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Supporting Information

An improved method for the synthesis and formation mechanism of $M_2B_{10}H_{14}$ based on the reactions of $B_{10}H_{14}$ with MNH_2BH_3 (M = Na, K)

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1. Experimental section：

1.1. General Procedures. All manipulations were carried out on a Schlenk line or in a glovebox filled with high-purity nitrogen. The ^{11}B NMR and ^{11}B {^{1}H} NMR spectra were recorded on a 193 MHz spectrometer and externally referenced to $BF_3{\cdot}OEt_2$ in C_6D_6 ($\delta = 0.00$ ppm). The ^{1}H NMR and ^{1}H {^{11}B} NMR spectra were obtained by a 600 MHz spectrometer. X-ray diffraction data were obtained with a Rigaku D/max 2500 diffractometer by using Cu-Ka radiation ($\lambda = 0.1542$ nm, 40 kV, 100 mA). IR spectra were measured by Spectrum 400F.

$B_{10}H_{14}$ was used as received. NaH and KH was washed with tetrahydrofuran (THF) and n-hexane and then dried in vacuo. $NaNH_2BH_3$, KNH_2BH_3, $NaB_{10}H_{13}$, and $NaB_{10}H_{15}$ were prepared according to the literature methods.[1-3] All solvents were distilled from standard drying agents and degassed before use.

1.2. Synthesis of $Na_2B_{10}H_{14}$. $B_{10}H_{14}$ (0.73 g, 6 mmol) and $NaNH_2BH_3$ (0.63 g, 12 mmol) were added to a 100 mL Schlenk flask. The flask was connected to a Schlenk line and 50 mL THF was injected. The reaction solution was stirred at room temperature for 30 min. During this time, a small amount of $[NH_2BH_2]_n$ precipitate was formed and then filtered out (Fig. S1). Then, 1,4-dioxane was added to the filtrate and formed a white precipitate $Na_2(C_4H_8O_2)_xB_{10}H_{14}$ (Fig. S2). After filtration, THF and 1,4-dioxane were removed from the filtrate under a dynamic vacuum to leave a white power containing the formed NH_3BH_3 (Fig. S3). And then, the precipitate $Na_2(C_4H_8O_2)_xB_{10}H_{14}$ was washed with CH_2Cl_2 (3 × 20 mL) and then dried under vacuum to yield a white powder product $Na_2B_{10}H_{14}$ (0.84 g, 83%). ^{11}B NMR (193 MHz, $(CD_3)_2SO$): δ −7.5 (*d*, *J* = 126 Hz), −22.1 (*d*, *J* = 122 Hz), −34.2 (*t*, *J* = 112 Hz), −40.8 (*d*, *J* = 129 Hz) ppm (Fig. 2a). ^{11}B{^{1}H} NMR (193 MHz, $(CD_3)_2SO$): δ −7.5 (*s*), −22.1 (*s*), −34.2 (*s*), −40.8 (*s*) ppm (Fig. 2b). ^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 1.44 (*m*, 2H), 0.68 (m, 4H), 0.47 (*m*, 4H), −2.03 (*m*, 2H), −4.96 (*br*, 2H) ppm (Fig. 3a). ^{1}H{^{11}B} NMR (600 MHz, $(CD_3)_2SO$): δ 1.44 (*s*, 2H), 0.68 (*s*, 4H), 0.47 (*s*, 4H), −2.03 (*s*, 2H), −4.96 (*s*, 2H) ppm (Fig. 3b). IR: 2520 (m), 2478 (m), 2425 (s), 2369 (s), 2332 (m), 2134 (w), 1388 (w), 1173 (s), 1005 (s), 738 (w) (Fig. S15).

