Supporting Information

Synthesis and decomposition of $Li_3Na(NH_2)_4$ and investigations of Li–Na–N–H based systems for hydrogen storage

Lars H. Jepsen[a], Peikun Wang[b], Guotao Wu[b], Zhitao Xiong[b], Flemming Besenbacher[c], Ping Chen[b*]

and Torben R. Jensen[a*]

[a]*Center for Materials Crystallography, Interdisciplinary Nanoscience Center and Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark*

[b]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences,116023, P.R. China*

[c]*Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark.*

*Corresponding authors

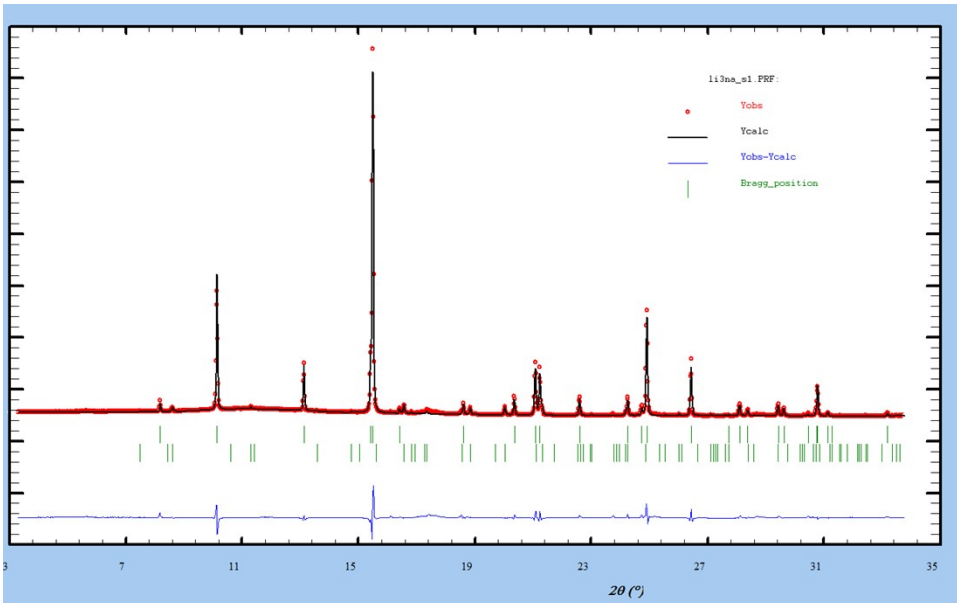

Figure S1 SR-PXD data collected at RT for $LiNH_2$-$NaNH_2$ (3:1) ball milled for 90 min and annealed at 150 °C for 6h (s4), λ = 0.82306 Å.

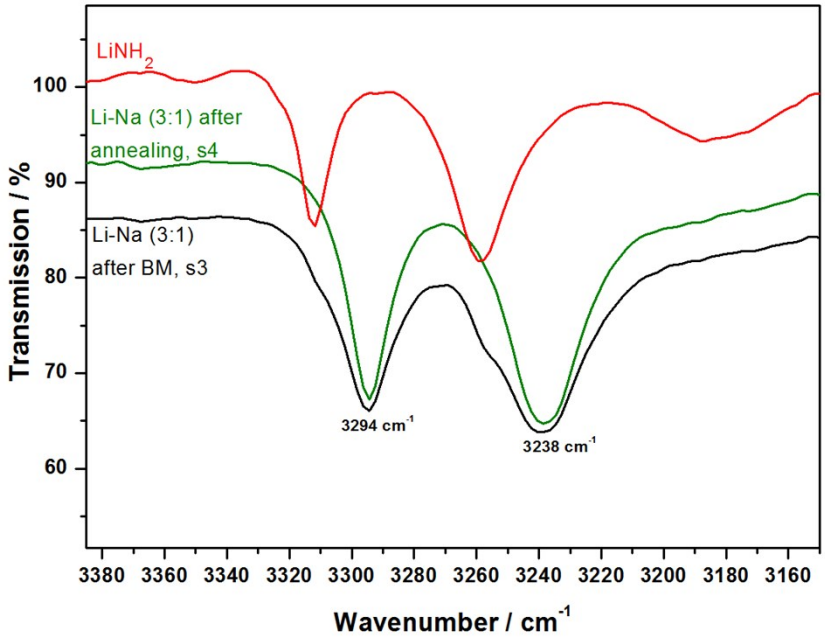

Figure S2 FTIR spectra recorded for $LiNH_2$-$NaNH_2$ (3:1) after 90 min ball milling (black, s3) and after annealing at 150 °C (green, s4) compared with $LiNH_2$ (red).

