

**Supplementary Information (SI)**

**On the concentration polarisation in molten Li salts  
and borate-based Li ionic liquids**

Keisuke Shigenobu <sup>1</sup>, Frederik Philippi,<sup>1</sup> Seiji Tsuzuki <sup>2</sup>, Hisashi Kokubo <sup>1</sup>, Kaoru Dokko <sup>1,2</sup>,

Masayoshi Watanabe <sup>2</sup> and Kazuhide Ueno <sup>1,2,\*</sup>

<sup>1</sup> Department of Chemistry and Life Science, Yokohama National University, 79-5 Tokiwadai,  
Hodogaya-ku, Yokohama 240-8501, Japan.

<sup>2</sup> Institute of Advanced Sciences, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku,  
Yokohama 240-8501, Japan.

CORRESPONDING AUTHOR: To whom correspondence should be addressed.

Kazuhide Ueno: Telephone/Fax: +81-45-339-3951. E-mail: ueno-kazuhide-rc@ynu.ac.jp

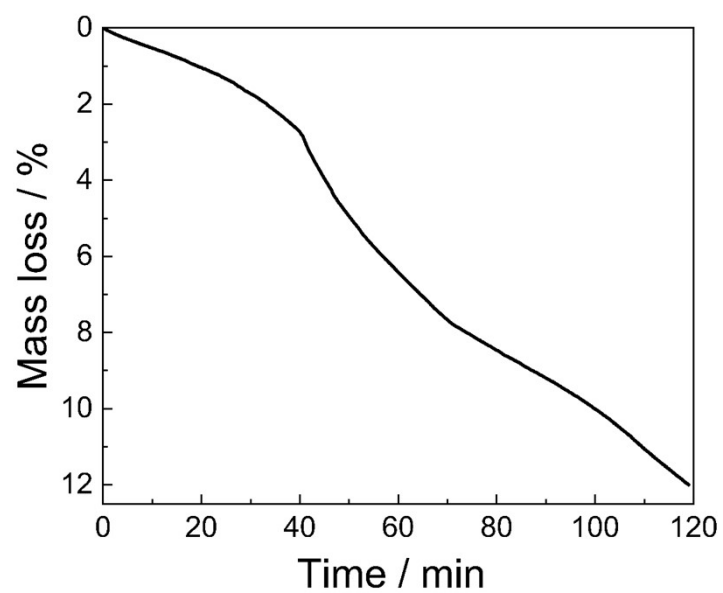
## Synthesis

Triethylene glycol monomethyl ether (mPEG3–OH), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP–OH) and trifluoroacetic acid (TFA–OH) were dehydrated by using the Zeolite molecular sieves. Under an argon atmosphere, to the  $2 \text{ mol dm}^{-3}$  solution of  $\text{LiBH}_4$  in tetrahydrofuran (THF) (20.0 mmol, 10.00 mL) at  $-78 \text{ }^\circ\text{C}$  was added the mixture of 2 mole equivalents of mPEG3–OH (40.0 mmol, 6.32 mL) and 15 mL dry THF dropwise over 10 min and the reaction mixture was stirred for 1 day with slowly and gradually elevating the temperature to  $40 \text{ }^\circ\text{C}$ . After the completion of the  $\text{H}_2$  gas evolution, to the reaction mixture at  $-78 \text{ }^\circ\text{C}$  was added the mixture of 2 mole equivalents of HFIP (40.0 mmol, 4.15 mL) for  $\text{Li}[\text{B}(\text{mPEG3})_2(\text{OHFIP})_2]$  or TFA–OH (40.0 mmol, 3.06 mL) for  $\text{Li}[\text{B}(\text{mPEG3})_2(\text{OTFA})_2]$  and 7 mL dry THF dropwise over 10 min under an argon atmosphere and the reaction mixture was stirred in the same way as the previous step. For the synthesis of Li salts:  $\text{Li}[\text{B}(\text{mPEG3})_4]$  and  $\text{Li}[\text{B}(\text{OTFA})_4]$ , the reaction was completed at the first step by adding 4 mole equivalents of mPEG3–OH (40.0 mmol, 6.32 mL) or TFA–OH (40.0 mmol, 3.06 mL) to the  $2 \text{ mol dm}^{-3}$  solution of  $\text{LiBH}_4$  in tetrahydrofuran (THF) (10.0 mmol, 5.00 mL).

