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Synthesis of a Series of Fluorinated Boronate Compounds and Their Use as Additives in Lithium Battery Electrolytes

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A new series of anion receptors based on boronate compounds have been synthesized. These compounds can be used as anion receptors in lithium battery electrolytes. The so-called boronate means that the compounds contain a boron bonded with two oxygen atoms and one carbon atom. This series includes various boronate compounds with different fluorinated aryl and fluorinated alkyl groups. When these anion receptors are used as additives in 1,2-dimethoxyethane (DME) solutions containing various lithium salts, the ionic conductivities of these solutions are greatly increased. The electrolytes tested in this study were DME solutions containing the following lithium salts: LiF, CF_3COOLi, and C_2F_5COOLi. Without the additive, the solubility of LiF in DME (and all other nonaqueous solvents) is very low. With some of these boronate compounds as additives, LiF solutions in DME with concentration as high as 1 M were obtained. The solubilities of the other salts were also increased by these additives. Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy studies show that I^- anions are complexed with these compounds in DME solutions containing LiI salts. The degree of complexation is also closely related to the structures of the fluorinated aryl and alkyl groups which act as electron-withdrawing groups. The NEXAFS results are in good agreement with ionic conductivity studies.

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Numerous studies on developing new cathode and anode materials for lithium batteries have been reported. In contrast, studies on developing new electrolyte systems somewhat lag behind. Recent studies[1,2] have shown that the low thermal stability of $LiPF_6$-based electrolyte plays an important role in the capacity fading of lithium-ion batteries during cycling. Therefore, the development of new electrolyte systems with high ionic conductivity, and good chemical and electrochemical stability will help to improve the cycling life of lithium-ion batteries. Studies on a new electrolyte using a boron-containing lithium salt bis(oxalato) borate (LiBOB)[3,4] have shown the advantages of the higher electrochemical stability of this new system. The potential of using boron-containing compounds in nonaqueous electrolytes is attracting more and more attention from both the academic and industrial communities. In our previous publications,[5,6] it has been demonstrated that using anion receptors as additives can significantly reduce ion pairing in nonaqueous electrolytes. These types of anion receptors can be used in two ways. One is to use them as additives to improve the properties of currently used electrolytes;[1] the other is to use them in combination with various salts to develop new electrolyte systems. Here we report the synthesis of a series of boronate compounds. The effect of these new compounds on conductivity of lithium salts in nonaqueous solution was studied. The molecular weights of most of these new boronate compounds are lower than our previously reported boron compounds, and many of them are liquids at room temperature. Therefore, their effects on conductivity enhancement are superior. The effects on anion complexation were investigated by near-edge X-ray absorption spectroscopy. Electrolytes using some compounds in this series display high electrochemical stability up to 5 V. Although the molecular structures and the synthesis of some compounds in this new series of boronate compounds had been briefly described in our previous publication,[7,8] detailed and systematic study of the series reported here provides more complete information about these compounds.

Experimental

Synthesis and characterization.—Fourteen fluorinated 1,3,2-benzodioxaborole and 1,3,2-dioxaborolane compounds synthesized in our laboratory are reported here. The chemical structures of these compounds were shown in Fig. 1. The starting materials were purchased from Aldrich Chemical Co. All the reactions and processes were performed under an argon atmosphere or under vacuum. Proton nuclear magnetic resonance (HNMR) spectra were recorded on a Hitachi R-1200 (60 MHz) spectrometer. The synthesis procedures of compounds (1), (2), and (3) are sketched in Fig. 2. The following are the outlines of these procedures:

Compound (1).—2-(2.4-Difluorophenyl)-4-fluoro-1,3,2-benzodioxaborole, or $(C_6H_3F)O_2B(C_6H_3F_2)$. 3-fluorocatechol (3.84 g, 0.03 mol) and 2,4-difluoroboronic acid (4.73 g, 0.03 mol) were mixed in 40 mL toluene. The mixture was heated to reflux. Water from condensation reaction was removed by azeotropic distillation. After 4 h of reaction, the solvent was evaporated from the 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) was obtained in 96% yield. Melting point: 112°C. HNMR ($CDCl_3$ ppm) δ: 6.7-7.2 (m, 5H), 7.8-8.3 (m, 1H). IR (neat cm^{-1}), ν 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.

