**Electronic Supplementary Information**

# Ionic conduction in ammonia functionalised closo-dodecaborates $MB_{12}H_{11}NH_3$ (M = Li and Na)

Steffen R. H. Jensen[a,b], Mathias Jørgensen[b], Thi Phuong Thao Nguyen[a], Greg Nolan[a], Craig E. Buckley[a], Torben R. Jensen[b]* and Mark Paskevicius[a]*

[a] Department of Physics and Astronomy, Institute for Energy Transitions, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

[b] Department of Chemistry, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Langelandsgade 140, DK-8000 Aarhus, Denmark.

* Corresponding authors
Torben R. Jensen (trj@chem.au.dk) and Mark Paskevicius (mark.paskevicius@gmail.com)

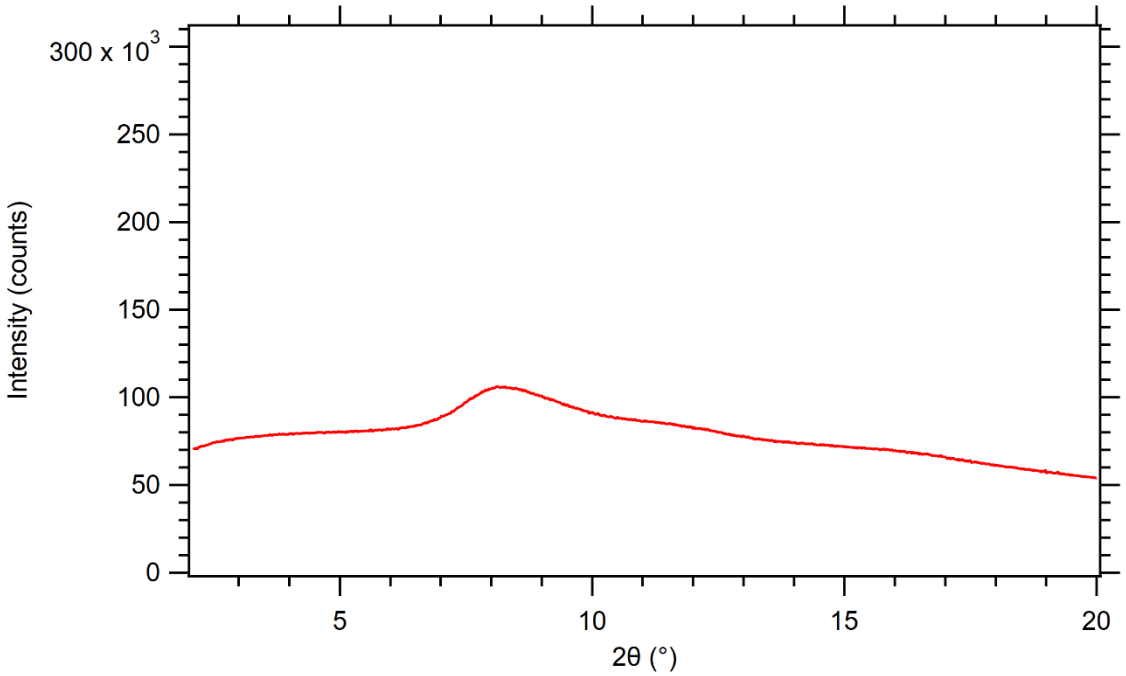



**Fig. S1** XRD data for solvated $LiB_{12}H_{11}NH_3$.MeCN after synthesis (before drying). λ = 0.824958 Å.

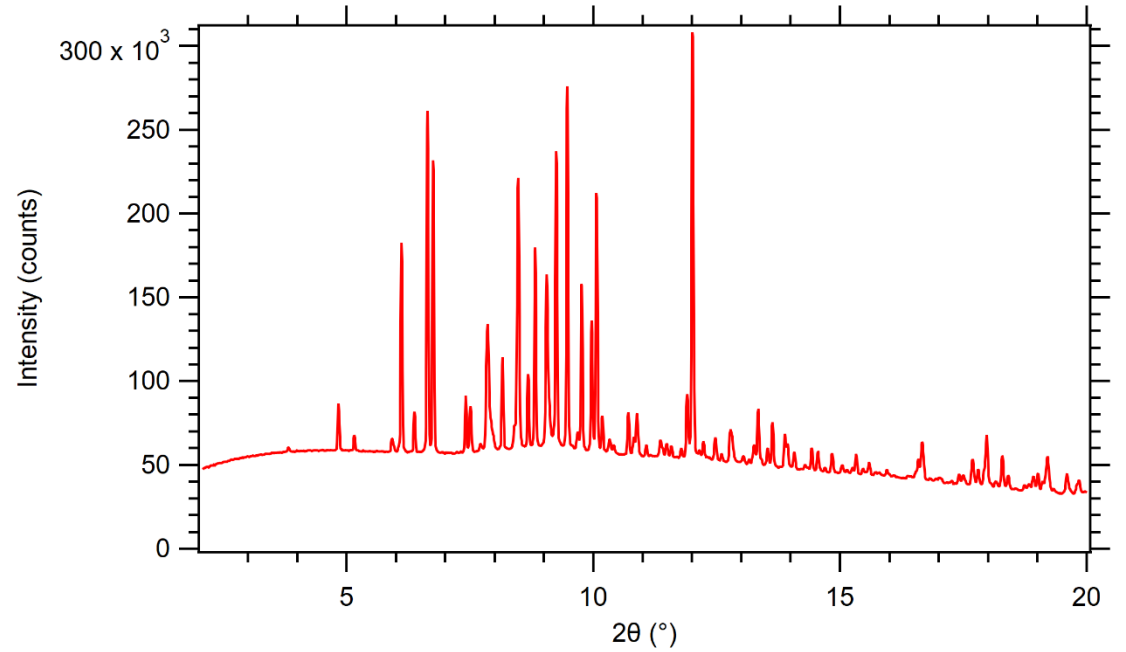



**Fig. S2** XRD data for solvated $NaB_{12}H_{11}NH_3.4H_2O$ after synthesis (before drying). λ = 0.824958 Å.

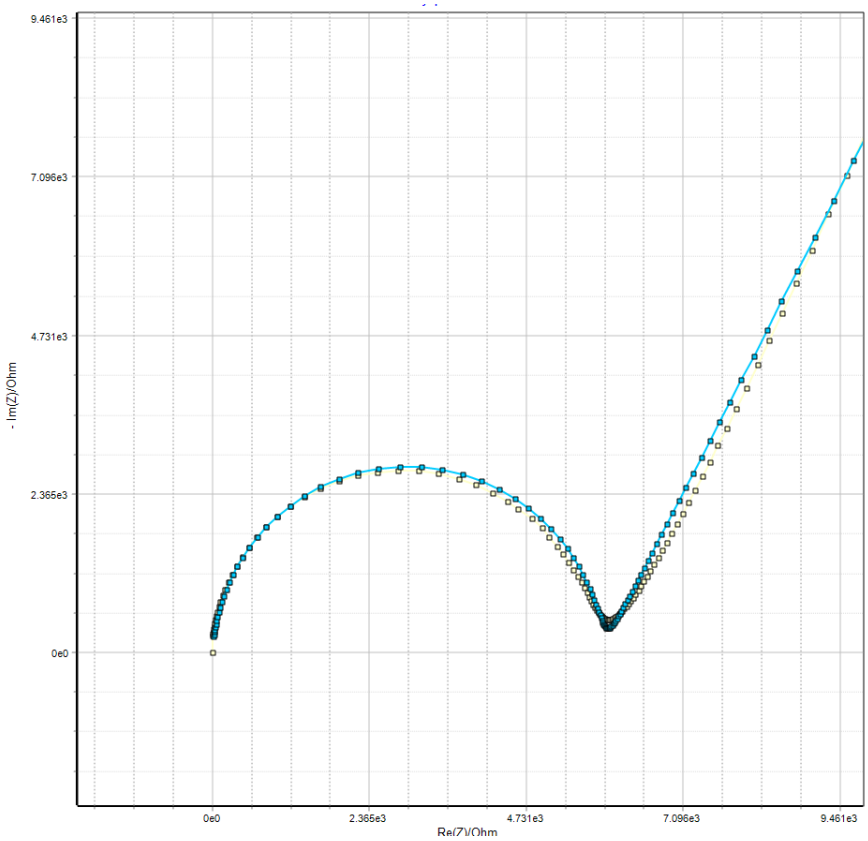



**Fig. S3** Example electrochemical impedance spectroscopy Nyquist plot for $LiB_{12}H_{11}NH_3$ at 110 °C (yellow) and the fit (blue) using a (*Q*/*R* + *W*) equivalent circuit with constant phase element (*Q*), resistor (*R*) and Warburg element (*W*).

