Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

Hydrogen Release from Alkali Metal Borohydrides in Ionic Liquids

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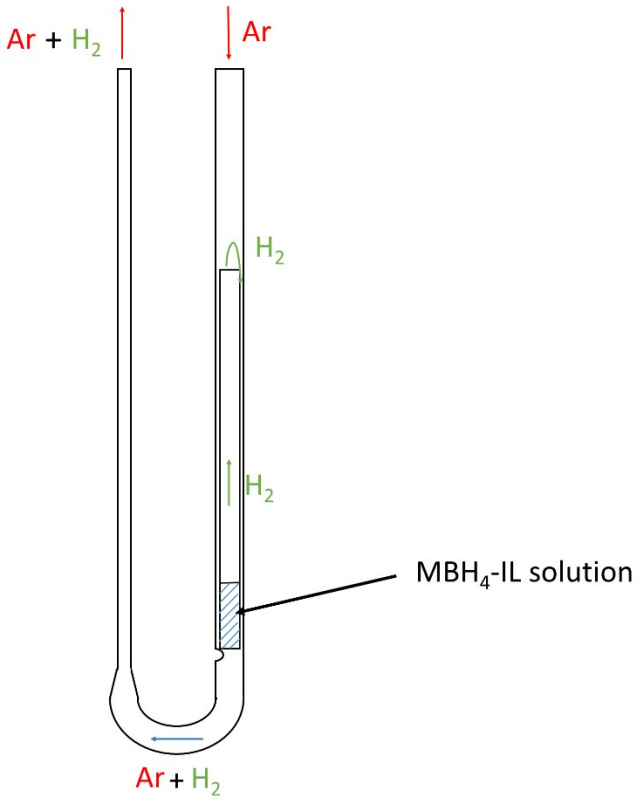

Fig. S1. Illustration of the sample tube used in TCD and TPD/MS measurements.

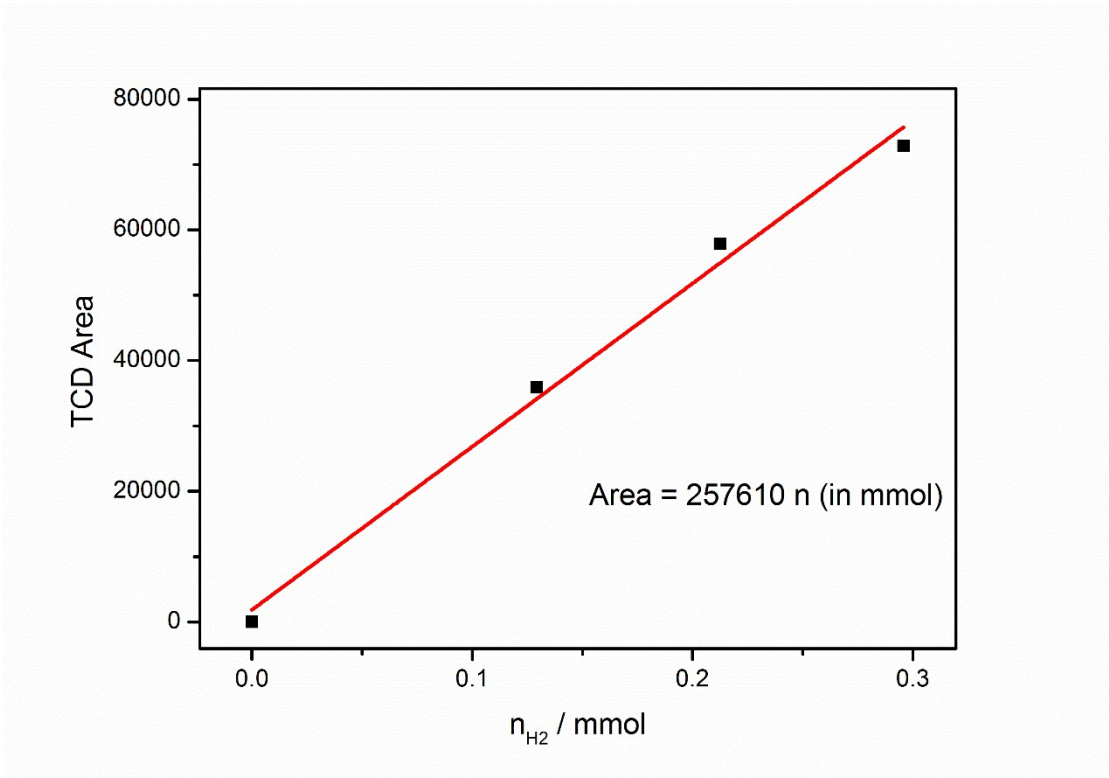

Fig. S2. The calibration curve for TCD measurement using MgH_2 as the standard material. A recovery test is performed in a typical Sievert-type apparatus to ensure the purity and dehydrogenation capacity of MgH_2.