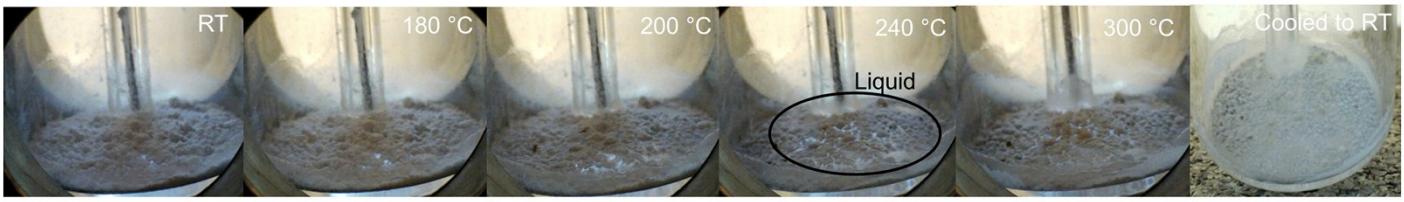

Figure S3 Temperature programmed photographic analysis of $Li_3Na(NH_2)_4$ (s4) during heating to 300 °C (4 °C/min) under argon atmosphere. A liquid is observed on the bottom of the glass vial at 240 °C. At 300 °C, the sample has a yellowish color which may suggest the presence of Li_2NH.

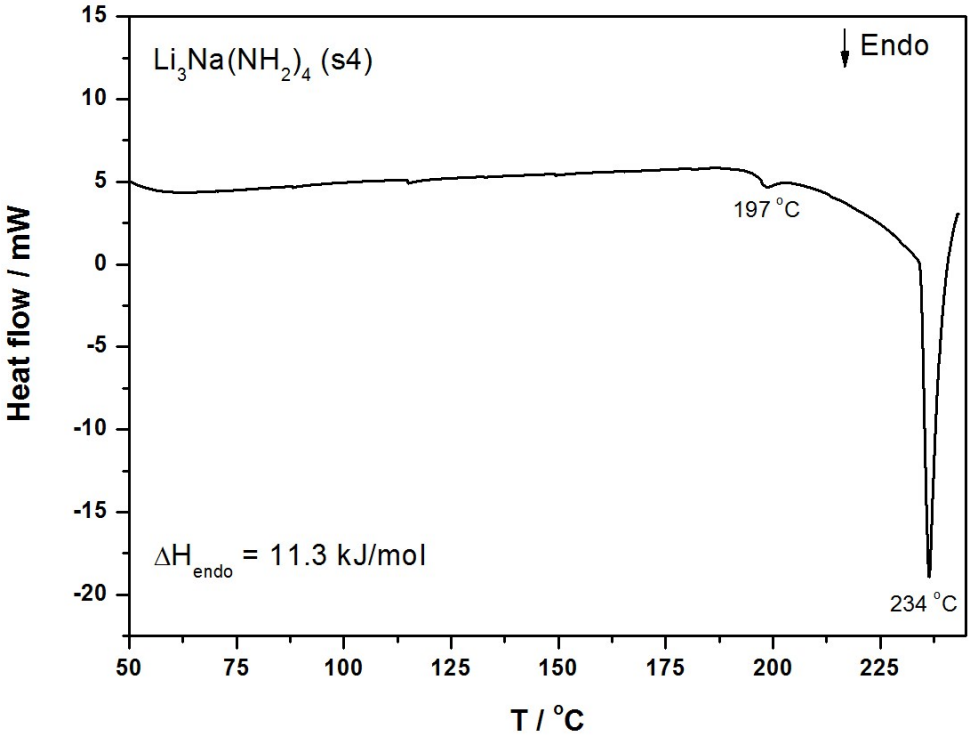

Figure S4 Calorimetric measurement of $Li_3Na(NH_2)_4$ (s4) heated to 245 °C (0.5 °C /min).

