium (+3) ion center. Indeed, the computed negative charge on the pyridyl nitrogens progressively becomes more negative as the putative donor strength in the 4-position of the pyridine ring increases, and by the same token the positive charge on the boron decreases as the

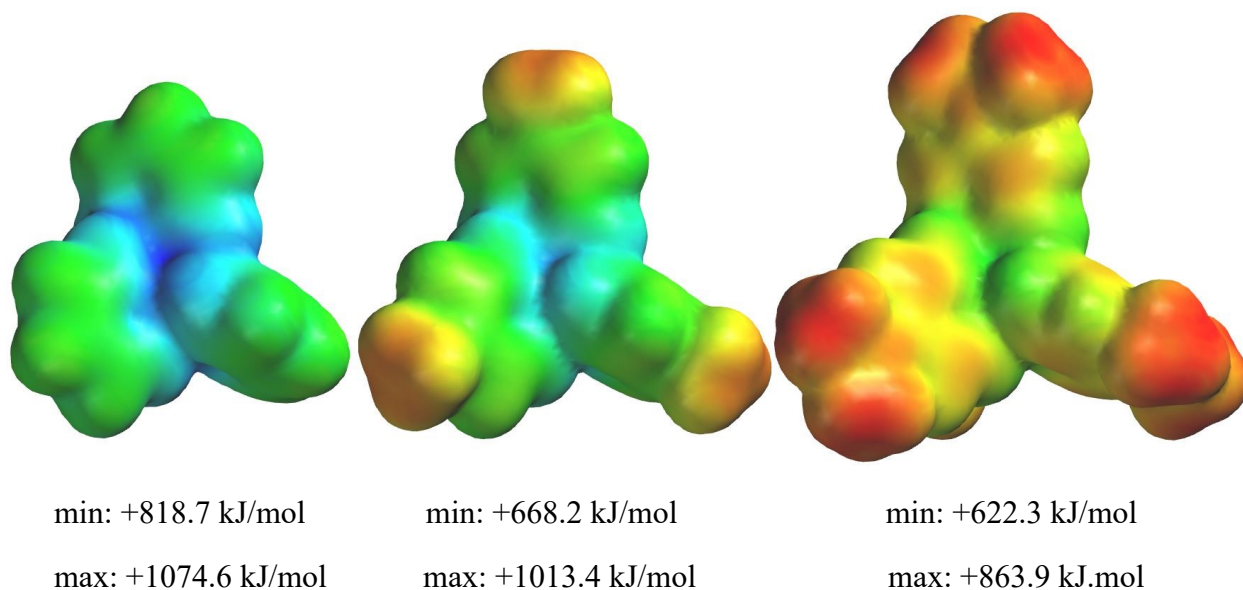
donor strength increases. These general trends can be visually appreciated by comparing the electrostatic potential maps for cations **1**, **6**, and **7** (Figure 2). Consistent with the foregoing, the N-B bond distances in **1-5** are shorter than those in **6** and **7**, suggesting stronger bonds between those atoms in the former group.



| Atom                       | 1      | 2      | 3      | 4      | 5      | 6                   | 7      |
|----------------------------|--------|--------|--------|--------|--------|---------------------|--------|
| Computed partial charges   |        |        |        |        |        |                     |        |
| B                          | 1.074  | 1.064  | 1.072  | 1.066  | 1.082  | 1.104               | 1.118  |
| N (1)                      | -0.579 | -0.582 | -0.583 | -0.581 | -0.568 | -0.543              | -0.536 |
| C (3)                      | 0.288  | 0.290  | 0.291  | 0.292  | 0.272  | 0.174               | -0.035 |
| N (2)                      | -0.306 | -0.315 | -0.313 | -0.318 | -0.332 | N/A                 | N/A    |
| Experimental B-N distances |        |        |        |        |        |                     |        |
|                            | 1.559  | 1.561  | 1.556  | N/A    | 1.561  | 1.585 <sup>12</sup> | N/A    |

**Table 1.** Computed partial charges for select atoms in cations **1-7**, and the experimental B-N bond distances from crystal structures of **1 – 3, 5 & 6**. Note that **6** and **7** are the Ryschkewitsch<sup>6</sup> and Bohl<sup>5</sup> cations, respectively.