1.3. Synthesis of $K_2B_{10}H_{14}$. $B_{10}H_{14}$ (0.73 g, 6 mmol) and KNH_2BH_3 (0.83 g, 12 mmol) were added to a 100 mL Schlenk flask. The flask was connected to a Schlenk line and 50 mL THF was injected. The reaction solution was stirred at room temperature for 12 hours. During this time, a large amount of white precipitate ($K_2B_{10}H_{14}$ and $[NH_2BH_2]_n$) was formed. After the reaction, the reaction solution was examined by ^{11}B NMR (NH_3BH_3, Fig. S6) and then a small amount of water (2 mL) was injected into the solution to destroy the formed $[NH_2BH_2]_n$. After filtration, the precipitate $K_2B_{10}H_{14}$ was washed with THF (3 × 30 mL) and then dried under vacuum to yield a white powder product $K_2B_{10}H_{14}$ (1.07 g, 89%). ^{11}B NMR (193 MHz, $(CD_3)_2SO$): δ −7.5 (*d*, J = 126 Hz), −22.1 (*d*, J = 117 Hz), −34.2 (*t*, J = 105 Hz), −40.9 (*d*, J = 129 Hz) ppm (Fig. S7a). $^{11}B\{^1H\}$ NMR (193 MHz, $(CD_3)_2SO$): δ −7.5 (*s*), −22.1 (*s*), −34.2 (*s*), −40.9 (*s*) ppm (Fig. S7b). ^1H NMR (600 MHz, $(CD_3)_2SO$): δ 1.44 (*m*, 2H), 0.68 (m, 4H), 0.49 (*m*, 4H), −2.03 (*m*, 2H), −4.97 (*br*, 2H) ppm (Fig. S8a). $^1H\{^{11}B\}$ NMR (600 MHz, $(CD_3)_2SO$): δ 1.44 (*s*, 2H), 0.68 (*s*, 4H), 0.49 (*s*, 4H), −2.03 (*s*, 2H), −4.97 (*s*, 2H) ppm (Fig. S8b). IR: 2521 (s), 2481 (s), 2274 (w), 2200 (w), 1411 (w), 1116 (w), 1027 (m), 928 (w), 718 (w) (Fig. S9).

1.4. The reaction of $B_{10}H_{14}$ with 1 equiv. of $NaNH_2BH_3$. $B_{10}H_{14}$ (0.24 g, 2 mmol) and $NaNH_2BH_3$ (0.11 g, 2 mmol) were added to a 50 mL Schlenk flask. The flask was connected to a Schlenk line and 20 mL THF was injected. The reaction solution was stirred at room temperature for 10 min and then was examined by ^{11}B NMR spectroscopy (Fig. S10).

1.5. The reaction of $NaB_{10}H_{13}$ with 1 equiv. of $NaNH_2BH_3$. The as-synthesized $NaB_{10}H_{13}$ (0.29 g, 2 mmol) and $NaNH_2BH_3$ (0.11 g, 2 mmol) were added to a 50 mL Schlenk flask. The flask was connected to a Schlenk line and 20 mL THF was injected. The reaction solution was stirred at room temperature for 30 min and then was examined by ^{11}B NMR spectroscopy (Fig. S11).

1.6. The reaction of $NaB_{10}H_{15}$ with 1 equiv. of $NaNH_2BH_3$. The as-synthesized $NaB_{10}H_{15}$ (0.29 g, 2 mmol) and $NaNH_2BH_3$ (0.11 g, 2 mmol) were added to a 50 mL Schlenk flask. The flask was connected to a Schlenk line and 20 mL THF was injected. The reaction solution was stirred at room temperature for 30 min and then was examined by ^{11}B NMR spectroscopy (Fig. S12).

1.7. The reaction of $B_{10}H_{14}$ with 0.5 equiv. of $NaNH_2BH_3$. $B_{10}H_{14}$ (0.24 g, 2 mmol) and $NaNH_2BH_3$ (0.05 g, 1 mmol) were added to a 50 mL Schlenk flask. The flask was connected to a Schlenk line and 20 mL THF was injected. The reaction solution was stirred at room temperature for 1 hour and then was examined by ^{11}B NMR spectroscopy (Fig. S13). After filtration, THF was removed from the filtrate under dynamic vacuum to leave an oily product, which was washed with methylbenzene (2 × 30 mL), and then dried under vacuum to yield a white powder product $NaB_{10}H_{15}$ which was not very pure (Fig. S14).