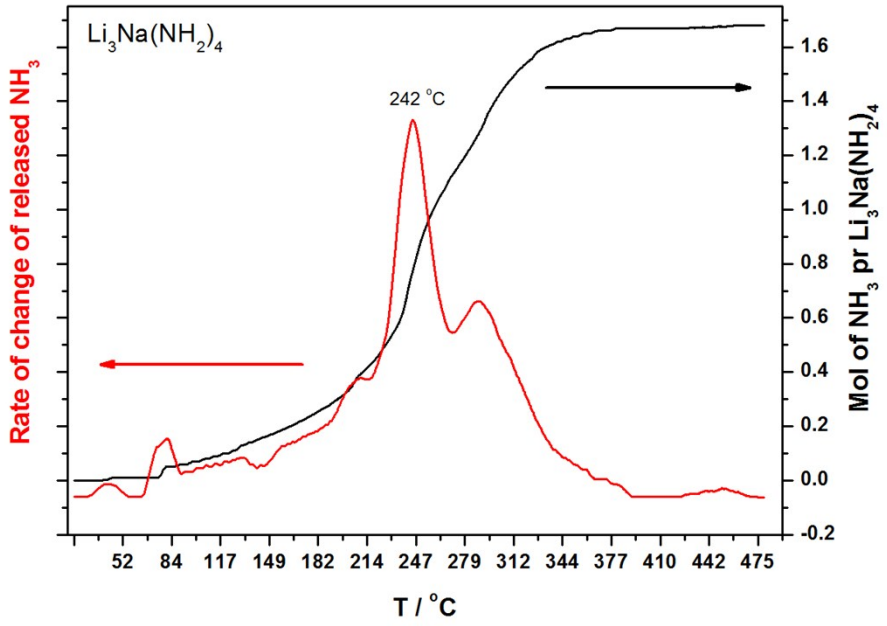

Figure S5 Determination of released NH_3 for $Li_3Na(NH_2)_4$ (s4) during heating from RT to 475 °C (2 °C/min). The black line shows the accumulated NH_3 released, while the red line (differentiated) reveals the rate of change in released NH_3.

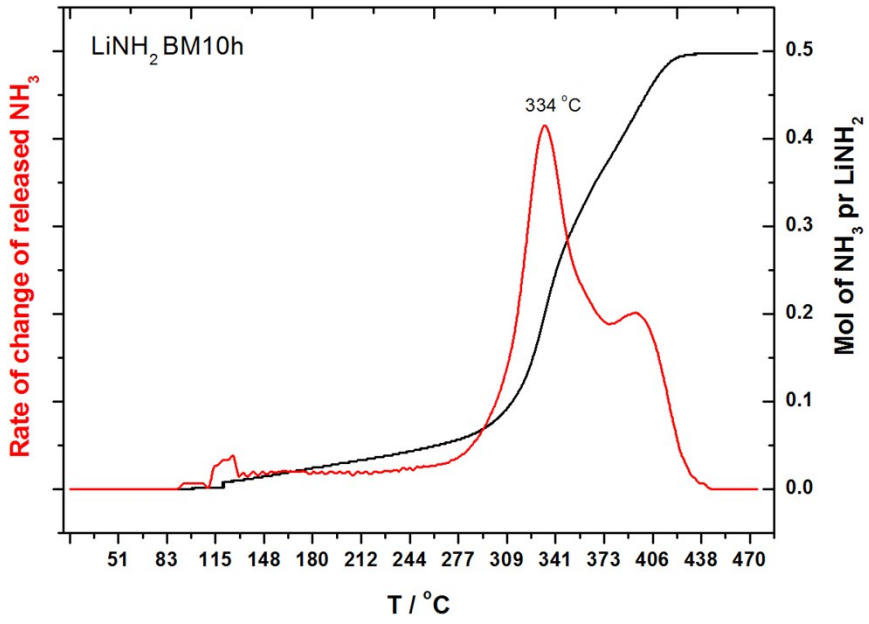

Figure S6 Determination of released NH_3 for $LiNH_2$ BM 10h (s12) during heating from RT to 475 °C (2 °C/min). The black line shows the accumulated NH_3 released during heating, while the red line (differentiated of black line) shows the rate of change of the NH_3 release.

