

## Supporting Information

### Unraveling Boron Oxidation and Structure in 2D $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$ via Solid-State NMR

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### Synthesize method:

**Synthesis of 3D  $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$  i-MAB phase:**  $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$  crystals were prepared using a modification of a reported procedure.<sup>1</sup> A tube furnace equipped with silicon carbide resistors was used. The starting materials were molybdenum metal powder, yttrium metal powder, crystalline boron powder, and aluminum metal chips. Various mixtures of these materials in various atomic ratios were placed in an alumina crucible and heated in an argon atmosphere. The tube was flushed with argon for 10 minutes before raising the temperature to 1400 °C. The sample was held at this temperature for 10 hours before cooling to 900 °C at a rate of 1 °C/min, then cooled to room temperature at 3 °C/min. After cooling to room temperature, the loosely sintered sample was pulverized and sieved through a 200-mesh screen.

**Derivation of 2D  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$  (boridene):** 2 g of the as-synthesized  $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$  i-MAB precursor was slowly added to 20 ml 40 wt% aqueous hydrofluoric (HF) acid at room temperature, then transferred to a silicone oil bath and magnetically stirred at 35°C for 210 min. After etching, the resulting suspension was diluted and transferred to a 50 ml centrifuge tube, then washed with degassed deionized water. Deionized water was used multiple times to eliminate any remaining acid and reaction byproducts, followed by centrifugation at 5000 rpm for 1 minute to remove excess water. To further delaminate the material, 10 mL of 20 wt% TBAOH was introduced into the centrifuge tube and shaken for 2 minutes. Subsequently, the tube underwent centrifugation at 6000 rpm for 2 minutes to discard the supernatant. Ethanol was then added to rinse off any residual TBAOH, and this was repeated three times by discarding the ethanol each time. After ethanol washing, degassed deionized water was used for additional rinsing, repeated three times. During this step, care was taken to avoid agitation and shaking to prevent delamination. Following the wash steps, 15 ml of water was added to the powder and shaken for 10 minutes to obtain single-layer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$  sheets. The centrifuge tube was then centrifuged at 3000 rpm for 10 minutes to remove undelaminated crystals, yielding a final colloidal suspension of delaminated  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$  sheets with an average concentration of approximately 4 mg/ml. The crystals were then separated from the etchant with vacuum filtration and rinsed with deionized water. By doing so, the conversion efficiency of multilayer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$  is 90%, and that of monolayer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$  is 5 - 10%.

### Characterization:

**X-ray Powder Diffraction (XRD):** XRD patterns were measured using a PANalytical Empyrean3 X-ray diffractometer operating at 45 kV and 40 mA, with Cu-K $\alpha$ 1 radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The data were collected by scanning from 4 to 60° (2 $\theta$ ) at 0.02° per step with a dwell time of 5 seconds.

**Scanning Electron Microscopy (SEM):** SEM measurements were performed on a Hitachi SU5000 Field Emission Scanning Electron Microscope.

**Transmission Electron Microscopy (TEM):** TEM images were obtained on a FEI Tecnai G<sup>2</sup> F30 transmission electron microscope, which is equipped with a field emission gun and operates at 300 kV.

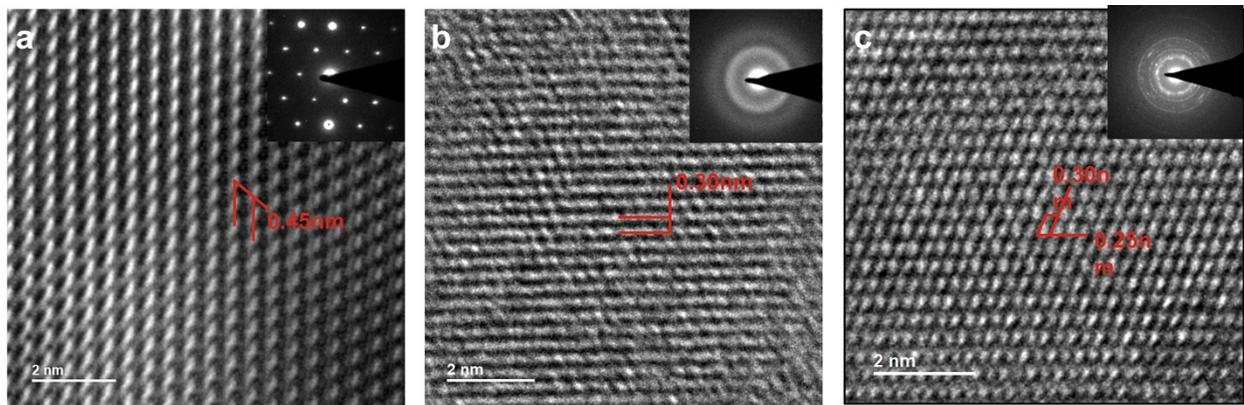
**X-ray Photoelectron Spectroscopy (XPS):** The chemical states and composition of the samples were analyzed by XPS on an ESCALAB 250 photoelectron spectrometer from Thermo Fisher Scientific, using a monochromatic Al K $\alpha$  X-ray beam (1486.6 eV). All binding energies were referenced to the C 1s peak (284.6 eV).

