Comment on "Bi-functional $Li_2B_{12}H_{12}$ for energy storage and conversion applications: solid-state electrolyte and luminescent down-conversion dye" by J. A. Teprovich Jr., H. Colón-Mercado, A. L. Washington II, P. A. Ward, S. Greenway, D. M. Missimer, H. Hartman, J. Velten, J. H. Christian and R. Zidan, *J. Mater. Chem. A*, 2015, 3, 22853

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Supporting Information

Experimental Details

Synthesis

Metal *closo*-boranes ($M_xB_{10}H_{10}$ and $M_xB_{12}H_{12}$) were prepared by solvent-mediated ion exchange techniques from either an $(NH_4)_2B_{10}H_{10}$ or $Li_2B_{12}H_{12}.xH_2O$ (Katchem) precursor.

$(NH_4)_2B_{10}H_{10}$ was synthesised from decaborane ($B_{10}H_{14}$, Katchem) by reaction with excess dimethyl sulphide (DMS) for 3 days at room temperature. The product, $B_{10}H_{12}DMS_2$, was separated and dried under vacuum 1 h, cooled to -33 °C, and stirred under liquid NH_3 for 2 h before being heated back to room temperature, followed by evacuation at 70 °C for 30 minutes, yielding a white powder, $(NH_4)_2B_{10}H_{10}$.

Cation exchange was undertaken by passing an aqueous solution of the precursor borane through an Amberlite IR-120-H resin (Sigma-Aldrich) to form the respective acid. The borane acid was then reacted with a metal source (LiOH, Na_2CO_3, $Sc_2(CO_3)_3$, $Y_2(CO_3)_3$, $La_2(CO_3)_3$, and $Eu_2(CO_3)_3$) until a neutral pH was obtained. The resulting solution was then concentrated by rotary evaporation at 65 °C and further dried on a Schlenk line for at least 3 hours at 45 – 65 °C. The resulting powders were obtained as crystalline hydrates.

'Sealed vessel annealing' was also undertaken to synthesise an 'impure' sample of $Li_2B_{12}H_{12}$. An attempt was made to replicate the 'sealed vessel annealed' $Li_2B_{12}H_{12}$ sample exactly as prepared in earlier work.[1] However, a lack of detail regarding the source and purity of starting reagents ($LiBH_4$ and $B_{10}H_{14}$) and the mill specifications made this challenging. A 2:1 molar ratio of $LiBH_4$ and $B_{10}H_{14}$ were ball milled together for 1 h (10:1 ball:powder ratio, 5 minute milling, 2 minute pause, 12 cycles, at 300 rpm in WC vials/balls within a Fritsch P4 mill). The milled powder was then annealed in a sealed vessel at 200 °C for 20 h, forming a slightly yellow powder.

Characterisation

Metal boranes were dissolved in MilliQ water (5 mg/ml). The stability of metal boranes is well known[2], where the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ anions do not even react with strong aqueous NaOH at 95 °C, and the $B_{12}H_{12}^{2-}$ is stable in 3 M HCl at 95 °C while the $B_{10}H_{10}^{2-}$ only reacts slowly. The absorption spectra were recorded on a Shimadzu UV3600 double-beam spectrophotometer. Fluorescence spectra were recorded using λ_{exc} = 250 nm on an L-

configuration fluorimeter (Fluoromax P, Horiba Jobin Yvon). Fluorescence quantum yields and instrument intensity calibration were determined using standard procedure.[3] L-tryptophan in water served as the fluorescence standard (φ_{fl} = 0.12 ± 0.01).[4]

Powder X-ray diffraction (PXRD) data were collected on a Rigaku Smartlab diffractometer using a Cu source (Cu Kα_1 radiation = 1.540593 Å) and a Rigaku D/tex detector. All samples were mounted in an argon-filled glovebox in 0.5 mm glass capillaries sealed with glue.

Coupled and ^{1}H-decoupled ^{11}B Nuclear Magnetic Resonance (NMR) were undertaken on a Bruker Avance III 400 MHz spectrometer with reference to a $BF_3{\cdot}Et_2O$ reference. Powder was dissolved in either D_2O or CD_3CN for analysis.