2. Supporting results:

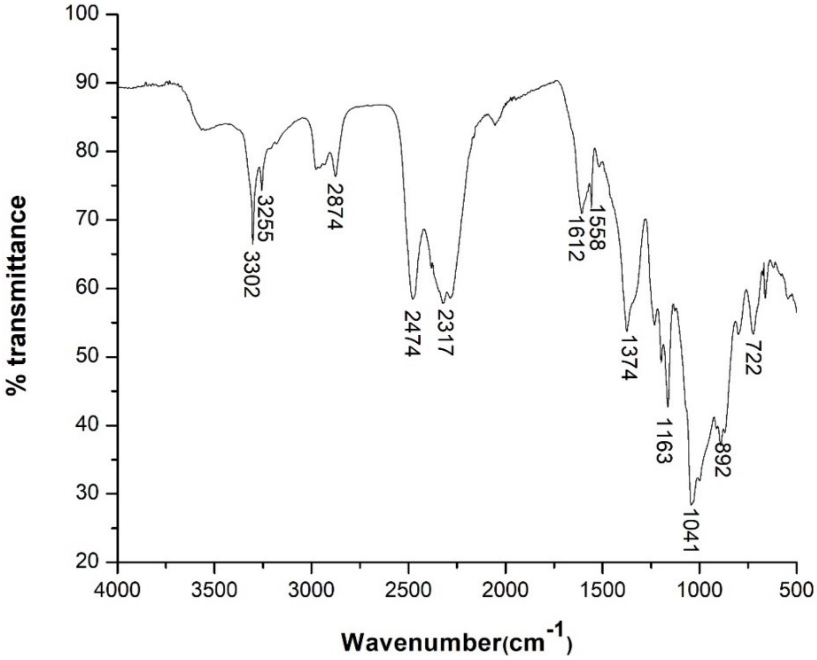

Fig. S1 IR spectrum of the formed $[NH_2BH_2]_n$ in the reaction of $B_{10}H_{14}$ with 2 equiv. of $NaNH_2BH_3$.

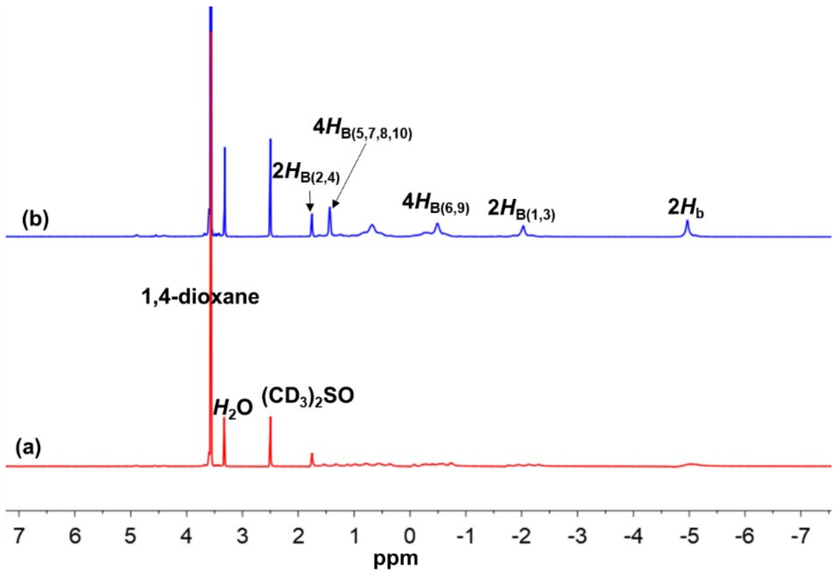

Fig. S2 ^{1}H NMR (a) and ^{1}H{^{11}B} NMR (b) spectra of the 1,4-dioxane-solvated $Na_2(C_4H_8O_2)_xB_{10}H_{14}$ in $(CD_3)_2SO$.

