Supplemental Information

Experimental Section:

Characterizations

XRD measurements were carried out using an automated Rigaku X-ray diffractometer with monochromatic Cu Kα radiation. XPS measurements were performed at room temperature utilizing a Kratos AXIS Ultra Imaging XPS Spectrometer using a monochromated Al Kα X-ray source operated at 150 W. The area of analysis was ~700 μm × 300 μm. Survey spectra and high resolution elemental region spectra were acquired using analyzer pass energies of 160 and 20 eV respectively. FTIR spectra was obtained using a Perkin-Elmer Spectrum One Instrument in conjunction with a Golden Gate ATP setup utilizing a spectral resolution of 2 cm^{-1}. Micro-FTIR spectra of pre/post decomposition samples were recorded against pure samples in the range of 4000 to 600 cm^{-1} using a Nicolet iN10 MX FTIR Microscope.

Solid-state ^{11}B and ^{27}Al MAS NMR spectra were obtained on a Varian NMR spectrometer (400 MHz). The experiments were performed at ambient temperatures using air-tight end-capped zirconia rotors, which were packed with the sample in the glovebox and spun at 12–15 kHz. The spectral frequencies were 160.5 and 130.3 MHz for the ^{11}B and ^{27}Al nuclei, respectively. The ^{27}Al NMR chemical shift scale (ppm) was referenced externally with $[Al(H_2O)_6]^{3+}$ in aqueous solution to 0 ppm while ^{11}B NMR were referenced to 0 ppm with $BF_3{\cdot}OEt_2$.

TPD measurements were performed on a Quantachrome Autosorb IQ Cor100 using a heating rate of 5 °C min^{-1} and a carrier gas of argon at a flow rate of 60 $mL{\cdot}min^{-1}$. Isothermal desorption/absorption and quantification of hydrogen evolution were obtained with a Hy-Energy PCT Pro-2000 instrument. Both MS signals were recorded using a mass spectrometer PrismaPlus PFEIFFER QME220.

Elemental analysis of carbon, hydrogen, and nitrogen were performed using an Elementar Vario MICRO CUBE analyzer. Elemental analysis of aluminum and boron were performed using a Leeman PROFILE SPEC Inductively Coupled Plasma-Atomic Emission Spectrometer.

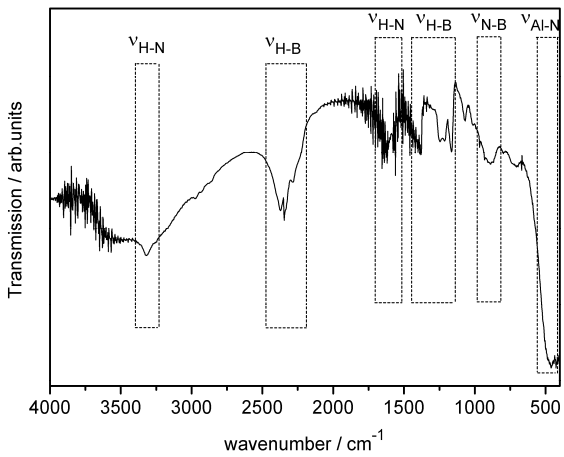

Figure S1. FTIR spectrum of as-prepared $Al(NH_2BH_3)_3{\cdot}3NH_3$.

Figure S2. Photograph of pressed shaped $Al(NH_2BH_3)_3 \cdot 3NH_3$ powder after exposure to dry air for 3 days.

Table S1. Experimentally measured vibrational modes of as-prepared $Al(NH_2BH_3)_3 \cdot 3NH_3$ (cm^{-1}). [a][b]

Molecule	Experimental	Theory [1,2]	Vibrational modes
$NH_3/Al(NH_3)_6^{3+}$	426	439	Al-N stretching
	1014, 1620	1027, 1620	H-N scissoring
	3319	3421	H-N symmetric stretching
	-	3540	H-N antisymmetric stretching
$AlAB/Al(NH_2BH_3)_6^{3-}$	461	-	H antisymmetric rocking with Al-N stretching/Al-N stretching
	726, 780, 798	-	antisymmetric H-N, H-B deformation/H wagging
	875	861	N-B stretching
	1066, 1112	987–1117	H wagging
	1165, 1248, 1380	1124–1211, 1380	H-B scissoring
	1555	1550	H-N scissoring
	2116	-	-
	2200, 2283	2178–2186	H-B symmetric stretching
	2341, 2372	2225–2309	H-B antisymmetric stretching
	3250	3335–3342	H-N symmetric stretching
	-	3412–3415	H-N antisymmetric stretching

[a] "-" indicates that no relevant data are available; [b] Part of the theory data are based on DFT studies of LiAB and AlH_3NH_3.