After the completion of the gas evolution, the reaction solvent was thoroughly evaporated off, and the residue was dried *in vacuo* at  $70 \text{ }^\circ\text{C}$  for 1 day to give  $\text{Li}[\text{B}(\text{mPEG3})_2(\text{OHFIP})_2]$  or  $\text{Li}[\text{B}(\text{mPEG3})_2(\text{OTFA})_2]$  as a viscous, colourless and transparent liquid,  $\text{Li}[\text{B}(\text{mPEG3})_4]$  as a sticky, colourless and transparent solid and  $\text{Li}[\text{B}(\text{OTFA})_4]$  as a white-coloured solid. 13.88 g (20.5 mmol) of  $\text{Li}[\text{B}(\text{mPEG3})_2(\text{OHFIP})_2]$  was obtained in 102 % yield, 11.22 g (19.7 mmol) of  $\text{Li}[\text{B}(\text{mPEG3})_2(\text{OTFA})_2]$  in 98 %, 6.45 g (9.61 mmol) of  $\text{Li}[\text{B}(\text{mPEG3})_4]$  in 96 % and 2.249 g (4.80

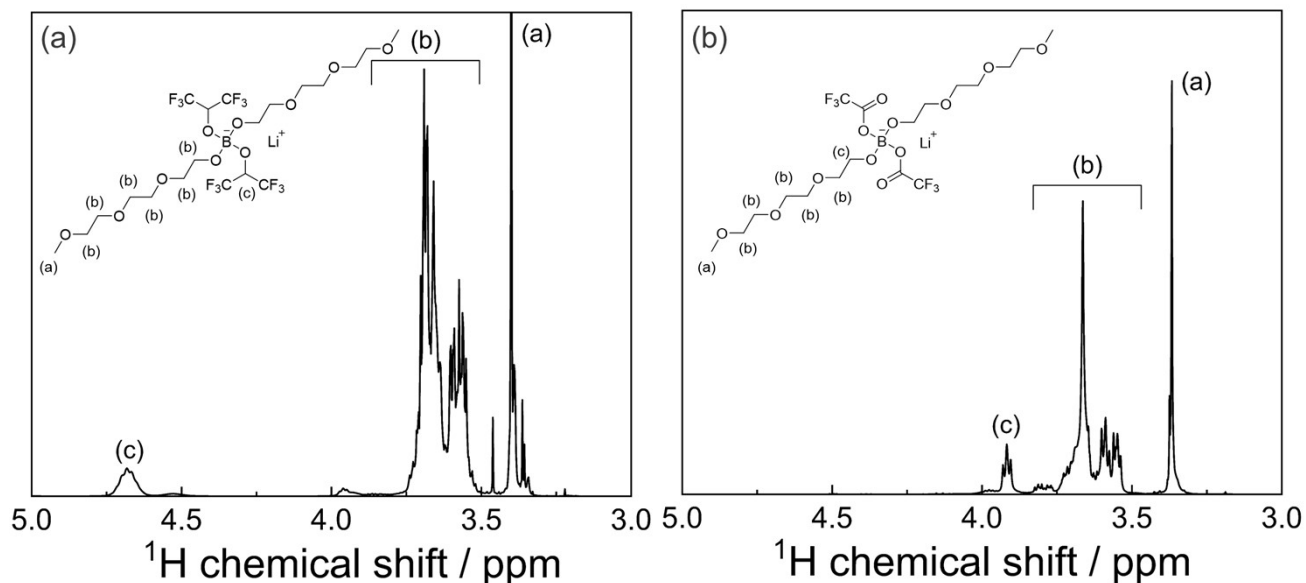
mmol) of Li[B(OTFA)<sub>4</sub>] in 48 %. The yield of Li ionic liquids depends on the accuracy in weighing and the remaining unreacted reagents or solvated-solvents such as mPEG3–OH and THF, however, almost 100 % yield (except Li[B(OTFA)<sub>4</sub>]) was achieved as expected two-step substitution reaction of LiBH<sub>4</sub>. The lowest conversion of Li[B(OTFA)<sub>4</sub>] would arise from its thermal stability; 12 % of its mass was reduced for 120 min at 70 °C under N<sub>2</sub> and atmospheric pressure (**Figure S1**). Thus, Li[B(OTFA)<sub>4</sub>] would be lost during the evaporation and drying process.

