# Supplementary Information

## Materials

Tetra-n-butylammonium chloride salt $(C_4H_9)_4NCl$ (TBACl) (SIGMA ALDRICH, purity ≥ 97%), sodium borohydride $NaBH_4$ (ACROS, purity 99%), sodium borodeuteride $NaBD_4$ (ACROS, purity 98%), sodium tetraphenylborate salt $(C_6H_5)_4BNa$ ($NaBPh_4$, purity ≥ 99.5%) (FLUKA), isopropanol (Fisher Chemical, analytical reagent grade 99.9%), magnesium bromide $MgBr_2$ (SIGMA ALDRICH, 98% purity) were used without any previous treatment. Dry dichloromethane (DCM) was obtained from the department of Organic Chemistry of the University of Geneva. TBACl, $NaBH_4$, $MgBr_2$, and $NaBD_4$ were stored and handled in a nitrogen-filled glove box (KLEINER AG, $H_2O$ < 0.1 ppm, $O_2$ < 0.1 ppm). All solvents were used under nitrogen flow to avoid any contamination. Ball milling (FRITSCH Pulverisette 7 Premium Line) was employed for tetrabutylammonium borohydride $(C_4H_9)_4NBH_4$ ($TBABH_4$), $Mg(B_3H_8)_2$, and $Mg(B_3D_8)_2$ synthesis. Nitrogen-vacuum line with standard Schlenk flasks were used for the syntheses. Autoclaves for solvothermal syntheses were built in-house. For solvothermal syntheses, a Heating Oven BINDER GmbH with R3 Controller was used. The device can be operated in an area temperature range of 5°C up to 300°C.

## Syntheses of $NaB_3H_8$ and $NaB_3D_8$

The syntheses are described by the following equations:

$$[CH_3(CH_2)_3N]_4Cl + 3NaBH_4 \rightarrow [CH_3(CH_2)_3N]_4BH_4 + NaCl + 2\,NaBH_4 \quad (1)$$

$$[CH_3(CH_2)_3N]_4BH_4 + 2NaBH_4 + 2CH_2Cl_2 \rightarrow [CH_3(CH_2)_3N]_4B_3H_8 + 2CH_3Cl + 2NaCl \quad (2)$$

$$[CH_3(CH_2)_3N]_4B_3H_8 + NaB(C_6H_5)_4 \rightarrow NaB_3H_8 + 4[CH_3(CH_2)_3N]B(C_6H_5) \quad (3)$$

- The salt metathesis described in Eq. 1 was carried out in planetary ball milling Fritsch Pulversiette 7 premium line. In a 20 mL airtight stainless steel grinding jar, 0.1450 g of $NaBH_4$ (0.1556g of $NaBD_4$) and 0.3550 g of TBACl (0.3444 g for $NaB_3D_8$) were placed together with five stainless steel balls with 10 mm diameters (balls-to-reactants mass ratio ~40). The mixture was milled for 1h at 500 rpm (15min milling and 5 min break). All manipulations were done in a nitrogen filled glovebox to avoid water contamination due to hygroscopic nature of the precursors.
- The reaction described in Eq. 2 was performed in a home-built Teflon line autoclave with 9g of the as-prepared mixture (30 mmol TBACl and 90 mmol $NaBH_4$ (or $NaBD_4$)) with 110 mL of dry dichloromethane. The autoclave was filled in the glovebox and then the autoclave was heated at 80°C during 16h for $TBAB_3H_8$ synthesis (65°C during 38 h for $NaBD_4$ for $TBAB_3D_8$ synthesis).

The solid (NaCl) was filtered out and the liquid evaporated on a rotavapor until dryness under ambient atmosphere. The solid was washed three times with 50 mL of distilled water upon Büchner.