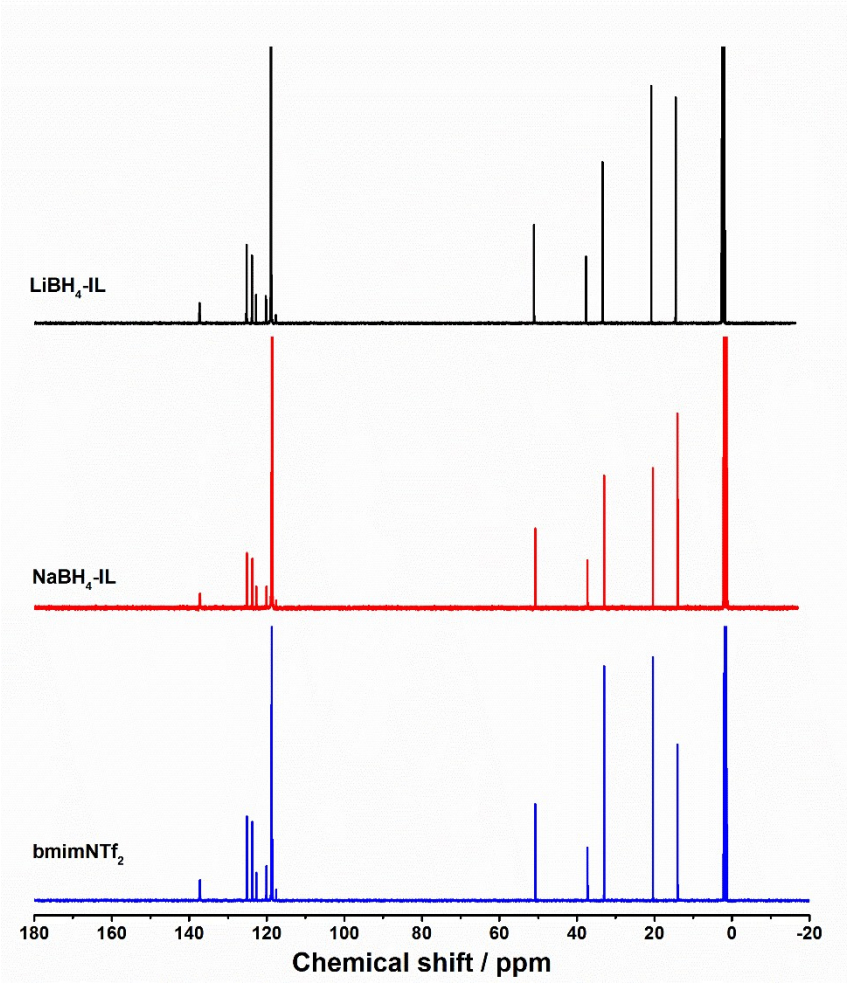

Fig. S3. ^{13}C NMR spectra of $LiBH_4$-IL, $NaBH_4$-IL and $bmimNTf_2$ samples in CD_3CN. The peaks at δ=118.26 and δ=1.79 are ascribed to the solvent. All the other peaks can be ascribed to the C atoms in $bmimNTf_2$.