## Thermogravimetric data

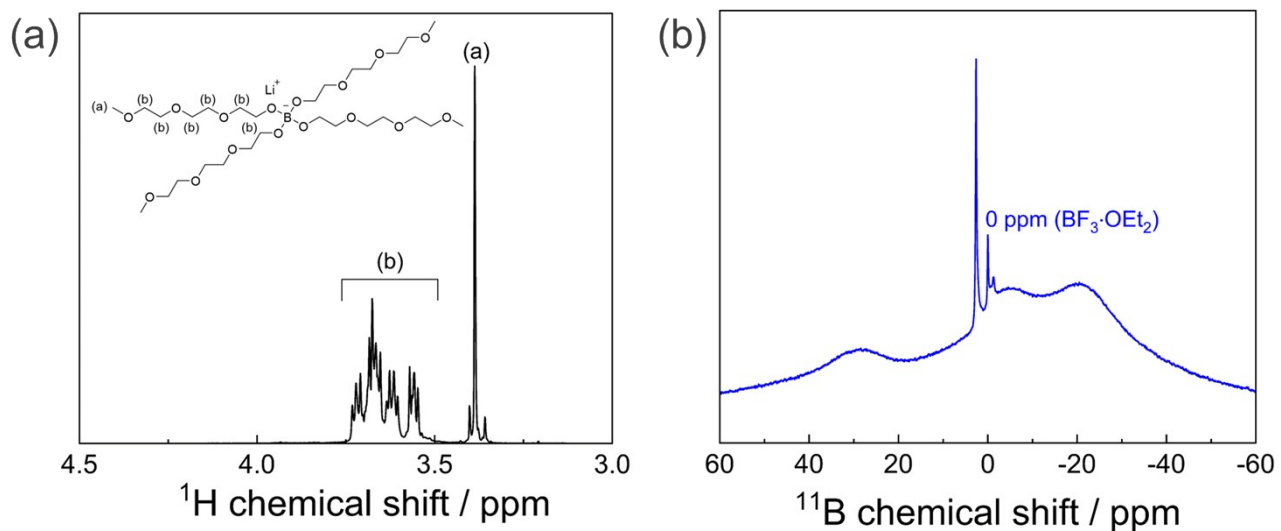


**Figure S1.** Isothermal thermogravimetric curve obtained for Li[B(OTFA)<sub>4</sub>] at 70 °C.

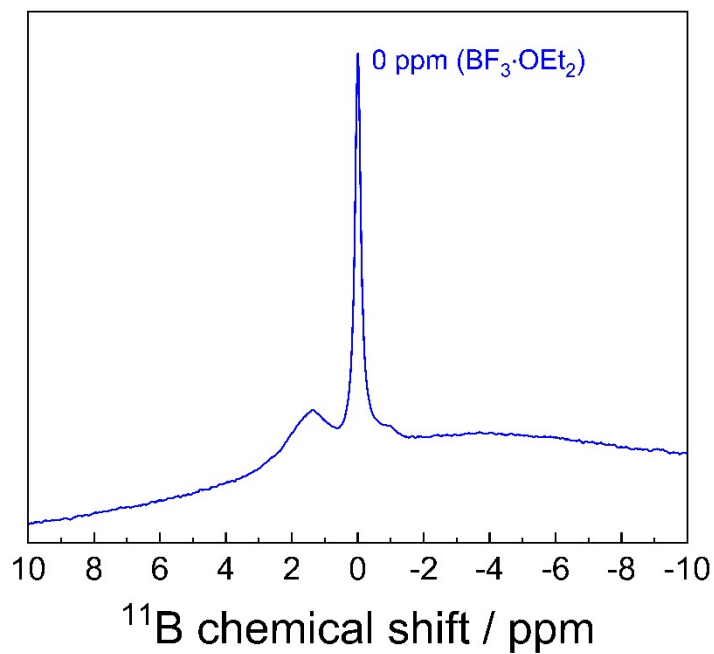
## NMR spectra



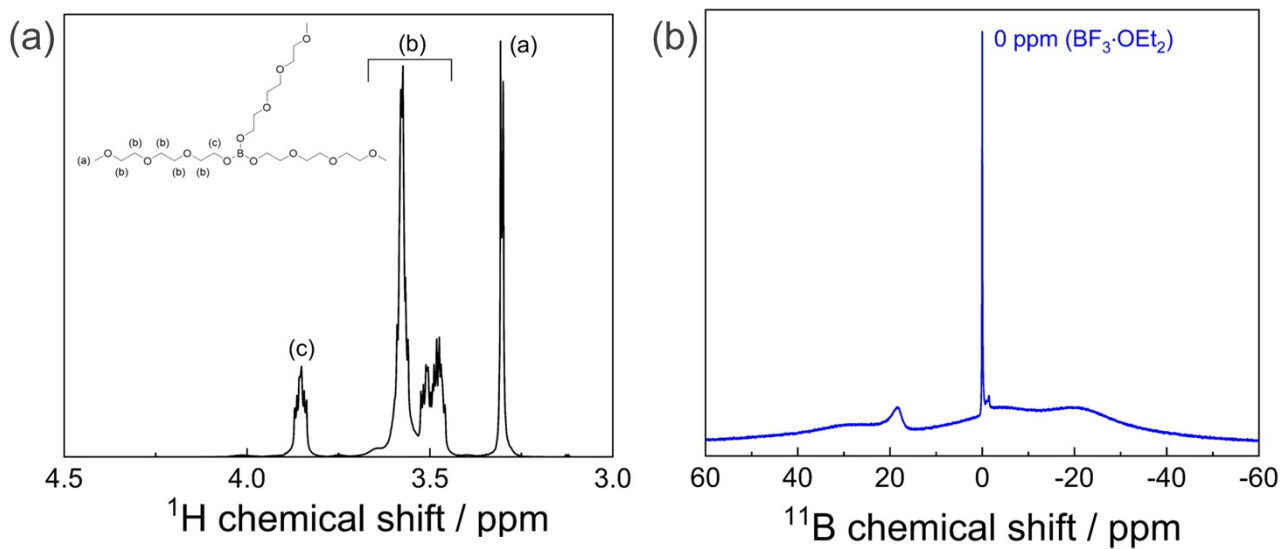
**Figure S2.**  $^1\text{H}$  NMR spectra of (a)  $\text{Li}[\text{B}(\text{mPEG}3)_2(\text{OHFIP})_2]$  