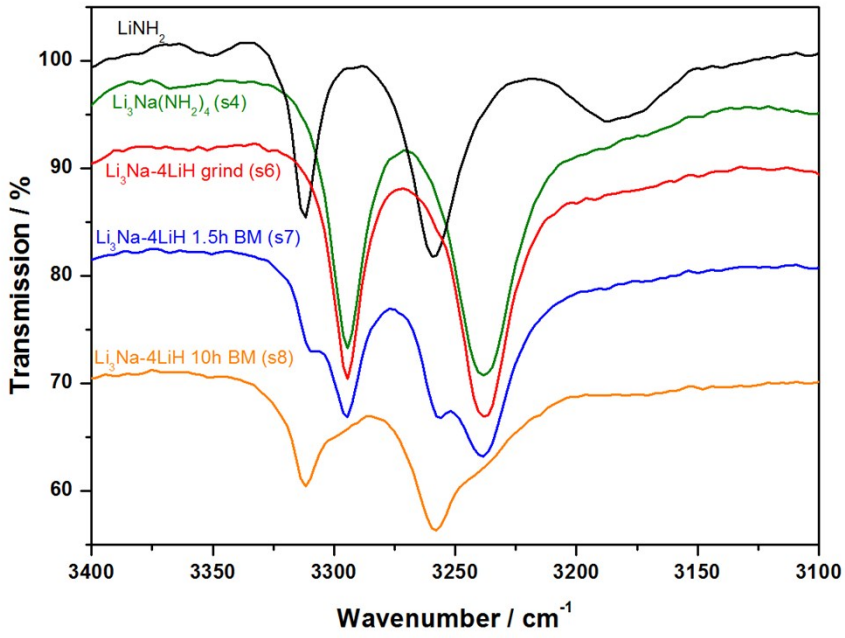

Figure S7 FTIR measured for $Li_3Na(NH_2)_4$–LiH (1:4) mixed in a mortar for 5 min (s6, red), ball milled for 1.5 h (s7, blue) and ball milled for 10 h (s8, orange).

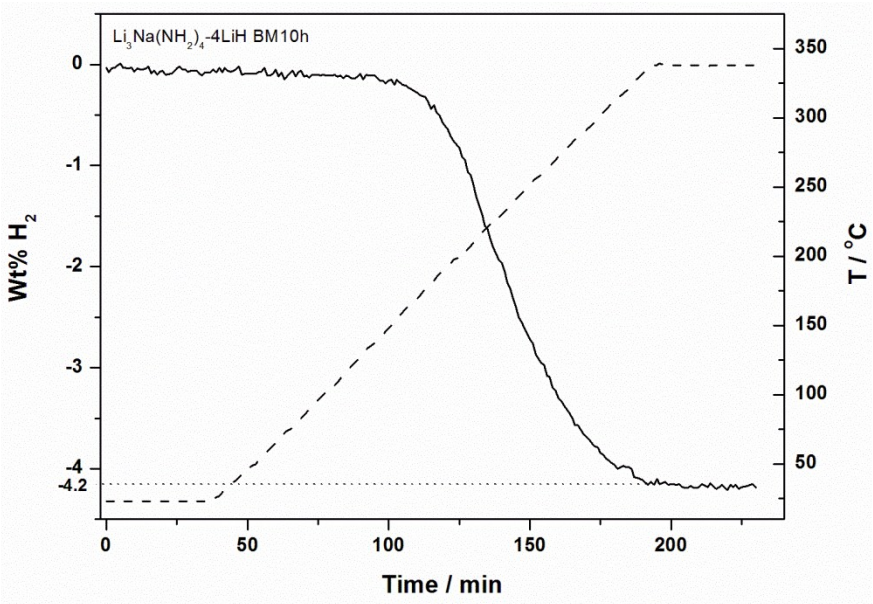

Figure S8 Sievert's measurement of $Li_3Na(NH_2)_4$–LiH (1:4, s8) heated to 340 °C (1 °C/min). The temperature is represented by the dashed line.