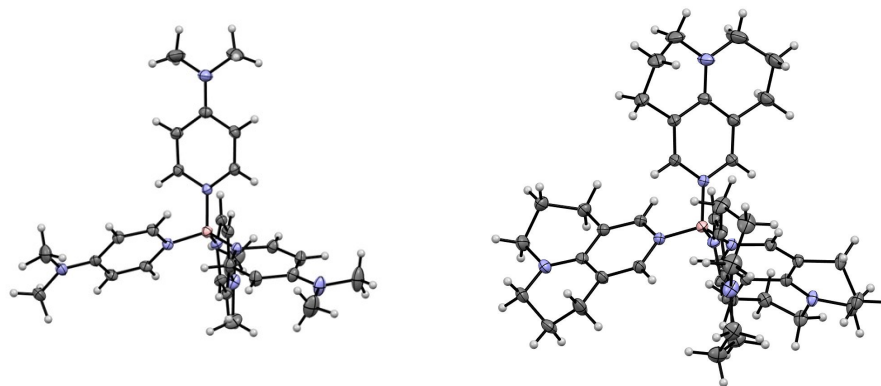




**Figure 2.** Electrostatic potential maps (Elstats) for (left to right) cations **7** (the Bohl cation), **6** (the Ryschkewitsch cation) and **1**, parent cation of the present series. Note how the centroid of the structures becomes less blue [e.g., less positive] from left to right, consistent with the boron center being provided more electron density by the coordinating pyridines. Common color scale: +622.3 (red) to +1074.6 (blue) kJ/mol.

### Crystallographic studies

Colorless, X-ray quality single crystals of the  $\text{Tf}_2\text{N}^-$  salts of cations **1**, **2**, **3** and **5** were obtained by recrystallization of the initial solid products from hot methanol or acetone-methanol mixtures, allowing us to acquire structures (Figure 3) that enabled us to compare the B-N bond distances in the present boroniums with that in the  $(4\text{-MePy})_4\text{B}^{+3}$  (Ryschkewitsch) cation (Table 1). Note that no comparison to the Bohl cation is possible as there is no published X-ray structure of any salt containing it. Also note that while the  $\text{Tf}_2\text{N}^-$  salt of cation **4** produced visually satisfactory crystals, they yielded hopelessly disordered structures even after multiple recrystallizations from different solvents.