**Fourier-transform Infrared Spectroscopy (FT-IR):** FT-IR spectra were acquired on a Nicolet 6700-Continuum Fourier-Transform Infrared Spectrometer from Thermo Fisher Scientific.

**Raman Spectroscopy:** Raman measurements were conducted on a Renishaw inVia Qontor Raman spectrometer, with laser excitations of 532 nm. During the measurements, the laser power on the sample surface was 250  $\mu\text{W}$ , and all integration times were 10 seconds.

**A Bruker Avance 600 NMR spectrometer** was used to record nuclear magnetic resonance (NMR) spectra. A typical Bruker MAS probe head with a rotor diameter of 1.9 mm and a spinning frequency of 25 kHz was employed for the <sup>27</sup>Al and <sup>11</sup>B magic angle spinning (MAS) NMR. Using a single 1 $\mu\text{s}$  excitation pulse and a 1 s interscan delay. The <sup>27</sup>Al chemical shift was referenced to a saturated Al(NO<sub>3</sub>)<sub>3</sub> solution. <sup>1</sup>H-<sup>11</sup>B HETCOR experiments were performed under a MAS frequency of 25 kHz and a recycle delay of 1.5 s. For <sup>1</sup>H, the lengths of  $\pi/2$  and  $\pi$  pulses were 0.9 and 1.8  $\mu\text{s}$ , respectively.

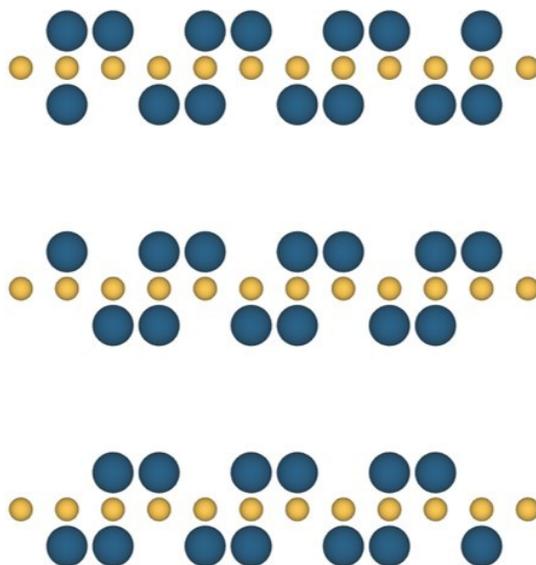
<sup>1</sup>H MAS NMR experiments were carried out using a 1.9 mm MAS probe at 25 kHz spin rates, typical  $\pi/2$ -pulse lengths of 1.5  $\mu\text{s}$ , and a recycle delay of 5 s. Adamantine is used as a secondary standard (1.78 ppm for <sup>1</sup>H). The back-to-back (BaBa) dipolar recoupling sequence was used to excite and reconvert double-quantum (DQ) coherences.<sup>2</sup>