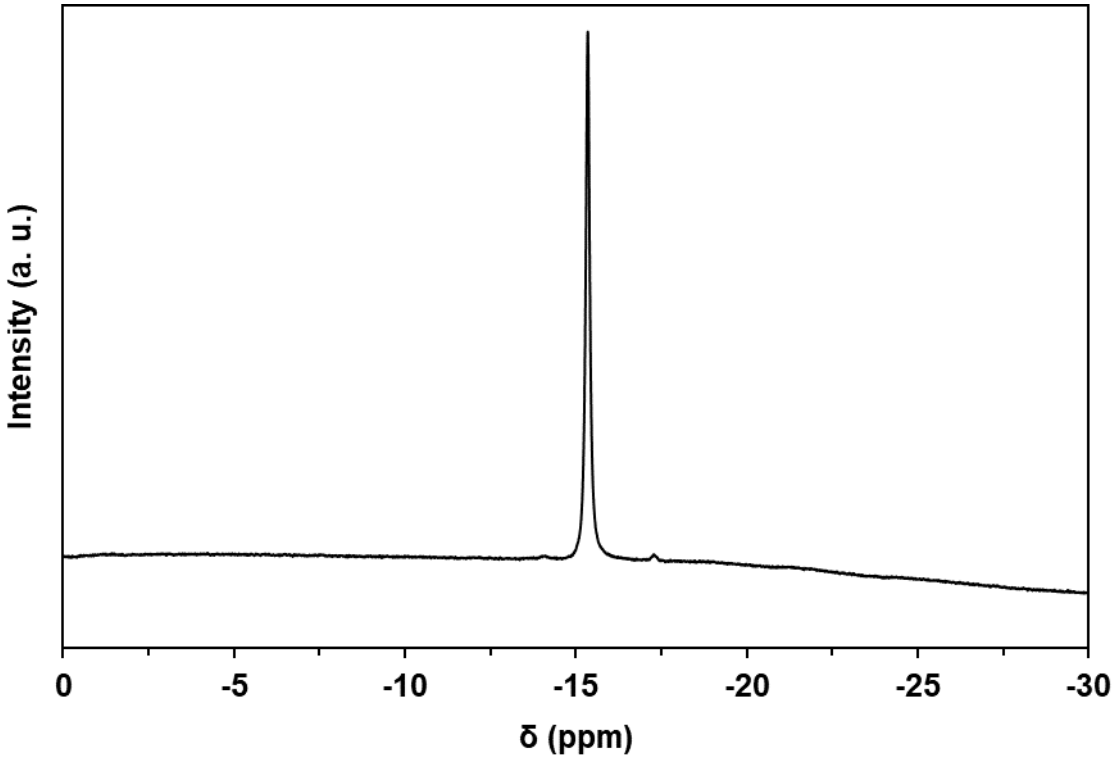



**Fig. S4** $^{11}B\{^{1}H\}$ NMR spectrum of the $NaB_{12}H_{12}$ precursor in $D_2O$.

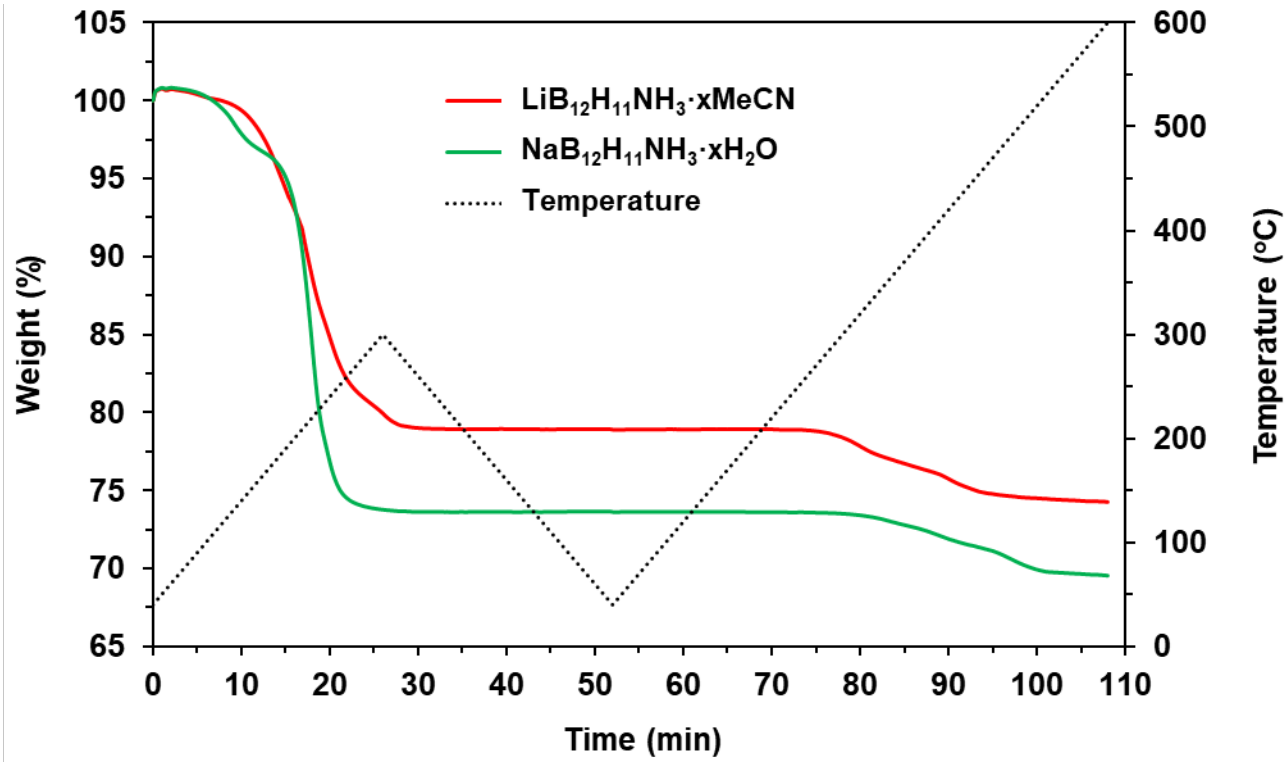



**Fig. S5** Thermogravimetric plots for $LiB_{12}H_{11}NH_3 \cdot x$MeCN and $NaB_{12}H_{11}NH_3 \cdot xH_2O$ heated from RT to 300 °C then cooled to 40 °C and finally re-heated to 600 °C in a 40 mLmin$^{-1}$ flow of Ar at 10 °C/min.

