

Supporting Information: Hydrogen Dissociation in Li-Decorated Borophene and Borophene Hydride: An Ab-Initio Study

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Comparison of heat of dehydrogenation results obtained from DFT-D2 and DFT-D3 for pristine and 3-Li doped borophene hydride and striped borophene; System size choice for borophene hydride and striped borophene; Convergence study for the number of k -points; Free energy and temperature plots as a function of time during Born-Oppenheimer Molecular dynamics simulations of 2D BH (with and without Li dopant); Different H₂ release paths on 2D BH; Different initial (chemisorbed) and final (physisorbed) H₂ configurations on striped-borophene; Different single Li adsorption sites on 2D BH; Different configurations of Li doped 2D BH at different (2, 3 and 4-Li) loadings; Minimum energy path for H₂ release on 3-Li doped 2D BH showing all stationary and transition states; Different single Li adsorption sites on striped borophene; Different configurations of Li doped striped borophene at different (2, 3 and 4-Li) loadings; Minimum energy path for H₂ release on 3-Li doped striped borophene showing all stationary and transition states.

Table S1: Heat of dehydrogenation calculated using DFT-D2 and DFT-D3 for different configurations of borophene hydride (2D BH) and striped borophene (B striped). The heat of dehydrogenation is calculated using the energy difference between the final (H_2 physisorbed) and initial (H-chemisorbed) state (ΔE_{FS-IS}). The Li doped structures for 2D BH and B-striped configuration are shown in figure S6 and S9, respectively. The use of DFT-D3 leads to a difference of ca. 0.05 – 0.15 eV compared to DFT-D2. However, it does not change the trend observed in the presence of Li dopants (lowering of heat of dehydrogenation).

Configuration	ΔE_{FS-IS} [eV] (DFT-D3)	ΔE_{FS-IS} [eV] (DFT-D2)
2D BH	1.88	1.94
3Li-2D BH	-0.02	0.02
B striped	1.38	1.41
3Li-B striped	0.58	0.73

Table S2: Influence of system size (in terms of conventional unit cell) on the substrate energy (E_S) per atom of borophene hydride (2D BH) and the energy difference between the single Li doped 2D BH and the pristine structure ($E_{S+M} - E_S$). Only system sizes that result in a nearly square 2D supercell are chosen. A system size of 3×4 conventional unit cell, with 48 B-atoms and 48 H-atoms (96 atoms in total) is chosen for further study. This system size is chosen to limit interaction between Li-atoms in the periodic images while ensuring that the computations do not become too expensive.

System size	No. B-atoms	E_S/atom [eV/atom]	$E_{S+M} - E_S$ [eV]
2×2	16	-4.943	-2.641
3×3	36	-4.945	-2.640
3×4	48	-4.944	-2.695
4×4	64	-4.944	-2.688

Table S3: Influence of system size (in terms of conventional unit cell) on the substrate energy (E_S) per atom of striped borophene (B striped) and the energy difference between the single Li doped B striped and the pristine structure ($E_{S+M} - E_S$). Only system sizes that result in a nearly square 2D supercell are chosen. A system size of 3×6 conventional unit cell, with 36 B-atoms is chosen for further study to limit interaction between Li-atoms in the periodic images while ensuring that the computations do not become too expensive.

System size	No. B-atoms	E_S/atom [eV/atom]	$E_{S+M} - E_S$ [eV]
2×4	16	-6.331	-3.409
3×6	36	-6.328	-3.538
4×8	64	-6.325	-3.535