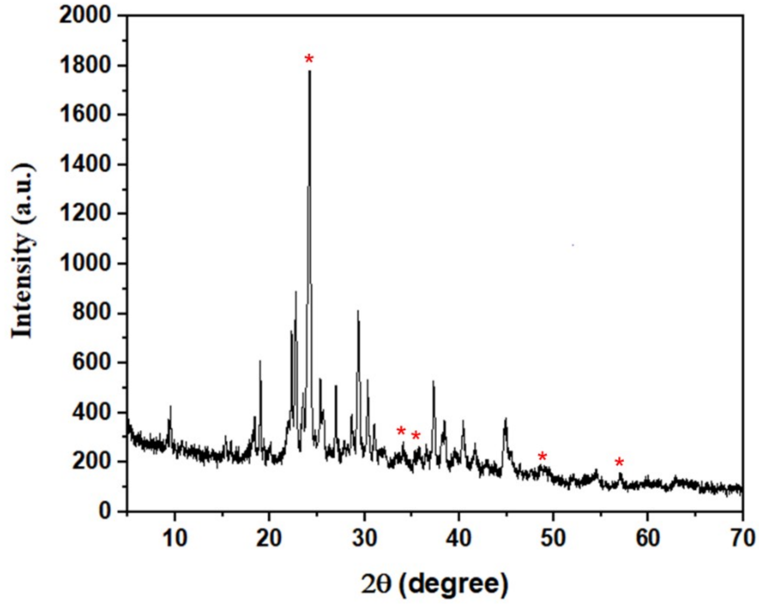

Fig. S3 X-ray powder diffraction data of the formed NH_3BH_3 (*) in the reaction of $B_{10}H_{14}$ with 2 equiv. of $NaNH_2BH_3$.

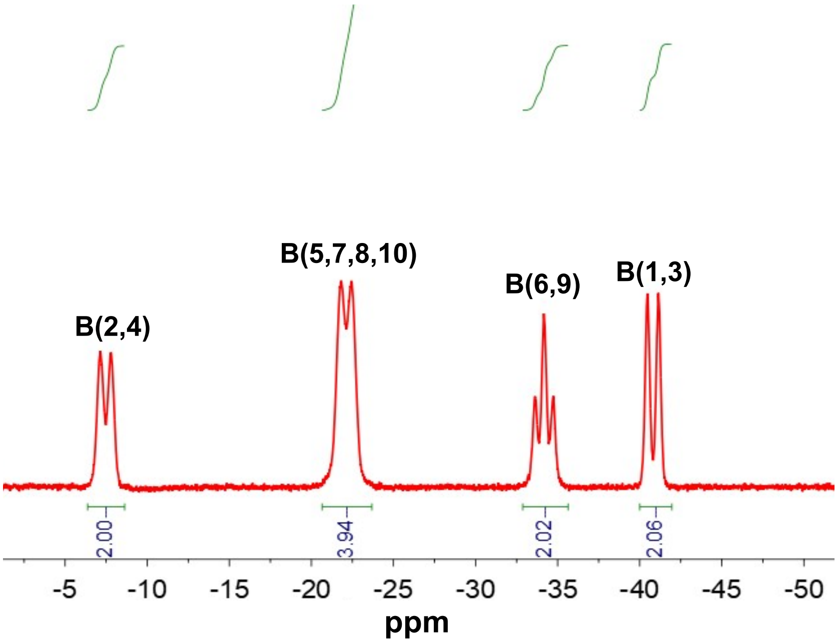

Fig. S4 The integration of the ^{11}B NMR spectrum of the prepared $Na_2B_{10}H_{14}$ in $(CD_3)_2SO$.

