Lithium ion conduction in an organoborate zwitterion–LiTFSI mixture

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An organoborate zwitterion–lithium salt mixture, prepared *via* selective borate formation of *N*-ethylimidazolium salt, exhibited ionic conductivity of 3.0 × 10^{-5} S cm^{-1} at 50 °C and a lithium transference number of 0.69.

Ionic liquids (ILs) have possible uses as electrolytes[1] because of their non-volatility, wide potential window, and high ionic conductivity.[2] However, without the addition of salt or acid, most ordinary ILs cannot be used as electrolyte solutions because of a lack of ions active toward electrodes. Moreover, even in IL–salt mixtures and IL–acid mixtures, the component ions tend to migrate under a potential gradient, thus causing the carrier ions in mixtures to have low transference numbers. For example, the transference numbers of the lithium cation t_{Li^+} in simple IL–lithium salt mixtures are reported to be about 0.2, which is not sufficiently large for most electrochemical applications.[3]

As a way to increase t_{Li^+}, we proposed the use of zwitterions as an ion conductive matrix. The zwitterions covalently bond to the component ions, thus reducing the mobility of the ions.[4] The zwitterions consisting of imidazolium cations and some anions (sulfonate, carboxylate, or imide) are solid at room temperature, despite their IL-like structure.[4–7] However, when these solid zwitterions were mixed with lithium bis(trifluoromethylsulfonyl) imide (LiTFSI), the resulting mixtures became liquid at room temperature. This is probably due to the formation of imidazolium–TFSI ion-pairs between zwitterions, which is a very good IL structure.[4,7] The ionic conductivity of the equimolar mixture of LiTFSI with a zwitterion that has both an *N*-ethylimidazolium site and a sulfonate site is about 10^{-5} S cm^{-1} at 50 °C with a t_{Li^+} value of 0.56.[5] These properties may be improved further by designing zwitterions to have a more dissociable structure and a smaller intermolecular electrostatic interaction.

In this report, we describe the preparation and testing of borate-type zwitterion–LiTFSI mixtures. The resulting borate-type zwitterion–LiTFSI showed high ability to transport mainly lithium cations at room temperature. The structure of the present zwitterion was designed by us based on the accumulated knowledge about zwitterions and molten salts.[1,4–7]

The ionic conductivity and t_{Li^+} values largely depend on the structure of the zwitterion. In particular, the structure of the anion site largely affects the thermal property of zwitterion–LiTFSI mixtures and also the t_{Li^+} values.[7] Therefore, to further increase both t_{Li^+} and the ionic conductivity, it is necessary to seek zwitterions with a novel anionic structure that is more dissociable than those of previously reported zwitterions.

Borate anions are promising as an anionic site for zwitterions because they are generally very stable due to the electron-deficient property of the boron atom and also because organoboron chemistry is diverse. In particular, tetrafluoroborate (BF_4^-) is well-known as a potential component of ILs. Because lithium salts have excellent electrolyte properties, a variety of dissociable lithium borates such as fluoromethylborate,[8] bis(oxalate)borate (BOB), and similar borate anions[9,10] have been reported.

Lately, we have reported on novel molten salts having an organoboron site.[11] For instance, the hydroboration of 1-allyl-3-propylimidazolium bromide with 9-borabicyclo[3.3.1]nonane (9-BBN), followed by an anion exchange reaction with LiTFSI, resulted in an alkylborate-type molten salt. It is thought that further reaction of the organoboron molten salt with an organolithium reagent would lead to the formation of an organoborate-type zwitterion. Generally, an alkyl chain length around 5–7 CH_2 units between the cation and anion sites produces high ionic conductivity in zwitterion–LiTFSI mixtures.[7] Therefore, a corresponding chain length was used in the present system.

For the synthesis shown in Scheme 1, the organoboron compound having an alkyl halide unit was prepared first *via* reaction of bromo 9-BBN with THF (tetrahydrofuran). After the quaternization of *N*-ethylimidazole with compound **A**, the resulting compound **B** was reacted with pentafluorophenyllithium. The bromide anion of compound **C** was converted with LiTFSI, and then the generated LiBr was removed. Details on the synthesis of borate-type zwitterion–LiTFSI mixtures are described below.† Hereafter, we use "**BZ**" as shorthand for "borate-type zwitterion".