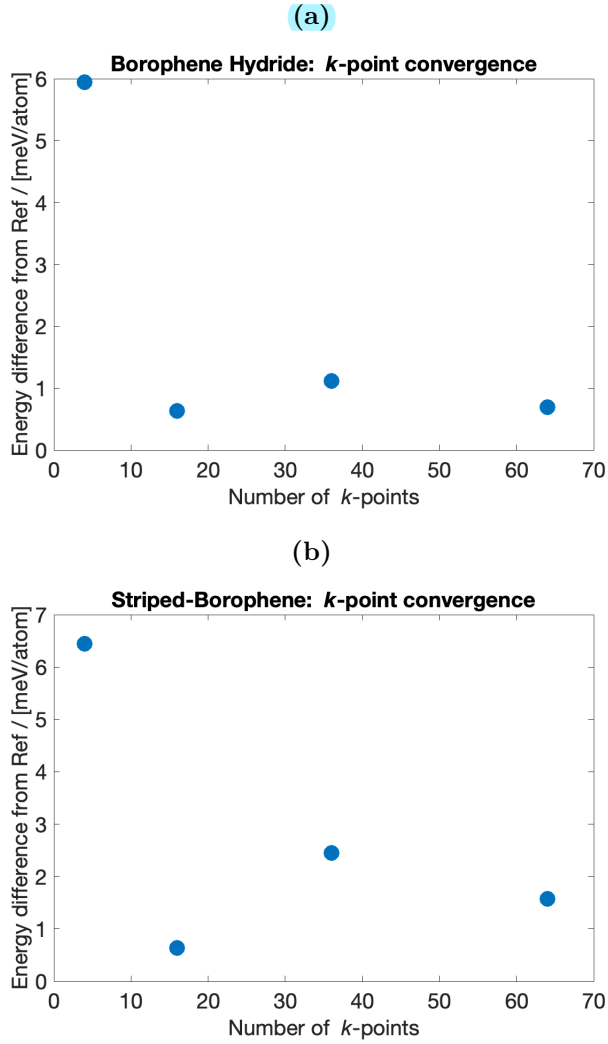


Figure S1: The k -point convergence for a Li decorated (a) 2×2 conventional cell of the borophene hydride structure (containing 16 B and 16 H atoms), and (b) 3×6 conventional cell of the striped borophene structure (containing 36 B atoms). On the y-axis, the relative energy difference with respect to an accurate reference, with a $27 \times 27 \times 1$ k -point mesh, an energy cut-off of 1400 eV, and a gaussian smearing with a sigma of 0.005 eV is shown. With the exception of the reference states, the simulations shown in these subfigures are run with varying k -point meshes, an energy cut-off of 550 eV, and a gaussian smearing with a sigma of 0.1 eV. It can be seen that for both simulations a k -point mesh of $4 \times 4 \times 1$ (number of k -points: 16) leads to a difference less than 1 meV per atom from the accurate reference states.

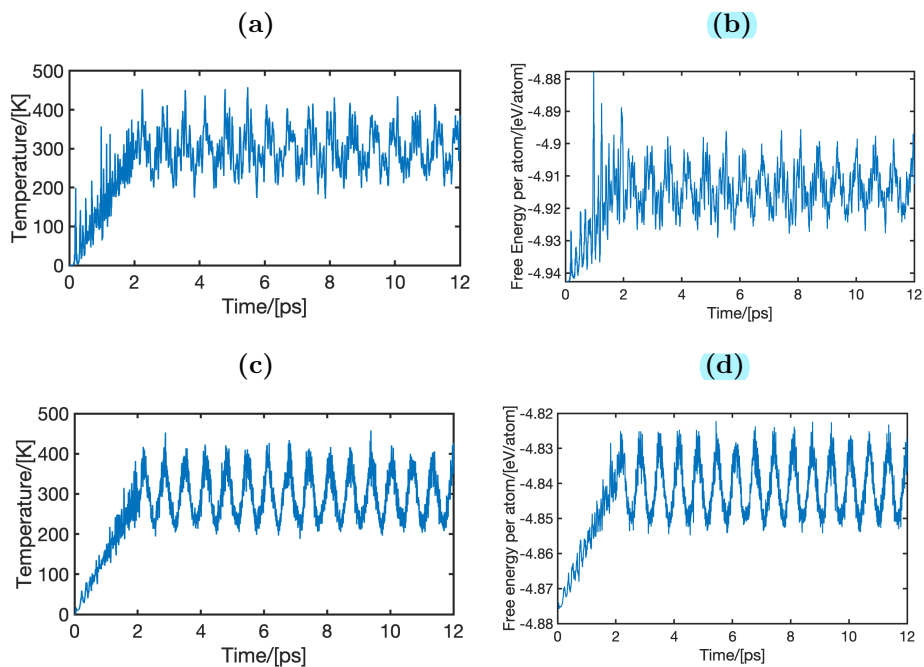


Figure S2: Temperature ((a),(c)), and free energy per number of atoms ((b), (d)) as a function of simulation time (ps) are shown for the Born-Oppenheimer Molecular Dynamics (BOMD) simulations of pristine borophene hydride ((a)-(b)) and 3-Li doped borophene hydride ((c)-(d)). In the initial 2 ps, the temperature is increased from 0 K to 300 K, following by a 10 ps production run. In the initial 2 ps run, a Nosé-Hoover mass parameter corresponding to a period of 40 timesteps is chosen. This allowed for the temperature to be increased from 0 to 300 K in 2000 timesteps in our simulations. In the subsequent 10 ps run, the period of temperature fluctuations is increased to ca. 1000 timesteps (1 ps) (weaker temperature coupling).