Results

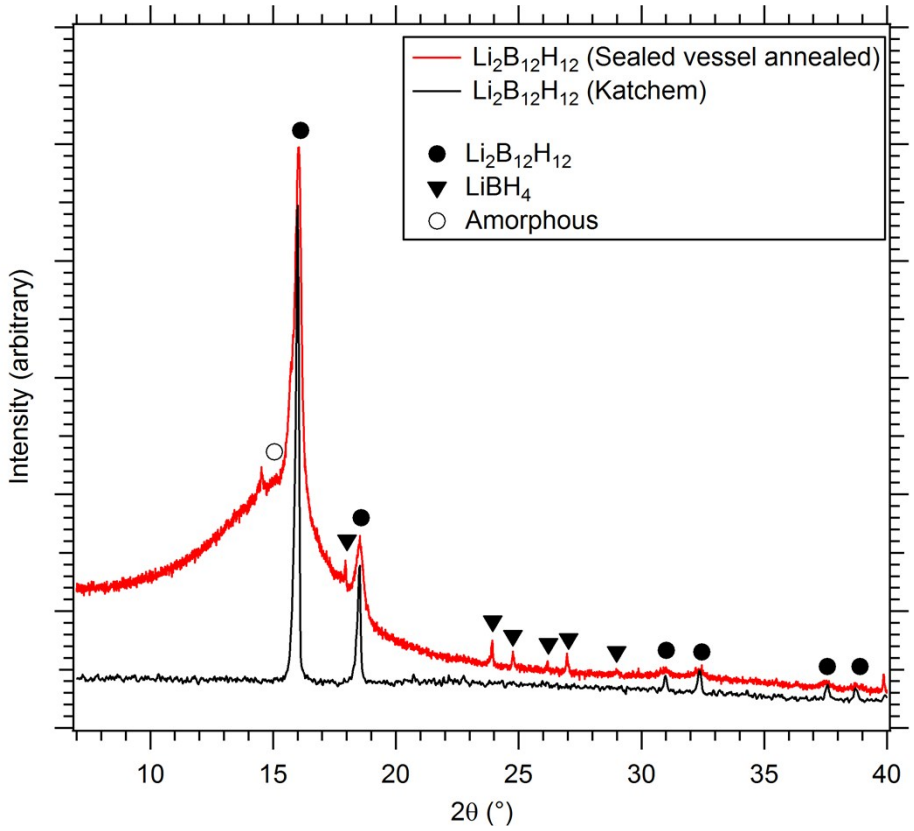


Figure S1: PXRD data of $Li_2B_{12}H_{12}$ from different sources (λ = 1.540593 Å).

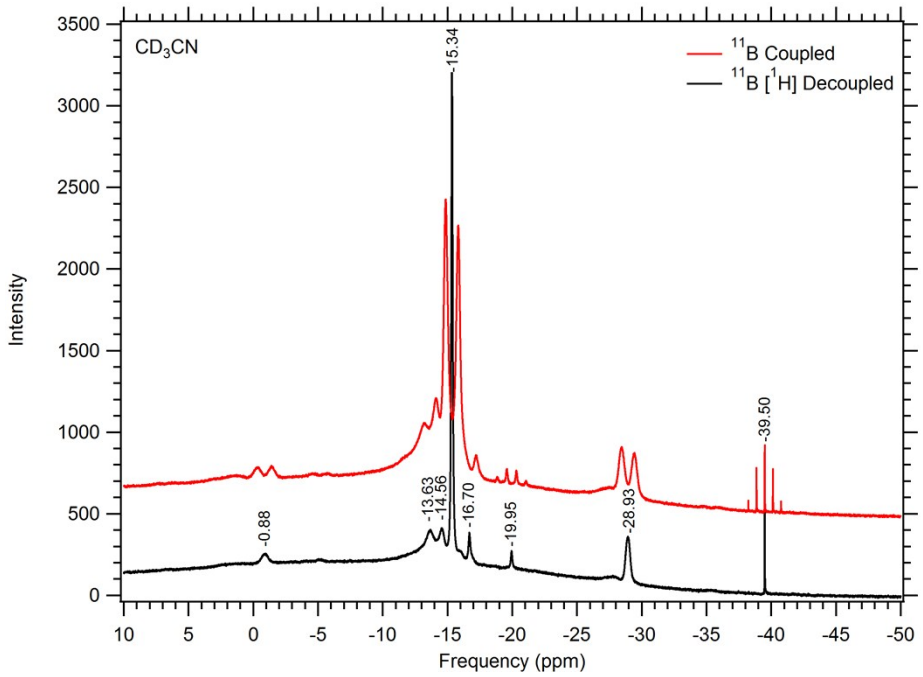


Figure S2: NMR data of 'impure' $Li_2B_{12}H_{12}$ from 'sealed vessel annealing' in CD_3CN.

