Electronic Supplementary Material (ESI) for Energy & Environmental Science

Structure and decomposition of zinc borohydride ammonia adduct: Towards a pure hydrogen release

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Table S1. Experimental and crystallographic details for $Zn(BH_4)_2 \cdot 2NH_3$

Chemical formula	Zn2 B4 N4 H28	
Formula weight	258.272 g/mol	
Crystal system	monoclinic	
Space group	$P\ 1\ 2_1\ 1$ (No. 4)	
Unit cell dimensions	a= 6.392(4) Å	α= 90°
	b= 8.417 (6) Å	β= 92.407(4) °
	c= 6.388(4) Å	γ =90°
Z	2	
Density (calculated)	1.24889 g/cm^3	
Volume	343.38(39) Å^3	
2theta, deg	$2\theta_{min} = 3$ $2\theta_{max} = 83$	
Detector	Mythen-II, AS	
Wavelength	0.6190 Å	
R_B	0.025	
R_{wp}	0.048	
GoF	1.41	

Table S2. Calculated structural parameters of the as-prepared $Zn(BH_4)_2 \cdot 2NH_3$.

H1	0.73810	0.38360	0.21140
H2	0.54760	0.50990	0.21220
H3	0.71230	0.49830	0.41410
H4	-0.11290	0.06460	0.75550
H5	-0.13690	0.26000	0.92930
H6	-0.32110	0.21670	0.69060
H7	-0.33050	0.09300	0.95690
H8	0.82800	0.93480	0.25730
H9	0.60690	0.84080	0.27300
H10	0.79630	0.81030	0.44730
H11	0.89040	0.53570	-0.13290
H12	0.65740	0.59600	-0.31380
H13	0.75950	0.74840	-0.12020
H14	0.94380	0.68910	-0.34210
B15	-0.22750	0.15890	0.83380
B16	0.81360	0.64210	-0.22940
N17	0.69970	0.49070	0.25530
N18	0.76420	0.83270	0.29320
Zn19	0.12230	0.15590	0.88000

Table S3. Interatomic bond distances (Å) in the crystal structure of $Zn(BH_4)_2{\cdot}2NH_3$ derived from the DFT calculation.

Atoms		Bond distances (Å)	Atoms		Bond distances (Å)
Zn19	H8	2.656	N17	H1	1.026
	H2	2.591		H2	1.032
	H1	2.657		H3	1.029
	H10	2.590	N18	H8	1.027
	H9	2.623		H9	1.028
	H3	2.691		H10	1.030
	H11	1.956	B15	H4	1.239
	H13	1.897		H5	1.229
	H4	1.887		H6	1.206
	H5	1.955		H7	1.207
	B15	2.281	B16	H11	1.230
	B16	2.286		H12	1.208
	N17	2.078		H13	1.237
	N18	2.078		H14	1.208

Table S4. Interatomic distances (Å) and Angles (°) for apparent dihydrogen Bonds in the calculated $Zn(BH_4)_2 \cdot 2NH_3$.

Distance		Angle		Angle	
H1···H5	2.298	B15-H5···H1	124.91	H5···H1-N17	139.25
H2···H7	1.905	B15-H7···H2	103.02	H7···H2-N17	154.62
H6···H9	2.178	B15-H6···H9	122.90	H6···H9-N18	142.87
H3···H12	2.003	B16-H12···H3	111.92	H12···H3-N17	153.26
H8···H11	2.210	B16-H11···H8	117.02	H11···H8-N18	141.69
H10···H14	1.961	B16-H14···H10	105.83	H14···H10-N18	148.88