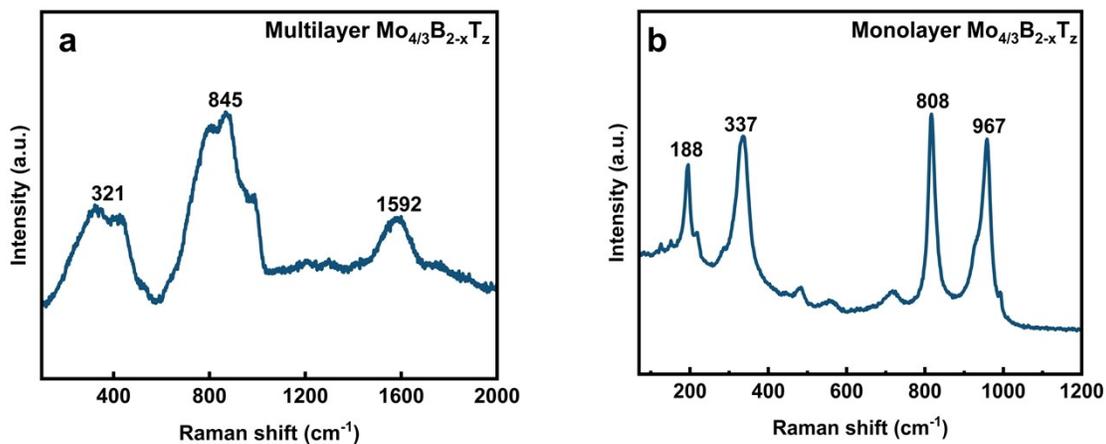
**Figure S1.** HRTEM picture of (a) 3D  $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ , (b) multilayer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$  and (c) 2D monolayer

Element	Mo	B	Al	Y	F	O	Sum[%]
Multilayer $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$	4.80	0.77	0.67	63.24	19.18	8.34	100
Monolayer $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$	36.73	-	3.09	37.27	12.18	12.13	100

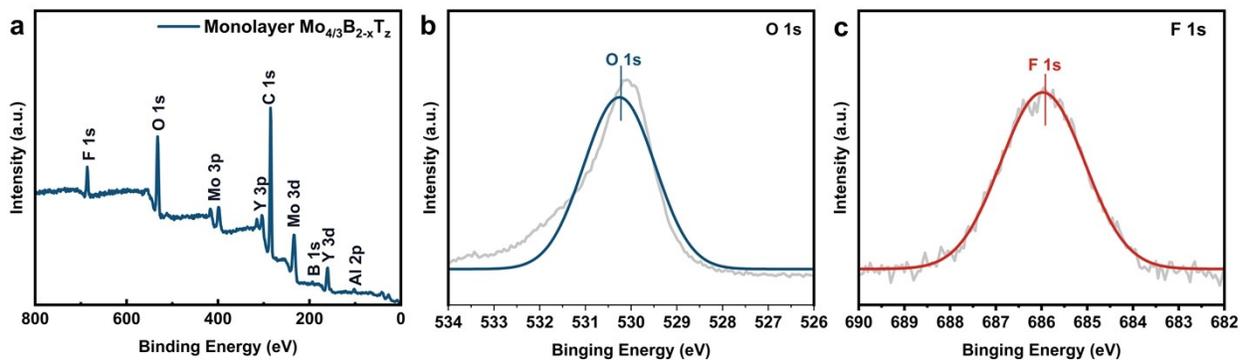
Table 1. Results of EDS analysis in TEM



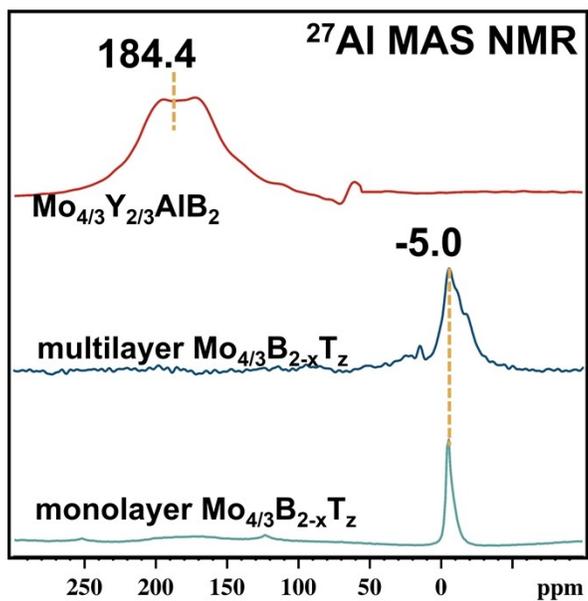
**Scheme S1.** The schematic atomic structure of  $\text{Mo}_{4/3}\text{B}_2$ .



**Figure S2.** Raman spectrum of multilayer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_x$  and monolayer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_x$ .