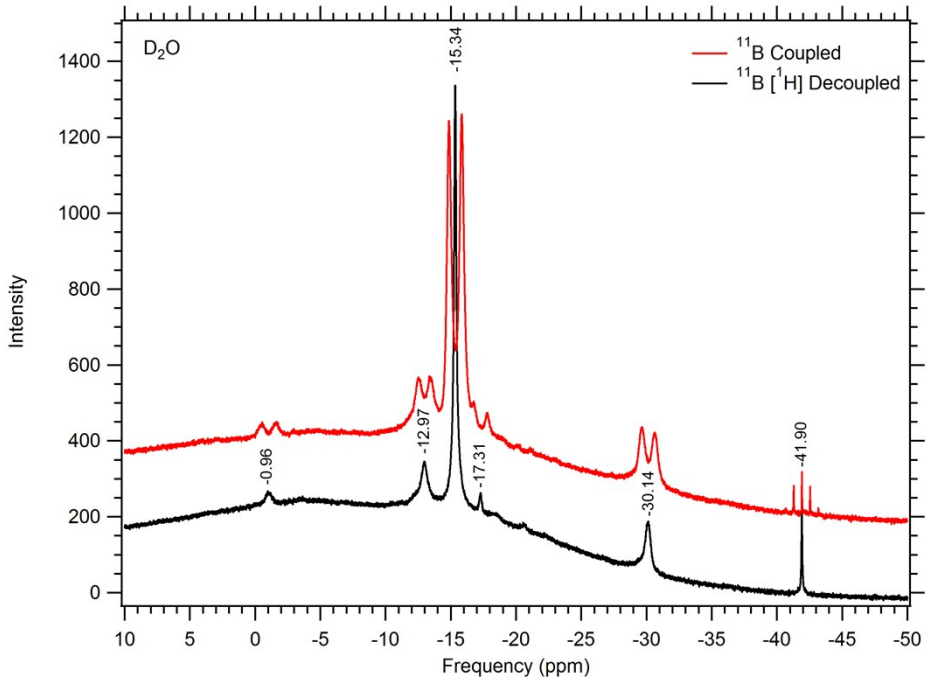


Figure S3: NMR data of 'impure' $Li_2B_{12}H_{12}$ from 'sealed vessel annealing' in D_2O.

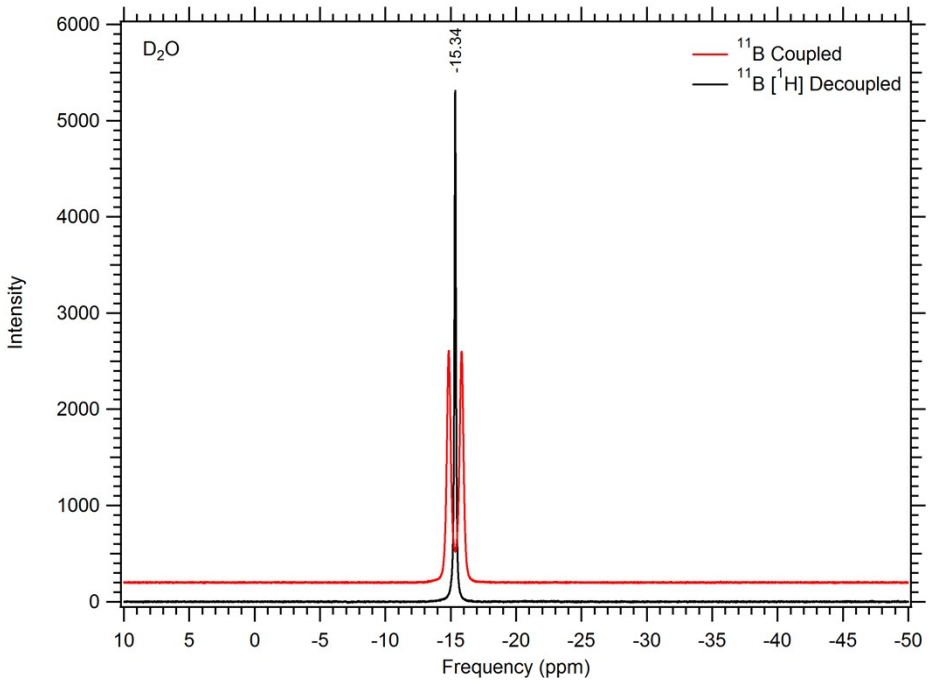


Figure S4: NMR data of $Li_2B_{12}H_{12}$ (Katchem) in D_2O.

