Design and evaluation of imidazolium cation-based ionic liquids having double-armed anions for selective cation conduction

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ABSTRACT

A series of triple ionic compounds consisting of double armed anions and one cation were prepared as lithium cation conductive matrices. As anions, lithium borates derived from lithium-9-borabicyclo[3,3,1]nonane hydride were introduced. The sterically hindered borate anion structures prevented the crystallization of triple ionic compounds. Introduction of ethylene oxide chains attached to the borate anions led to lower glass transition temperature, and also improved ionic conductivity. A lithium transference number of 0.73 was observed in spite of the presence of ethylene oxide chains.

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1. Introduction

Ionic liquids (ILs) are receiving attention as alternative to volatile organic solvents due to their negligible vapor pressure. Moreover, ILs possess intriguing properties such as high thermal and electrochemical stability and high ionic conductivity [1,2].

Particularly in the field of electrochemistry, ILs are expected as a key materials which might give a solution to the safety problems of batteries due to their non-flammable property. However, selectivity of carrier ion transport is one of problems when ionic liquids are applied for batteries. Since ionic liquids do not include electroactive species, it is necessary to add salts or acids prior to their use. The mobility of electroactive ions greatly affects on the electrical power of the batteries as lithium cation does on lithium (ion) batteries and protons does on fuel cells. In ILs, it is quite difficult to rapidly transport these small cations because of strong electrostatic interactions with neighboring anions. These interactions of small cations induce increase of both glass transition temperature and viscosity. Moreover, the migration of component ions of ILs prevents efficient electrochemical reactions at electrodes. These two problems are the crucial points that prevent the application of ILs for battery technologies.

To enable efficient transport of small cations in ILs and also to reduce migration of the component ions, we have proposed two major strategies; polymerized ionic liquids (PILs) [3–5] and zwitterions (ZIs) [6–9]. Although the ionic conductivity has been lowered as a result of these approaches due to restricted ionic motion and/or increase in viscosity, it is worth while to analyze relationship between structures and ion conductive properties of these systems for the design of better single ion conductive matrices.

PILs are easily obtained by the polymerization of IL type monomers, for example, by radical polymerization of dialkylimidazolium vinylsulfonates. Various types of PILs such as polycations [3], polyanions [3], copolymers [4], polymer composites [5,10] have been designed so far. These polymers gave thin film conductors suitable as light and thin polymer electrolytes. On the other hand, ZIs in which cation was tethered with anion via covalent bonding were designed to restrict migration of component ions under the potential gradient (Fig. 1). Although most ZIs show high Tm of above 100 °C, mixtures of ZIs and strong acids or salts melt at room temperature, and show high ionic conductivity [6–9]. PILs and ZIs systems showing relatively high transference number of lithium cations [4,8,9] were also successfully designed.

In order to further improve the selectivity of lithium cation transport, we have reported double armed ionic liquids, termed triple ions (TIs) [11] (Fig. 1). TI is ZI tethered with another anion as depicted in Scheme 1. Differently from ZIs in which both cation and anion originating from salt additive are still mobile, in the case of TIs, only target cations are expected to migrate. These TIs were
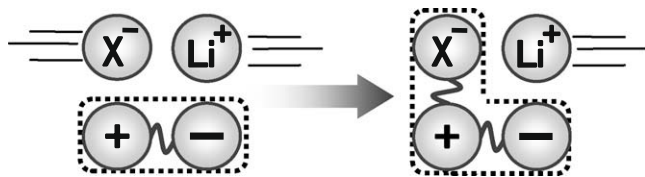
Fig. 1. Schematic illustration of lithium cation transport in zwitterion (ZI; left) and triple ion (TI: right).

consisted of imidazolium cation and two anionic arms having one lithium cation. Although these TIs show target ion transporting property, the T_m of most TIs were about 250 °C which were much higher than those for ordinary ILs. Accordingly, ionic conductivity of double sulfonate type TIs was below $10^{-8}\,S\,cm^{-1}$ at 100 °C [11]. However, the improvement of physicochemical properties of TIs is a challenging and attractive approach for the design of ideal single ion conductive matrices.