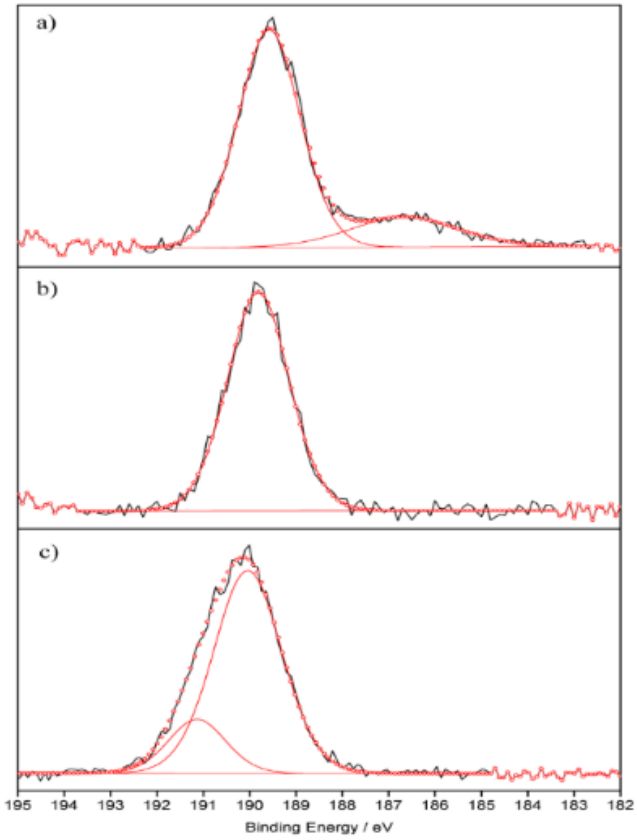

Figure S3. The B 1s XPS results of $Al(NH_2BH_3)_3 \cdot 3NH_3$ before (**a**) and after thermal decomposition in an open system (**b**)/in a closed system (**c**). The experiment data are in black, while the fitted ones are in red.