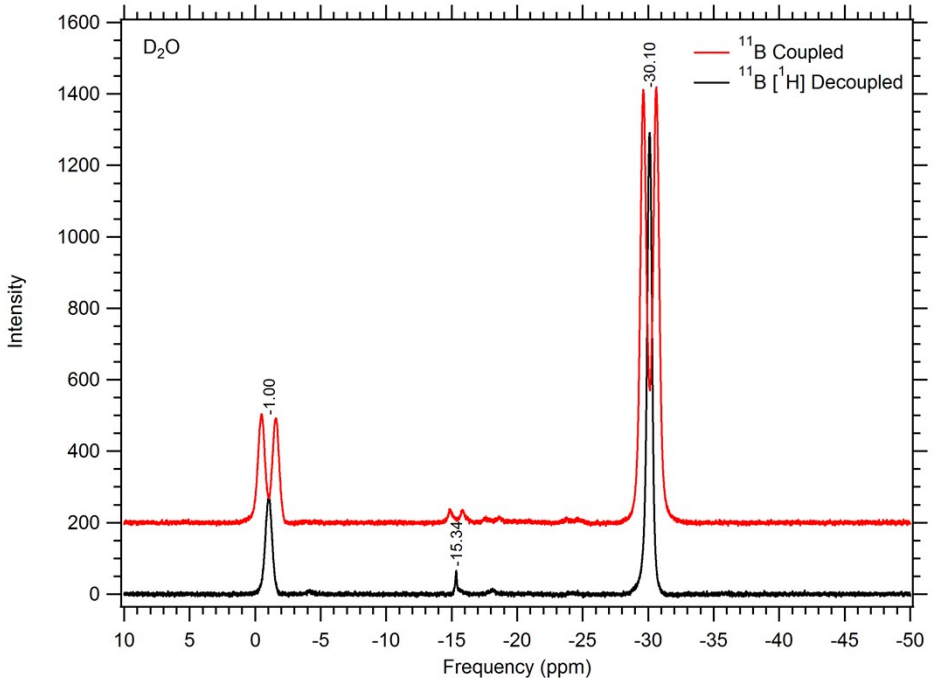
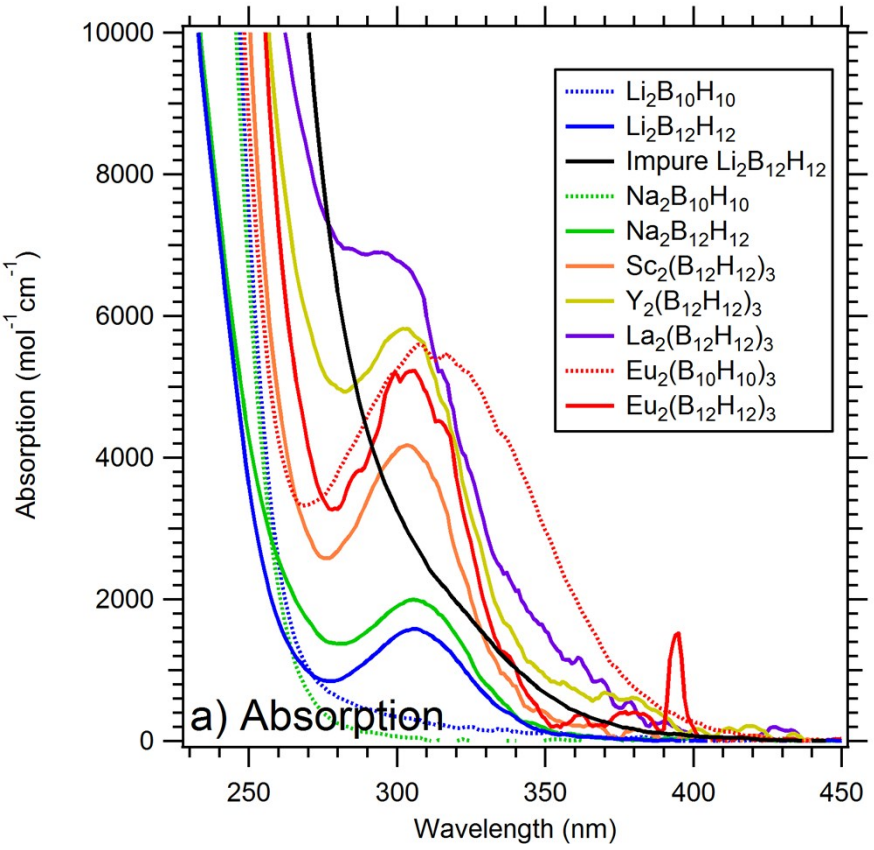


Figure S5: NMR data of wet chemically synthesised $Li_2B_{10}H_{10}$ in D_2O.