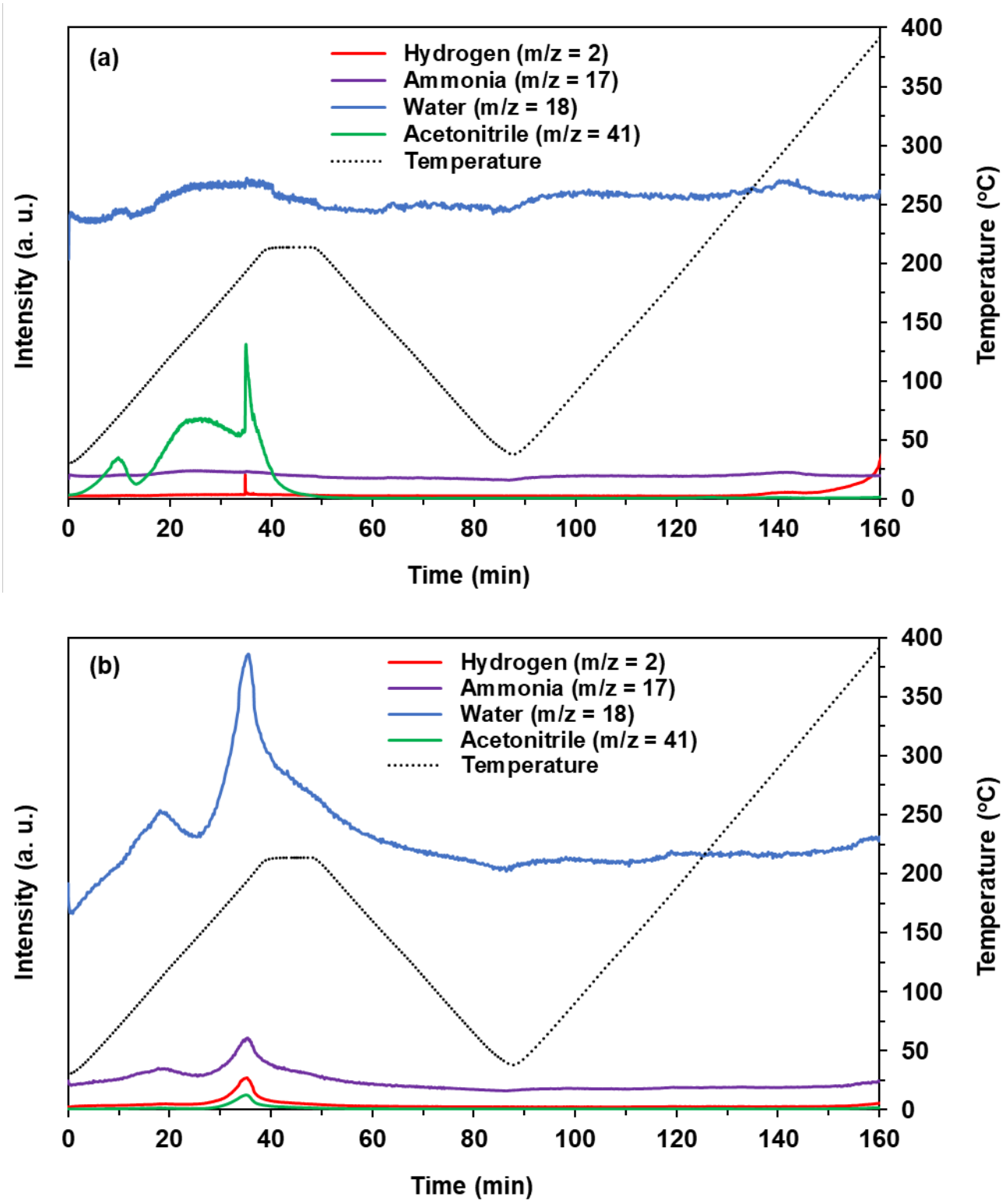



**Fig. S6** TPD plots for (a) $LiB_{12}H_{11}NH_3 \cdot x$MeCN and (b) $NaB_{12}H_{11}NH_3 \cdot xH_2O$. Temperature program: heating from RT to 220 °C ($\Delta T/\Delta t$ = 5 °Cmin$^{-1}$), isothermally holding at 220 °C for 1 h, cooling to RT, and heating again to 400 °C ($\Delta T/\Delta t$ = 5 °Cmin$^{-1}$). The signals for $NaB_{12}H_{11}NH_3 \cdot xH_2O$ at 35 minutes for $m/z$ = 2 and 17 are likely related to water fractionation in the mass spectrometer.