and (b)  $\text{Li}[\text{B}(\text{mPEG}3)_2(\text{OHFIP})_2]$  from 3.0 ppm to 5.0 ppm.



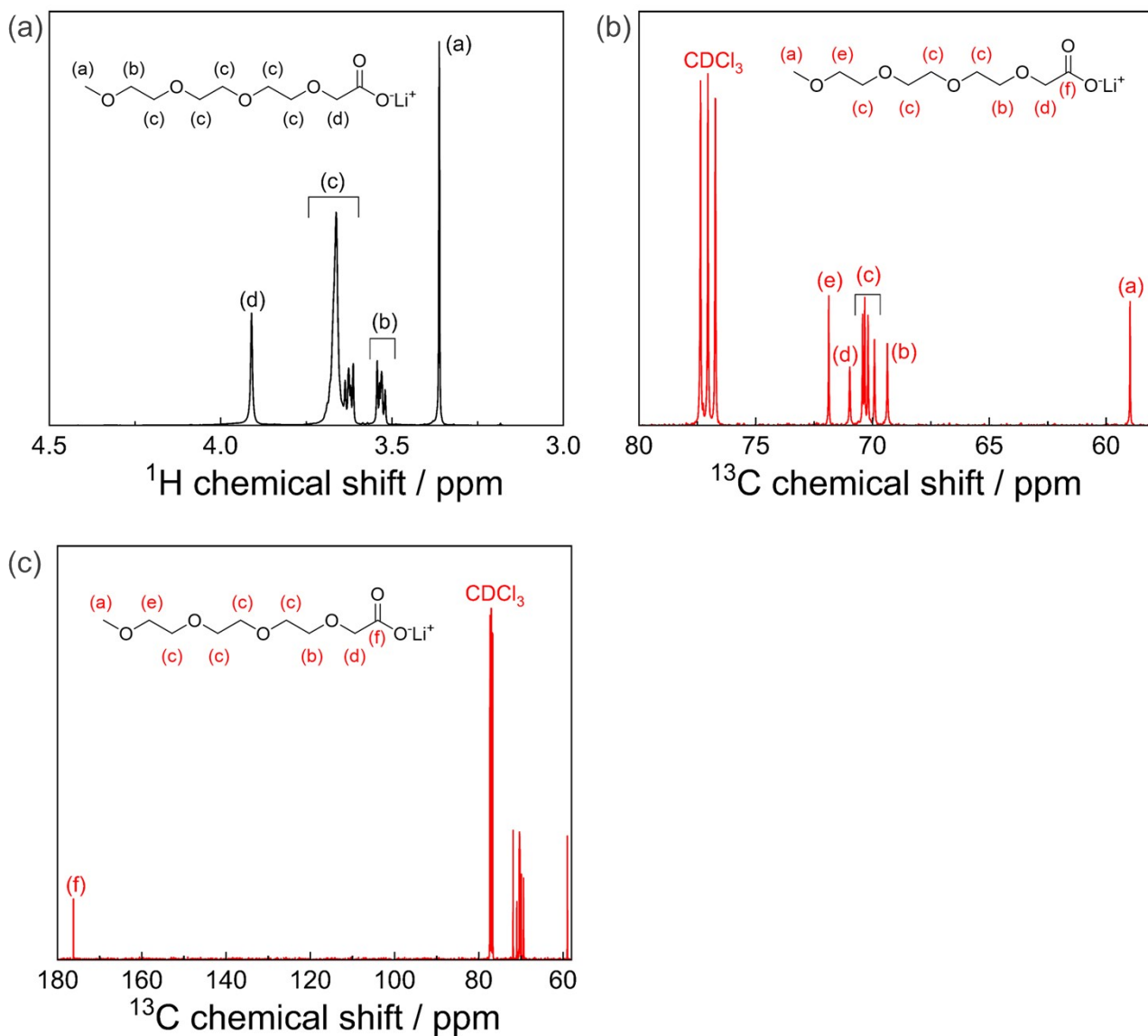
**Figure S3.** (a)  $^1\text{H}$  NMR spectra of  $\text{Li}[\text{B}(\text{mPEG}3)_4]$  from 3.0 ppm to 4.5 ppm and (b)  $^{11}\text{B}$  NMR spectra of  $\text{Li}[\text{B}(\text{mPEG}3)_4]$  from -60 ppm to 60 ppm.



