Crystalline Low Molecular Weight Cyclic Organoboron Compound for Efficient Solid State Lithium Ion Transport

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1. Materials and Instruments:

Dehydrated ethylene glycol was purchased from WAKO Co. Ltd. and used as received. Hexane, for washing the product, was purchased from WAKO Co. Ltd. and was used as received. NMR spectroscopic analysis was done by using Bruker model Avance III 400. Thermogravimetric analysis was done on a Perkin Elmer model TGA7. Ionic conductivity was measured with a complex-impedance gain phase analyzer Solartron model 1260, under the frequency range from 0.1 Hz to 1 MHz. Raman spectroscopic analysis was done using Raman scattering equipment of Horiba, Jobin-Yvon make; model T64000. TEM micrographs were obtained using Transmission Electron Microscope, Hitachi H-7650. DC current measurements were carried out on a Potentiostat/ Galvanostat of Princeton Applied Research make; model Versastat-3. Potential Window measurement was done using Potentiostat/ Galvanostat made by Princeton Applied Research model Versastat-3.

2. Experimental

Mesityl borane was synthesized according to the literature[1]. Dehydrated ethylene glycol (0.598 mL, 0.0107 moles) was added to the synthesized mesitylborane (1.42 g, 0.0107 moles) at 0 °C. Reaction was carried for stirring for 5 hours at room temperature under N_2 atmosphere **(Scheme 1)**. The resulting mixture was washed with hexane and dried under reduced pressure for 3 hours to obtain a white crystalline powder. The final product, denoted as **1** (EGMB), was recrystallized using hexane to obtain needle shaped crystals.
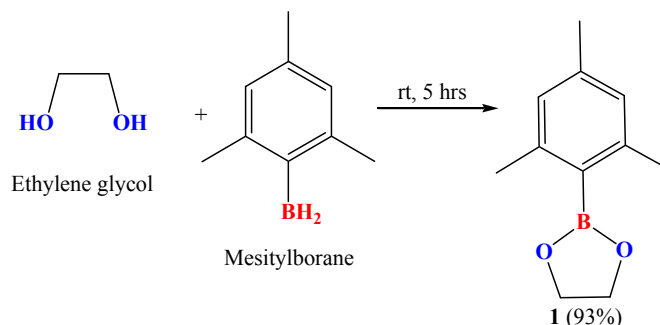
Scheme 1

3. Characterization:

The synthesized low molecular weight cyclic organoboron electrolyte **1**, obtained as needle shaped crystals was characterized by NMR spectroscopy, TGA, Raman Spectroscopy and HRTEM. Then, it was subjected to electrochemical measurements for further analysis.

a. NMR Spectroscopy:

^{11}BNMR (400MHz, δ ppm, DMSO-d_6): 31.3 ppm (RB (OR`)$_2$)
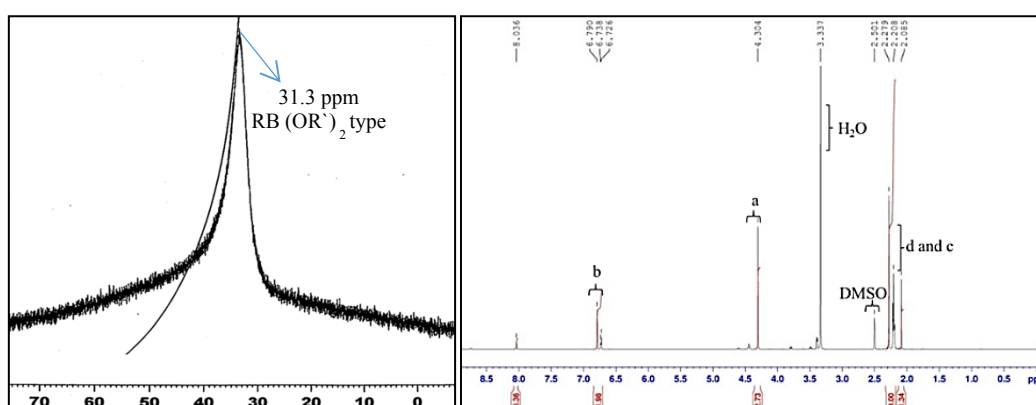
Fig. 1 ^{11}B-NMR and ^{1}H-NMR of **1** in DMSO-d_6