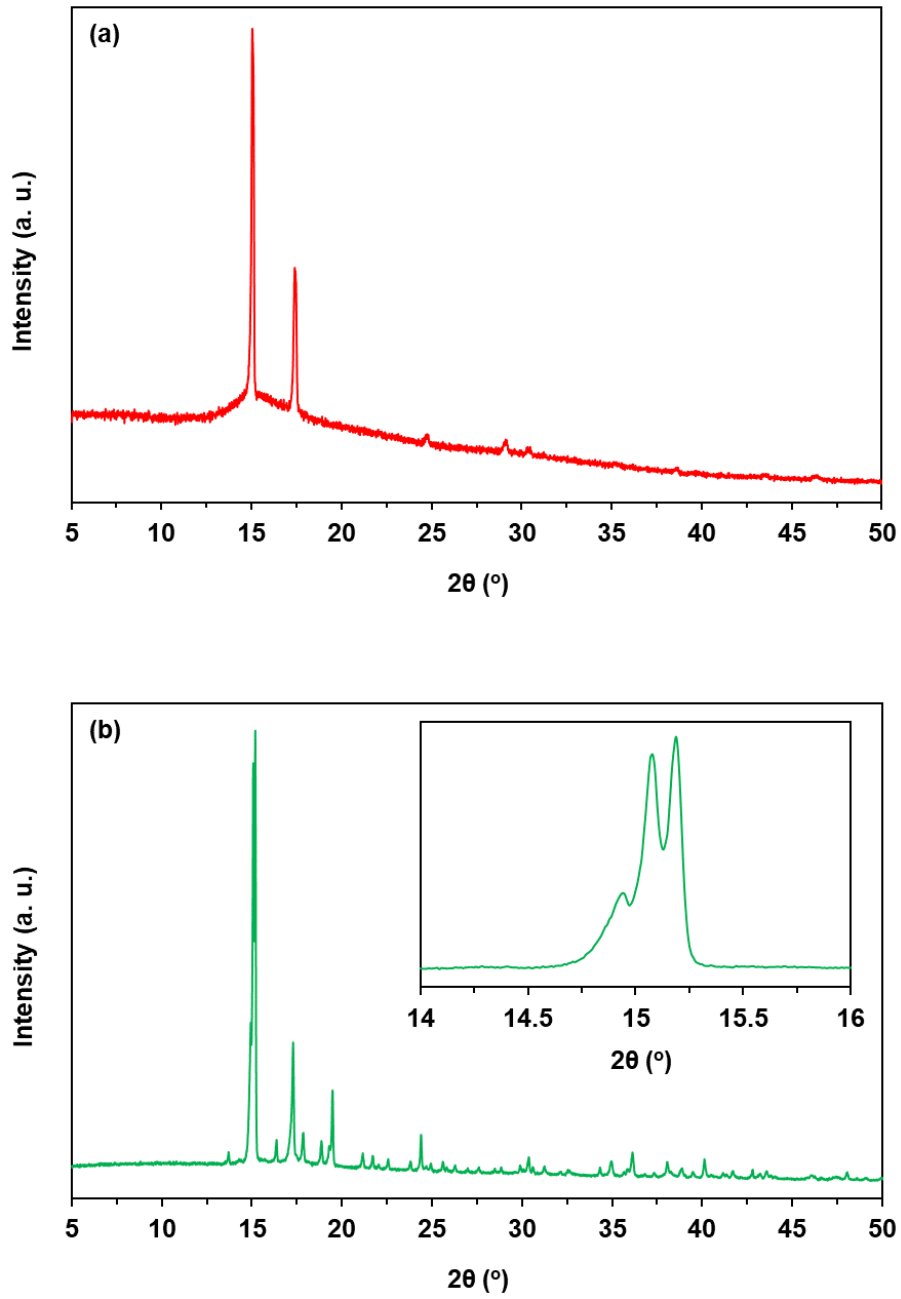
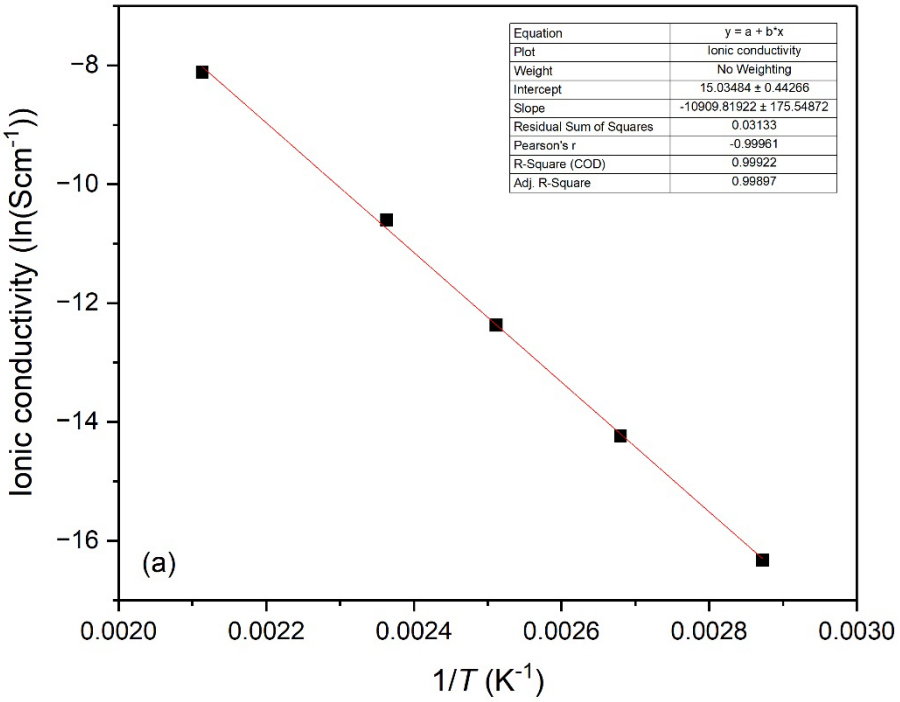