Compound (2).—2-(3-Trifluoromethyl phenyl)-4-fluoro-1,3,2-benzodioxaborole, or $(C_6H_3F)O_2B(C_7H_4F_3)$. The same synthesis procedure as for compound (1) was used. 3-Fluorocatechol reacted

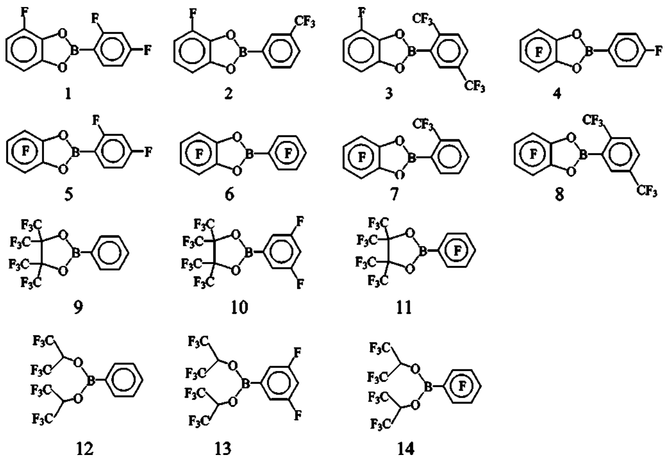

Figure 1. Chemical structure of boronate-based anion receptors. The numbers under the structures correspond to the compound number in the text.

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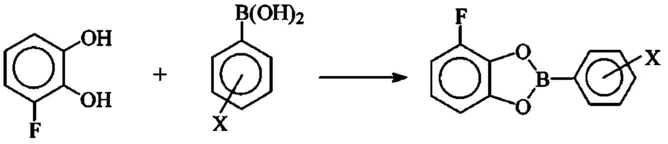


1, 2, 3

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

Figure 2. Scheme of synthesis steps of compounds (1-3).

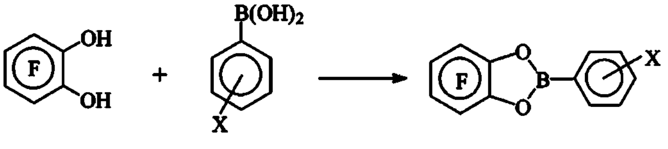
with equivalent 3-trifluoromethylboronic acid to yield 95% pure product. Melting point: 81-82°C. HNMR ($CDCl_3$ ppm) δ 6.8-7.4 (m, 3H), 7.5-8.1 (m, 2H), 8.2-8.5 (m, 2H). IR (neat cm^{-1}), ν 3059.5, 1632.7, 1499.7, 1462.5, 1376.1, 1301.9, 1171.3, 1131.0, 1080.0, 1026.9, 917.7, 847.7, 808.7, 774.7, 721.7, 701.1, 605.7.

2,5-Bis(trifluoromethyl)phenylboronic acid, an intermediate compound. 160 mL of 2.5 M butyl lithium in hexane was mixed with 400 mL of anhydrous ether. 77.2 g (0.27 M) of 1,4-bis(trifluoromethyl)benzene was added dropwise to this solution at room temperature. After refluxing for 6 h, the solution was added dropwise, over a 1 h period, from a dropping funnel, to a flask in an ice bath containing 100 mL trimethylborate mixed with 400 mL ether. The mixture was further stirred for 2 h at room temperature. Then the mixture was poured into an aqueous ammonium chloride solution. The ether layer was separated and washed with water. The product was dried over magnesium sulfate. The solvent was evaporated and a crystalline of the product was formed. Pentane was added to precipitate out all the crystals. The crude product was filtered out and further purified through recrystallization. The yield was 21 g, and the melting point was 133-135°C.

Compound (3).—2,5-Bis(trifluoromethyl)phenyl-4-fluoro-1,3,2-benzodioxaborole, or $(C_6H_3F)O_2B(C_8H_3F_6)$. The same synthesis procedure as for compound (1) was used. 2.56 g of 3-fluorocatechol was condensed with 5.16 g of 2,5-bis(trifluoromethyl)phenylboronic acid to obtain 6.8 g of pure product (sublimed at 120°C/0.3 mm Hg). The yield was 92%. The melting point of the compound was 81-83°C. HNMR (Acetone-d6 ppm) δ: 7-7.4 (m, 3H), 8.1-8.25 (m, 2H), 8.6 (s, 1H).

The synthesis procedure of compounds (4-8) was similar as described for compound (1) and is sketched in Fig. 3.

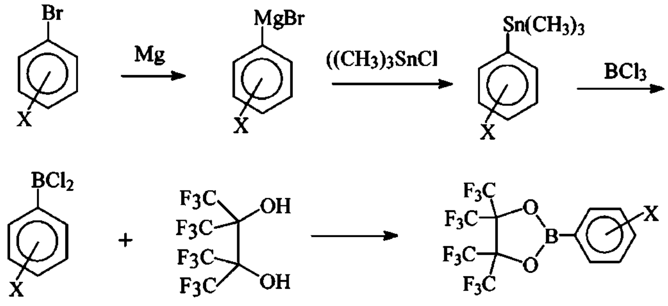
Compound (4).—2-(4-Fluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole or $(C_6F_4)O_2B(C_6H_4F)$. 3.3 g of tetrafluorocatechol was condensed with 2.5 g of 4-fluoroboronic acid to obtain 5 g of crude product. It was sublimed at 135°C/(0.15 mm Hg) twice to obtain 4 g of pure product. The melting point of the compound was 128-130°C.