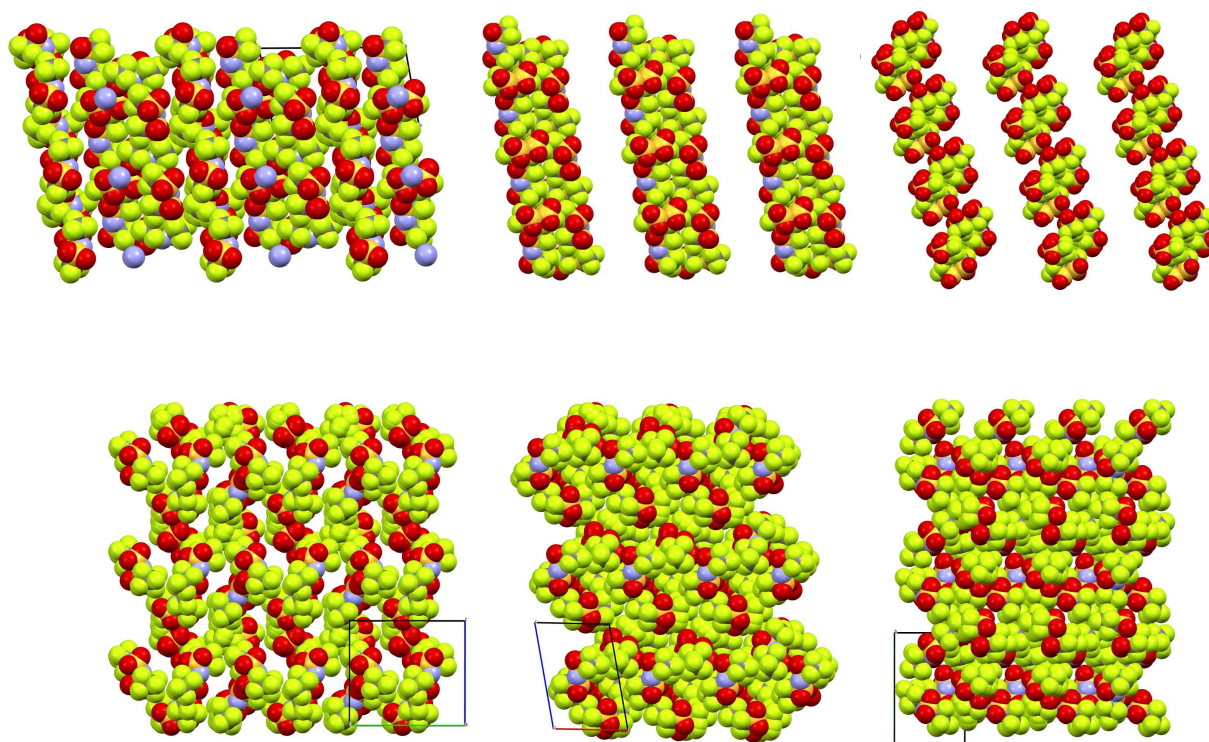


**Figure 3.** ORTEPs of boronium (+3) cations **1** and **5**. The associated  $\text{Tf}_2\text{N}^-$  anions have been omitted for clarity. Additional structures and crystallographic data are provided as Supporting Information.

As shown in Table 1, the B-N bond distances in **1**, **2**, **3**, and **5** are the same within experimental error, consistent with the five DMAP-family ligands having similar electron-donating strength to the boronium center. Further, these distances are significantly shorter than that between N and B in the Ryschkewitsch cation **6**, suggesting a weaker B-N bond in the latter. This is consistent with the longstanding understanding that amine groups are more “electron donating” (better *ortho-para* directors) than are alkyl groups. In accord with the foregoing, the C(3)-N(2) distances in **1**, **2**, **3**, and **5** are such as to suggest that the capacity of their 4-amino groups to ‘push’ electron density into the pyridines were fundamentally the same. Complimenting these data are the computed charges (Table 1) for the boron and pyridine N atoms in boroniums **1-7**. Note that the partial charge on the pyridine Ns in **1-4** are quite close, and that of **5** is relatively close as well, but that there is a sharp drop-off for those in **6** and **7**. Even more significant, the computed degree of positive charge on the Bs of **1-5** are close, but there is a noticeable increase for those in **6** and **7**, the Ryschkewitsch and Bohl cations, respectively.