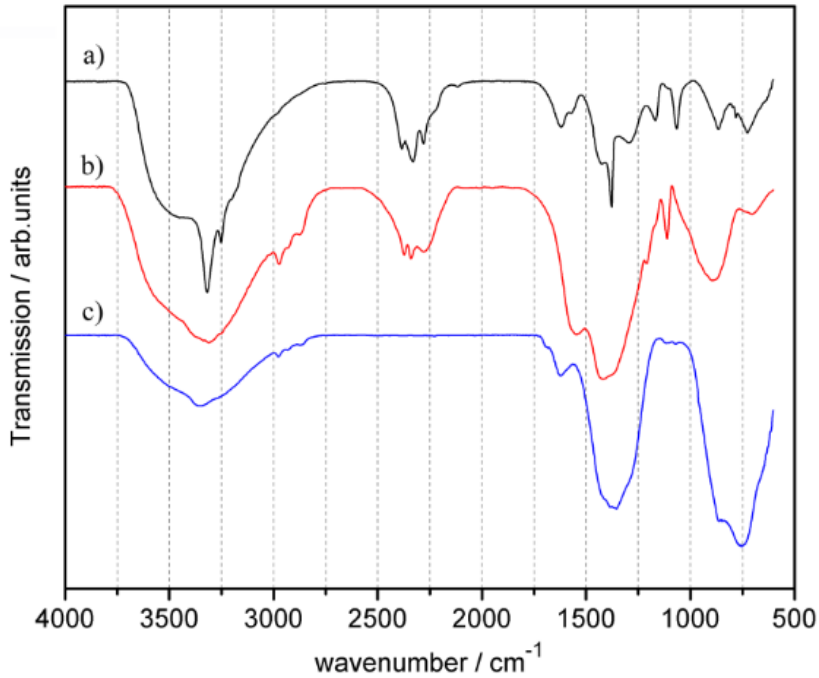

Figure S4. Micro-FTIR spectra: (**a**) $Al(NH_2BH_3)_3 \cdot 3NH_3$, (**b**) $AlN_3B_3H_6$, (**c**) $AlN_6B_3H_{6.5}$*. $AlN_3B_3H_6$ (open system) and $AlN_6B_3H_{6.5}$* (closed system) are generated from $Al(NH_2BH_3)_3 \cdot 3NH_3$ decomposition.

Table S2. Experimentally measured vibrational modes of $AlN_3B_3H_6$ and $AlN_6B_3H_{6.5}$* (cm^{-1}).

Molecule	Experimental	Vibrational modes
$AlN_3B_3H_6$	706, 893	Al-N stretching/AlN [3–5]
	1108	H wagging
	1170, 1207	H-B scissoring
	1390, 1544	N-B stretching/*h*-BN [6,7]
	2283	H-B symmetric stretching
	2340, 2373	H-B antisymmetric stretching
	2877, 2929, 2969	H-N or H-O deformation
$AlN_6B_3H_{6.5}$*	748, 858	Al-N stretching/AlN [3–5]
	1068, 1114	H wagging
	1367, 1627	N-B stretching/*h*-BN [6,7]
	2868, 2931, 2979	H-N or H-O deformation

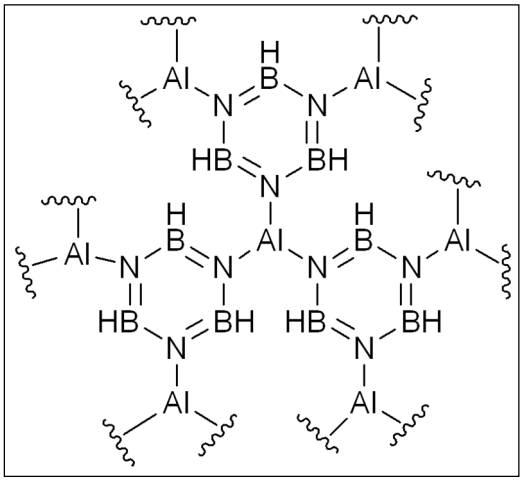

Figure S5. Structural representation borazine-derivated $AlN_3B_3H_6$.

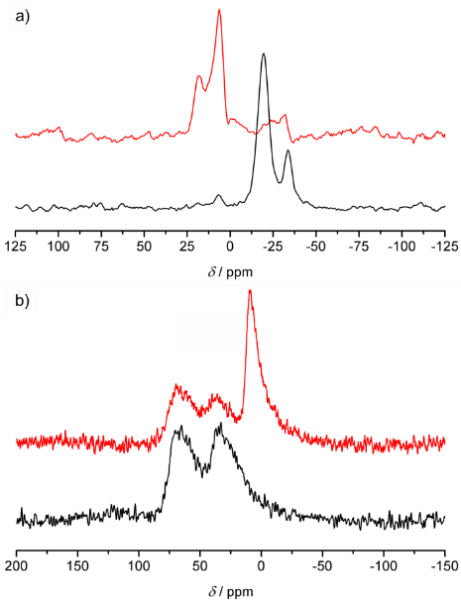

Figure S6. (**a**) ^{11}B CPMAS NMR spectra and (**b**) ^{27}Al CPMAS NMR spectra of as-prepared (black) $Al(NH_2BH_3)_3 \cdot 3NH_3$ and after desorption at 105 °C (red) in a closed vessel.

Table S3. Elemental analysis of $Al(NH_2BH_3)_3 \cdot 3NH_3$ before and after thermal decomposition in an open system/in a closed system (%).

Sample	Al	N	B	H	C
$Al(NH_2BH_3)_3 \cdot 3NH_3$	15.16	44.74	18.45	13.51	–
$AlAB \cdot 3NH_3$ decomposition open system	20.19	37.54	23.65	6.28	0.16
$AlAB \cdot 3NH_3$ decomposition closed system	15.83	48.18	18.36	3.83	0.13

References

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