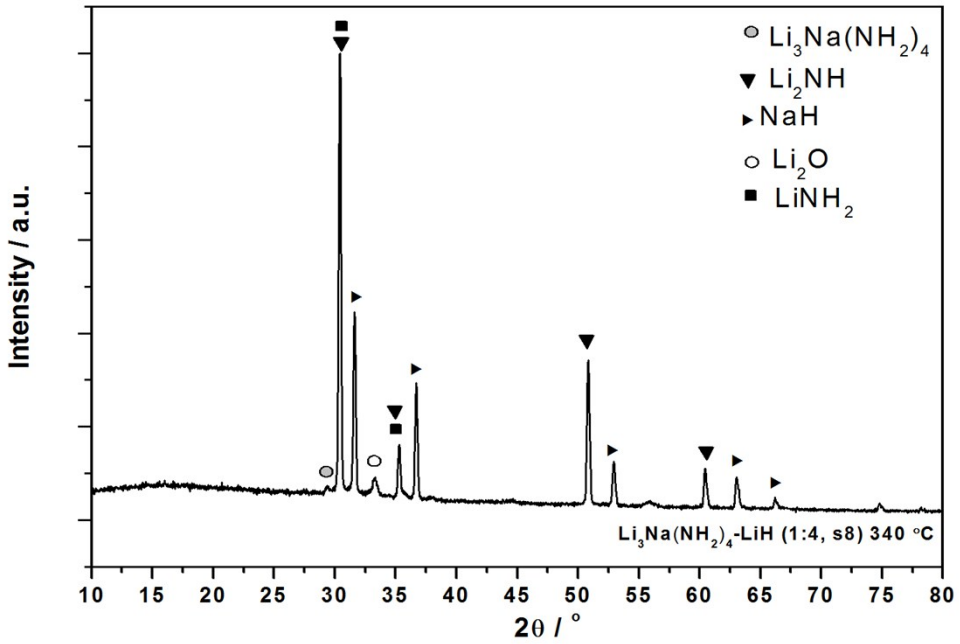

Figure S9 PXD data for $Li_3Na(NH_2)_4$–LiH (1:4, s8) after heating to 340 °C, λ = 1.54056 Å. Symbols: ■ $LiNH_2$; ▲ NaH; ● $Li_3Na(NH_2)_4$; ▲ Li_2NH; ○ Li_2O.

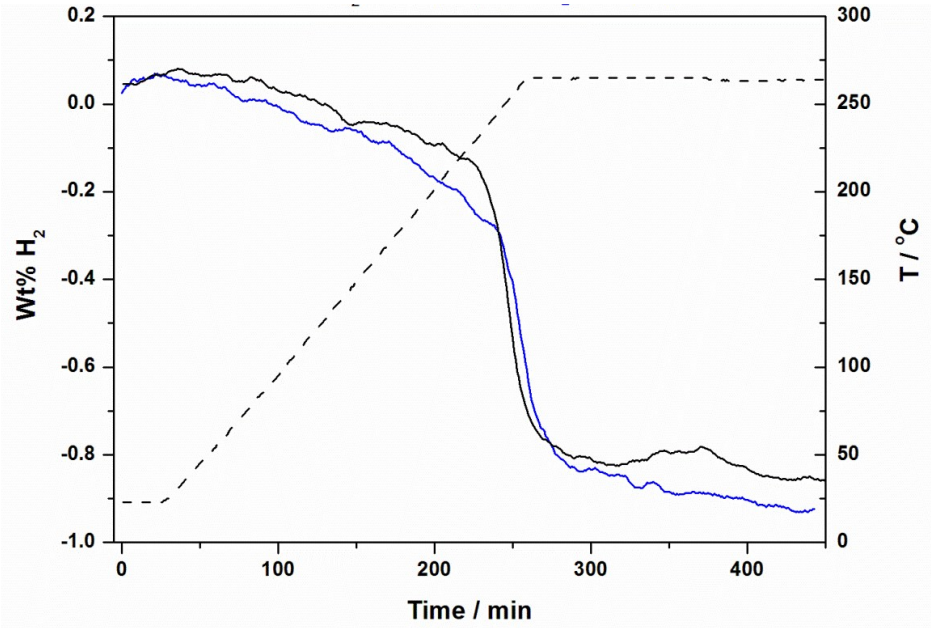

Figure S10 Sieverts measurements of $LiNH_2$─NaH (1:1, s10, black line) and $NaNH_2$─LiH (1:1, s11, blue line) heated to 340 °C (1 °C/min). The temperature is represented by the dashed line.