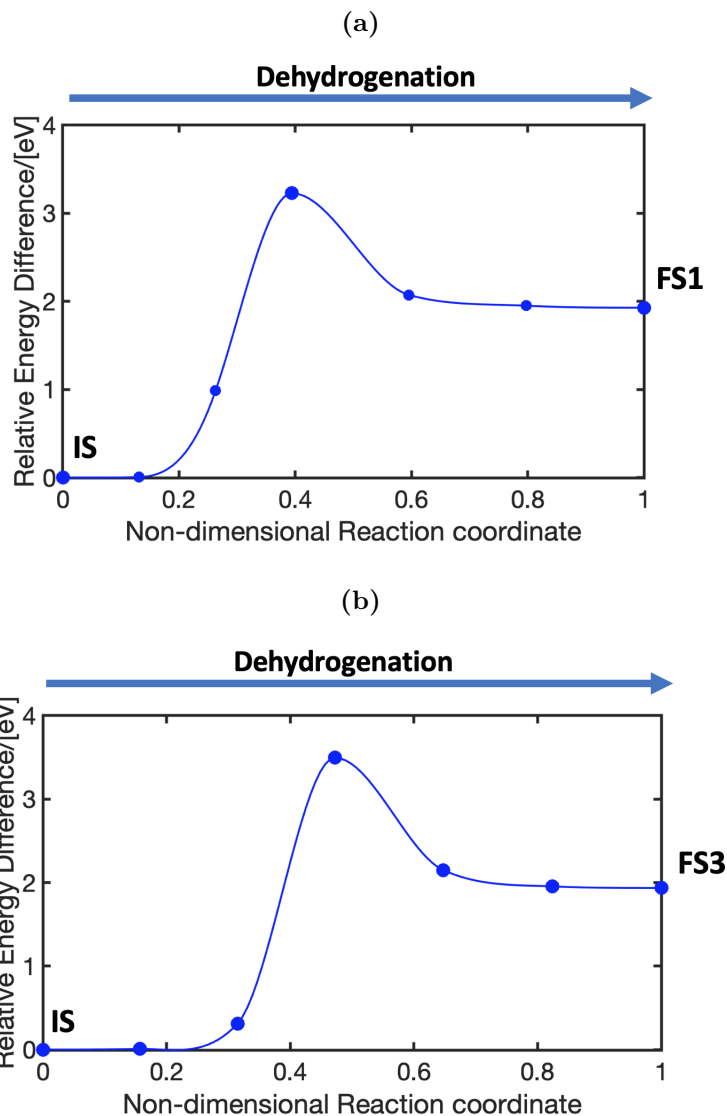


Figure S3: The minimum energy pathways (one-step process with no stationary states) for a single H_2 release for V1 and V3 (discussed in the main paper (Figure 1) along with the corresponding initial state (IS) and final states (FS1 and FS3)) H_2 formation routes are shown in subfigures (a) and (b), respectively. It is seen that V1 has a lower activation energy by around 0.27 eV compared to V3. In the main paper, a two-step process (with an initial H-diffusion step) for H_2 desorption on 2D BH (V1) is presented, which has a lower overall activation energy than the 1-step process shown in this figure.

