Electronic Supplementary Material (ESI) for Dalton Transactions.
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Electronic Supplementary Information (ESI)

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Experimental

$LiBH_4$ (purity: 95%) and $ZnCl_2$ (purity: 98%) were purchased from Alfa Aesar and nano-porous SiO_2 (SBA15) was from ACS Material. SBA15 was pretreated under vacuum lower than 10^{-4} mbar and at 500 °C for 12 h. To synthesize nanoconfined $LiBH_4$, the mixture of $LiBH_4$ and SBA15 was first hand-milled for 15 min using a mortar and a pestle and thereafter transported into a steel autoclave. Subsequently, the autoclave was evacuated for 30 min and 100 bar H_2 was introduced at RT. The autoclave was heated to 300 °C with a ramp of 5 °C/min and kept for 25 min, while the pressure reached 120 bar H_2. Nanoconfined $LiBH_4$ with two different loading ratios of 20 mass% and 39 mass% were prepared, respectively. All the handlings were performed in a Braun Ar-circulated glove box (M-Braun) with $O_2 < 0.1$ ppm and $H_20 < 0.1$ ppm.

To synthesize nanoconfined $Li_2B_{12}H_{12}$, nanoconfined $LiBH_4$ with the loading ratio of 20 mass% was treated under B_2H_6 atmosphere at 150 °C for 15 h. Thereby, $LiZn_2(BH_4)_5$, synthesized by milling a mixture of $ZnCl_2$ and $LiBH_4$, was used as a B_2H_6 source which releases B_2H_6 and H_2 above 90 ºC according to eq. s1.

$$LiZn_2(BH_4)_5 \rightarrow LiBH_4 + 2Zn + 52B_2H_6 + 2H_2 \quad \text{(eq. s1)}$$

XRD measurements were performed on a Bruker D8 diffractometer equipped with a Goebel mirror selecting Cu Kα radiation (λ= 1.5418 Å) and a linear detector system (Vantec) using sample powders sealed in glass capillaries under argon atmosphere. The Rietveld refinement was performed using Topas5 software.

N_2-physisorption (Micromeritics TriStar 3000) was performed at 77 K for porosity analysis. The total pore volume was obtained at $P/P_0 = 0.997$. The samples were prepared in a capped quartz sample tube in the glovebox and were directly measured. The mesopore size distribution was analyzed with the Barrett-Joyner-Halenda (BJH) method from the adsorption branch of the isotherm with a carbon black thickness equation as reference.

Solid-state NMR experiments were performed on a Bruker Advance III 400 MHz NMR spectrometer using a 4 mm cross polarization magic angle spinning probe. ^{7}Li and ^{11}B NMR spectra were recorded at 155.5 and 128.4 MHz, respectively. The bearing gas pressure was set to 400 mbar and the temperature dependent measurement performed without sample rotation. The samples were equilibrated for 10 min at each temperature for these experiments. The ^{11}B MAS NMR spectra were recorded at 12 kHz sample rotation applying a Hahn echo pulse sequence to suppress the broad background resonance of boron nitride in the probe. Pulse lengths of 1.5 μs ($\pi/12$ pulse) and 3.0 μs were applied for the excitation and echo pulses, respectively. For selected samples, ^{1}H-^{11}B cross polarization magic angle spinning (CP-MAS) NMR spectra were recorded using weak radio-frequency powers for spin locking of the ^{11}B nucleus on resonance. ^{11}B NMR chemical shifts are reported in parts per million (ppm) externally referenced to a 1M $B(OH)_3$ aqueous solution at 19.6 ppm.

Ionic conductivity was measured by alternating current (AC) impedance spectroscopy using a Zahner IM6ex electrochemical workstation in 2-electrode stainless steel cells. The frequency was varied between 3 MHz and 10 Hz. Lithium metal were used as electrodes. All powder samples were pressed into pellets with a diameter of 12 mm and a thickness of ca. 1.0 mm under a pressure of 0.9 GPa.