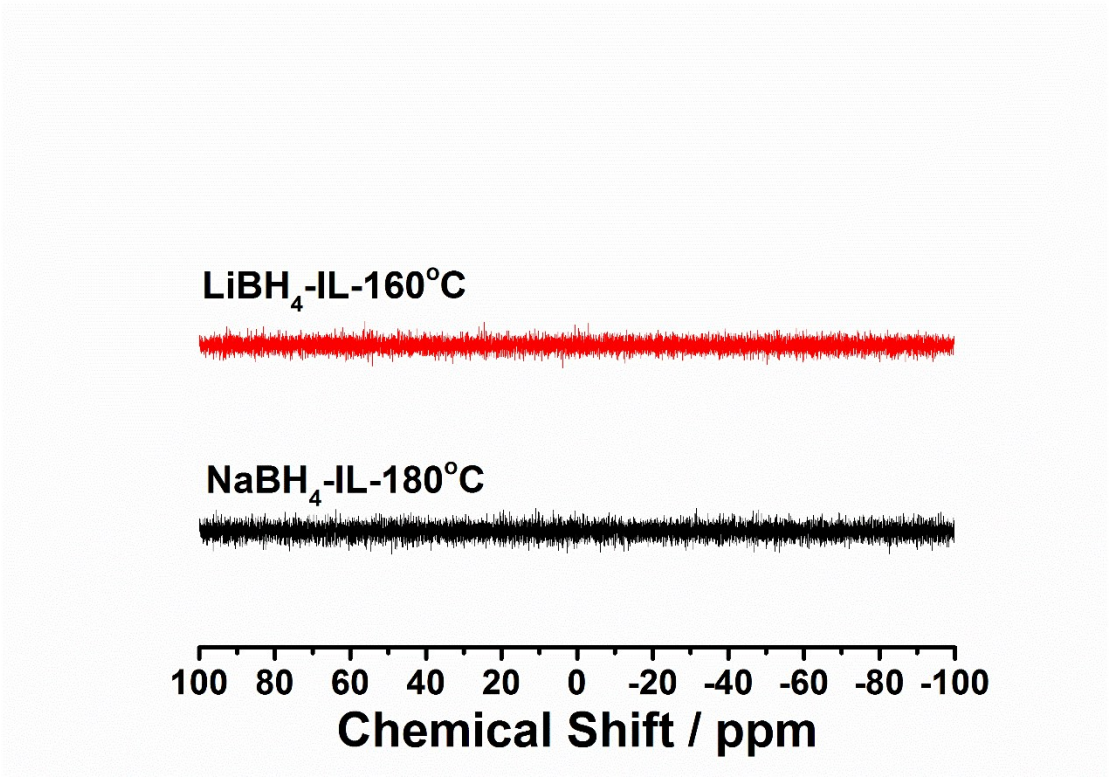

Fig. S4. Full-ranged ^{11}B NMR spectra of $NaBH_4$-IL-180 ˚C and $LiBH_4$-IL-160 ˚C samples. No soluble boron containing species can be found in these samples.

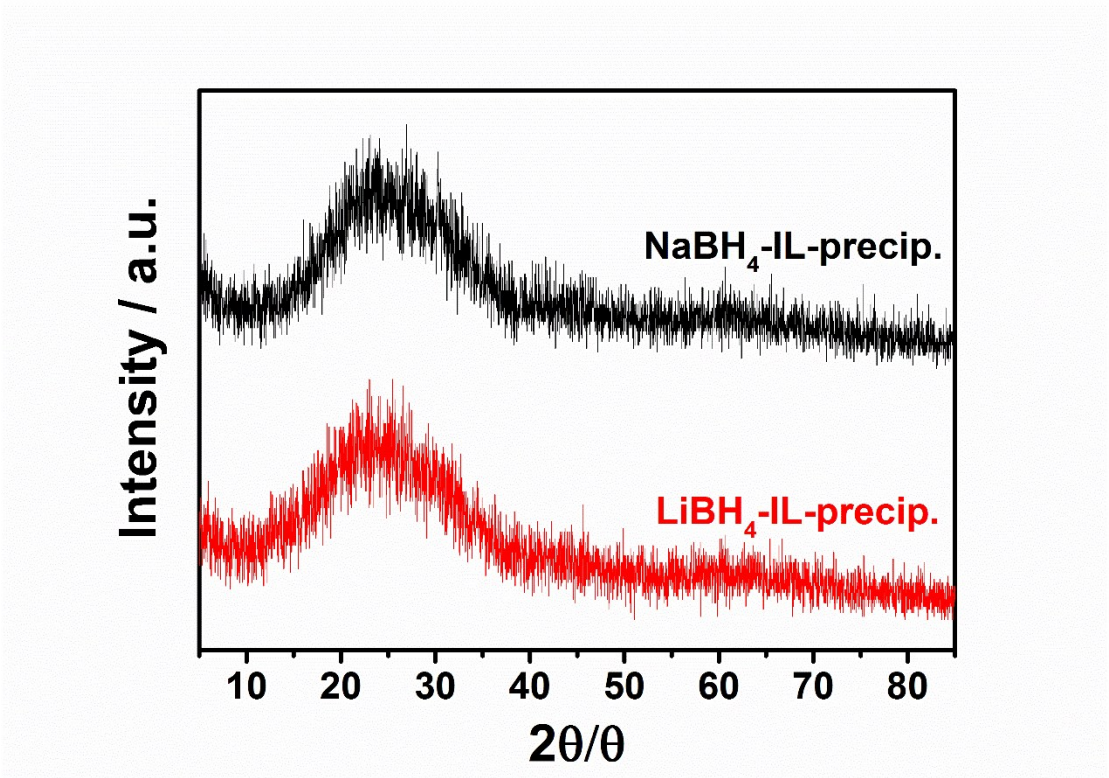

Fig. S5. XRD patterns of the dehydrogenated products (precipitation) of $NaBH_4$-IL and $LiBH_4$-IL samples.