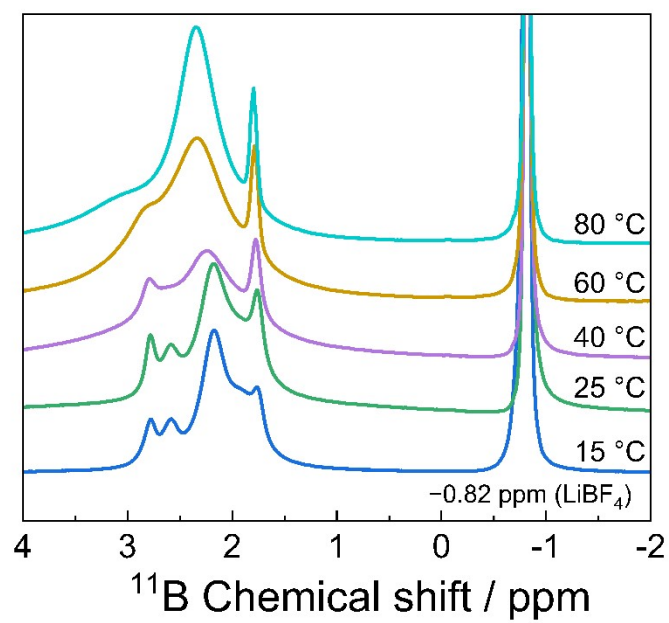
**Figure S4.**  $^{11}\text{B}$  NMR spectrum of  $\text{Li}[\text{B}(\text{OTFA})_4]$  from  $-10$  ppm to  $10$  ppm.



**Figure S5.** (a)  $^1\text{H}$  NMR spectra of  $\text{B}(\text{mPEG}3)_3$  from  $3.0$  ppm to  $4.5$  ppm and (b)  $^{11}\text{B}$  NMR spectra of  $\text{B}(\text{mPEG}3)_3$  from  $-60$  ppm to  $60$  ppm.