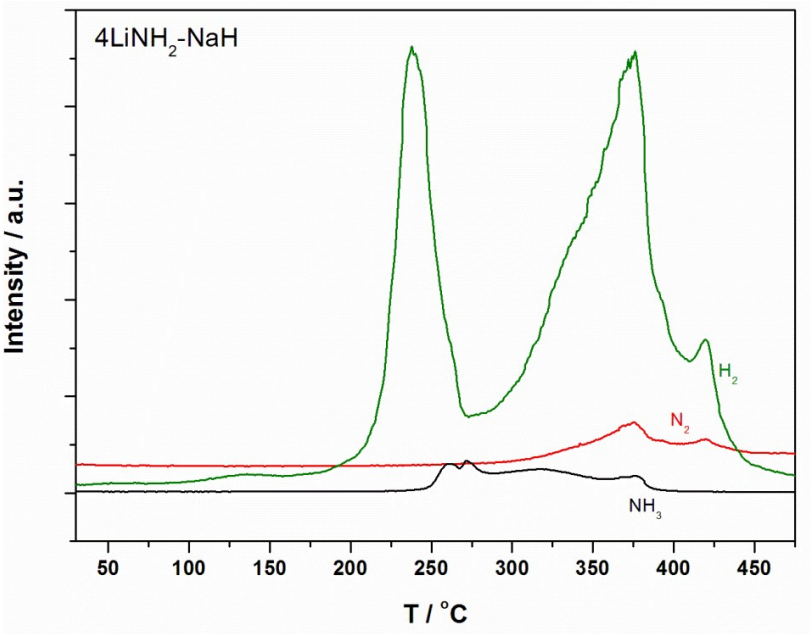

Figure S11 TPD-MS for $LiNH_2$─NaH (4:1) during heating from RT to 475 °C (2 °C/min).

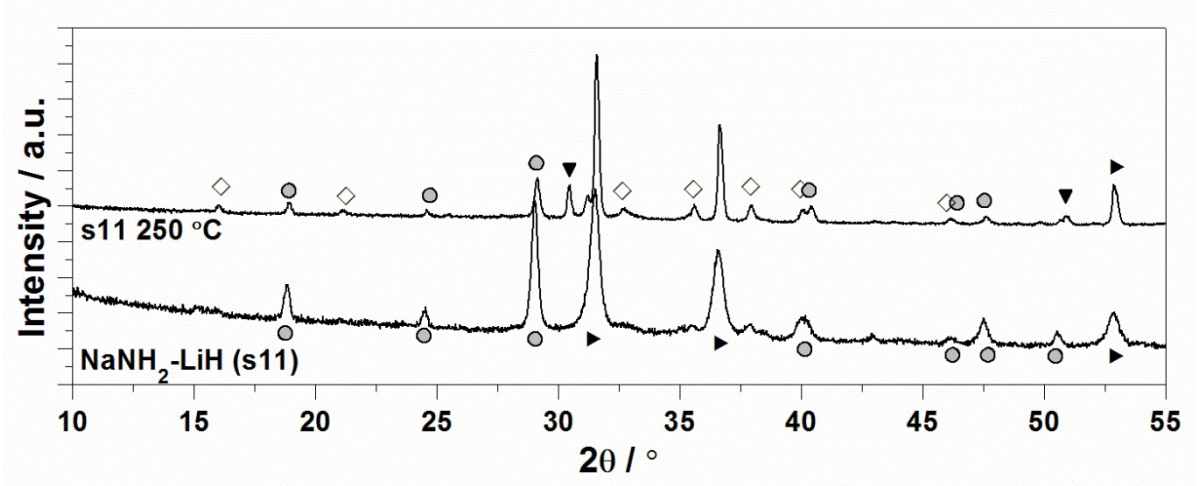

Figure S12 PXD data for $NaNH_2$–LiH (s11) and after heating s11 to 270 °C. Both PXD patterns were measured at RT, λ = 1.54056 Å. Symbols: ■ $LiNH_2$; ▲ NaH; ● $Li_3Na(NH_2)_4$;◇ $LiNa_2(NH_2)_3$; ▲Li_2NH.