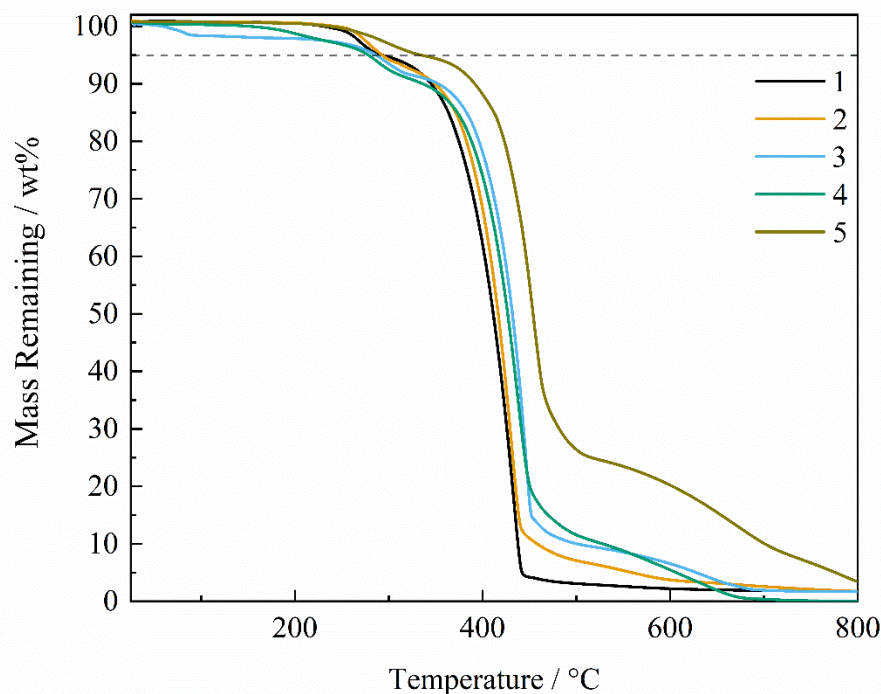
As mentioned earlier, we envision that the present boronium (+3) cations might be useful in crystal engineering, bringing together around them large anions which might ‘overlap’ to create chemically continuous domains. That such an outcome might occur can already be anticipated from the structure of **1**· $\text{Tf}_2\text{N}^-$ , as shown in the cation-free anion packing diagrams shown in Figure 4. Consequently, in order to more fully explore the possibility, we prepared and acquired an X-

ray structure on its counterpart salt **1**·BETI, the latter anion having two additional CF<sub>2</sub> units compared to Tf<sub>2</sub>N<sup>-</sup>. As can likewise be seen in Figure 4, this indeed leads to the formation of continuous, fluorine-rich ribbons in two of the three dimensions of the crystal lattice, strongly supporting our conjecture.



**Figure 4.** Three-axis packing diagrams of the anions in **1**·Tf<sub>2</sub>N (top) and **1**·BETI (bottom). Note the incipient formation of continuous fluorous domains in the former salt, whereas in the latter continuous domains are achieved with the BETI<sup>-</sup> anion, which has an additional CF<sub>2</sub> group on each side of the anion.

#### Thermal and electrochemical stability of boronium (+3) cations



INSERT

**Figure 5.** Thermal decomposition curves of the  $\text{Tf}_2\text{N}^-$  salts of boronium ions **1-5**.

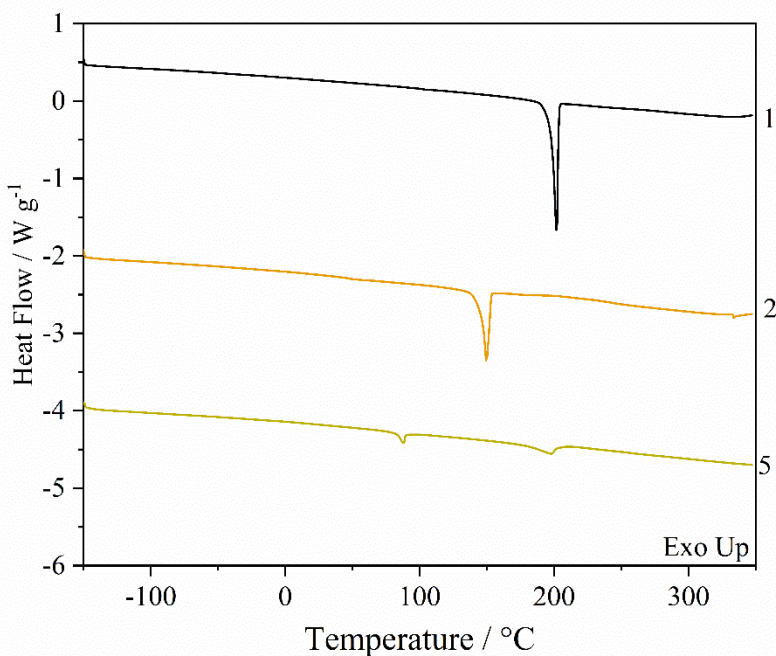
Thermal properties of the suite of the  $\text{Tf}_2\text{N}^-$  salts of cations **1-5** were measured using both TGA and DSC. Though only a single trace is shown, thermal decomposition temperatures ( $T_5$ ) were measured in duplicate to ensure consistency (Figure 5). Remarkably, the boronium (+3) cations exhibited thermal stabilities ( $T_5$ , Table 2) up to 336 °C, nearly 50 °C higher than past reported boronium salts in which the cation contained at least one trialkylamine moiety. Cation **5** exhibited the highest thermal stability (336 °C), on par with some of the highest reported thermal stabilities for both past reported boronium salts and other *onium* salts such as imidazolium, phosphonium, and pyrrolidinium cations.<sup>13,14,15,16,17,18</sup> The increase in  $T_5$  from cations **1-4** to cation **5** suggests that increasing the bulk of the cation may lead to a delay in the onset of whatever mechanism is operative in the thermal decomposition of the salt.<sup>19,20</sup>