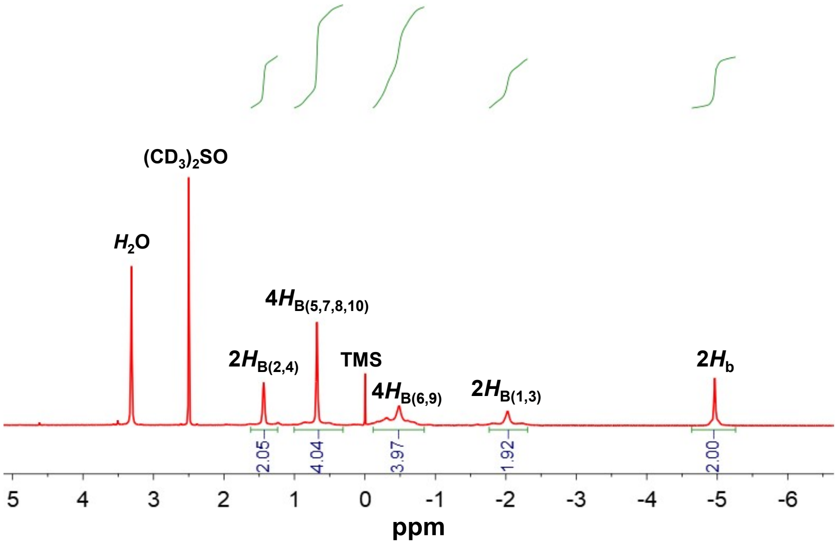

Fig. S5 The integration of the $^1H\{^{11}B\}$ NMR spectrum of the prepared $Na_2B_{10}H_{14}$ in $(CD_3)_2SO$.

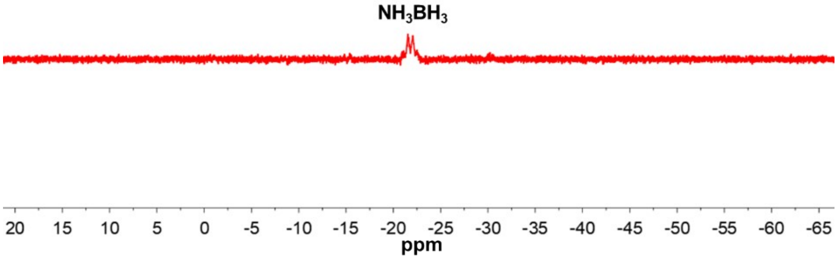

Fig. S6 ^{11}B NMR spectrum of the formed NH_3BH_3 in the reaction of $B_{10}H_{14}$ with 2 equiv. of KNH_2BH_3.

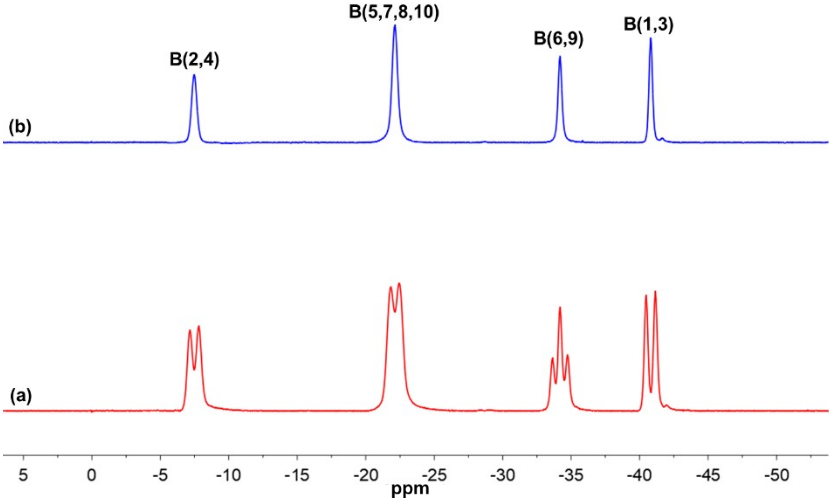

Fig. S7 ^{11}B NMR (a) and ^{11}B{^{1}H} NMR (b) spectra of the prepared $K_2B_{10}H_{14}$ in $(CD_3)_2SO$.

