

# Synthesis of a new family of fluorinated boronate compounds as anion receptors and studies of their use as additives in lithium battery electrolytes

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## 1. Introduction

Numerous studies have been done on developing new electrolytes for lithium batteries with high ionic conductivity, and good chemical and electrochemical stability. In addition to the research on new salts and solvents, the use of cation receptors to reduce ion pairing in non-aqueous electrolytes has been considered as an approach to improve the properties of electrolytes [1]. Although, both cation and anion receptors enhance the dissociation of ion pairs and increase the conductivity of electrolytes, the use of anion receptors is more attractive for a lithium battery electrolyte, because anion receptors increase the lithium transference number in the electrolyte. However, most available neutral anion receptors complex with anions through hydrogen binding and cannot be used in lithium batteries [2]. Recently, we have reported on synthesis of a series of new neutral boron compounds as anion receptors based on the idea that electron-deficient boron would complex the anion of the ion pair. The anion complexation effect of these boron compounds was further enhanced by attaching electron-withdrawing groups [3,4]. Here we report synthesis of another new family of boronate compounds. The effect of these new compounds on conductivity of lithium salts in non-aqueous solution was studied. The molecular weights of these new boronate compounds are lower than our previously reported boron compounds. Therefore, their effects on conductivity enhancement are superior. They also display high electrochemical stability up to 5 V.

## 2. Experimental

Nine fluorinated 1,3,2-benzodioxaborole and 1,3,2-dioxaborolane compounds were synthesized in our laboratory.

The chemical structure of these compounds was shown in Fig. 1. The synthesis procedure of compounds (1), (2) and (3) are sketched in Fig. 2. The followings are the outlines of these procedures.

### 2.1. 2-(2,4-Difluorophenyl)-4-fluoro-1,3,2-benzodioxaborole (1)

3-Fluorocatechol (3.84 g, 0.03 mol) and 2,4-difluoroboric acid (4.73 g, 0.03 mol) were mixed in 40 ml of toluene. The mixture was heated to reflux. Water from condensation reaction was removed by distillation. After 4 h of reaction, the solvent was evaporated from reaction mixture under reduced pressure. The residue was sublimed at 98–100°C/0.1 mm-Hg. The final product (7.2 g of white crystal powder) was obtained in 96% yield. Melting point: 112°C. NMR (CDCl<sub>3</sub> ppm),  $\delta$ : 6.7–7.2 (m, 5H), 7.8–8.3 (m, 1H). IR (neat per cm),  $\nu$ : 3082.7, 1613.0, 1499.4, 1462.4, 1422.6, 1393.3, 1368.5, 1331.9, 1268.9, 1173.6, 1140.3, 1103.5, 1057.7, 1025.0, 968.7, 853.3, 774.7, 725.5, 653.4.

### 2.2. 2-(3-Trifluoromethyl phenyl)-4-fluoro-1,3,2-benzodioxaborole (2)

The same synthesis procedure as for compound (1) was used. 3-fluorocatechol reacted with equivalent 3-trifluoromethylboronic acid to yield 95% pure product. Melting point: 81–82°C. NMR (CDCl<sub>3</sub> ppm),  $\delta$ : 6.8–7.4 (m, 3H), 7.5–8.1 (m, 2H), 8.2–8.5 (m, 2H). IR (neat per cm),  $\nu$ : 3059.5, 1632.7, 1499.7, 1462.5, 1376.1, 1301.9, 1171.3, 1131.0, 1080.0, 1026.9, 917.7, 847.7, 808.7, 774.7, 721.7, 701.1, 605.7.

### 2.3. 2,5-Bis(trifluoromethyl phenyl)-4-fluoro-1,3,2-benzodioxaborole (3)

The same synthesis procedure as for compound (1) was used.