Table S1: ^{11}B NMR weight fractions

Sample	**Chemical Shift (ppm)**	**Assignment**	**wt.%**
$Li_2B_{10}H_{10}$ (D_2O)	-1.00	$Li_2B_{10}H_{10}$	98.2
	-30.10		
	-15.34	$Li_2B_{12}H_{12}$	1.8
$Li_2B_{12}H_{12}$	-15.34	$Li_2B_{12}H_{12}$	100

(D_2O)			
Sealed vessel annealed $Li_2B_{12}H_{12}$ (Acetonitrile)	-15.34	$Li_2B_{12}H_{12}$	54
	-0.88	$Li_2B_{10}H_{10}$	20
	-28.93		
	-13.63	$LiB_{11}H_{14}$	12
	-14.56		
	-16.70		
	-19.95	Acetonitrile.BH_3	10
	-39.50	$LiBH_4$	4



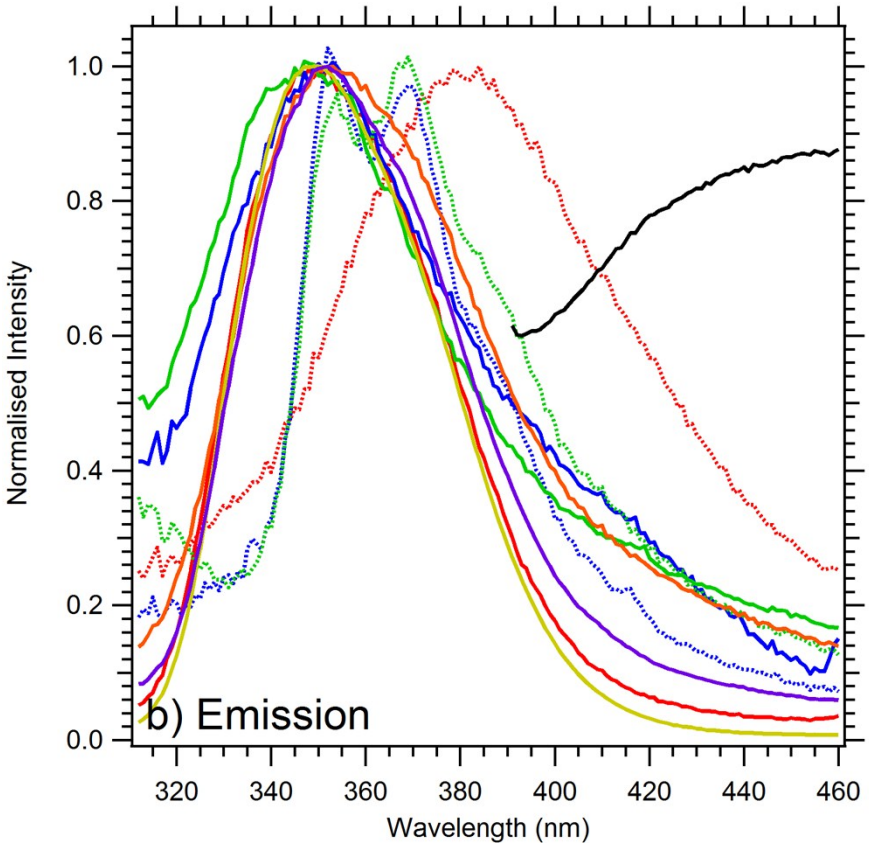


Figure S4:a) absorption and b) emission spectra of aqueous metal closo-boranes.

References

1. J. A. Teprovich, H. Colon-Mercado, A. L. Washington Ii, P. A. Ward, S. Greenway, D. M. Missimer, H. Hartman, J. Velten, J. H. Christian and R. Zidan, *J. Mater. Chem. A*, 2015, **3**, 22853-22859.
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3. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, 2006.
4. M. Brouwer Albert, *Pure Appl. Chem.*, 2011, **83**, 2213.