- The salt metathesis described in Eq. 3 was carried out in isopropanol with 1.2 equivalent of $TBAB_3H_8$ (or $TBAB_3D_8$) reacting with 1 equivalent of $NaBPh_4$ during 1h at room temperature. The supernatant was removed using cannula and the solid was washed 3 times with dry dichloromethane. The as-prepared solid was then dried under dynamic vacuum at 50°C during 2h and then it was stored in the glovebox. The yield of the synthesis is around 80% for both $TBAB_3H_8$ and $TBAB_3D_8$.

**Ex- situ Liquid $^{11}B$ NMR of $TBAB_3D_8$**

To gain insight into the reaction mechanism of the formation of $TBAB_3D_8$, ex-situ liquid $^{11}B$ NMR experiments of the liquid phase were performed at different reaction time (12, 24, 29, 32 and 38 h) (Figure S3). For this particular experiment, a reaction temperature of 65°C was chosen in order to slow down the reaction and identifies the intermediates (figure S3). The ex-situ measurements show the complete conversion of $BD_4^-$ ($\delta$ = -38.8ppm) into $B_3D_8^-$ ($\delta$ = -30ppm) by increasing the reaction time. The signal corresponding to $B_2D_7^-$ ($\delta$ = -26.0ppm) confirms the mechanism proposed by Moury et al and Gigante et al [1, 2] for the formation of tetrabutylammonium octahydrotriborate ($TBAB_3H_8$). In this experiment, the conversion of $BD_4^-$ into $B_2D_7^-$ is more obvious than in the previous study of $TBAB_3H_8$ revealing that the reaction involves two steps, i.e. $BD_4^- \rightarrow B_2D_7^- \rightarrow B_3D_8^-$. The intermediate $B_2D_7^-$ starts to appear after 12h and it is converted completely into $B_3D_8^-$ after 38h. This result demonstrates that the B-D bond breaking to form $B_3D_8^-$ is the rate limiting step. Moreover, through this experiment, it is demonstrated that the procedure can be adapted to synthesize deuterated $B_3D_8^-$ and $B_2D_7^-$ salts in liquid phase starting from $NaBD_4$, which is of high interest for neutron diffraction studies.

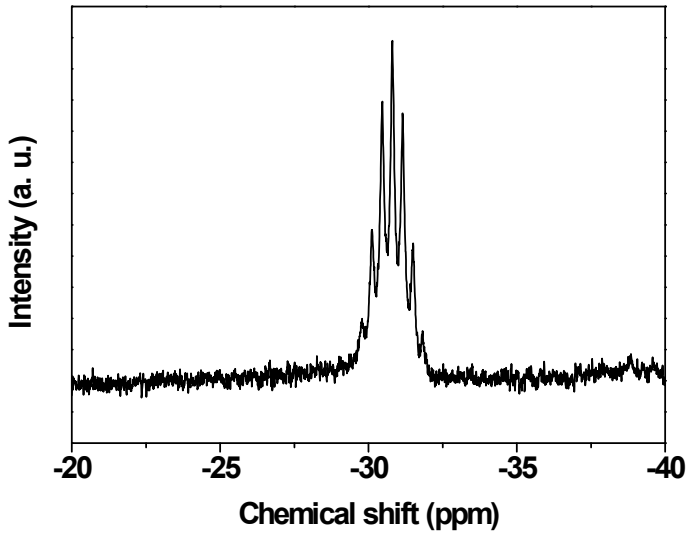


**Figure S1.** $^{11}B\{^{1}H\}$ NMR spectra of $Mg(B_3H_8)_2$ in $d_8$-toluene. Experiment performed on the 300 MHz spectrometer