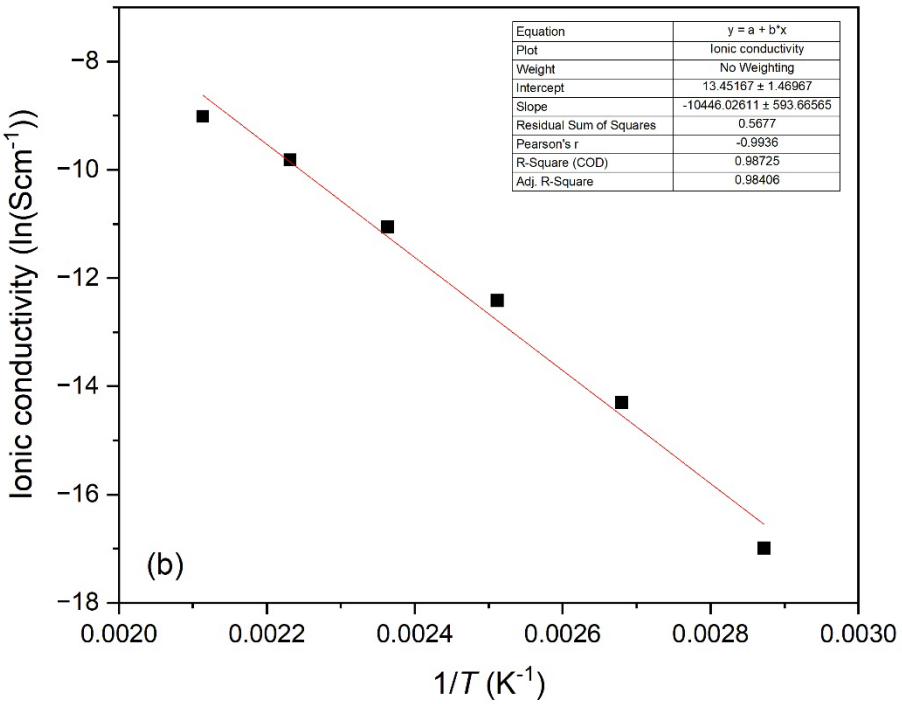