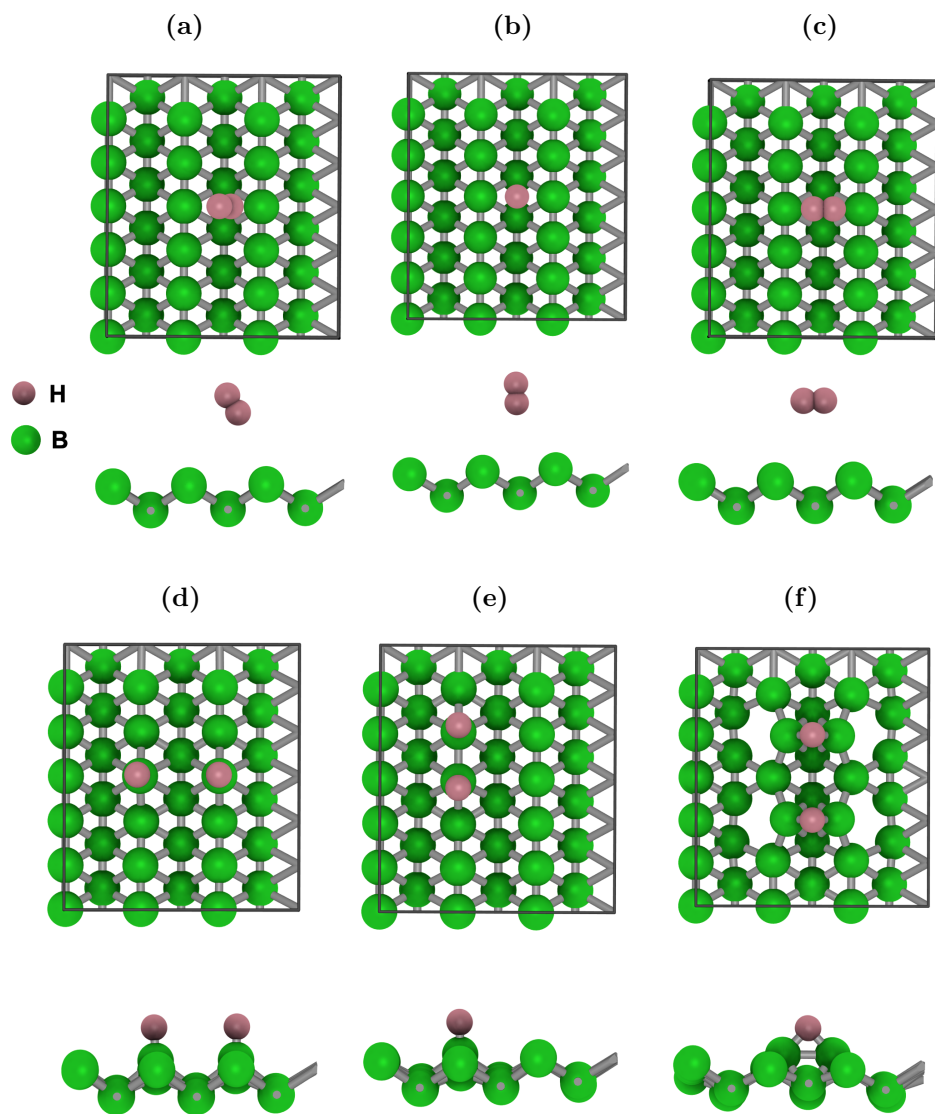


Figure S4: Top and side view of different variations of physisorbed and chemisorbed H₂ on striped borophene are shown in structures (a)-(c) (physisorbed), and (d)-(f) (chemisorbed). Structure (a) is the most stable physisorbed configuration with a H₂ adsorption energy of -0.049 eV/H₂. Structures (b), and (c) have an H₂ adsorption energy of -0.048 , and -0.045 eV/H₂, respectively. Structure (d) is the most stable chemisorbed structure with a heat of hydrogenation of (difference between chemisorbed and most stable physisorbed state (a)) -1.41 eV/H₂. Structures (e), and (f) have heat of reactions of -0.75 , and -0.63 eV/H₂, respectively.