^{1}HNMR (400MHz, δ ppm, DMSO-d_6): 6.79-6.72(2H phenyl ring protons), 4.30(4H, -CH$_2$- groups of ethylene glycol), 2.27-2.08 (9H, -CH$_3$ protons of mesityl group)

b. Thermogravimetric Analysis:

Thermogravimetric analysis to study the thermal stability of the cyclic organoboron electrolyte showed that the compound is thermally stable up to 100ºC. In total, 5 samples were studied, out of which, 4 samples were prepared by the facile grinding technique under nitrogen atmosphere which can be listed as below:

Pure: **1** (pure)

Sample 1: **1**:LiTFSI = 4:1 (molar ratio with **lowest** concentration of **1**)

Sample 3: **1**:LiTFSI = 1:1 (**equimolar** ratio of **1** and LITFSI)

Sample 6: **1**:LiTFSI = 1:4 (molar ratio with **highest** concentration of **1**)

Sample <u>4</u>: **1**:LiTFSI = 1:2 (molar ratio showing **highest ionic conductivity**)

TGA for all the samples were done under argon atmosphere between 30°C to 300°C at

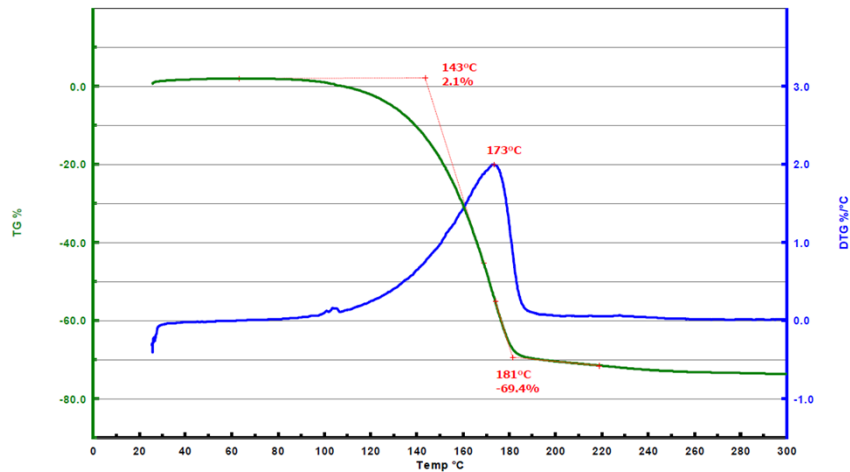the rate of 10°C/min. Fig. 2 to 6 shows the TGA profiles of the prepared samples.
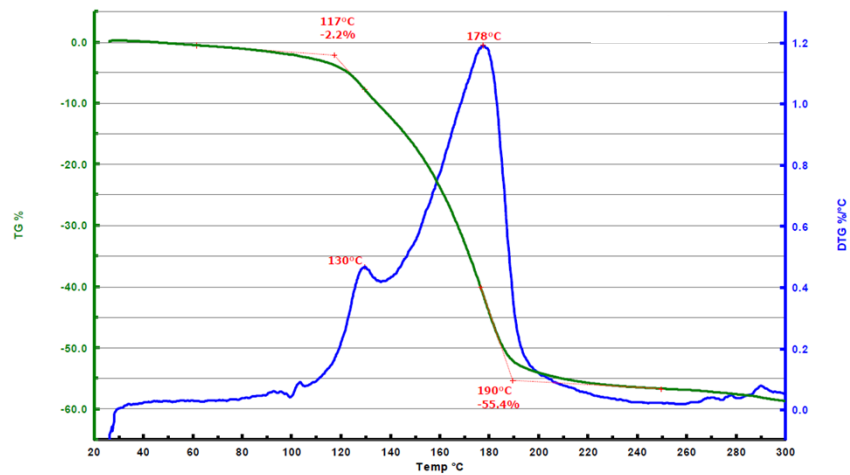