4, 5, 6, 7, 8

4 X= 4- difluoro
5 X= 2,4-difluoro
6 X= pentafluoro
7 X= 2-trifluoromethyl
8 X= 2,5-ditrifluoromethyl

Figure 3. Scheme of synthesis steps of compounds (4-8).



9, 10, 11

9 X= 5H
10 X= 3,5- difluoro
11 X= pentafluoro

Figure 4. Scheme of synthesis steps of compounds (9-11).

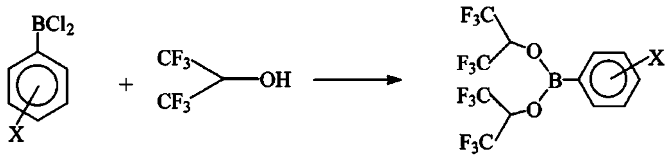
Compound (5).—2-(2,4-Difluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole (5) or $(C_6F_4)O_2B(C_6H_3F_2)$. The crude product was obtained from 3.64 g of tetrafluorocatechol and 3.16 g of 2,4-difluorophenylboronic acid. The crude product was sublimed at 125°C/0.2 mm Hg to obtain 5.7 g of pure compound. The melting point of the compound was 112-114°C. HNMR [dimethyl sulfoxide (DMSO)-d6 ppm] δ: 6.7-7.2 (m, 2H), 7.3-7.7 (m, 1H).

Compound (6).—2-(Pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole or $(C_6F_4)O_2B(C_6F_5)$. 3.64 g of tetrafluorocatechol was condensed with 4.2 g pentafluoroboronic acid. The crude product was then sublimed at 110°C/0.1 mm Hg to obtain 6.2 g of pure compound. The melting point of the compound was 131-132°C.

Compound (7).—2-(2-Trifluoromethyl phenyl)-tetrafluoro-1,3,2-benzodioxaborole or $(C_6F_4)O_2B(C_7H_4F_3)$. 3.3 g of tetrafluorocatechol was reacted with 3.42 g of 2-trifluoromethylphenylboronic acid to obtain 5.9 g of crude product. The crude product was then sublimed at 110°C/0.1 mm Hg to obtain 5.2 g of pure compound. The melting point of the compound was 102-103°C. HNMR (acetone-d6 ppm) δ: 7.8-8.1 (m, 3H), 8.2-8.4 (m, 1H).

Compound (8).—2,5-Bis(trifluoromethyl phenyl)-tetrafluoro-1,3,2-benzodioxaborole or $(C_6F_4)O_2B(C_8H_3F_6)$. 3.2 g of tetrafluorocatechol was condensed with 5.16 g of 2,5-bis(trifluoromethyl)phenylboronic acid to obtain the crude compound. The crude product was distilled using a Kugelrohr at 105-110°C/0.3 mm Hg. After cooling, crystals were formed and the yield was 7.4 g. The melting point of the compound was 81-83°C. HNMR (Acetone-d6 ppm) δ: 8.05-8.2 (m, 2H), 8.6 (s, 1H).

The synthesis procedure of compounds (9-11) are sketched in Fig. 4. The following are the outlines of these procedures:



12, 13, 14

12 X= 5H
13 X= 3,5- difluoro
14 X= pentafluoro

Figure 5. Scheme of synthesis steps of compounds (12-14).

Table I. Ionic conductivity of 0.8 M boronate compounds + lithium salts in DME.

Boronate compounds	Conductivity CF_3COOLi (S/cm)	Conductivity C_2F_5COOLi (S/cm)	Conductivity LiF (S/cm)	Group number of compounds
	3.3×10^{-5}	2.1×10^{-5}	[a]	
1. $(C_6H_3F)O_2B(C_6H_3F_2)$	4.20×10^{-3}	4.07×10^{-3}	[a]	1
2. $(C_6H_3F)O_2B(C_7H_4F_3)$	4.59×10^{-3}	3.57×10^{-3}	[a]	1
3. $(C_6H_3F)O_2B(C_8H_3F_6)$	4.67×10^{-3}	4.57×10^{-3}	[a]	1
4. $(C_6F_4)O_2B(C_6H_4F)$	4.20×10^{-3}	4.07×10^{-3}	1.00×10^{-3}	2
5. $(C_6F_4)O_2B(C_6H_3F_2)$	7.50×10^{-3}	7.09×10^{-3}	2.75×10^{-3}	2
6. $(C_6F_4)O_2B(C_6F_5)$	8.24×10^{-3}	8.10×10^{-3}	9.54×10^{-3}	2
7. $(C_6F_4)O_2B(C_7H_4F_3)$	6.56×10^{-3}	6.14×10^{-3}	3.06×10^{-3}	2
8. $(C_6F_4)O_2B(C_8H_3F_6)$	6.60×10^{-3}	6.00×10^{-3}	3.42×10^{-3}	2
9. $(C_6F_{12})O_2B(C_6H_5)$	5.65×10^{-3}	5.79×10^{-3}	2.31×10^{-3}	3
10. $(C_6F_{12})O_2B(C_6H_3F_2)$	7.37×10^{-3}	6.44×10^{-3}	6.97×10^{-3}	3
11. $(C_6F_{12})O_2B(C_6F_5)$	6.74×10^{-3}	6.27×10^{-3}	7.48×10^{-3}	3
12. $(C_3HF_6O)_2B(C_6H_5)$	6.45×10^{-3}	[b]	4.78×10^{-3}	4
13. $(C_3HF_6O)_2B(C_6H_3F_2)$	7.80×10^{-3}	[b]	4.75×10^{-3}	4
14. $(C_3HF_6O)_2B(C_6F_5)$	8.33×10^{-3}	[b]	4.03×10^{-3}	4