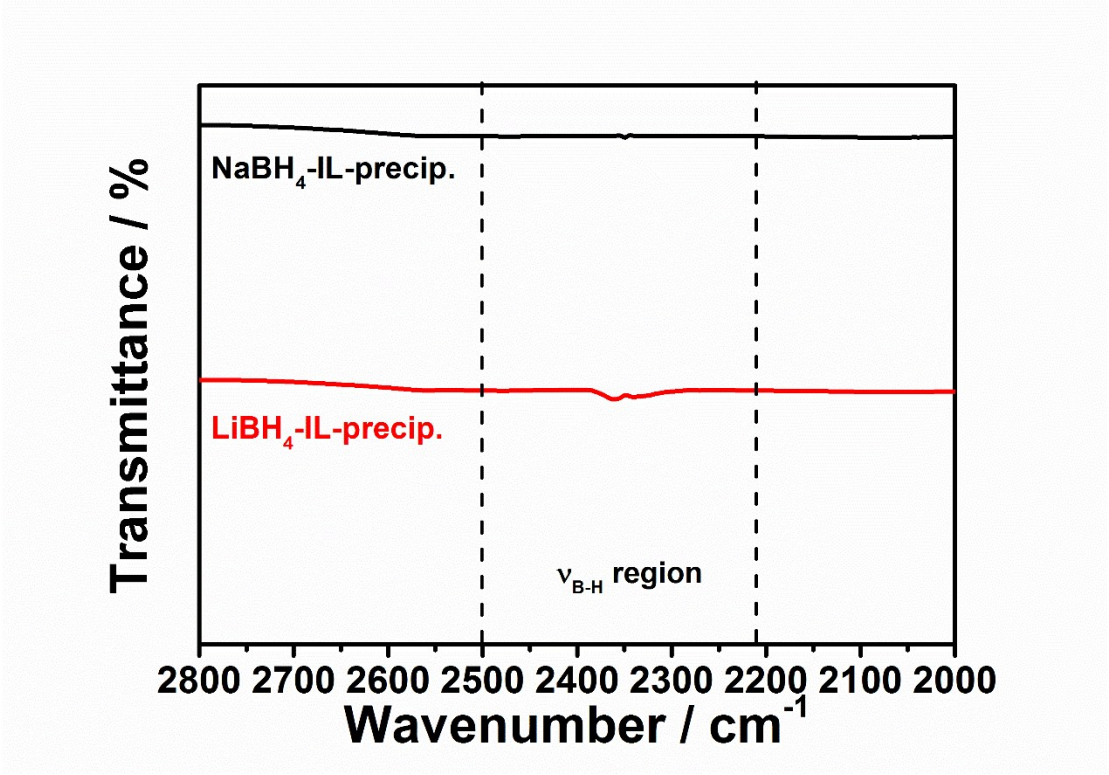

Fig. S6. IR spectra of the dehydrogenated products (precipitation) of $NaBH_4$-IL and $LiBH_4$-IL samples.