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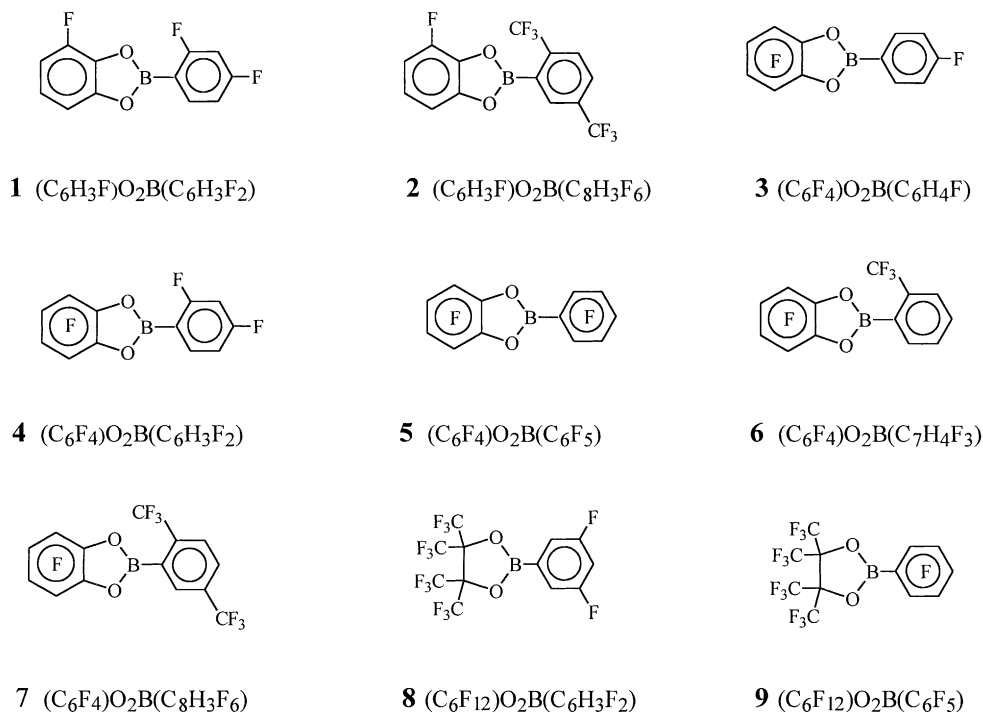
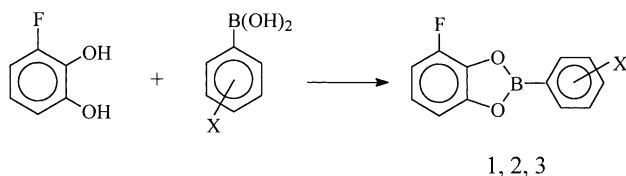


Fig. 1. Chemical structures of boronate-based anion receptors.



- 1 X= 2,4- difluoro
- 2 X= 3-trifluoromethyl
- 3 X= 2,5-ditrifluoromethyl

Fig. 2. Synthesis procedure of fluorinated 1,3,2-benzodioxaborole compounds (1), (2), and (3).

Electrolyte conductivity measurements were made on a Hewlett-Packard 4129A Impedance Analyzer using a cell with Pt electrodes. Electrochemical stability measurements were performed using a Solatron SI 1287 Electrochemical Interface in the potential dynamic mode.

### 3. Results and discussion

The ionic conductivity of electrolytes based on the lithium salts,  $CF_3CO_2Li$  and  $C_2F_5CO_2Li$ , dissolved in DME are very low, with respective conductivities of only  $3.3 \times 10^{-5}$  and  $2.1 \times 10^{-5}$  S/cm at concentrations of 0.2 M. LiF is insoluble in this solvent. With addition of stoichiometric amounts of compound (1) as an additive, the conductivities of 0.2 M solutions of  $CF_3CO_2Li$  and  $C_2F_5CO_2Li$  salts in DME were greatly increased to  $1.24 \times 10^{-3}$  and  $1.1 \times 10^{-3}$  S/cm, respectively, as shown in Table 1. The conductivity enhancement effect of these compounds increases with increasing number of the electron withdrawing groups. When compound (4) was used as an additive, even LiF was dissolved in DME at concentrations as high as 1.2 M. The conductivity of the solutions containing  $CF_3CO_2Li$  and  $C_2F_5CO_2Li$  salts were increased to  $7.5 \times 10^{-3}$  and  $7.59 \times 10^{-3}$  S/cm, respectively at a concentration of 0.8 M in DME, as shown in