It should be noted that the reaction of **B** with pentafluorophenyllithium was done in the presence of an IL. Generally, selective formation of a borate structure is impossible due to the reactive proton in the 2 position of the imidazolium ring.[12] Recently, some ionic liquids composed of aliphatic cations, such as ammonium and phosphonium, were reported to be highly stable toward strong bases[13] such as Grignard reagents. Such chemistry is very interesting because it might further broaden the potential of ILs, both as a reaction medium, and as a designer matrix for various applications. Here, for selective borate formation, we have examined the use of pentafluorophenyllithium as an organolithium reagent. Pentafluorophenyllithium was used because of its relatively weak basicity due to the presence of electron-withdrawing fluorine atoms. In the ^{1}H-NMR spectrum of the product, the peak attributable to proton at the 2 position was observed at 8.6 ppm (CD_3OD, relative to Me_4Si), which is a typical chemical shift for proton at the 2 position of a dialkylimidazolium ring. In

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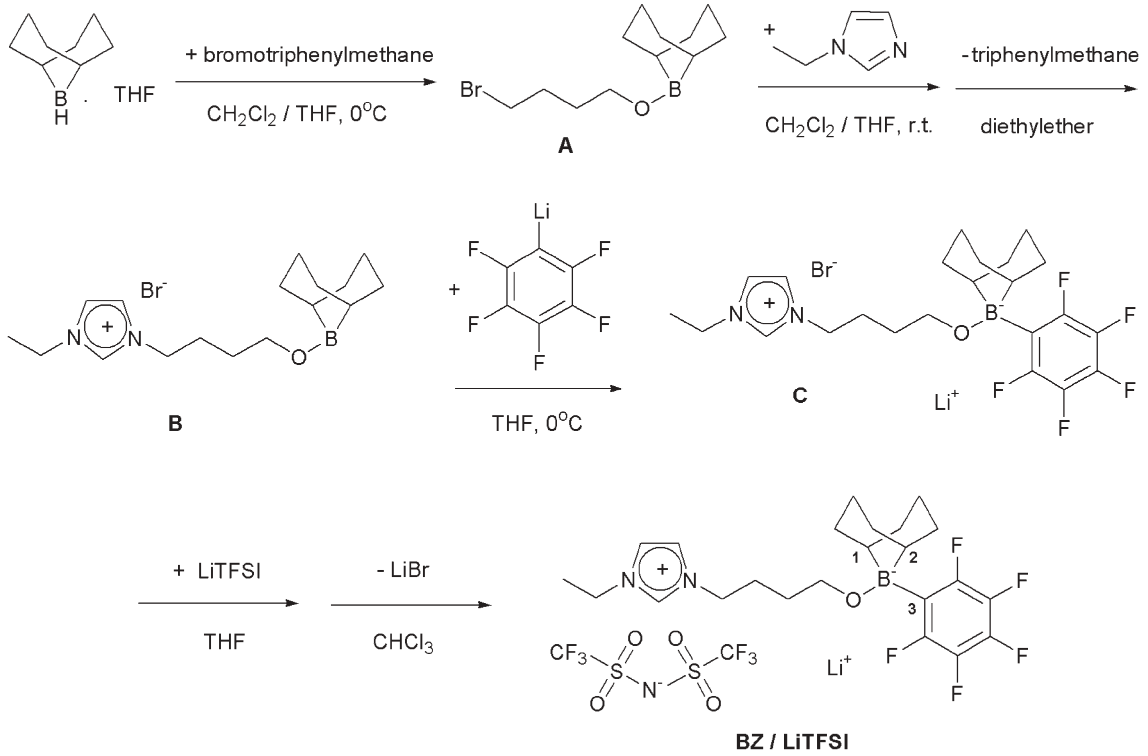

Scheme 1 Synthesis of the organoborate-type zwitterion–LiTFSI mixture.

the ^{11}B-NMR spectrum, the main peak at -18.79 ppm (CD_3OD, relative to BF_3OEt_2) also indicated the formation of borate.

We followed this synthesis procedure two times, and in all cases the ^{11}B-NMR spectrum indicated borate formation. However, peaks attributable to the imidazolium ring were not observed when the synthesis was carried out using n-butyllithium or phenyllithium. This fact suggests that the weak basicity of the pentafluorophenyllithium is essential for the selective borate formation.

This procedure differs from those used to make previously reported zwitterion–LiTFSI mixtures in that the previous mixtures were prepared by adding LiTFSI to pure zwitterions.