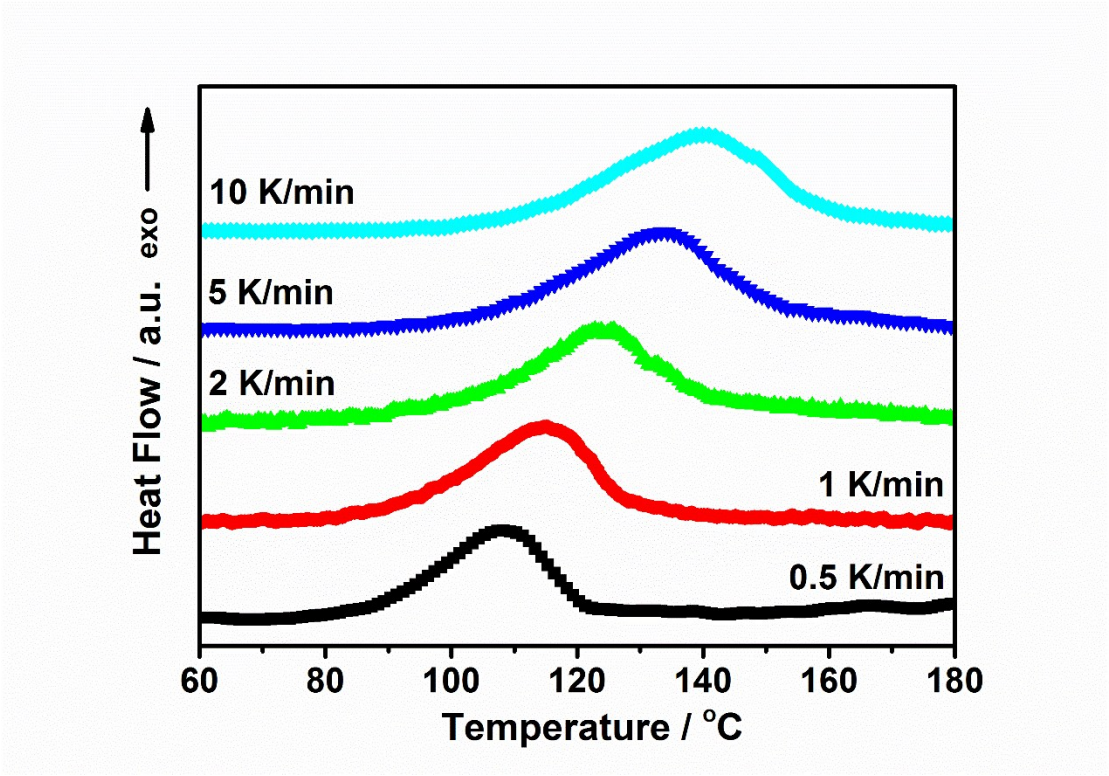

Fig. S7. DSC curves of $NaBH_4$-IL samples at heating rate of 0.5, 1, 2, 5, 10 K/min.

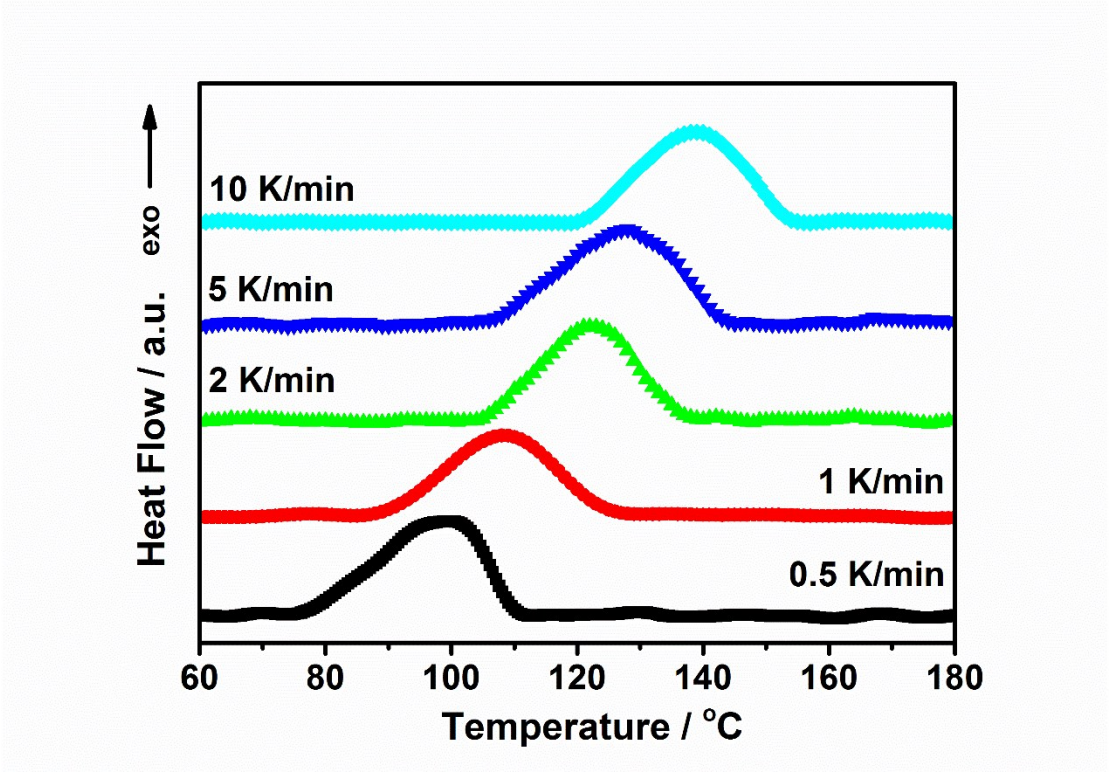

Fig. S8. DSC curves of $LiBH_4$-IL samples at heating rate of 0.5, 1, 2, 5, 10 K/min.