Table 1  
Ionic conductivity of compound (1) + lithium salt in DME solutions

Concentration of compound (1) (M)	Concentration of lithium salt (M)	Conductivity $CF_3COOLi$ (S/cm)	Conductivity $C_2F_5COOLi$ (S/cm)	Conductivity LiF (S/cm)
0	0.2	$3.3 \times 10^{-5}$	$2.1 \times 10^{-3}$	a
0.2	0.2	$1.24 \times 10^{-3}$	$1.1 \times 10^{-3}$	a
0.4	0.4	$2.83 \times 10^{-3}$	$2.73 \times 10^{-3}$	a
0.6	0.6	$3.83 \times 10^{-3}$	$3.69 \times 10^{-3}$	a
0.8	0.8	$4.20 \times 10^{-3}$	$4.07 \times 10^{-3}$	a
1.0	1.0	$3.96 \times 10^{-3}$	$3.86 \times 10^{-3}$	a
1.2	1.2	$3.40 \times 10^{-3}$	$3.35 \times 10^{-3}$	a

<sup>a</sup> The solubility of LiF was very low, therefore, the conductivity was not measured.

Table 2  
Ionic conductivity of compound (4) + lithium salt in DME solutions

Concentration of compound (4) (M)	Concentration of lithium salt (M)	Conductivity CF <sub>3</sub> COOLi (S/cm)	Conductivity C <sub>2</sub> F <sub>5</sub> COOLi (S/cm)	Conductivity LiF (S/cm)
0	0.2	$3.3 \times 10^{-5}$	$2.1 \times 10^{-5}$	<sup>a</sup>
0.2	0.2	$3.50 \times 10^{-3}$	$3.92 \times 10^{-3}$	<sup>a</sup>
0.4	0.4	$6.15 \times 10^{-3}$	$6.60 \times 10^{-3}$	<sup>a</sup>
0.6	0.6	$7.47 \times 10^{-3}$	$7.59 \times 10^{-3}$	$2.20 \times 10^{-3}$
0.8	0.8	$7.50 \times 10^{-3}$	$7.09 \times 10^{-3}$	$2.75 \times 10^{-3}$
1.0	1.0	$6.91 \times 10^{-3}$	$5.62 \times 10^{-3}$	$3.03 \times 10^{-3}$
1.2	1.2	$5.25 \times 10^{-3}$	$4.15 \times 10^{-3}$	$3.15 \times 10^{-3}$

<sup>a</sup> LiF was only partially dissolved in these solutions, therefore, the conductivity was not measured.

Table 3  
Ionic conductivity of compound (5) + lithium salt in DME solutions

Concentration of compound (5) (M)	Concentration of lithium salt (M)	Conductivity CF <sub>3</sub> COOLi (S/cm)	Conductivity C <sub>2</sub> F <sub>5</sub> COOLi (S/cm)	Conductivity LiF (S/cm)
0	0.2	$3.3 \times 10^{-5}$	$2.1 \times 10^{-5}$	<sup>a</sup>
0.2	0.2	$4.11 \times 10^{-3}$	$4.52 \times 10^{-3}$	$3.58 \times 10^{-3}$
0.4	0.4	$7.51 \times 10^{-3}$	$7.67 \times 10^{-3}$	$6.85 \times 10^{-3}$
0.6	0.6	$9.00 \times 10^{-3}$	$8.92 \times 10^{-3}$	$8.98 \times 10^{-3}$
0.8	0.8	$8.24 \times 10^{-3}$	$8.10 \times 10^{-3}$	$9.54 \times 10^{-3}$
1.0	1.0	$7.76 \times 10^{-3}$	$6.49 \times 10^{-3}$	$9.00 \times 10^{-3}$
1.2	1.2	$6.62 \times 10^{-3}$	$4.67 \times 10^{-3}$	$7.68 \times 10^{-3}$

<sup>a</sup> The solubility of LiF was very low, therefore, the conductivity was not measured.