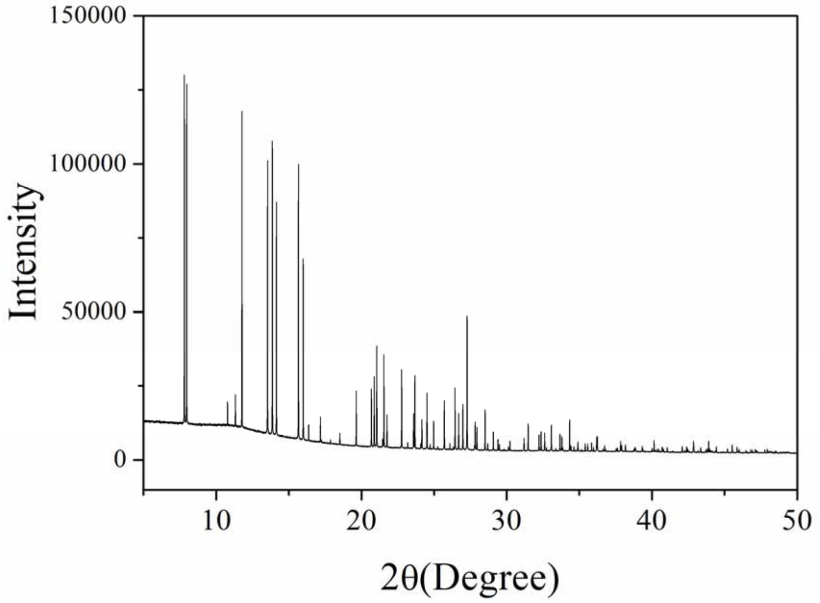

Figure S1. High-resolution XRD patterns of $ZnCl_2\cdot2NH_3$.

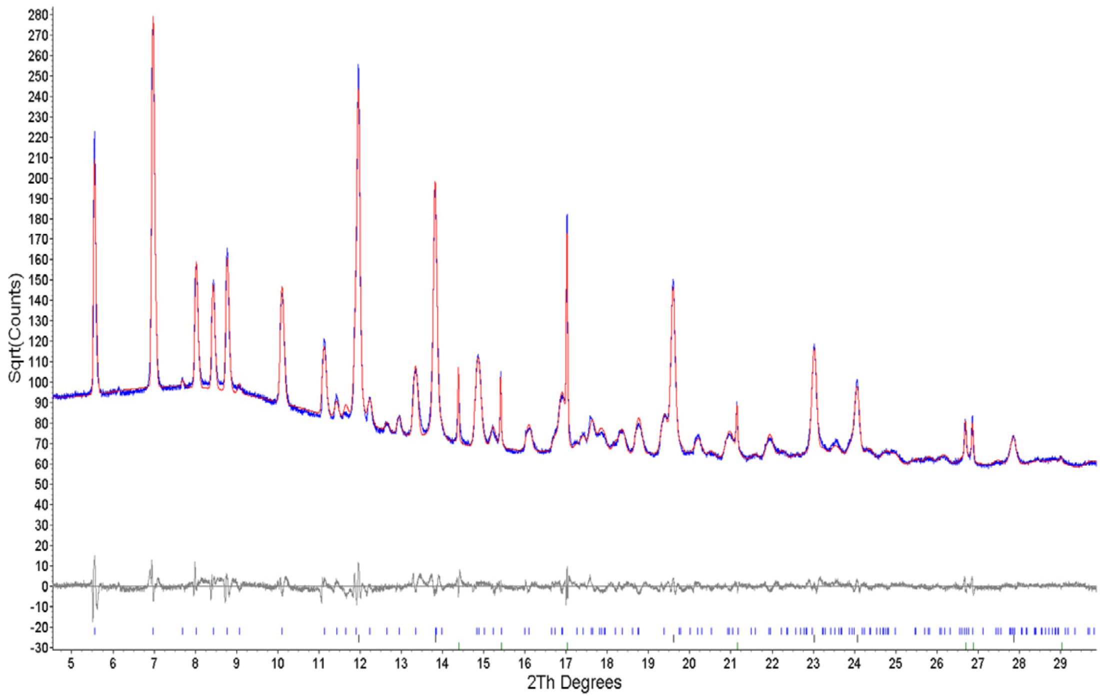

Figure S2. Rietveld refinement profile for $Zn(BH_4)_2{\cdot}2(NH_3)$ phase showing observed (blue), calculated (red), difference (grey) plots. The position of Bragg reflections (tick marks) are shown for $Zn(BH_4)_2{\cdot}2(NH_3)$ (upper), LiCl (middle), and Zn (lower).