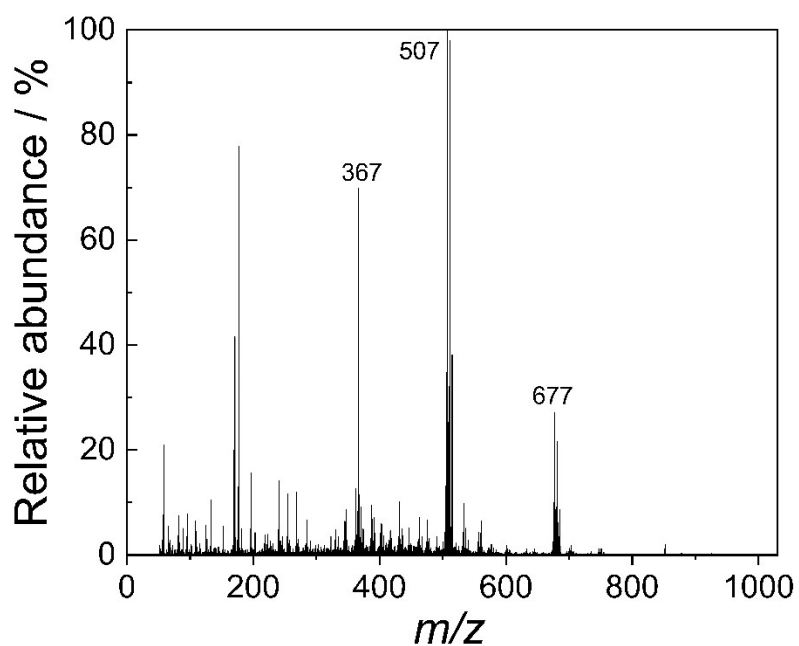
**Figure S6.** (a)  $^1\text{H}$  NMR spectra of Li[TOTO] from 3.0 ppm to 4.5 ppm and  $^{13}\text{C}$  NMR spectra of Li[TOTO] (b) from 58 ppm to 80 ppm and (c) from 58 ppm to 180 ppm.



**Figure S7.** VT NMR spectra regarding  $^{11}\text{B}$  of  $\text{Li}[\text{B}(\text{mPEG}3)_2(\text{OHFIP})_2]$ .

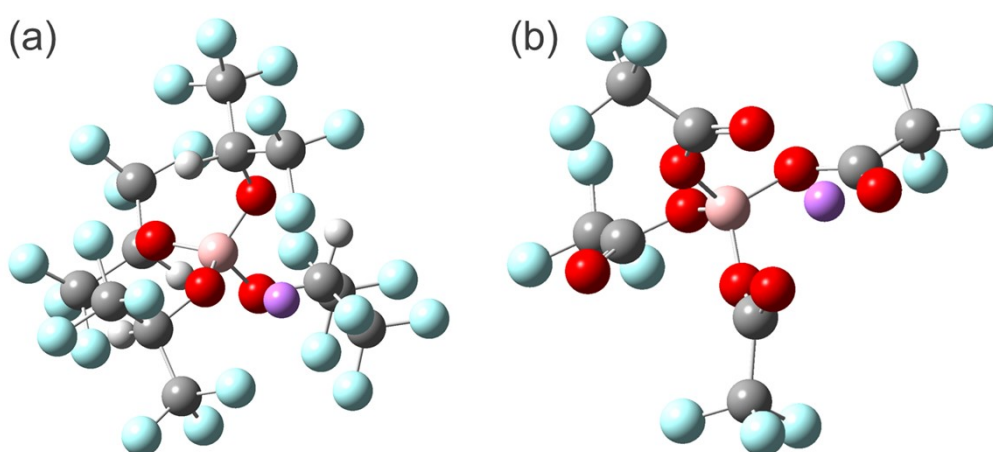


## FAB-MS Spectra



**Figure S8.** FAB-MS spectrum of  $^{11}\text{B}$  of  $\text{Li}[\text{B}(\text{mPEG}3)_2(\text{OHFIP})_2]$ .

## DFT calculations



**Figure S9.** The B3LYP/6-311++G\*\* level optimised geometries of (a)  $\text{LiB}(\text{OHFIP})_4$  and (b)  $\text{LiB}(\text{OTFA})_4$ . Purple:  $\text{Li}^+$ , pink: B, red: O, grey: C, light grey: H and sky blue: F.

**Table S1** The energies of Li ionic liquids, borate esters, and Li salts <sup>a</sup>.

	$E_{LiIL}^b$	$E_{sol}^b$	$E_{salt}^b$
Li[B(OHFIP) <sub>4</sub> ]	-3190.4562	–	–
B(OHFIP) <sub>3</sub>	–	-2393.3599	–
LiOHFIP	–	–	-797.0386
-----			
Li[B(OTFA) <sub>4</sub> ]	-2138.103	–	–
B(OTFA) <sub>3</sub>	–	-1604.0537	–
LiOTFA	–	–	-533.9721

a: The geometries were optimised at the B3LYP/6-311++G\*\* level.

b: Energy in atomic units.