It should also be noted that **BZ**–LiTFSI was liquid at room temperature. The DSC curve (differential scanning calorimetry, SII DSC EXSTAR6000, Seiko Instruments, sweep rate: 5 °C min^{-1} from -100 to 120 °C) showed only the glass transition temperature (T_g) at -35 °C, whereas no melting point was observed. As described in previous reports, pure zwitterions that contain a phenyl group generally have a high melting point.[6] When a zwitterion with a high melting point was mixed with LiTFSI, the resulting matrices also tended to have a relatively high T_g.[7] However, the **BZ**–LiTFSI had a relatively low T_g, close to that of carboxylate- and (carbonyl)(sulfonyl)imide-type zwitterion–LiTFSI mixtures (around -35 °C),[6] in spite of the presence of a phenyl group. This is likely due to the large steric hindrance around the anionic charge centre in BZ, which effectively reduces the inter-zwitterion electrostatic interaction.

The ionic conductivity of **BZ**–LiTFSI was measured using the complex impedance method (Solartron 1260 impedance/gain-phase analyzer) under a nitrogen atmosphere. The temperature sweeping rate was 10 °C min^{-1} from 60 to 30 °C. The resulting ionic conductivity of 3.0×10^{-5} S cm^{-1} at 50 °C (Fig. 1) is almost the same as that for mixtures of carboxylate-type or (carbonyl)(sulfonyl)imide-type zwitterions with LiTFSI.[7] This high ionic conductivity of **BZ**–LiTFSI is likely to be due to its low T_g.

The t_{Li^+} value was estimated using a combination of the AC impedance and the DC polarization methods (potential-static field: 10 mV, lithium metal electrode). Cell preparation and measurement procedures have been carried out in an argon atmosphere at room temperature. The t_{Li^+} value for the **BZ**–LiTFSI system was 0.69 at room temperature. This is a significantly higher value than that for ILs containing lithium salts,[3] and even higher than that of lithium bis(perfluoropinacolato)borate dissolved in organic solvents (0.55).[14]

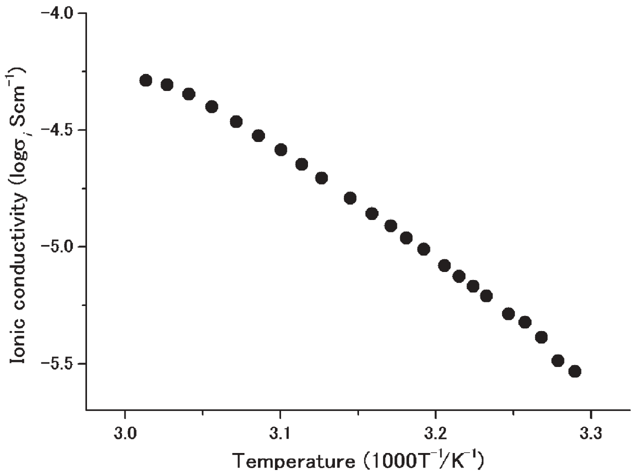

Fig. 1 Temperature dependence of the ionic conductivity of **BZ**–LiTFSI.

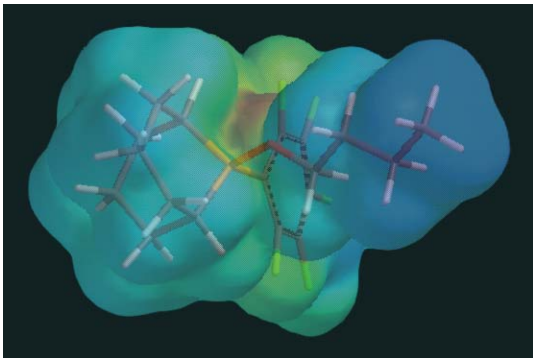

Fig. 2 Calculated electrostatic potential surface for only the borate anion site as a model of **BZ** having 9-BBN and pentafluorophenyl groups which have steric hindrance around the exposed negative charge (red: negative, blue–green: neutral, blue: positive).

Table 1 Calculated bond lengths and bond angles around boron atom for borate-type zwitterion (**BZ**)[a]

Length/Å		Angle/°	
B–C1	1.664	C1–B–C2	101.05
B–C2	1.658	C1–B–C3	111.55
B–C3	1.656	C2–B–C3	116.53
B–O	1.476	C1–B–O	108.19
		C2–B–O	113.99
		C3–B–O	105.40

[a] All carbons shown here are next to the boron atom. These numbers are shown in Scheme 1.