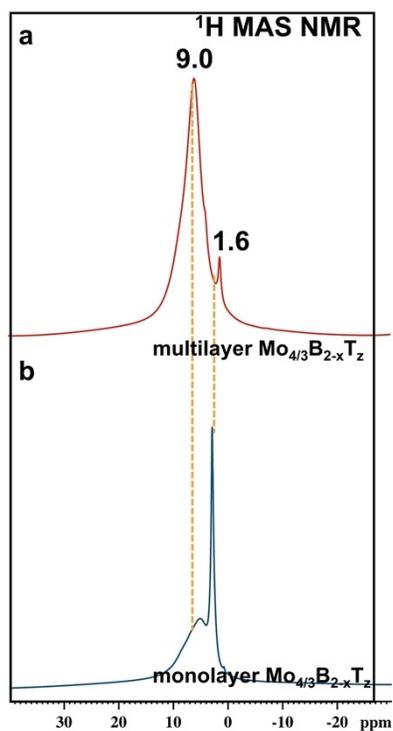


**Figure S3.** High-resolution XPS spectra of a) full region, b) O 1s region, and (c) F 1s region for monolayer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_x$  along with their fittings representing various species.

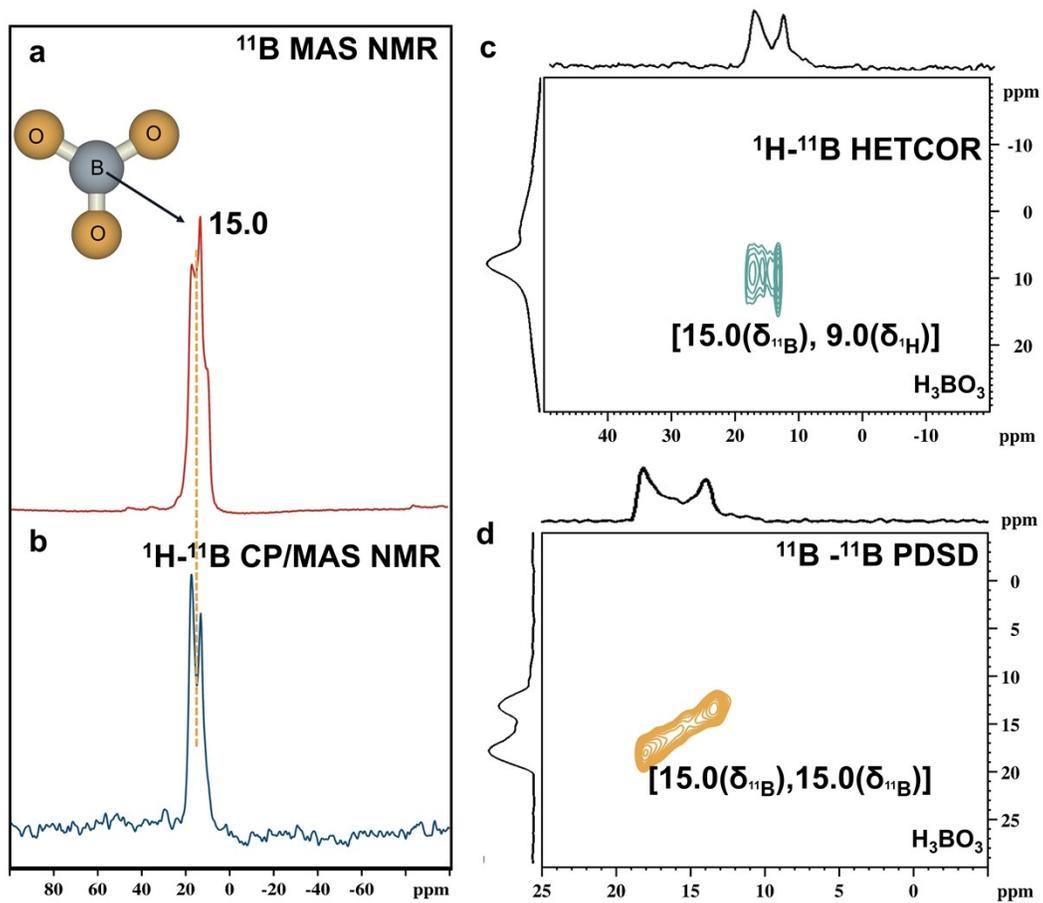


**Figure S4.**  $^{27}\text{Al}$  MAS NMR spectra of (a)  $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ , (b) multilayer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$ , and (c) monolayer