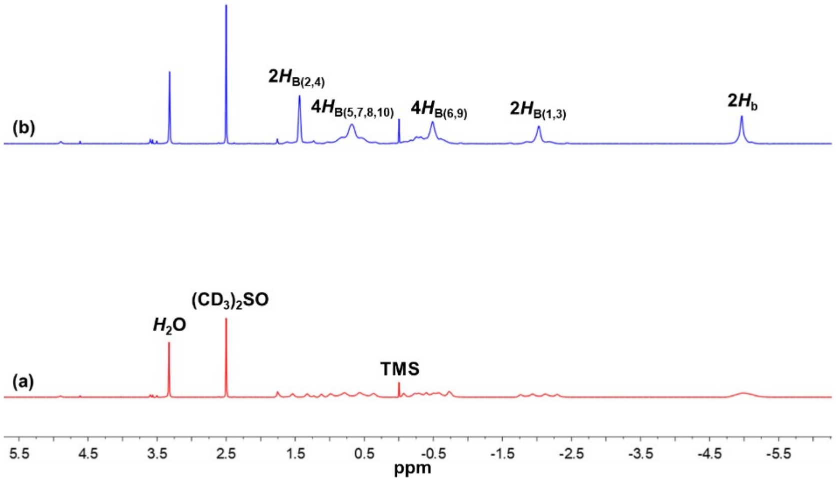

Fig. S8 ^{1}H NMR (a) and ^{1}H{^{11}B} NMR (b) spectra of the prepared $K_2B_{10}H_{14}$ in $(CD_3)_2SO$.

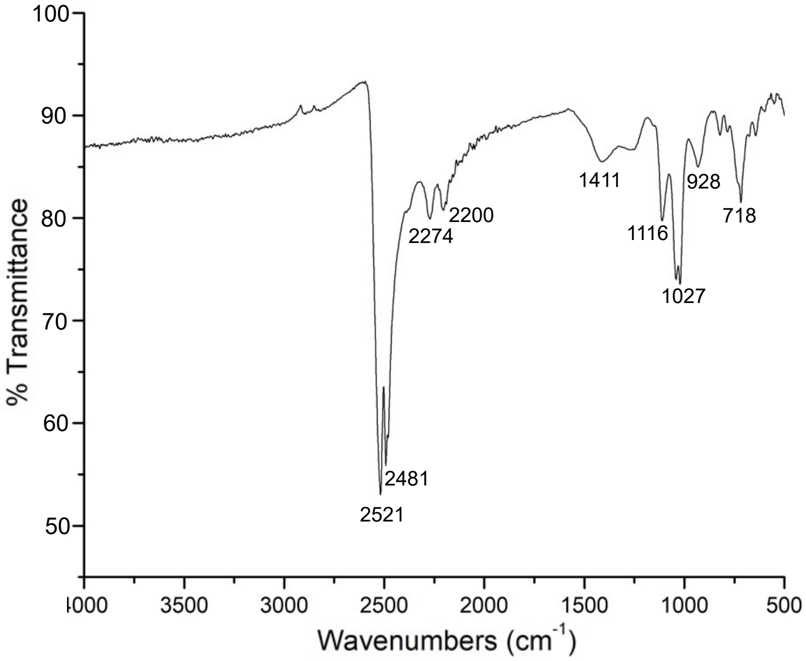

Fig. S9 IR spectrum of the prepared $K_2B_{10}H_{14}$.