Generally, the anionic structure largely influences on thermal and ion conductive properties of ILs [8]. As anionic structure in electrolytes, borate anions such as tetrafluoroborate are frequently employed because of their reasonable stability and high ionic conductivity [12,13]. We have also reported several solid polymer electrolytes bearing dissociable borate salt structures [14–16]. Particularly, the polymer electrolyte bearing a pentafluorophenylborate showed markedly improved ionic conductivity. Recently, a borate type ZI including pentafluorophenylborate was also reported by us, which showed both high ionic conductivity and good selectivity for lithium ion transport at the same time. It is also advantageous that borate anion can be readily modified with a various substituents via dehydrocoupling reaction of hydroborates with various alcohols.

In the present work, TIs having 9-BBN type anion were synthesized using lithium 9-BBN hydride (Scheme 1). These new TIs have electron-withdrawing and plasticizing group attached to the borate unit, which resulted in remarkably improved ion conductive characteristics in comparison with previously reported double sulfonate type TIs.
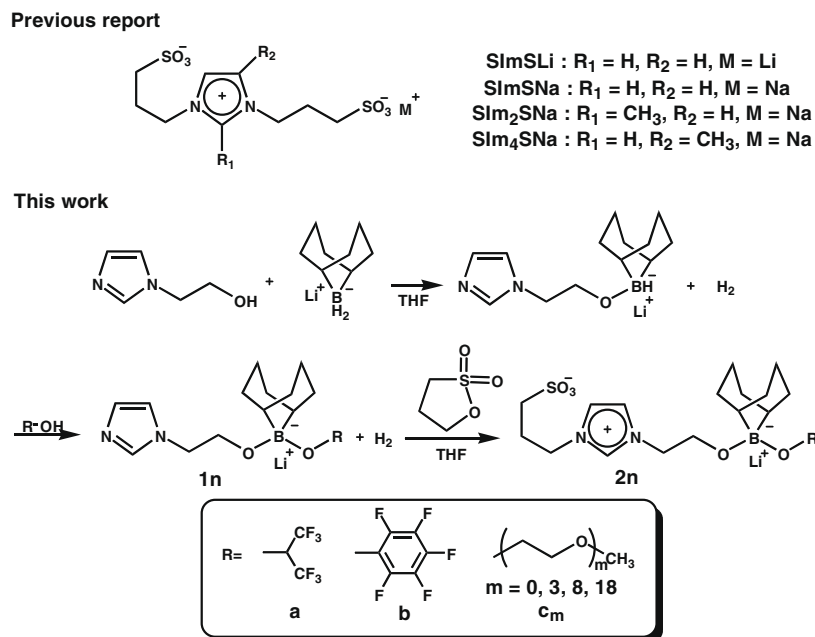
2. Results and discussion

Borate-type TIs were synthesized according to the synthetic route shown in Scheme 1. All the obtained borate-type TIs were white solid at room temperature. Although, all the TIs were insoluble in dimethyl sulfoxide, dichloromethane and acetonitrile, they were easily dissolved in methanol. In each ^{11}B NMR spectrum of borate-type TI, one peak was observed at −15 to −16 ppm. It was indicated that lithium 9-BBN hydride was quantitatively reacted with a hydroxyl proton of 2-hydroxylethyl imidazole.

The phase transition temperatures of the obtained borate-type TIs are shown in Table 1. Although sulfonate-type TIs SImSLi and SImSNa showed T_m, borate-type TIs **2a** and **2b** showed only T_g. This should be because of plasticizing effect of fluorinated substituents on the borate units. In order to reduce the T_g of TIs, ethylene oxide (EO) chains were introduced to the borate unit. The effect of EO chains on T_g was studied as a function of EO chain length. The lowest T_g of −25 °C was observed for **2c$_{18}$** among the series of borate type TIs.

The ionic conductivities of the borate-type TIs were shown in Fig. 2. **2c$_8$** showed the highest ionic conductivity of $2.5 \times 10^{-6}\,S\,cm^{-1}$ at 100 °C. This conductivity is five hundred times higher than that of double sulfonate type TI, SImSLi (see Scheme 1) at 100 °C [11]. Fig. 3 shows the effect of EO chain length on ionic conductivity and T_g of borate-type triple ions. Although elongation of EO chain lowered the T_g, the maximum ionic conductivity was observed when $m = 8$.