Fig. 2: TGA profile of pure EGMB

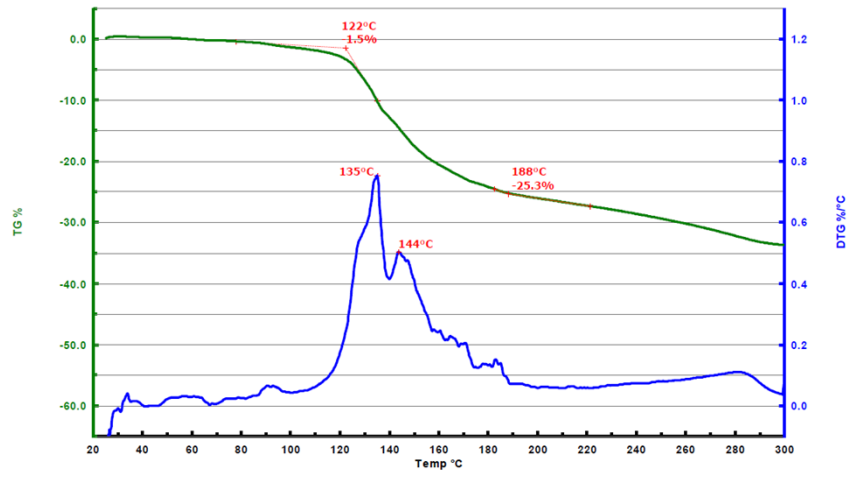**Fig. 3:** TGA profile of Sample EGMB:LiTFSI = 4:1
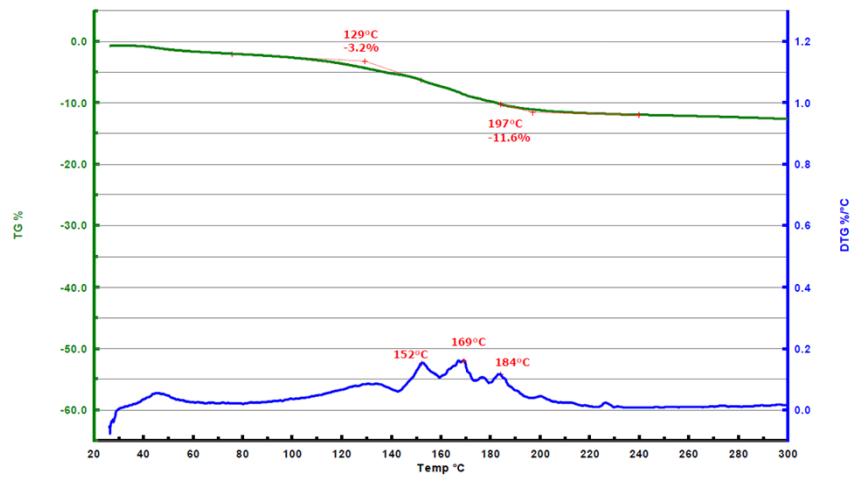
Fig. 4: TGA profile of Sample EGMB:LiTFSI = 1:1

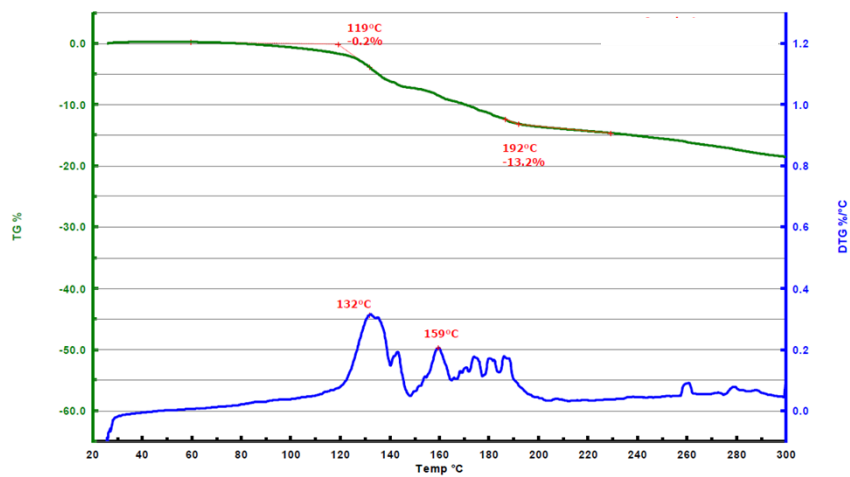
Fig. 5: TGA profile of Sample EGMB:LiTFSI = 1:4