[a] The solubility of LiF was low; therefore, the conductivity was not measured.
[b] Conductivity was not measured.

Compound (9).—2-Phenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaborolane or $(C_6F_{12})O_2B(C_6H_5)$. The synthesis of this compound followed the procedure described by Allan *et al.*[9] By reacting perfluoropinacol with dichlorophenylborane, the product was obtained with a yield of 78%. The boiling point of the compound was 68°C/18 mm Hg.

Compound (10).—2-(3,5-Difluorophenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaborolane or $(C_6F_{12})O_2B(C_6H_3F_2)$. 1-bromo-3,5-difluorobenzene (38.6 g, 0.2 mol) was added slowly to a mixture of magnesium turnings (4.8 g, 0.2 mol) in 200 mL anhydrous ethyl ether. After the reaction mixture was refluxed for 2 h, trimethyltin chloride (40 g, 0.2 mol) was added dropwise to the solution and refluxing continued for one more hour. Then the reaction mixture was hydrolyzed by saturated ammonium chloride. The organic layer of 3,5-difluorophenyltrimethyltin was separated and purified by distillation with a 62% yield. Then the 3,5-difluorophenyltrimethyltin (11 g, 0.04 mol) was reacted with boron trichloride (11 g, 0.093 M) in a sealed tube at 0°C for 1 h and then at room temperature for 12 h. Dichloro-3,5-difluorophenylborane (6.3 g, 0.032 mol) was obtained from the reaction with a yield of 81%. Dichloro-3,5-difluorophenylborane (5.84 g, 0.03 mol) was added to a solution containing perfluoropinacol (10 g, 0.03 M) in 50 mL of anhydrous chloroform at −40°C. Then the reaction mixture was stirred continuously at room temperature for 4 h. The insoluble material was filtered off from the solution. The chloroform solvent was removed by evaporation. The pure product was obtained by distillation of the residue with a yield of 73%. The boiling point of the compound was 80°C/14 mm Hg. HNMR ($CDCl_3$ ppm) δ: 6.9-7.4 (m, 1H), 7.35-7.7 (m, 2H). IR (neat cm^{-1}), ν 3092.0, 1593.8, 1480.6, 1432.0, 1388.2, 1248.9, 1109.8, 1080.5, 986.9, 952.8, 889.6, 870.4, 748.2, 721.8.

Compound (11).—2-pentafluorophenyl-4,4,5,5-tetrakis(trisfluoromethyl)-1,3,2-dioxaborolane or $(C_6F_{12})O_2B(C_6F_5)$. This compound was synthesized with the same procedure for compound (10). Bromopentafluorobenzene and perfluoropinacol were used as starting materials. The final product had a boiling point: 87-90°C/12 mm Hg. IR (neat cm^{-1}), ν 1657.6, 1493.5, 1426.4, 1368.4, 1246.5, 1083.7, 989.9, 952.2, 889.0, 749.2, 718.2.

The synthesis procedure of compounds (12-14) are sketched in Fig. 5. Following are the outlines of these procedures.

Compound (12).—Bis(1,1,1,3,3,3-hexafluoroisopropyl)phenylboronate, or $(C_3HF_6O)_2B(C_6H_5)$. To a mixture of 4.8 g (0.2 M) of sodium hydride in 200 mL of anhydrous ether, 33.6 g (0.2 M) of 1,1,1,3,3,3-hexafluoro-2-propanol was added dropwise at room temperature. After the addition was completed, the ether was evaporated from the solution. The residue was dried under vacuum to obtain the solid alkoxide. 200 mL of pentane was added to the alkoxide, then 15.9 g (0.1 M) of dichlorophenylborane (purchased from Aldrich) was dropped into the mixture. After stirring the mixture for 20 h, the sodium chloride was filtered off. The ether was removed by evaporation under atmospheric pressure from the filtrate. The liquid residue was distilled under vacuum using a Kugelrohr. 22 g of the pure product was obtained. The boiling point of the compound was 90-95°C/15 mm Hg. HNMR ($CDCl_3$ ppm) δ: 5.2 (q, 2H), 7.55 (s, 5H). IR (neat cm^{-1}), ν 3061.1, 2966.9, 1603.9, 1344.9, 1267.9, 1110.4, 905.8, 874.4, 693.2.