| <b>Boronium</b> | <b>T<sub>5</sub> (°C)</b> | <b>T<sub>m</sub> (°C)</b> |
|-----------------|---------------------------|---------------------------|
| <b>1</b>        | 291 ± 2                   | 202                       |
| <b>2</b>        | 295 ± 3                   | 149                       |
| <b>3</b>        | 278 ± 10                  |                           |
| <b>4</b>        | 280 ± 2                   |                           |
| <b>5</b>        | 336 ± 4                   | 89                        |

**Table 2.** Thermal properties for the Tf<sub>2</sub>N<sup>-</sup> salts of boroniums **1-5**.

In addition to thermal stability, the phase behavior of the boronium (+3) herein is also of interest. The high formal charge on each cation, and consequentially higher number of associated anions, leads to salts with melting temperatures well above room temperature for the Tf<sub>2</sub>N<sup>-</sup> salts of **1-5**. Across the board, no glass transitions at low temperatures were observed in the DSC, again likely due to the high formal charge.<sup>12,13,14</sup> On heating, the Tf<sub>2</sub>N<sup>-</sup> salts of **1**, **2**, and **5** all exhibit clean melting behavior at 202, 149, and 89 °C, respectively (Figure 5). We note that the T<sub>m</sub> of **5**•Tf<sub>2</sub>N makes it ‘classifiable’ as an ionic liquid by the frequently used (but arbitrary) metric of being < 100°C.





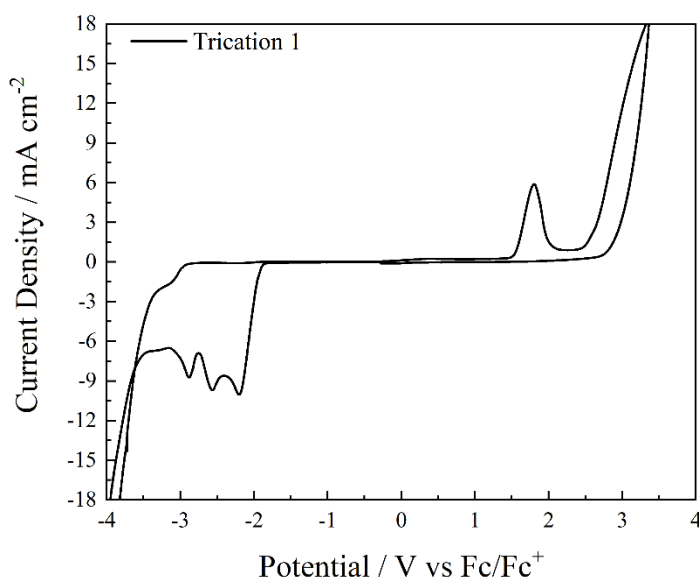
**Figure 6.** Differential scanning calorimetry heating traces of the  $\text{Tf}_2\text{N}^-$  salts of **1**, **2**, and **5**. Samples were first preconditioned at  $50\text{ }^\circ\text{C}$ , then cooled to  $-150\text{ }^\circ\text{C}$  before heating to  $350\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C min}^{-1}$ .