The negative charge of borate anion was stabilized by introducing electron-withdrawing group. Both **2a** and **2b** bearing electron-withdrawing group showed the relatively high ionic conductivity. Especially, **2b** bearing pentafluorophenyl group showed higher ionic conductivity than **2a** in spite of its high T_g. This should be because the interaction between 9-BBN-OC$_6$F$_5$ and the imidazolium cation was weak due to sterically more hindered borate structure.

The temperature dependence of the ionic conductivity was fitted to VFT (Vogel–Fulcher–Tamman) equation to analyze the ion conductive behavior after optimizing the ideal glass transition temperature T_0. These VFT plots were fitted to linear lines, suggest-

Scheme 1. Synthetic scheme for organoborate type triple ions.

Previous report

SImSLi : R$_1$ = H, R$_2$ = H, M = Li
SImSNa : R$_1$ = H, R$_2$ = H, M = Na
SIm$_2$SNa : R$_1$ = CH$_3$, R$_2$ = H, M = Na
SIm$_4$SNa : R$_1$ = H, R$_2$ = CH$_3$, M = Na

This work

m = 0, 3, 8, 18

Table 1
Thermal properties of triple ions determined by DSC measurements.

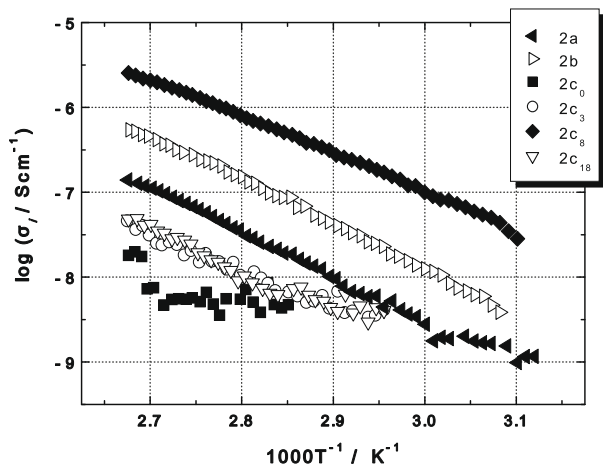| TIs	T_m (°C)	T_g (°C)	TIs	T_m (°C)	T_g (°C)
2a	–	0	SImSLi	287	–
2b	–	6	SImSNa	254	–
2c$_0$	–	23	SIm$_2$SNa	–	20
2c$_3$	–	11	SIm$_4$SNa	–	23
2c$_s$	–	–17			
2c$_{18}$	–	–25			

Fig. 2. Temperature dependence of ionic conductivity for organoborate type triple ions.
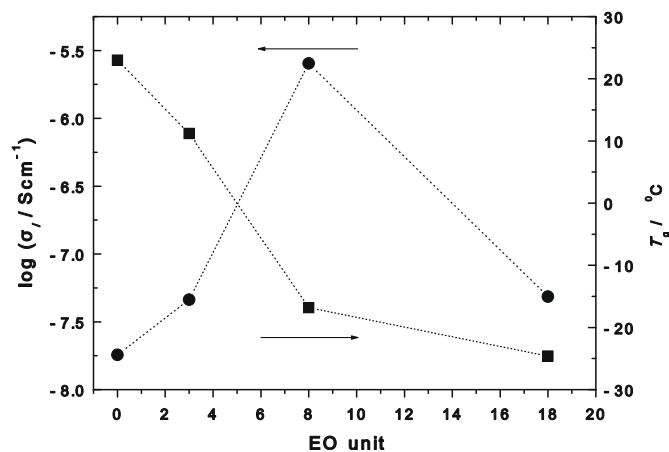

Fig. 3. Effect of EO chain length on both ionic conductivity (●) and glass transition temperature (■) of organoborate type triple ions having EO chains.

Fig. 4. Relation between T_g and ionic conductivity (at 100 °C) of TIs.

ing that the ionic conduction was based on the diffusion of lithium cations in a viscous matrix. This also implies that ionic conductivity should be correlated with T_g of the systems similarly to the case of ordinary ionic liquids.

The relationship between T_g and the ionic conductivity (at 100 °C) for all the obtained TIs is shown in Fig. 4. The ionic conductivity for all the TIs except for **2c$_{18}$** correlated well with their T_g. On the other hand, borate-type TIs having longer EO chain deviated from the relation line. This suggested that the mobility of lithium cation was dependent not only on the molecular motion of TIs but also on the segmental motion of EO chain.