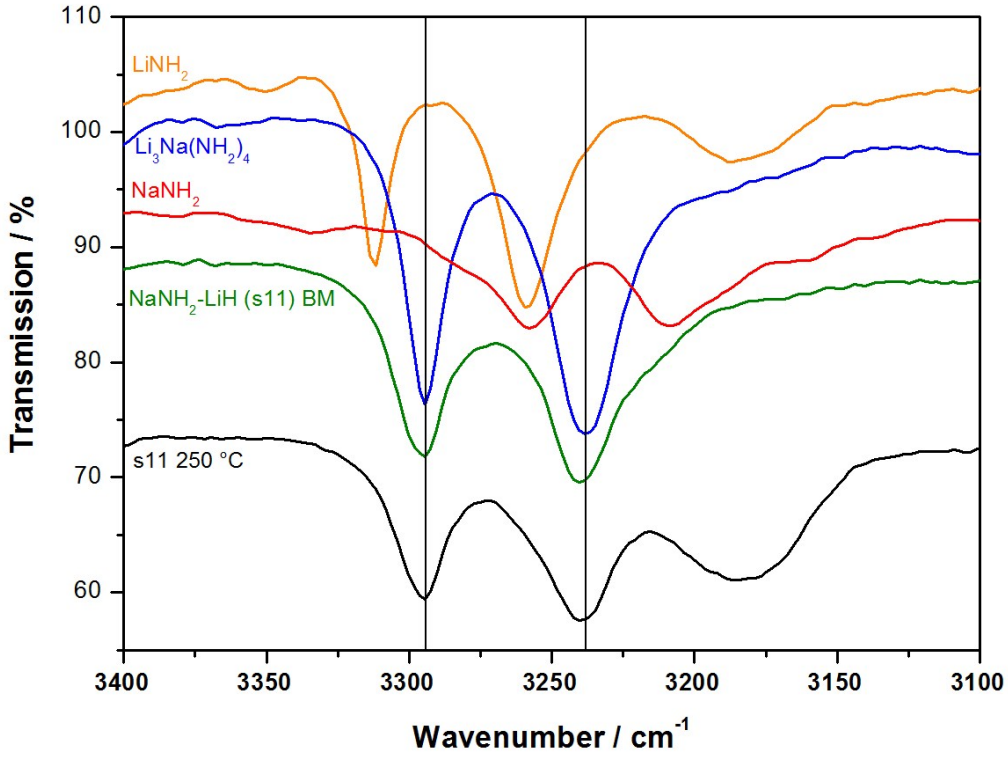

Figure S13 FTIR spectra for $NaNH_2$–LiH (s11) and after heating s11 to 270 °C. All spectra were collected at RT.

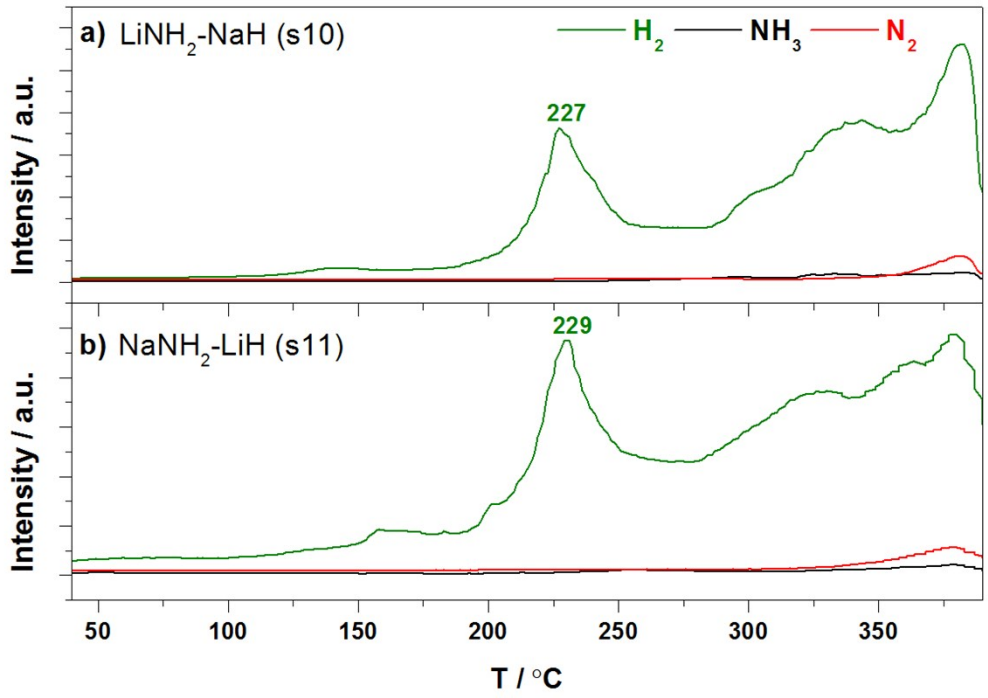

Figure S14 TPD-MS for a) $LiNH_2$–NaH (s10) and b) $NaNH_2$–LiH (s11) during heating from RT to 400 °C (2 °C/min).