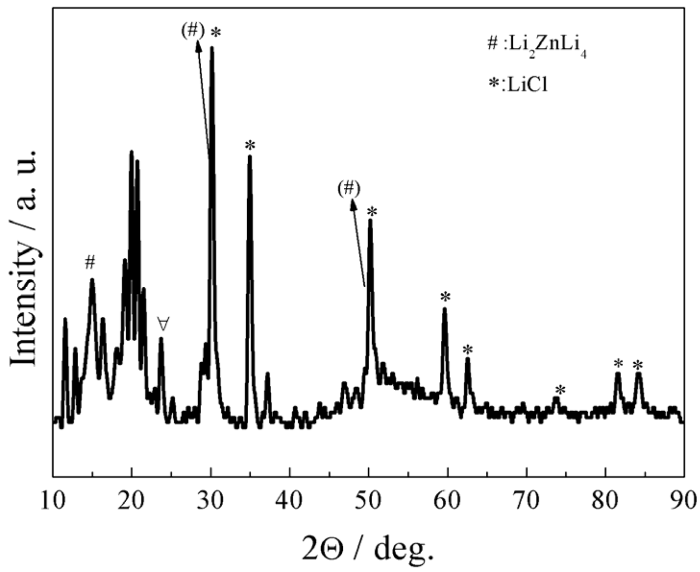

Figure S3. Laboratory XRD patterns of the post milled 1:2 $ZnCl_2/2LiBH_4$. The asterisks and pound sign indicate the position of diffraction peak arising from LiCl and Li_2ZnCl_4, respectively. According to the previous literature,[S1] the ball milled product of $ZnCl_2/2LiBH_4$ turns out to be mixed-metal(Zn-Li) borohydride. So it is highly possible that the synthesis via $ZnCl_2/2LiBH_4$ should follow the pathway below:

$3ZnCl_2+6LiBH_4 \rightarrow 2LiZn(BH_4)_3+2LiCl+Li_2ZnCl_4$

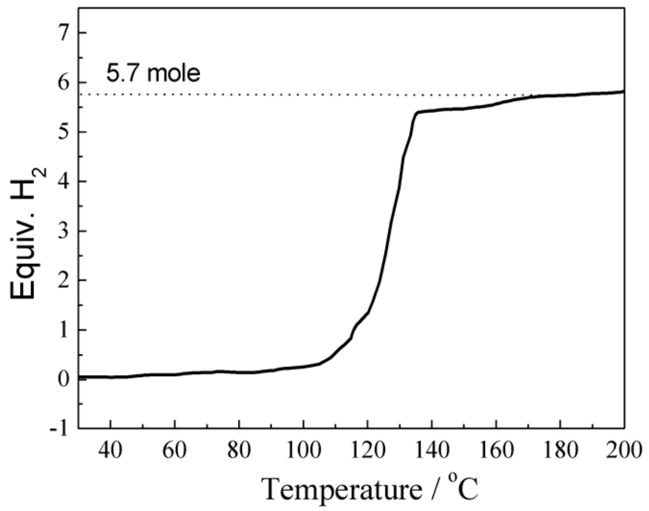

Figure S4. The TPD result of $Zn(BH_4)_2{\cdot}(NH_3)_2$, which gave a release of 5.7 equiv. gas. By combination with the TG results, this 5.7 equiv. gas can be safely ascribed to the quantity of H_2.

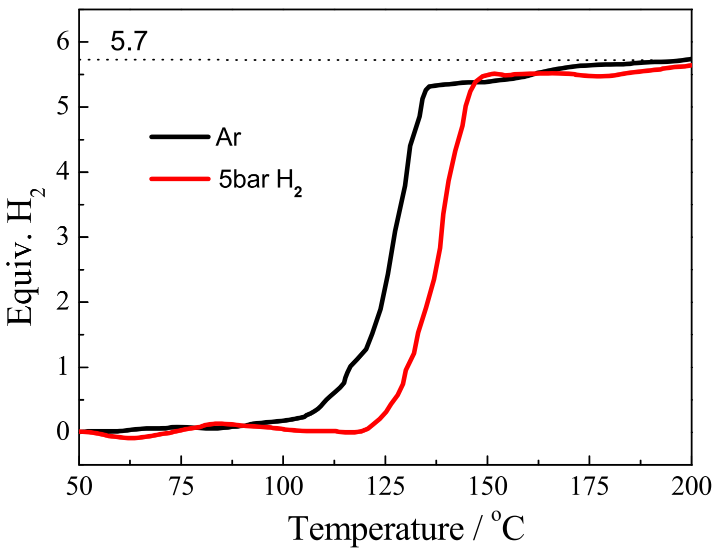

Figure S5. The TPD results for $Zn(BH_4)_2{\cdot}(NH_3)_2$ under 1bar Ar and 5 bar H_2 atmosphere.