Compound (13).—Bis(1,1,1,3,3,3-hexafluoroisopropyl)-3,5-difluoro phenylboronate, or $(C_3HF_6O)_2B(C_6H_3F_2)$. This compound was synthesized with the same procedure as described for compound (12), but using dichloro-3,5-difluorophenylborane to replace the dichlorophenylborane. The yield was 62%. The boiling point of the compound was 70-73°C/15 mm Hg. HNMR ($CDCl_3$ ppm) δ: 5.1 (q, 2H), 6.9-7.35 (m, 3H). IR (neat cm^{-1}), ν 3092.3, 1590.6, 1348.7, 1267.7, 1204.4, 1117.0, 987.2, 872.4, 698.2.

Compound (14).—Bis(1,1,1,3,3,3-hexafluoroisopropyl)pentafluorophenylboronate, or $(C_3HF_6O)_2B(C_6F_5)$. This compound was synthesized with the same procedure as described for compound (12),

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

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	3.3×10^{-5}	2.1×10^{-5}	[a]
0.2	0.2	1.24×10^{-3}	1.1×10^{-3}	[a]
0.4	0.4	2.83×10^{-3}	2.73×10^{-3}	[a]
0.6	0.6	3.83×10^{-3}	3.69×10^{-3}	[a]
0.8	0.8	4.20×10^{-3}	4.07×10^{-3}	[a]
1.0	1.0	3.96×10^{-3}	3.86×10^{-3}	[a]
1.2	1.2	3.40×10^{-3}	3.35×10^{-3}	[a]

[a] The solubility of LiF was low; therefore, the conductivity was not measured.

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

Concentration of compound (2) (M)	Concentration of lithium salt (M)	Conductivity CF_3COOLi (S/cm)	Conductivity C_2F_5COOLi (S/cm)	Conductivity LiF (S/cm)
0	0.2	3.3×10^{-5}	2.1×10^{-5}	[a]
0.2	0.2	1.93×10^{-3}	7.60×10^{-4}	[a]
0.4	0.4	3.57×10^{-3}	1.94×10^{-3}	[a]
0.6	0.6	4.53×10^{-3}	2.90×10^{-3}	[a]
0.8	0.8	4.59×10^{-3}	3.57×10^{-3}	[a]
1.0	1.0	3.95×10^{-3}	3.79×10^{-3}	[a]
1.2	1.2	3.00×10^{-3}	3.68×10^{-3}	[a]

[a] The solubility of LiF was low; therefore, the conductivity was not measured.

Table IV. Ionic conductivity of compound (6) + lithium salt in DME solutions.

Concentration of compound (6) (M)	Concentration of lithium salt (M)	Conductivity CF_3COOLi (S/cm)	Conductivity C_2F_5COOLi (S/cm)	Conductivity LiF (S/cm)
0	0.2	3.3×10^{-5}	2.1×10^{-5}	[a]
0.2	0.2	4.11×10^{-3}	4.52×10^{-3}	3.58×10^{-3}
0.4	0.4	7.51×10^{-3}	7.67×10^{-3}	6.85×10^{-3}
0.6	0.6	9.00×10^{-3}	8.92×10^{-3}	8.98×10^{-3}
0.8	0.8	8.24×10^{-3}	8.10×10^{-3}	9.54×10^{-3}
1.0	1.0	7.76×10^{-3}	6.49×10^{-3}	9.00×10^{-3}
1.2	1.2	6.62×10^{-3}	4.67×10^{-3}	7.68×10^{-3}

[a] The solubility of LiF was low; therefore, the conductivity was not measured.

Table V. Ionic conductivity of compound (8) + lithium salt in DME solutions.

Concentration of compound (8) (M)	Concentration of lithium salt (M)	Conductivity CF_3COOLi (S/cm)	Conductivity C_2F_5COOLi (S/cm)	Conductivity LiF (S/cm)
0	0.2	3.3×10^{-5}	2.1×10^{-5}	[a]
0.2	0.2	3.60×10^{-3}	3.92×10^{-3}	[a]
0.4	0.4	6.16×10^{-3}	6.56×10^{-3}	[a]
0.6	0.6	6.95×10^{-3}	7.15×10^{-3}	[a]
0.8	0.8	6.60×10^{-3}	6.00×10^{-3}	3.42×10^{-3}
1.0	1.0	5.22×10^{-3}	4.11×10^{-3}	3.78×10^{-3}
1.2	1.2	3.47×10^{-3}	2.23×10^{-3}	3.46×10^{-3}

[a] LiF was only partially dissolved in these solutions; therefore, conductivity was not measured.