Table 4  
Ionic conductivity of compound (9) + lithium salt in DME solutions

Concentration of compound (9) (M)	Concentration of lithium salt (M)	Conductivity CF <sub>3</sub> COOLi (S/cm)	Conductivity C <sub>2</sub> F <sub>5</sub> COOLi (S/cm)	Conductivity LiF (S/cm)
0	0.2	$3.3 \times 10^{-5}$	$2.1 \times 10^{-5}$	<sup>a</sup>
0.2	0.2	$4.30 \times 10^{-3}$	$4.57 \times 10^{-3}$	$3.47 \times 10^{-3}$
0.4	0.4	$7.07 \times 10^{-3}$	$7.16 \times 10^{-3}$	$6.13 \times 10^{-3}$
0.6	0.6	$7.83 \times 10^{-3}$	$7.72 \times 10^{-3}$	$4.53 \times 10^{-3}$
0.8	0.8	$6.74 \times 10^{-3}$	$6.27 \times 10^{-3}$	$7.48 \times 10^{-3}$
1.0	1.0	$4.69 \times 10^{-3}$	$3.97 \times 10^{-3}$	$6.55 \times 10^{-3}$
1.2	1.2	$2.86 \times 10^{-3}$	$1.91 \times 10^{-3}$	$5.10 \times 10^{-3}$

<sup>a</sup> The solubility of LiF was very low, therefore, the conductivity was not measured.

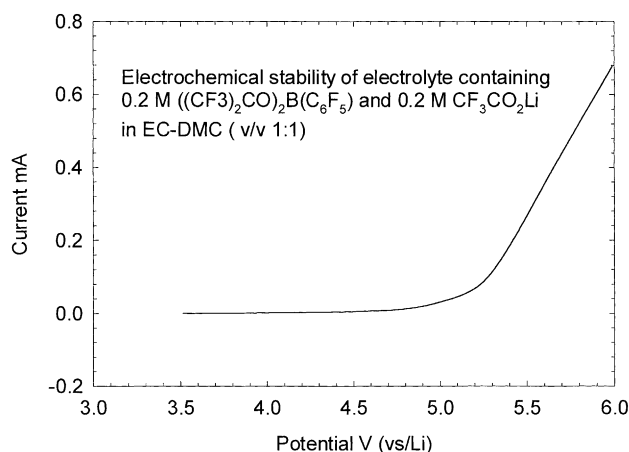


Fig. 3. Electrochemical stability of boronate-based anion receptors.

Table 2. When the fully fluorinated compound (5) was used as an additive, the conductivity of LiF solutions in DME reached as high as  $9.54 \times 10^{-3}$  S/cm at 0.8 M, as shown in Table 3. The conductivity results for DME solutions containing compound (9) and lithium salts are listed in Table 4.

The electrochemical stability studies were carried out using a Solatron SI 1287 Electrochemical Interface in potential dynamic mode at a scan rate of 20 mV/s. The resulting curve is plotted in Fig. 3. The electrolyte made of compound (9), LiF salt and EC/DMC solvent has excellent electrochemical stability at voltage versus Li as high as 5 V.

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### **References**

- [1] M.C. Lonergan, M.A. Ratner, D. Shriver, *J. Am. Chem. Soc.* 117 (1995) 2344.
- [2] F.P. Schmidtchen, M. Berger, *Chem. Rev.* 97 (1997) 1609.
- [3] H.S. Lee, X.Q. Yang, C.L. Xiang, J. McBreen, L.S. Choi, *J. Electrochem. Soc.* 145 (1998) 2813.
- [4] X. Sun, H.S. Lee, S. Lee, X.Q. Yang, J. McBreen, *Electrochem. Solid State Lett.* 1 (1998) 39.