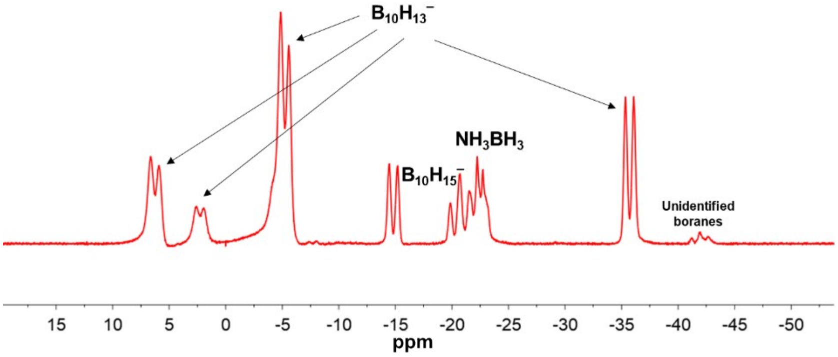

Fig. S10 ^{11}B NMR spectrum of the reaction solution of $B_{10}H_{14}$ with 1 equiv. of $NaNH_2BH_3$.

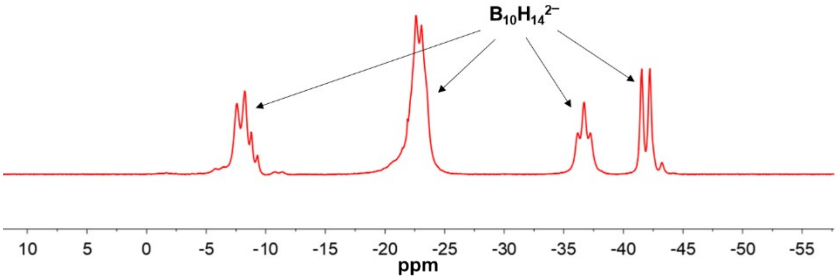

Fig. S11 ^{11}B NMR spectrum of the reaction solution of $NaB_{10}H_{13}$ with 1 equiv. of $NaNH_2BH_3$.

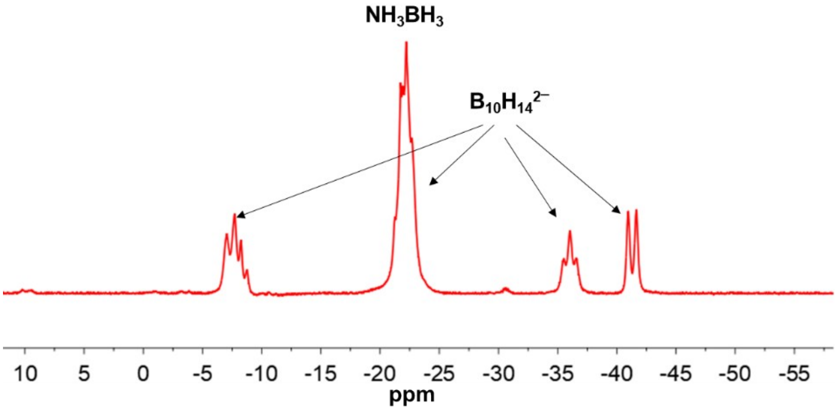

Fig. S12 ^{11}B NMR spectrum of the reaction solution of $NaB_{10}H_{15}$ with 1 equiv. of $NaNH_2BH_3$.

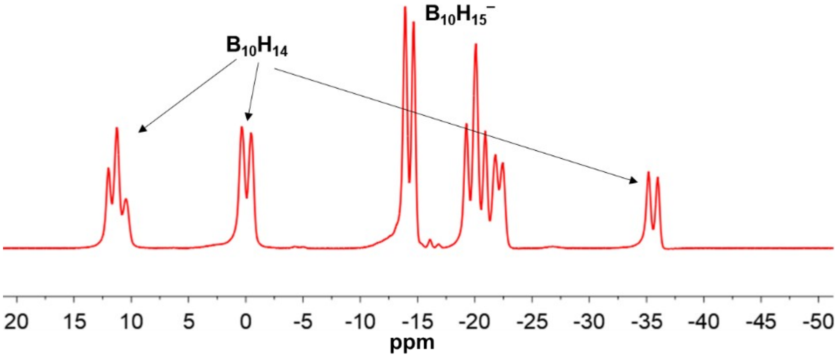

Fig. S13 ^{11}B NMR spectrum of the reaction solution of $B_{10}H_{14}$ with 0.5 equiv. of $NaNH_2BH_3$.