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

Concentration of compound (9) (M)	Concentration of lithium salt (M)	Conductivity CF_3COOLi (S/cm)	Conductivity C_2F_5COOLi (S/cm)	Conductivity LiF (S/cm)
0	0.2	3.3×10^{-5}	2.1×10^{-5}	[a]
0.2	0.2	3.15×10^{-3}	3.46×10^{-3}	7.40×10^{-4}
0.4	0.4	4.95×10^{-3}	5.33×10^{-3}	1.38×10^{-3}
0.6	0.6	5.89×10^{-3}	6.14×10^{-3}	1.90×10^{-3}
0.8	0.8	5.65×10^{-3}	5.79×10^{-3}	2.31×10^{-3}
1.0	1.0	4.59×10^{-3}	4.46×10^{-3}	2.47×10^{-3}
1.2	1.2	3.02×10^{-3}	2.78×10^{-3}	2.40×10^{-3}

[a] The solubility of LiF was low; therefore, the conductivity was not measured.

Table VII. Ionic conductivity of compound (11)+ lithium salt in DME solutions.

Concentration of compound (11) (M)	Concentration of lithium salt (M)	Conductivity CF_3COOLi (S/cm)	Conductivity C_2F_5COOLi (S/cm)	Conductivity LiF (S/cm)
0	0.2	3.3×10^{-5}	2.1×10^{-5}	[a]
0.2	0.2	4.30×10^{-3}	4.57×10^{-3}	3.47×10^{-3}
0.4	0.4	7.07×10^{-3}	7.16×10^{-3}	6.13×10^{-3}
0.6	0.6	7.83×10^{-3}	7.72×10^{-3}	4.53×10^{-3}
0.8	0.8	6.74×10^{-3}	6.27×10^{-3}	7.48×10^{-3}
1.0	1.0	4.69×10^{-3}	3.97×10^{-3}	6.55×10^{-3}
1.2	1.2	2.86×10^{-3}	1.91×10^{-3}	5.10×10^{-3}

[a] The solubility of LiF was low; therefore, the conductivity was not measured.

but using dichloro-pentafluorophenylborane to replace the dichlorophenylborane. The yield was 43%. The boiling point of the compound was 73-75°C/15 mm Hg. HNMR ($CDCl_3$ ppm) δ: 4.9 (q, CH). IR (neat cm^{-1}), ν 2972.8, 1654.8, 1491.3, 1379.6, 1271.7, 1209.0, 1113.7, 982.5, 874.5, 693.4.

Conductivity measurements.—Conductivity measurements were made at 25°C using a Hewlett-Packard 4129A impedance analyzer in the frequency range from 5 Hz to 10 MHz. Cells with Pt electrodes were used for the measurements. The cell constants were calibrated by measuring a 0.05 N KCl standard aqueous solution. The ionic conductivities of dimethoxyethane (DME) solutions containing various boron-based compounds and lithium salts were compared with the conductivities of DME solutions containing lithium salts only.

Near-edge absorption X-ray fine structure measurements.—Near-edge absorption X-ray fine structure (NEXAFS) measurements were made at the iodine L_I edge for LiI/DME solutions with and without boron-based anion receptors. The measurements were done at Beam Line X19A of the National Synchrotron Light Source (NSLS). The data were collected using a large solid angle ionization chamber as the fluorescence detector. The solutions containing LiI salt and various boronate compounds were poured into cells with thin Mylar windows for NEXAFS studies.

Electrochemical stability measurements.—Electrochemical stability measurements were performed using a Solatron SI 1287 electrochemical interface in the potential dynamic mode.