In addition to an initial solid-liquid transition, cation **5** exhibits a second endothermic peak at  $198\text{ }^\circ\text{C}$ , which appears to be a high temperature liquid-liquid transition.<sup>19</sup> Salts **3** and **4** also undergo endothermic transitions at elevated temperatures, though the peaks are broader compared to those of **1**, **2**, and **5**. While less defined, two endothermic peaks can be distinguished from the heating curve of **3**, much like **5**, suggesting similar thermal behavior for the two samples.

### Electrochemical analysis

Preliminary electrochemical analysis was performed on cation **1** to determine a baseline behavior for this novel suite of multivalent boronium salts. The high  $T_m$  for the suite of boronium (+3) salts prevents their direct study as neat electrolytes; Accordingly, solutions in acetonitrile were used to investigate their electrochemical behavior, particularly with respect to electrochemical degradation or the buildup of solid-electrolyte interface (SEI) layers.<sup>20,21</sup>

Sweeping negative from the open circuit potential (OCP) in the presence of cation **1** reveals three irreversible reductions at  $-2.19\text{ V}$ ,  $-2.55\text{ V}$ , and  $-2.87\text{ V}$  (vs  $\text{Fc}/\text{Fc}^+$ ) (Figure 6).



**Figure 7.** Representative cyclic voltammogram of the  $\text{Tf}_2\text{N}^-$  salt of **1**. All scans were conducted at  $50 \text{ mV s}^{-1}$  from  $V_{\text{ocp}}$ , first negative than positive.

For comparison, the structurally similar cation tetraphenylphosphonium ( $\text{PPh}_4^+$ ) monocation exhibits a single reduction potential of  $-3.25 \text{ V}$  (vs  $\text{Fc}/\text{Fc}^+$ ). Many factors, including the formal charge on the cation, electronic nature of the ligands, and the nature of any prospective leaving group can contribute to vastly different reduction potentials between two cations despite similarities in structure.<sup>24</sup> On the return sweep, a single oxidation can be seen at  $1.8 \text{ V}$  (vs  $\text{Fc}/\text{Fc}^+$ ) which is consistent with studies on neat boronium electrolytes. The presence of this peak, which is dependent on initial sweeps beyond the cathodic limit of the cell, is believed to be the oxidation of the solid-electrolyte interface (SEI) layer which assembles at the onset of cation degradation. Continuous sweeping of the electrode reveals reduced cathodic activity, likely due to surface passivation from SEI accumulation, while the intensity and position of the oxidative peak remains consistent. In addition, the  $\text{Tf}_2\text{N}^-$  salts of **2** and **3** were also tested for electrochemical activity in acetonitrile. Unlike the  $\text{Tf}_2\text{N}^-$  salt of cation **1**, both compounds exhibited broad, single step reductions when sweeping from OCP to negative potentials. The oxidation peak observed on return sweeps for cations **2** and **3** was also present, though significantly altered in shape from what was observed for cation **1**. The difference in behavior between these samples suggest potentially different decomposition pathways as the test cell approaches either the cathodic or anodic limiting

potential, warranting further studies on the reductive products of any future boronium (+3) salts as well.

### Conclusions

By using strongly electron-donating 4-aminopyridines as ligands, bromide salts of boronium (+3) cations can be formed which are stable in water on a pH-independent basis, a heretofore unprecedented achievement. The salts produced undergo clean but irreversible electrochemical reductions. That, coupled with the high thermal stabilities measured for the  $\text{Tf}_2\text{N}^-$  salts of these cations, indicates that further studies on these species as electrolytes or additives to existing electrolytic cell designs is warranted. Additionally, X-ray crystal structures support the proposition that these cations of 3+ charge can serve as templating tectons for the assembly around them of large anions, leading to the creation of continuous anion domains in the crystal lattice, making them promising materials for application in crystal engineering.