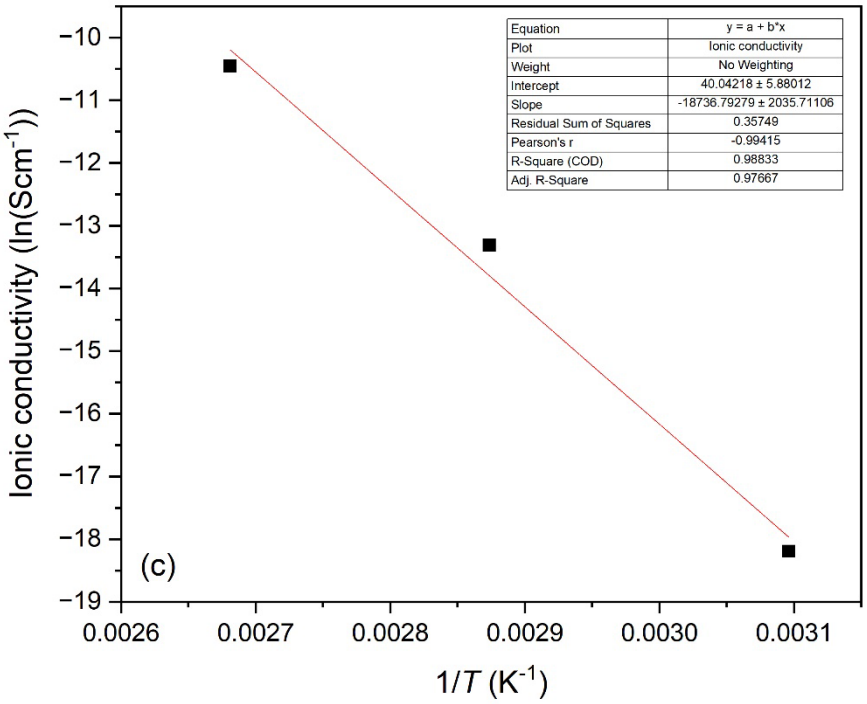

**Fig. S7** XRD patterns of (a) $LiB_{12}H_{11}NH_3$ and (b) $NaB_{12}H_{11}NH_3$ at RT ($\lambda$ = 1.54060 Å).

**Table S1** Atomic coordinates for α-$NaB_{12}H_{11}NH_3$ in $P2_12_12_1$ ($a$ = 7.1972(3) Å, $b$ = 9.9225(4) Å, $c$ = 14.5556(5) Å, and $V$ = 1038.19 Å$^3$).