Fig. 6: TGA profile of Sample EGMB:LiTFSI = 1:2

c. VFT plots (Temperature dependence of ionic conductivity)

The temperature dependence of ionic conductivity was studied by the VFT analysis of the samples prepared by both the methods.
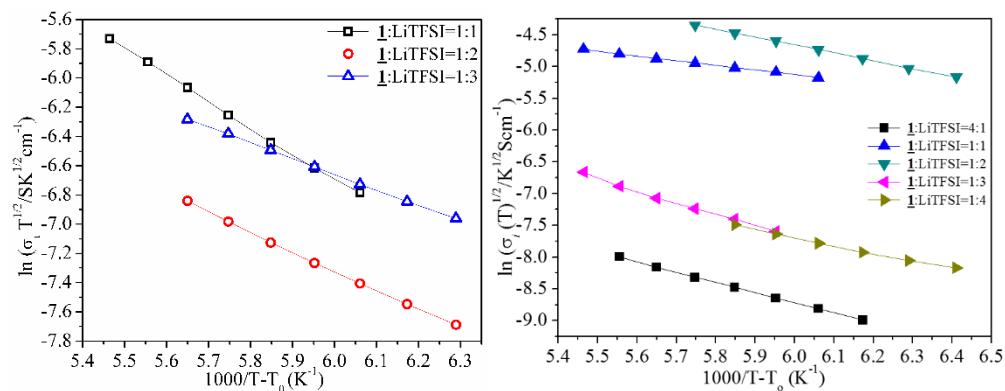

Fig. 7 VFT plots for the samples doped with LiTFSI (a) by conventional method of dissolving in THF and (b) by grinding method

d. Raman Spectroscopy (Theoretical and Experimental):

Raman spectrum was also studied under 531 nm. The Raman spectrum obtained experimentally was confirmed through a simulated spectrum for an optimized structure of **1** (EGMB) using Gaussian 09 software with a density functional theory (DFT) calculations using a basis set of B3LyP-6-311G.
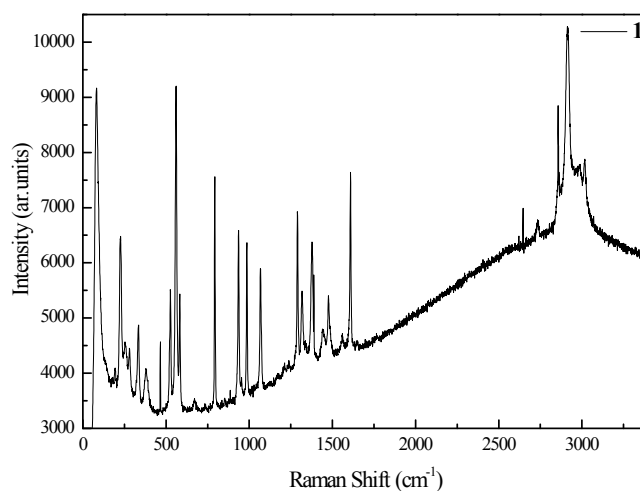

Fig. 8 Raman Spectrum of **1** under 531nm

The observed Raman frequencies are listed below:

2950 – 3000 cm^{-1},C=C, C-H (alkyl free) vibrations; 1580- 1620 cm^{-1},Aromatic CH_2=CH_2 stretch; 1350 -1450 cm^{-1}, Aromatic ring vibrations; 950 – 1000 cm^{-1}, Aromatic ring vibrations; 50 cm^{-1} and 550 cm^{-1}, Ethylene CH_2 stretch and bend.

e. <u>HRTEM</u>:

<u>Fig. 9</u> shows the transmission electron micrographs of the crystalline material EGMB (**1**). A definite geometry and an unresolved lattice fringes like pattern apparently evinces the formation of organic crystals.
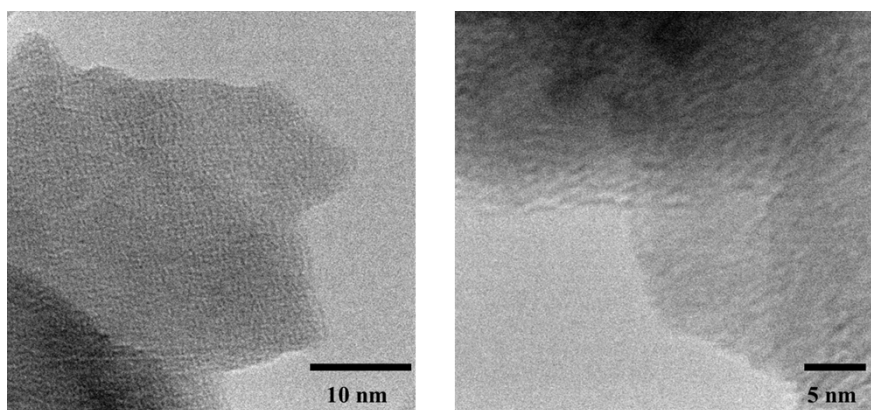

<u>Fig. 9 </u>Transmission Electron Micrographs of **1**

4. <u>Electrochemical Analysis</u>:

a. Lithium transference number

The measure was carried out using Li/electrolyte/Li type cell. A combination of DC polarization and AC impedance was used to determine the lithium ion transference number of the samples[2]. Firstly, the initial interfacial resistance is observed by AC impedance followed by DC polarization of the cell applying small, constant potential difference between the electrodes. Finally, the

interfacial resistance is again determined by using the AC impedance method after the cell had attained a steady current during the DC polarization technique.

At a constant DC of 0.03 V, the Li ion transference number, calculated by the formula,

$$t_{Li+} = i_f (V - i_0 R_0)/i_0 (V - i_t R_f), \qquad\qquad \text{----- (1)}$$

where t_{Li^+} =Li-cation transference number; V =Applied DC voltage; I_0 =Initial current; I_f =Final current; R_0 =Initial resistance; R_f =Final resistance

b. Potential window measurement of **1**:

The potential window of the sample was determined to be 5.3 V. Potential window measurement was done in a 3E configuration cell under Argon atmosphere. Electrolyte used was 0.01M **1** in 0.1M LiTFSI in 15mL EC: DC =1:1. The potential window of the cell was analyzed by cyclic voltammetric analysis between -3.5 V to +3.5 V using Pt-Pt electrode (wire) vs $Ag/AgNO_3$ at a scan rate of 5mV/s. From -3.3 V to +2.5V there occurred no electrochemical reaction.
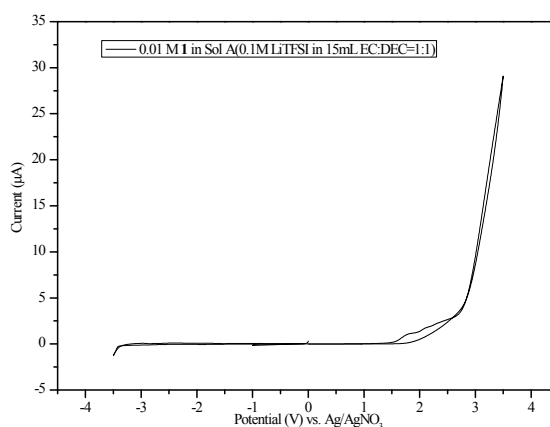

Fig. 10 Cyclic Polarization scan for the sample **1** in 0.1M LiTFSI in 15mL EC:DC=1:1 vs

$Ag/AgNO_3$

References

1. M. Ranger and M. Leclerc, *Macromolecules*, 1999, **32**, 3306–3313

2. B. M. Wiers, M.-L. Foo, N. P. Balsara, and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 14522–14525.