### **Acknowledgements**

The authors thank the National Science Foundation (NSF Award number CHE 2102978 and subaward A21-0189-S001) for support of this work. Computational work was made possible in part by a grant of high-performance computing resources and technical support from the Alabama Supercomputer Authority. A portion of this work was also funded through a grant from the Army Research Office (MIPR #12005747). Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the U.S. Navy or the U.S. Army.

### **References**

1. Ling, I., Skelton, B. W., Sobolev, A. N., Alias, Y., Khor, Z. C., Raston, C. L. Effects of anions on the solid-state interplay of symmetric and unsymmetric phosphonium cations, *New J. Chem.*, **2020**, *44*, 10220-10228. Doi: 10.1039/d0nj01975e



2. Teodoro, J. S., Palmeira, C. M., Rolo, A. P., Mitochondrial membrane potential ( $\Delta P\Psi$ ) fluctuations associated with the metabolic states of mitochondria, *Methods in Molecular Biology*, **2018**, 1782, 109-119. ISBN-13: 978-1493978304
3. Díaz Morales, U. M., Corma Canós, A. Organic-Inorganic Hybrid Materials: Multi-Functional Solids for Multi-Step Reaction Processes. *Chem. Eur. J.*, **2018**, 24(16), 3944-3958. Doi: 10.1002/chem.201704185
4. Kore, B., Jamshidi, M., Gardner, J. M. The impact of moisture on the stability and degradation of perovskites in solar cells, *Mater. Adv.*, **2024**, 5, 2200-2217. Doi: 10.1039/D3MA00828B
5. Bohl, R. D., Galloway, G. L., The Synthesis of some compounds containing trivalent boron cations, *J. Inorg. Nucl. Chem.* **1971**, 33, 885-887. Doi: 10.1016/0022-1902(71)80494-3
6. Makosky, C. W., Galloway, G. L., Ryschkewitsch, G. E., The Synthesis of some compounds containing trivalent boron cations, *Inorg. Chem.*, **1967**, 6, 1972-1974. Doi: 10.1021/ic50057a006
7. Tandom, R., Unzner, T., Nigst, T. A., De Rycke, N., Mayer, P., Wendt, B., David, O. R. P. Zipse, K., Annelated Pyridines as Highly Nucleophilic and Lewis Basic Catalysts for Acylation Reactions, *Chem. Eur. J.*, **2013**, 19, 6435-6442. Doi: 10/1002/chem.201204452
8. Wilde, J. H., Smith, J. A., Dickie, D. A., Harman, W. D. Molybdenum-Promoted Synthesis of Isoquinuclidines with Bridgehead CF<sub>3</sub> Groups, *J. Am. Chem. Soc.*, **2019**, 141(47), 18890-18899. Doi: 10.1021/jacs.9b10781

9. Forsythe, P.; Frampton, R.; Johnson, C. D.; Katritzky, A. R., Acidity functions and the protonation of weak bases. Part VII. The protonation behaviour of dimethylaminopyridines and their N-oxides, *J. Chem. Soc., Perkin Trans. 2* **1972**, 671-673. Doi:10.1039/P29720000671
10. Gaussian 16, Revision C.01, Frisch, M. J., et al.; Wallingford CT, 2016; NBO Version 3.1, Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.
11. Wavefunction Inc., Irvine, CA, 2024
12. Vargas-Baca, I, Findlater, M., Powell, A., Vasudevan, K. V., Cowley, A. H., Boron di- and tri-cations, *Dalton Trans.*, **2008**, 6421-6426. Doi: 10.1039/b810575h
13. Fox, P. A.; Griffin, S. T.; Reichert, W. M.; Salter, E. A.; Smith, A.B.; Tickell, M.D.; Wicker, B. F.; Cioffi, E.A.; Davis, J.H., Jr.; Rogers, R. D.; Wierzbicki, A. Exploiting isolobal relationships to create new ionic liquids: novel room-temperature ionic liquids based upon (N-alkylimidazole) (amine)BH<sub>2</sub><sup>+</sup>"boronium" ions. *Chem. Commun.* **2005** (Aug 7): 3679-3681; Doi: 10.1039/B504631A
14. Ruther, T.; Huynh, T. D.; Huang, J.; Hollenkamp, A. F.; Salter, E. A.; Wierzbicki, A.; Mattson, K.; Lewis, A.; Davis, J. H., Jr. Stable cycling of lithium batteries using novel Boronium-cation-based ionic liquid electrolytes. *Chem.Mater.* **2009** (Dec. 16); 22(3):1038-1045. Doi: 10.1021/cm9019815
15. Stachurski, C. D.; Davis, J. H., Jr.; Cosby, T.; Crowley, M. E.; Larm, N. E.; Ballentine, M. G.; O'Brien, R. A.; Zeller, M.; Salter, E. A.; Wierzbicki, A.; Trulove, P. C.; Durkin, D. P. Physical and Electrochemical Analysis of N-Alkylpyrrolidinium-Substituted