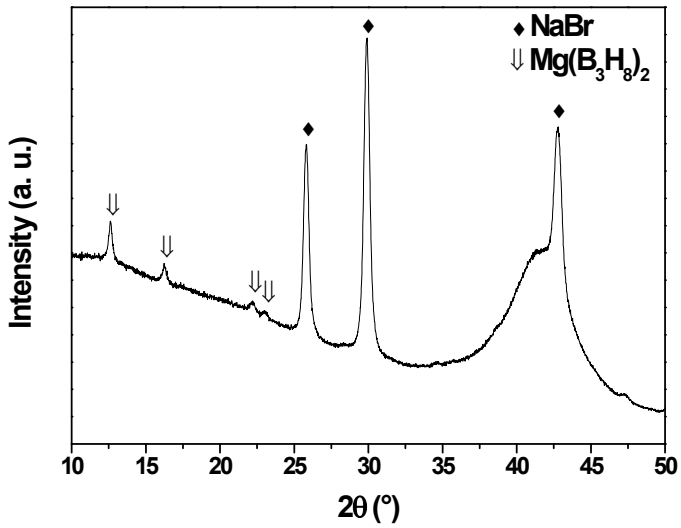


**Figure S2.** X-ray diffraction pattern of the mixture $Mg(B_3H_8)_2$ and NaBr

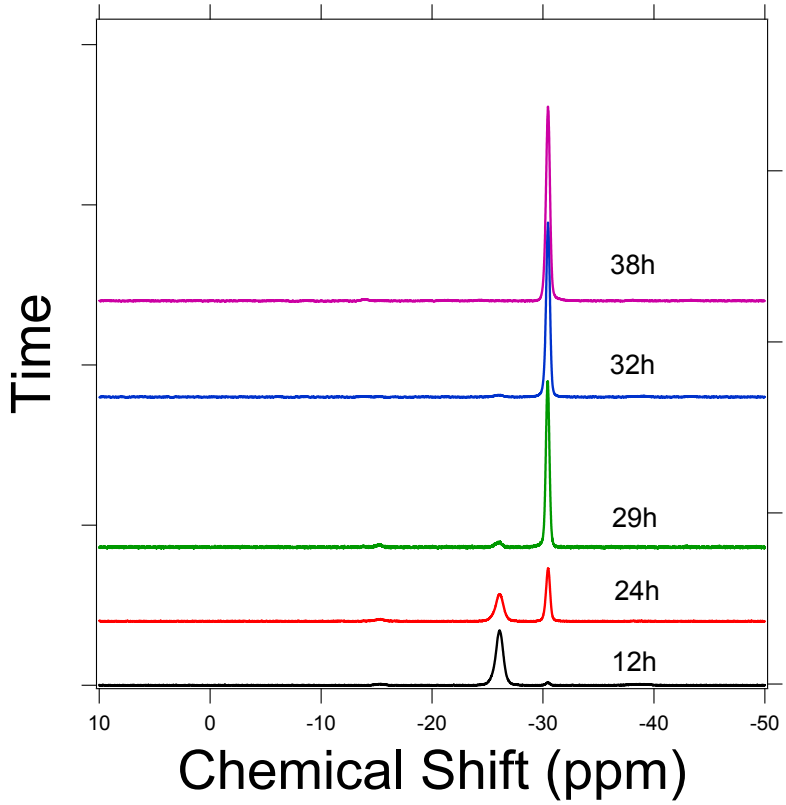


**Figure S3.** Ex-situ liquid $^{11}$B NMR spectra of the liquid phase of the reaction mixtures $TBABD_4$+2$NaBD_4$ at 65°C after different reaction times. Experiments performed in $CD_2Cl_2$ on the 300 MHz spectrometer

**References:**

[1]. Moury, R.; Gigante, A.; Hagemann, H., An alternative approach to the synthesis of $NaB_3H_8$ and $Na_2B_{12}H_{12}$ for solid electrolyte applications. *International Journal of Hydrogen Energy* **2017,** *42* (35), 22417-22421.

[2]. Gigante, A.; Duchêne, L.; Moury, R.; Pupier, M.; Remhof, A.; Hagemann, H., Direct Solution-Based Synthesis of $Na_4(B_{12}H_{12})(B_{10}H_{10})$ Solid Electrolyte. *ChemSusChem* **2019,** *12* (21), 4832-4837.