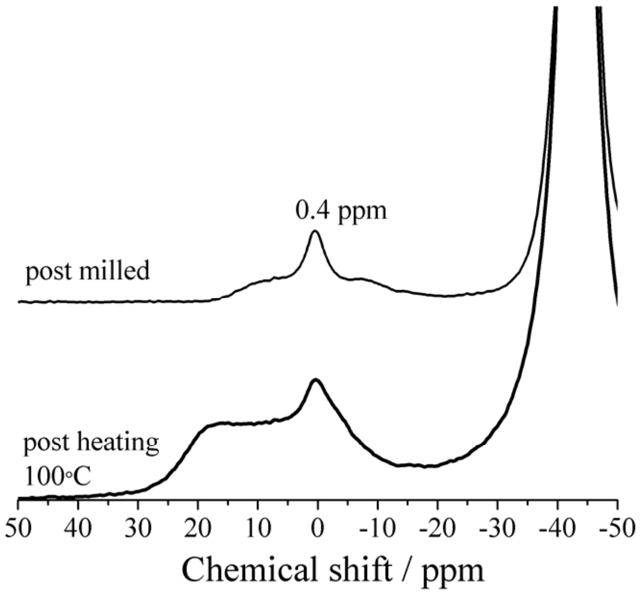

Figure S6. The ^{11}B NMR spectra of as-prepared $Zn(BH_4)_2 \cdot 2NH_3$ and the sample after heating to 100 ^{o}C. The heating rate was 10 ^{o}C min^{-1}.

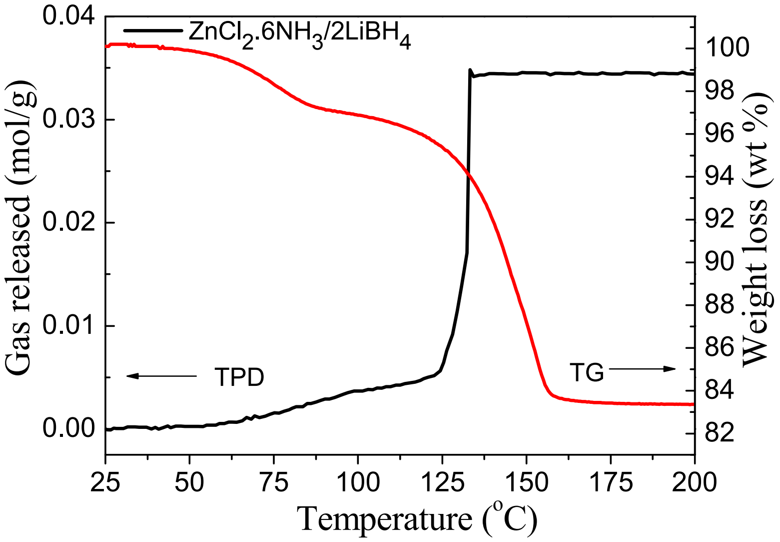

Figure S7. The TPD and TG results for the $Zn(BH_4)_2{\cdot}6NH_3/2LiCl$. By combination of the TG and TPD results, the mole ratios of the H_2 and NH_3 in the total released gas are 81.6 and 18.4%, respectively.

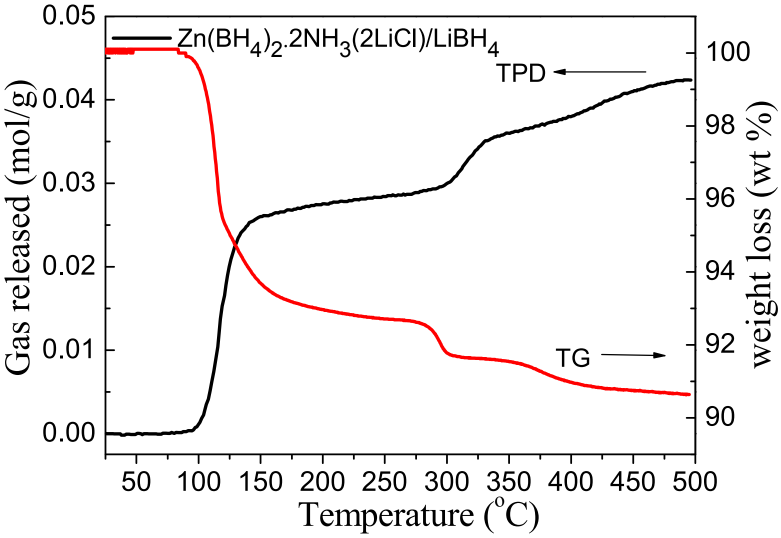

Figure S8. The TPD and TG results for the $Zn(BH_4)_2{\cdot}2NH_3(2LiCl)/LiBH_4$. TG result shows that this sample gave a weight loss of 9.2 wt.% by 500 °C. From the TPD, the total gas released is 4.6 mol/g by 500 °C. It fairly confirms that only hydrogen is released for this sample by heating to 500 °C.

References:

(S1)Ravnsbaek, D.; Filinchuk, Y.; Cerenius, Y.; Jakobsen, H. J.; Besenbacher, F.; Skibsted, J.; Jensen, T. R. *Angew. Chem. Int. Ed.* **2009**, *48*, 6659.