| Name | Atom | *x* | *y* | *z* |
|---|---|---|---|---|
| B1 | B | 0.083674 | 1.091983 | 0.125373 |
| B2 | B | 0.317307 | 0.910132 | 0.035607 |
| B3 | B | 0.446004 | 0.899962 | 0.125812 |
| B4 | B | 0.219115 | 1.081069 | 0.215647 |
| B5 | B | 0.090674 | 0.939005 | 0.071653 |
| B6 | B | 0.223529 | 1.069163 | 0.030440 |
| B7 | B | 0.438638 | 1.054724 | 0.181270 |
| B8 | B | 0.308428 | 0.922975 | 0.221984 |
| B9 | B | 0.444761 | 1.050055 | 0.066006 |
| B10 | B | 0.088670 | 0.943867 | 0.184933 |
| B11 | B | 0.229939 | 0.832731 | 0.131668 |
| B12 | B | 0.303679 | 1.160967 | 0.119196 |
| N13 | N | -0.097088 | 1.192367 | 0.130071 |
| H14 | H | 0.363236 | 0.843547 | -0.029550 |
| H15 | H | 0.583923 | 0.823510 | 0.120187 |
| H16 | H | 0.184284 | 1.143193 | 0.280134 |
| H17 | H | -0.033967 | 0.900349 | 0.030299 |
| H18 | H | 0.195675 | 1.117917 | -0.041169 |
| H19 | H | 0.561703 | 1.099626 | 0.226027 |
| H20 | H | 0.340518 | 0.872810 | 0.294518 |
| H21 | H | 0.578936 | 1.088863 | 0.025622 |
| H22 | H | -0.037544 | 0.902957 | 0.228729 |
| H23 | H | 0.207572 | 0.711737 | 0.138838 |
| H24 | H | 0.330684 | 1.272477 | 0.113484 |
| Na | Na | 0.015603 | 0.878269 | 0.881189 |


Equation | y = a + b*x
Plot | Ionic conductivity
Weight | No Weighting
Intercept | 15.03484 ± 0.44266
Slope | -10909.81922 ± 175.54872
Residual Sum of Squares | 0.03133
Pearson's r | -0.99961
R-Square (COD) | 0.99922
Adj. R-Square | 0.99897
Ionic conductivity (ln(Scm-1))
1/T (K-1)
(a)
−8
−10
−12
−14
−16
0.0020
0.0022
0.0024
0.0026
0.0028
0.0030


Equation | y = a + b*x
Plot | Ionic conductivity
Weight | No Weighting
Intercept | 13.45167 ± 1.46967
Slope | -10446.02611 ± 593.66565
Residual Sum of Squares | 0.5677
Pearson's r | -0.9936
R-Square (COD) | 0.98725
Adj. R-Square | 0.98406
Ionic conductivity (ln(Scm-1))
1/T (K-1)
(b)
−8
−10
−12
−14
−16
−18
0.0020
0.0022
0.0024
0.0026
0.0028
0.0030



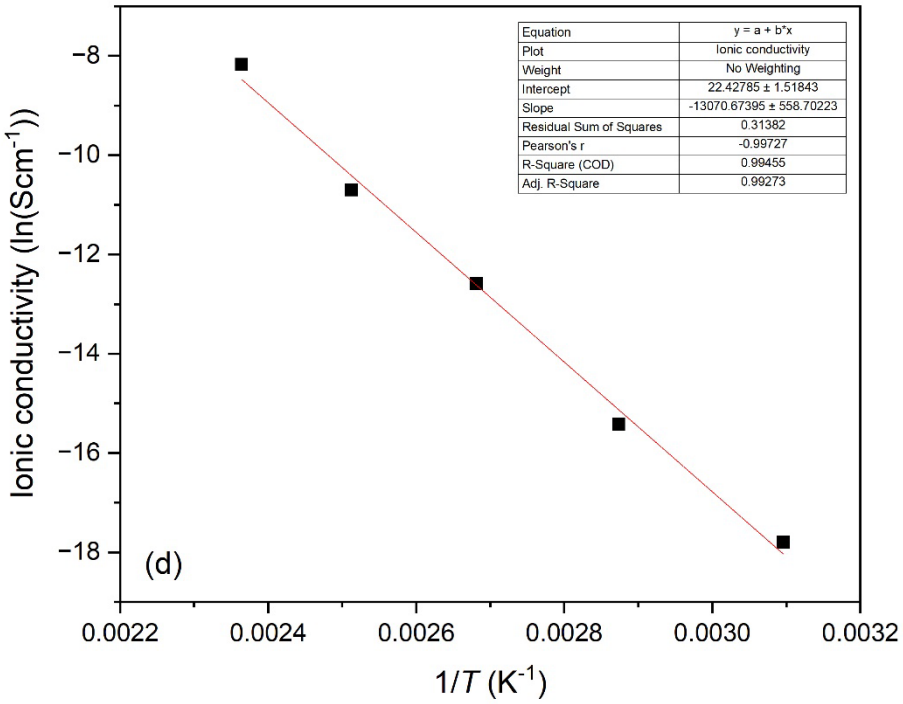




**Fig. S8** Arrhenius plots for the ionic conductivity of dehydrated (a) $LiB_{12}H_{11}NH_3$ and (b) $NaB_{12}H_{11}NH_3$, and hydrated (c) $LiB_{12}H_{11}NH_3$ and (d) $NaB_{12}H_{11}NH_3$.