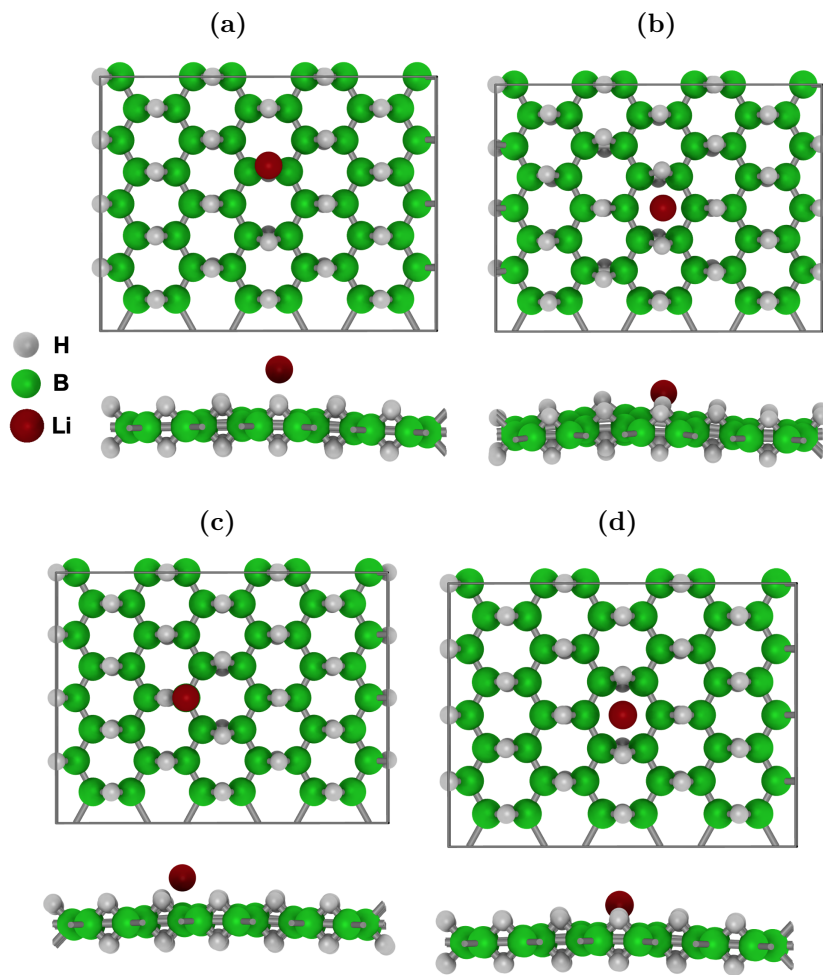


Figure S5: Different initial configurations tested for Li adsorbed on borophene hydride are shown in (a)-(c). In (a) Li is placed on top of an H atom, while in (b), and (c) it is placed on the vacant site and B-atom, respectively. After relaxing the initial configurations (with a force convergence criteria of $1 \text{ meV}/\text{\AA}$), structure (d) (vacant site) is obtained for all three initial configurations. Structure (d) leads to a Li adsorption energy of $-0.66 \text{ eV}/\text{Li}$.