Results and Discussion

The ionic conductivity of electrolytes containing lithium salts only, such as CF_3CO_2Li and $C_2F_5CO_2Li$, dissolved in DME are low, with respective conductivities of only 3.3 and 2.1×10^{-5} S/cm at concentrations of 0.2 M. LiF is insoluble in this solvent. The conductivity enhancement effects of the boronate compounds are summarized in Table I for 0.8 M concentrations of both the lithium salts and the anion receptors. All measurements were done at 25°C. According to the chemical structures in Fig. 1, the 14 compounds can be divided into four groups: compounds (1-3), compounds (4-8), compounds (9-11), and compounds (12-14). The 0.8 M concentration data are given because this is close to the optimized concentration. With the addition of stoichiometric amounts of compounds (1-3) as additives, the conductivities of 0.8 M solutions of CF_3CO_2Li and $C_2F_5CO_2Li$ salts in DME were significantly increased to a range around 4×10^{-3} S/cm, as shown in Table I. However, their anion complexation effects of these compounds were still rather weak and the solubility of LiF remained low. When the second group compounds [compounds (4-8)] were used as additives, their effects were strong enough to dissolve LiF salt to concentrations as high as 1.2 M. The main difference between the first group and the second is the fully fluorinated left ring in group 2. This is consistent with our previous results on the increased conductivity enhancement effects of other boron-based anion receptors with the increasing number of the electron-withdrawing groups.[6,7] The largest conductivity enhancement in group 2 is from compound (6), which has fully fluorinated rings on both sides. Compound 6 has the strongest effect in group 2. This tells us that the conductivity enhancement (obtained from the anion complexation effect) strongly depends on the electron-withdrawing effect of the substituting group, but it is also affected by steric hindrance effects. Compound (8) has a greater conductivity enhancement effect than compound (5), due to the two stronger CF3 electron-withdrawing groups as compared to the two single fluorine atoms in compound (5). It has a weaker effect than compound (6) due to the steric hindrance effect of the bulky CF_3 structure. All compounds in groups (3) and (4) are liquids at room temperature due to their partial branch structures. This liquid nature makes them much easier to be dissolved in nonaqueous solvents. In group 3, the conductivity enhancement increases with the increased number of substituting fluorine atoms. However, in group 4, the conductivity enhancement does not have clear correlation with the number of fluorine atoms. This may be due to the more flexible branch structure of group 4. Although we have measured conductivity data for all 14 compounds at various concentrations, only selected data are presented here for each group. The ionic conductivity data of compound 1 and compound 2 as additives in DME with various concentrations are listed in Tables II and III. The corresponding data for compound (6) and compound (8) are listed in Tables IV and V. Table VI contains data for compound (9) and Table VII contains data for compound (11). The results for compound (14) are listed in Table VIII. For most compounds, the conductivity has a maximum at around 0.8 M concentration. For compounds with CF_3 substituting groups attached to phenol rings, the conductivity decreases rapidly with increasing concentration after the maximum was reached, while the others with fluorine substituting atoms only decrease slightly. We would like to point out that

Table VIII. Ionic conductivity of compound (14)+ lithium salt in DME solutions.

Concentration of compound (11) (M)	Concentration of lithium salt (M)	Conductivity CF_3COOLi (S/cm)	Conductivity LiF (S/cm)
0	0.2	3.30×10^{-5}	[a]
0.2	0.2	3.67×10^{-3}	1.45×10^{-3}
0.4	0.4	4.49×10^{-3}	2.70×10^{-3}
0.6	0.6	8.96×10^{-3}	3.56×10^{-3}
0.8	0.8	8.33×10^{-3}	4.03×10^{-3}
1.0	1.0	6.30×10^{-3}	4.09×10^{-3}
1.2	1.2	3.68×10^{-3}	3.77×10^{-3}

[a] The solubility of LiF was low; therefore, the conductivity was not measured.

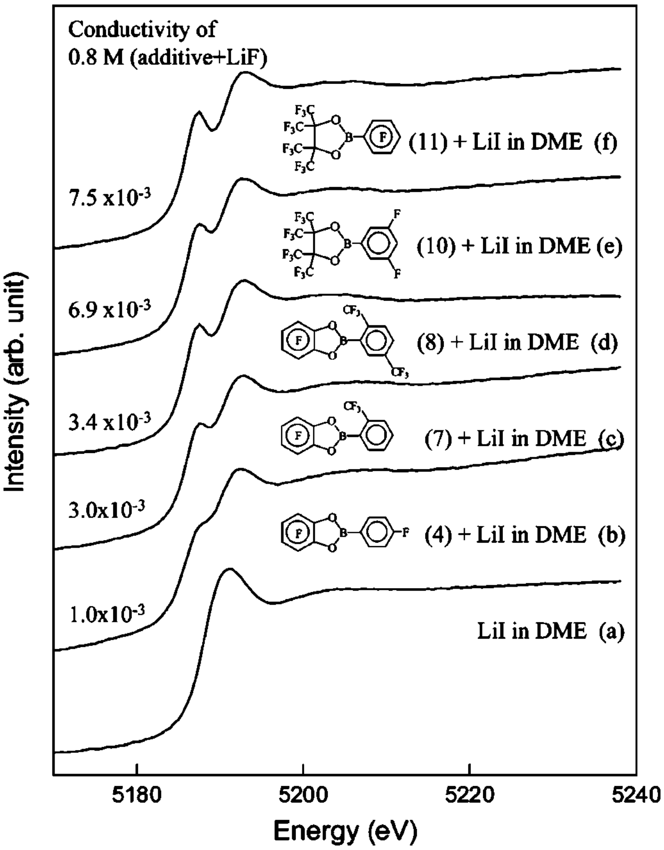


Figure 6. NEXAFS at the I L_I edge for DME solutions of: (a) 0.2 M LiI salt, (b) 0.2 M [LiI + compound (4)], (c) 0.2 M [LiI + compound (7)], (d) 0.2 M [LiI + compound (8)], (e) 0.2 M [LiI + compound (10)], and (f) 0.2 M [LiI + compound (11)].