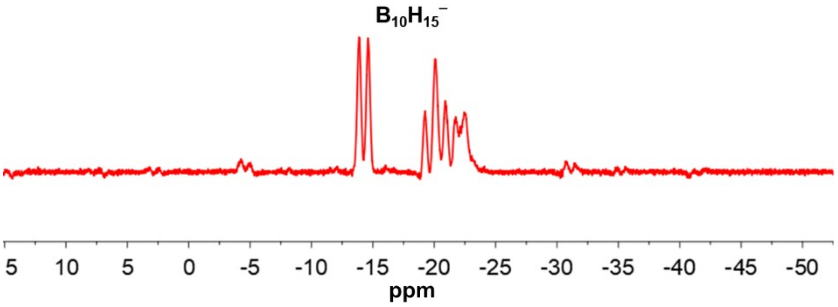

Fig. S14 ^{11}B NMR spectrum of the isolated $NaB_{10}H_{15}$ which is not very pure.

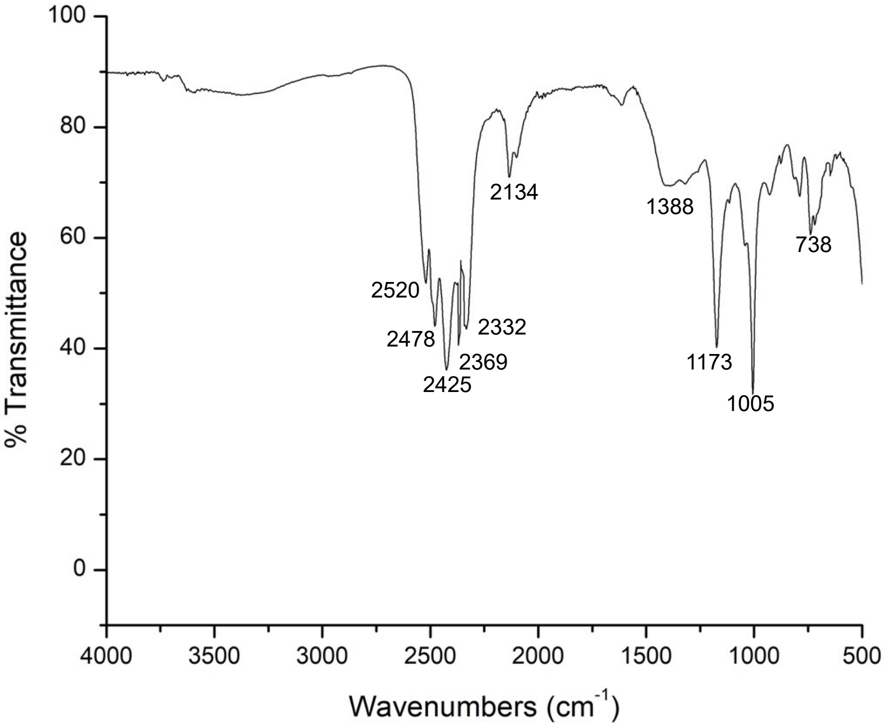

Fig. S15 IR spectrum of the prepared $Na_2B_{10}H_{14}$.

3. References

1 (a) Z. Xiong, G. Wu, Y. S. Chua, J. Hu, T. He, W. Xu and P. Chen, *Energy Environ. Sci.,* 2008, **1**, 360−363; (b) Z. Xiong, C. K. Yong, G. Wu, P. Chen, W. Shaw, A. Karkamkar, T. Autrey, M. O. Jones, S. R. Johnson, P. P. Edwards and W. I. F. David, *Nat. Mater.,* 2008, **7**, 138−141.

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