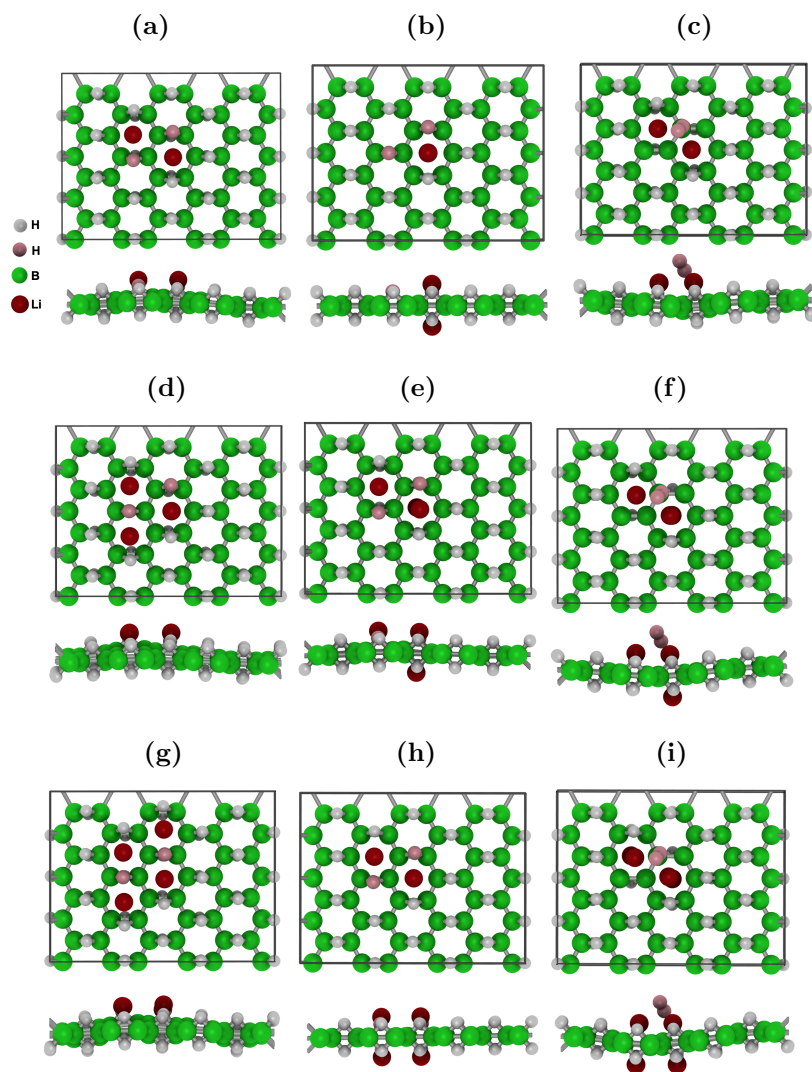


Figure S6: Top and side view of different 2-Li (a)-(c), 3-Li (d)-(f), and 4-Li (g)-(i) configurations of 2D BH are shown. In structures (a), (d), and (g), the Li-atoms are decorated on the top-surface, surrounding the H-atoms that undergo dissociation (shown in pink). In structures (b), (e), and (h) the Li-atoms are decorated in the top-bottom surface alternatively. Structures (a), (e), and (h) are more energetically stable than structure (b) (19% Li adsorption energy difference), (d) (43% Li adsorption energy difference), and (g) (75% Li adsorption energy difference), respectively. The H_2 -physisorbed (dehydrogenated) states on the most stable 2-Li, 3-Li, and 4-Li configurations are shown in structures (c), (f) and (i), respectively. The equation for calculating the Li-adsorption energy is defined in the main paper.