The electrostatic potential surface of **BZ** was then calculated using MNDO semi-empirical MO method (Wavefunction, model Spartan '04) for only the anion site of **BZ** (Fig. 2). In the anion site of **BZ**, the bulky alkyl group causes steric hindrance around the anionic site, whereas the pentafluorophenyl group works as an electron-withdrawing group. The results in Fig. 2 show that negative charge is exposed only in one direction, with the other directions being surrounded by alkyl groups. Such a bulky anion shows weaker interaction with relatively large cations like imidazolium. To estimate the effect of the steric hindrance on the electrostatic interaction among zwitterions, the equilibrium structure of **BZ** was also calculated with the MNDO method. Bond lengths and bond angles around the boron atom are summarized in Table 1. The distances between the boron atom and the two nitrogen atoms in the imidazolium ring were calculated to be 5.670 and 5.099 Å, respectively. The distances are longer than that for the case when the anion site was substituted with BF_3^- (4.268 and 4.312 Å). This indicates that both steric hindrance and the presence of an electron-withdrawing pentafluorophenyl group weaken the electrostatic interactions among **BZ**.

In summary, a novel lithium ion conductive ionic liquid based on a borate-type zwitterion has been prepared *via* selective borate formation of *N*-ethylimidazolium salt bearing a 9-BBN tail using pentafluorophenyllithium. The t_{Li^+} value for the ionic liquid **BZ**–LiTFSI was estimated from measurements to be 0.69. The markedly low T_g value (−35 °C) and high ionic conductivity (3.0×10^{-5} S cm^{-1} at 50 °C) of **BZ**–LiTFSI are ascribed to a high degree of dissociation of the lithium borate site. The results indicated that **BZ** has steric hindrance around its negative charge that inhibits the electrostatic interactions among the component zwitterions.

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Notes and references

† Reagents were purchased from the following companies. *N*-ethylimidazole, triphenylmethylbromide, bromopentafluorobenzene: Tokyo Chemical Industry Co., Ltd.; 9-borabicyclo[3.3.1]nonane (9-BBN): Aldrich Co. Ltd.; n-butyllithium: Kanto Chemical Co. Ltd. LiTFSI was a gift from Sumitomo 3M Co Ltd. All the procedures were carried out under a dry argon atmosphere.

Preparation of a solution of pentafluorophenyllithium: dried diethyl ether was added to 0.13 ml (1.1 mmol) of pentafluorobromobenzene in a flask flushed with dry argon gas. Then, n-butyllithium 0.68 ml (1.1 mmol) was added slowly to the solution at 0 °C.

Preparation of BZ–LiTFSI in Scheme 1: a tetrahydrofuran (THF) solution (8.0 ml of 0.5 M) of the 9-BBN–THF complex was added slowly to 1.3 g (4.0 mmol) of dried bromotriphenylmethane in dichloromethane at 0 °C. The resulting mixture was stirred for 6 h at room temperature. And then, 0.4 ml (4.0 mmol) of *N*-ethylimidazole was added slowly to the mixture. The mixture was further stirred for 24 h, solvent was partly evaporated, and then the concentrated solution was added to 40 ml of dried diethyl ether. After the solution was stirred swiftly for 10 min, the supernatant was removed by syringe. This reprecipitation was repeated twice. The solution of pentafluorophenyllithium prepared as mentioned above, was added slowly to the precipitation at 0 °C, and the mixture was stirred for 2 h at room temperature. After solvent was removed, the residue was dissolved in 30 ml of diethylether. The supernatant was removed by syringe again, and then 30 ml of dichloromethane was added and stirred. The soluble fraction was separated by syringe and the solution was evaporated. 6.0 ml of a THF solution of LiTFSI (0.1 M) was added to the residue, and the mixture was stirred for 2 days at room temperature. After solvent was evaporated, 30 ml of chloroform was added. The solvent of the soluble part was removed, and then the product was dried under vacuum to afford a yellow viscous liquid. NMR: δ_H (500 MHz, CD_3OD, δ (ppm) Me_4Si) 1.28 (2H × 2, m, 9-BBN), 1.42 (3H, t, $NCH_2\mathit{CH_3}$), 1.58 (2H × 4, m, 9-BBN), 1.72 (2H × 2, t, 9-BBN), 1.74 (2H, t, $NCH_2CH_2CH_2\mathit{CH_2}O$) 1.83 (2H × 2, m, $NCH_2\mathit{CH_2CH_2}CH_2O$), 4.18 (2H, q, $N\mathit{CH_2}CH_3$), 4.20 (2H, t, $N\mathit{CH_2}CH_2CH_2CH_2O$), 7.40 (1H × 2, w, imidazolium), and 8.76 (1H, s, imidazolium), δ_B(500 MHz, CD_3OD, δ (ppm) $(CH_3O)_3B$) −18.79 (s).

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