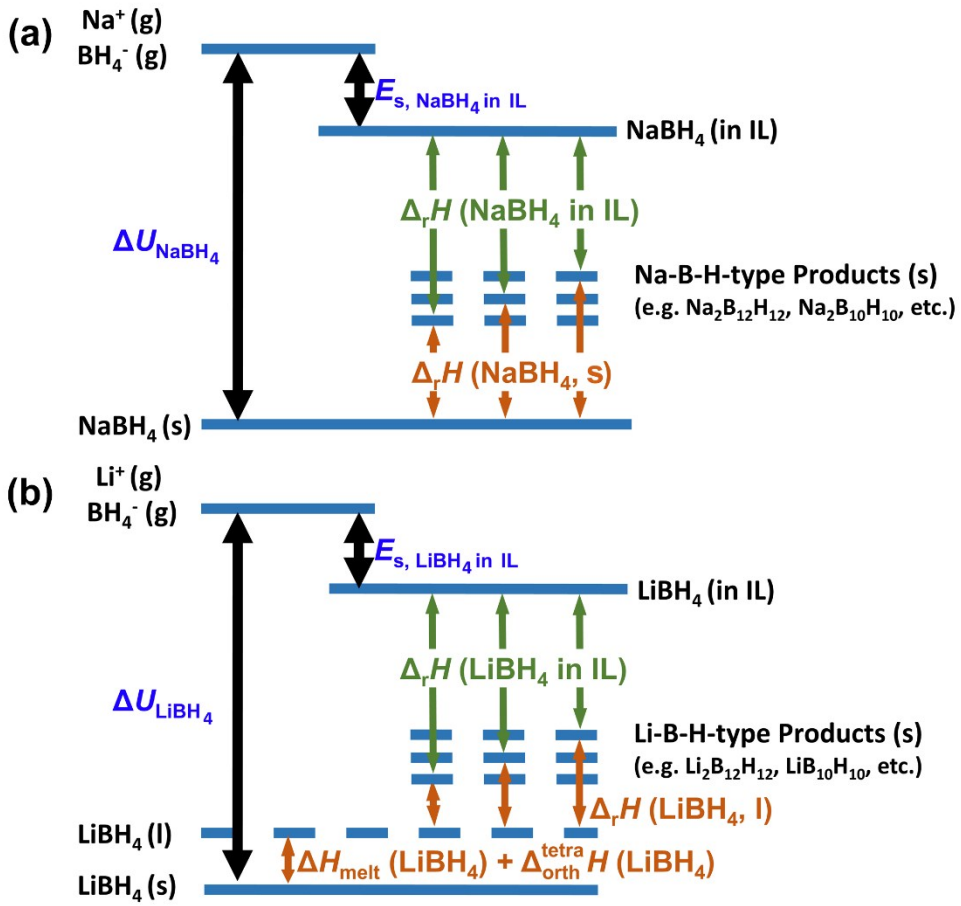

Fig. S9. Energetic diagrams of the dehydrogenation reaction of $NaBH_4$-IL (a) and $LiBH_4$-IL (b), considering different M-B-H type products and the phase change of $LiBH_4$.

This diagram is a modified version of Scheme 1 in the main text, including the following two issues which were omitted in Scheme 1

1) The dehydrogenation products could be other compounds/mixtures composed of M-B-H. This is represented by a band instead of a single energy level. As all the M-B-H compounds/mixtures are thermodynamically less stable compared to MBH_4, this band remain above the solid state MBH_4 level.

2) The solid state phase change and melting of $LiBH_4$ is considered. Since the enthalpy of phase change and melting is small compared to the lattice enthalpy, the melted $LiBH_4$ can be simply represented by a level slight upshift compared to the solid state $LiBH_4$. The energy level of the melted $LiBH_4$ remains well below the dehydrogenation products.

Therefore, including the above two issues will only affect the exact position of the species and the absolute value of the dehydrogenation enthalpy. Scheme 1 in the main text describes the stability order and the signs of the dehydrogenation enthalpy in the solid state and in IL correctly.