The transference number of lithium cation (t_{Li^+}) for **2c** was 0.73. Generally, it is known that EO chain strongly interacts with lithium cation due to their 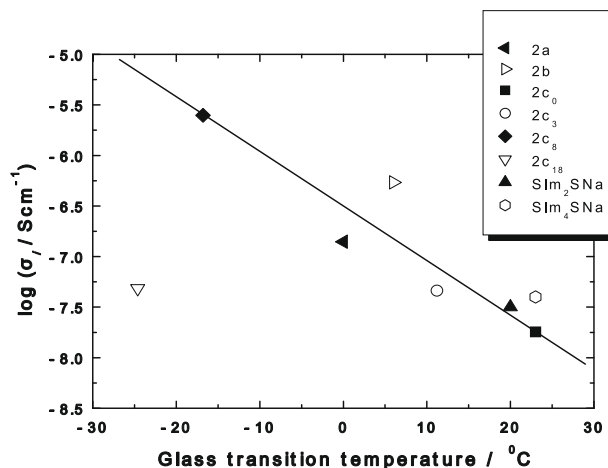Lewis basicity to reduce (t_{Li^+}). However, in spite of the presence of EO chain, **2c$_8$** showed relatively high (t_{Li^+}). The modification of TI with moderate length of EO chain resulted in both high ionic conductivity and high lithium transference number.

In conclusion, both borate and sulfonate anions were covalently tethered at 1- and 3-positions of imidazolium cation. The obtained triple ions which contain lithium cation as small counter cation were capable of transporting lithium cations in good efficiency and selectivity. As borate anion units, 9-borabicyclo-3,3,1-nonane (9-BBN) was employed because of their relatively high chemical and thermal stability. The triple ion having oligo(oxyethylene) tail onto the borate anion showed the highest ionic conductivity of 2.5×10^{-6} S cm^{-1} at 100 °C due to the relatively low T_g (–17 °C). Its ionic conductivity was about 500 times higher than those for TIs having sulfonate anionic arms both at 1- and 3-positions of imidazolium cation. The transference number of lithium cation for this salt was 0.73, which was significantly higher than those for ZIs reported so far. Furthermore, introduction of fluorinated groups such as hexafluoroisopropoxy or pentafluorophenoxy groups onto the borate moiety also led to moderate ionic conductivity. This should be because of high dissociation degree of lithium borate structure and also of plasticizing effect of fluorinated substituents. It was demonstrated that good ion conductive properties can be achieved without utilizing segmental motion of polyether in the TI systems.

3. Experimental

3.1. Materials

One molar THF solution of lithium-9-borabicyclo[3,3,1]nonane hydride was purchased from Aldrich and used as received. 1,1,1,3,3,3-Hexafluoropropanol, pentafluorophenol, and 1,3-propanesultone were purchased from Tokyo Chemical Industry. Poly(ethyleneglycol) monomethyl ether was kindly donated from NOF corporation. All the reactions were carried out under inert atmosphere.

3.2. Preparation of **2a**

N-2-(hydroxyethyl)imidazole (0.20 ml, 2.0 mmol, prepared according to the reported method [17,18]) was dissolved in THF (20 ml). The solution was added to 2.0 ml of 1 M THF solution of lithium-9-borabicyclo[3,3,1]nonane hydride (2.0 mmol) during 3 min at 0 °C. After the solution was stirred for 8 h at room temperature, 0.2 ml of 1,1,1,3,3,3-hexafluoropropanol (2.0 mmol, 0.211 ml) was added during a minute and the resulting mixture

was further stirred for 8 h. After the solvent was removed under a reduced pressure, the residue was washed with 30 ml of diethyl ether. Then the residue was dissolved in 10 ml THF, and 1,3-propanesultone (2.0 mmol, 0.175 ml) was added to the solution during a minute. After the mixture was stirred for 3 days, the supernatant was removed by a syringe. **2a** was obtained as a white solid after washed with THF.