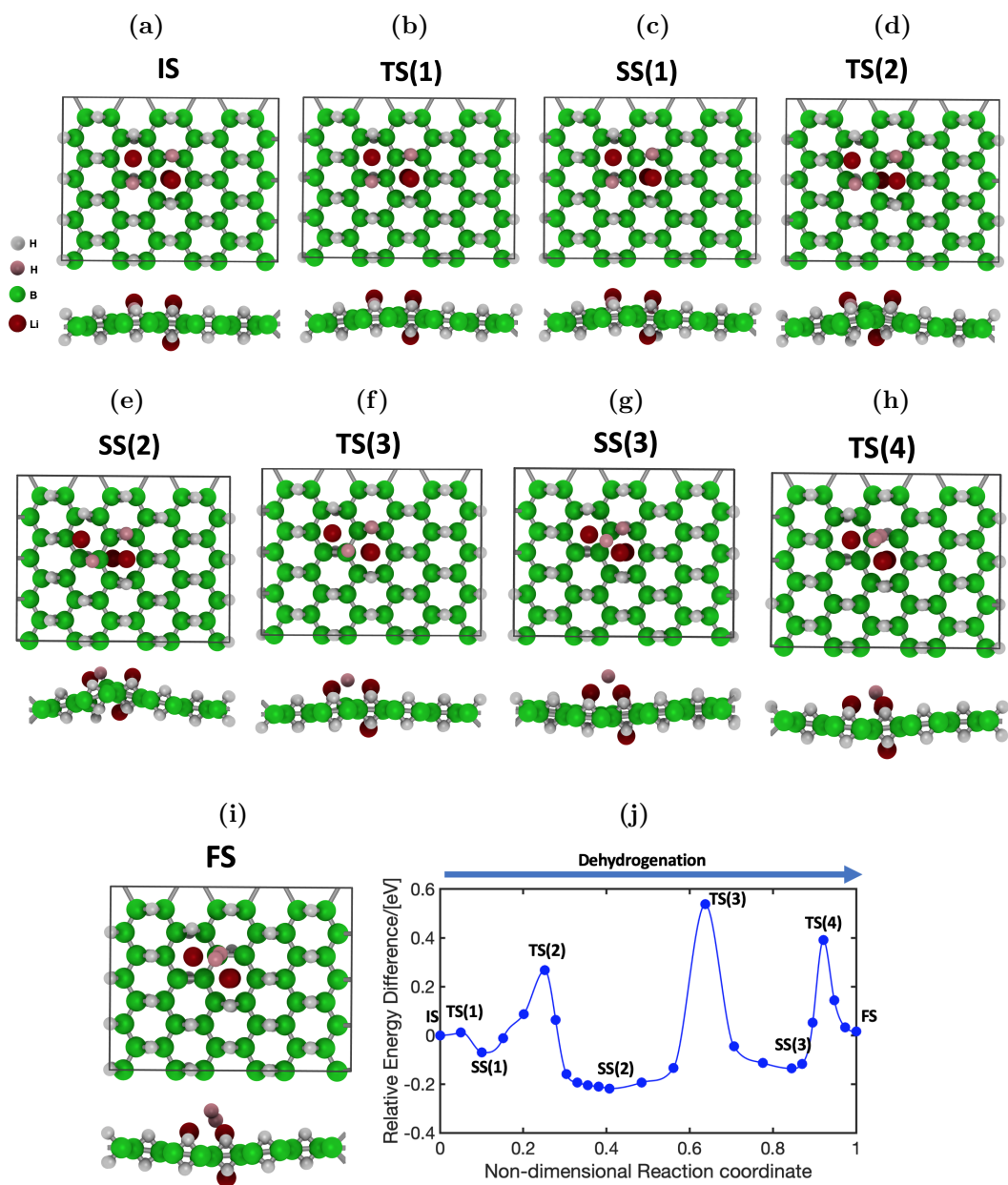


Figure S7: All the stationary states (SS) and transition states (TS) for H-dissociation on 3 Li doped 2D BH are shown in (b)-(h), along with the corresponding initial (IS), and final (FS) states shown in (a), and (i), respectively. The corresponding minimum energy pathway is shown in subfigure (j). The H-atoms that are undergoing dehydrogenations are colored in pink, while the rest of H-atoms are colored in grey.