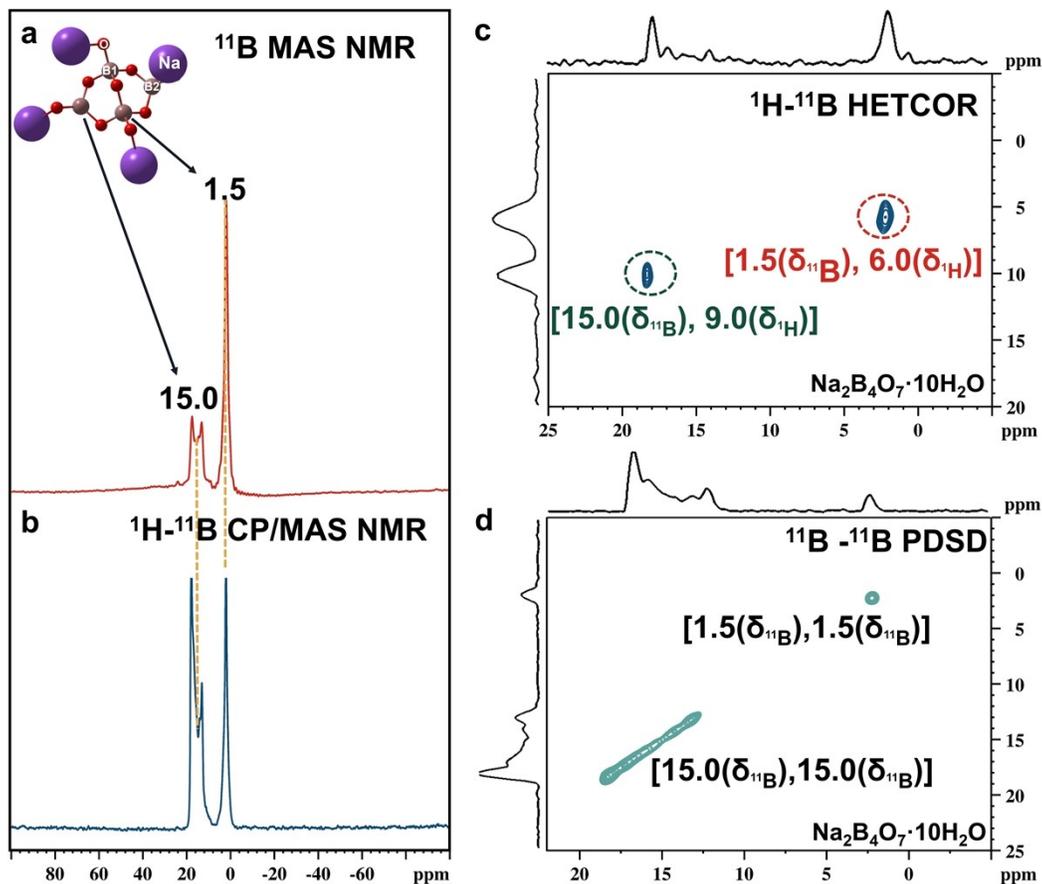
$\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$ .



**Figure S5.**  $^1\text{H}$  MAS NMR spectra of (a) multilayer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$  and (b) monolayer  $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$ .



**Figure S6.** NMR spectra of  $\text{H}_3\text{BO}_3$  (a)  $^{11}\text{B}$  MAS NMR spectra and (b)  $^1\text{H}$ - $^{11}\text{B}$  CP/MAS NMR spectra and (c)  $^1\text{H}$ - $^{11}\text{B}$  HETCOR NMR spectra and (d)  $^{11}\text{B}$ - $^{11}\text{B}$  PDS NMR spectra.



**Figure S7.** NMR spectra of borax (a)  $^{11}\text{B}$  MAS NMR spectra and (b)  $^1\text{H}$ - $^{11}\text{B}$  CP/MAS NMR spectra and (c)  $^1\text{H}$ - $^{11}\text{B}$  HETCOR NMR spectra and (d)  $^{11}\text{B}$ - $^{11}\text{B}$  PDS NMR spectra.

- 1 L. T. Alameda, P. Moradifar, Z. P. Metzger, N. Alem and R. E. Schaak, *J. Am. Chem. Soc.*, 2018, **140**, 8833–8840.
- 2 L. Mafra, R. Siegel, C. Fernandez, D. Schneider, F. Aussenac and J. Rocha, *J. Magn. Reson.*, 2009, **199**, 111–114.