^{1}H NMR (CD$_3$OD): δ_H (in ppm, Me$_4$Si) = 1.37∼1.96 (m, 14H, 9-BBN), 2.35 (m, 2H, NCH$_2$CH$_2$CH$_2$SO$_3$), 2.84 (t, 2H, NCH$_2$CH$_2$CH$_2$SO$_3$), 3.88 (t, 2H, NCH$_2$CH$_2$OB), 4.34 (t, 2H, CH$_2$OB), 4.45 (t, 2H, NCH$_2$CH$_2$CH$_2$SO$_3$), 7.64 (s, 1H, imidazolium), 7.70(s, 1H, imidazolium)

^{11}B NMR (CD$_3$OD): δ_B (in ppm, (CH$_3$O)$_3$B) = −15.34 (s).

3.3. Preparation of **2b**

N-2-(Hydroxyethyl)imidazole (0.20 ml, 2.0 mmol) was reacted with 2.0 ml of 1 M THF solution of lithium-9-borabicyclo[3,3,1]nonane hydride (2.0 mmol) in a similar manner with the case of **2a**. To the reaction mixture, 0.36 ml of pentafluorophenol (2.0 mmol) was added at r.t. and the resulting solution was stirred for 8 h at r.t. After the solvent was removed under a reduced pressure, the residue was washed with 30 ml of diethyl ether. Then the residue was dissolved in 10 ml THF, and 1,3-propanesultone (2.0 mmol, 0.175 ml) was added to the solution during a minute. After the mixture was stirred for 3 days, the supernatant was removed by a syringe. Compound **2b** was obtained as a white solid after washed with THF.

^{1}H NMR (CD$_3$OD): δ_H(in ppm) = 1.37∼1.96 (m, 14H, 9-BBN), 2.35 (m, 2H, NCH$_2$CH$_2$CH$_2$SO$_3$), 2.84 (t, 2H, NCH$_2$CH$_2$CH$_2$SO$_3$), 3.88 (t, 2H, NCH$_2$CH$_2$OB), 4.34 (t, 2H, CH$_2$OB), 4.45 (t, 2H, NCH$_2$CH$_2$CH$_2$SO$_3$), 7.64 (s, 1H, imidazolium), 7.70(s, 1H, imidazolium).

^{11}B NMR (CD$_3$OD): δ_B (in ppm, (CH$_3$O)$_3$B) = −15.76 (s).

3.4. Preparation of **2c$_8$**

EO modified TIs were typically prepared as follows. *N*-2-(Hydroxyethyl)imidazole (0.20 ml, 2.0 mmol) was reacted with 2 ml of 1 M THF solution of lithium-9-borabicyclo[3,3,1]nonane hydride (2.0 mmol) in a similar manner with the case of **2a**. To the reaction mixture, 0.64 ml of poly(ethyleneglycol) methyl ether (Mw:350; 2.0 mmol) was added and the resulting solution was stirred for 8 h at r.t. After the solvent was removed under a reduced pressure, residue was washed with 30 ml of diethyl ether. Then the residue was dissolved in 10 ml THF, and 1,3-propanesultone (2.0 mmol, 0.175 ml) was added to the solution during a minute. After the mixture was stirred for 3 days, the supernatant was removed by a syringe. **2c$_8$** was obtained as a white solid after washed with THF.

^{1}H NMR (CD$_3$OD): δ_H(in ppm) = 1.43∼2.02 (m, 14H, 9-BBN), 2.33 (m, 2H, NCH$_2$CH$_2$CH$_2$SO$_3$), 2.82 (t, 2H, NCH$_2$CH$_2$CH$_2$SO$_3$), 3.55 (s, 3H, CH$_3$O(PEO)), 3.65 (m, 32H, OCH$_2$CH$_2$O(PEO)), 3.87 (t, 2H, NCH$_2$CH$_2$OB), 4.30 (t, 2H, CH$_2$OB), 4.44 (t, 2H, NCH$_2$CH$_2$CH$_2$SO$_3$), 7.68 (s, 1H), 7.70(s, 1H).

^{11}B NMR (CD$_3$OD): δ_B (in ppm, (CH$_3$O)$_3$B) = −15.49 (s).

3.5. Measurements

The structures of TIs were determined by ^{1}H NMR and ^{11}B NMR spectra recorded on an α-500 (JEOL). The phase transition temperatures were determined by differential scanning calorimetry (DSC-6200 SEIKO Instruments Inc.) at the heating rate of 10 °C/min. The ionic conductivities were measured by complex ac impedance method using Solartron model 1260 (Schlumberger) using stainless steel electrodes.

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