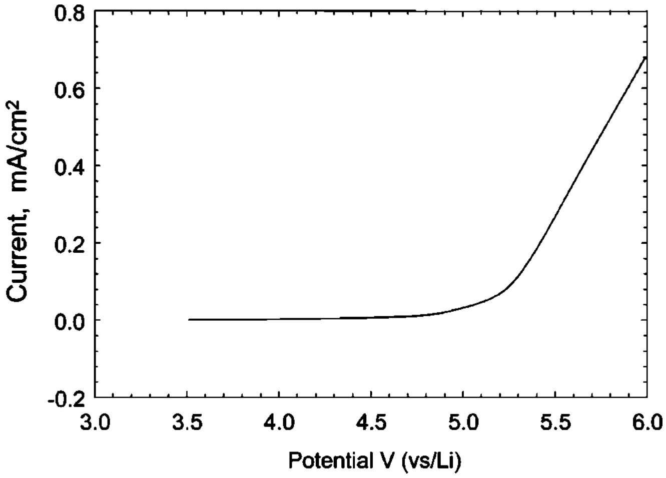


Figure 7. Electrochemical stability of electrolyte containing 0.2 M LIF and compound (14) in EC-DMC solution (v/v 1:1).

for the practical lithium battery electrolyte, DME is not a good choice due to its poor electrochemical stability compared with other solvents such as dimethyl carbonate (DMC).

In our previous publication,[5] NEXAFS was used to study the anion complexation of boron compounds. This technique is used here to study the anion complexation effect of boronate compounds.

NEXAFS spectra at the iodine L_I edge were used to study the coordination symmetry of the I^- ion in solutions. It would be better if we could get spectroscopic evidence for complex formation in LiF solutions directly by studying the fluorine *K* edge. Unfortunately, the energy of fluorine *K* edge is too low and difficult to apply to solution studies. Therefore, the spectroscopy was done at the chlorine *K* edge and iodine *L* edges. We report our iodine *L* edge spectroscopy results here. In an iodine *L* edge NEXAFS experiment, as the incident X-ray energy is scanned through the iodine *L* edge, the ejected 2*s* photoelectrons can undergo bound state transitions to empty 5*p* states. Coordination symmetry can affect the energy levels of the final states. Therefore, the fine structure of the absorption spectra near the edge provides information about the coordination symmetry of the I^- anion.

Figure 6 shows how the boron-based additives with different electron-withdrawing groups have a dramatic effect on fine structure of the absorption spectra. NEXAFS data at the iodine *K* edge are given for DME solutions of (a) 0.2 M LiI, (b) 0.2 M LiI + 0.2 M compound (4), (c) 0.2 M LiI + 0.2 M compound (7), (d) 0.2 M LiI + 0.2 M compound (8), (e) 0.2 M LiI + 0.2 M compound (10), (f) 0.2 M LiI + 0.2 M compound (11). The "white line" peak, between 5185 and 5195 eV, above the edge, is due to dipole-allowed transitions to final states of *p* symmetry. The structure of the white line is sensitive to the coordination of the absorbing atom, I^-, in these spectra. This technique has been used to study the complexation between Cl^- and aza-based anion receptors[10] and other types of boron-based anion receptors.[5] The white line in curve (a) for LiI in DME is a broad peak. When LiI salt was dissolved in solvent, the I^- ion experiencing a spherical symmetric environment, the 5*p* final states of the I^- are close to being degenerate, and the transition feature is a broad peak. White-line peak splitting can occur if there is an asymmetric distribution of atoms (or molecules) surrounding the I^- with strong bonding. The more asymmetric the distribution is, the stronger the splitting effect will be. The asymmetric local field experienced by each of the degenerate 5*p* final states of I^- is different and the degeneracy is lifted. This results in a splitting of the absorption peak. In curve (a), when the LiI salt was dissolved in DME, the white-line splitting is almost undetectable, because the distribution of the solvent molecules has a spherical symmetry surrounding the I^- ions, and the interaction between the solvent and I^- is weak. We classify these anions as uncomplexed anions. In curve (b), white-line splitting was observed when compound (4) was added into the solution. This gives strong evidence that the I^- is indeed complexed with the boron atom in compound (4). In curves (c-f), for solutions containing LiI and compounds (7-10), respectively, the white-line splitting becomes more and more obvious, indicating stronger and stronger anion complexing effects of these compounds. For easy comparison, the chemical structures and the ionic conductivities of these compounds used as additives for LiF salts are also shown in Fig. 6. It is quite clear that the stronger the electron-withdrawing power of the substituting groups in the boronate compounds, the higher the conductivity enhancement, and also the larger white-line splitting of the NEXAFS spectra.

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. A three-electrode cell with a glassy carbon as working electrode (7.0 mm^2), platinum wire as counter electrode, and metal lithium foil as reference electrode was used for this study. The resulting curve is plotted in Fig. 7. The electrolyte made of compound (14), LiF salt, and ethylene carbonate/diethyl carbonate (EC/DMC) solvent has excellent electrochemical stability at voltage *vs.* Li as high as 5 V.

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