Boronium Ionic Liquids. *Inorg. Chem.* **2023** (Oct. 23); 62(44): 18280-18289. Doi: 10.1021/acs.inorgchem.3c02971

16. Fredlake, C. P., Crosthwaite, J. M., Hert, D. G., Aki, S. N. V. K., Brennecke, J. F., Thermophysical Properties of Imidazolium-Based Ionic Liquids, *J. Chem. Eng. Data*, **2004**, 49(4), 954-964. Doi: 10.1021/je034261a
17. Del Sesto, R. E., Corley, C., Robertson, A., Wilkes, J. S., Tetraalkylphosphonium-based ionic liquids, *J. Organomet. Chem.*, **2005**, 690(10), 2536-2542.  
Doi:10.1016/j.jorganchem.2004.09.060
18. M. Malarz, K., Mrozek-Wilczkiewicz, A., Musiol, R., Zorębski, E., Dzida, M., Pyrrolidinium-Based Ionic Liquids as Sustainable Media in Heat-Transfer Processes, *ACS Sus. Chem. Eng.*, **2017**, 5 (11), 11024-11033. Doi: 10.1021/acssuschemeng.7b02918
19. Cao, Y., Mu, T, Comprehensive Investigation on the Thermal Stability of 66 Ionic Liquids by Thermogravimetric Analysis *Ind. Eng. Chem. Res.*, **2014**, 53 (20), 8651-8664  
Doi: 10.1021/ie500959
20. Soltani, M., McGeehee, J. L., Stenson, A. C., O'Brien, R. A., Duranty, E. R., Salter, E. A., Wierzbicki, A., Glover, T. G., Davis, J. H., Jr., Ionic liquids of superior thermal stability. Validation of PPh<sub>4</sub><sup>+</sup> as an organic cation of impressive thermodynamic durability, *RSC Adv.*, **2020**, 10, 35, 20521-20528. Doi: 10.1039/D0RA03220D
21. Harris, M. A., Kinsey, T. Wagle, D. V., Sangoro, J., Evidence of a liquid–liquid transition in a glass-forming ionic liquid, *Proc. Nat. Acad. Sci.*, **2021**, 118 (11), e2020878118. Doi:10.1073/pnas.2020878118

22. Clarke-Hannaford, J., Breedon, M., R  ther, T., Spencer, M. J. S., Stability of Boronium Cation-Based Ionic Liquid Electrolytes on the Li Metal Anode Surface, *ACS Appl. Energy Mater.*, **2020** 3 (6), 5497-5509. Doi:10.1021/acsaem.0c00482
23. Clarke-Hannaford, J., Breedon, M., R  ther, T., Johansson, P., Spencer, M. J. S. Spectroscopic and Computational Study of Boronium Ionic Liquids and Electrolytes, *Chemistry*, **2021**, 27(50), 12826-12834. Doi: 10.1002/chem.202101576
24. Lang, C. M., Kim, K., Guerra, L., Kohl, P. A., Cation Electrochemical Stability in Chloroaluminate Ionic Liquids, *J. Phys. Chem. B* **2005** 109 (41), 19454-19462. Doi: 10.1021/jp053106v