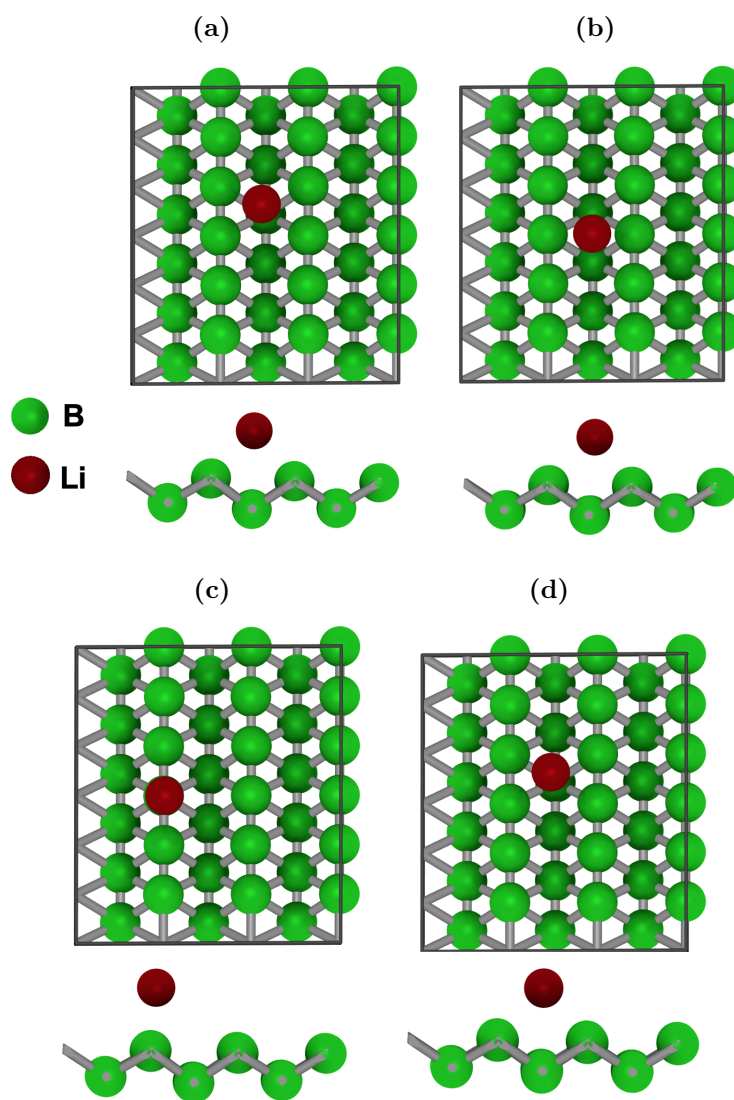


Figure S8: Different initial configurations tested for Li adsorption on striped-borophene are shown in (a)-(c). Striped-borophene is a corrugated structure, consisting of lines of B-atoms layered at 2 different heights (upper and lower layer). In (a) Li is placed on top of a B atom in the lower layer. In (b) Li is placed at the bridge site of 2 B atoms in the lower layer, and in (c) it is placed on a B atom in the upper layer. After relaxing the initial configurations (with a force convergence criteria of $1 \text{ meV}/\text{\AA}$), structure (d) (Li on B atom at the lower layer) is obtained for all three initial configurations. Structure (d) leads to a Li adsorption energy of $-1.52 \text{ eV}/\text{Li}$.

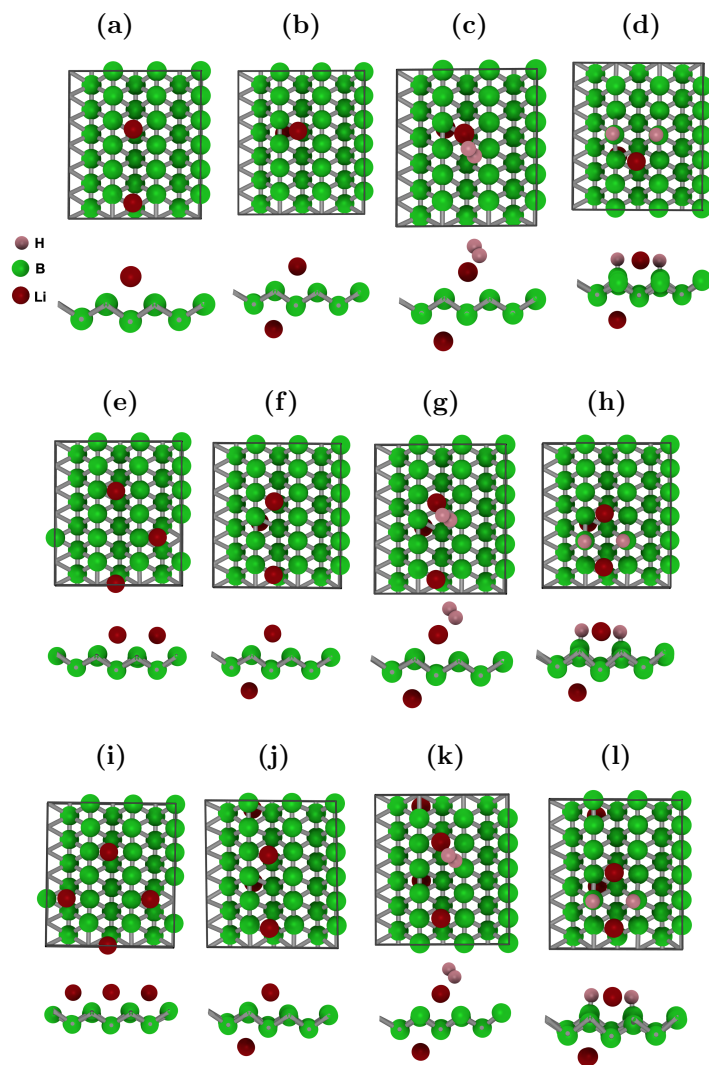


Figure S9: Top and side view of different 2-Li (a)-(d), 3-Li (e)-(h), and 4-Li (i)-(l) configurations of striped borophene are shown. In structures (a), (e), and (i), the Li-atoms are decorated on the top-surface, surrounding the H-atoms that undergo dissociation (shown in pink). In structures (b), (f), and (j) the Li-atoms are decorated in the top-bottom surface alternatively. Structures (b), (f), and (j) are more energetically stable than structure (a) (1.4% Li adsorption energy difference), (e) (16% Li adsorption energy difference), and (i) (26% Li adsorption energy difference), respectively. The H_2 -chemisorbed and physisorbed (dehydrogenated) states on the most stable 2-Li, 3-Li, and 4-Li configurations are shown in structures (c)-(d), (g)-(h) and (k)-(l), respectively. The equation for calculating the Li-adsorption energy is defined in the main paper.

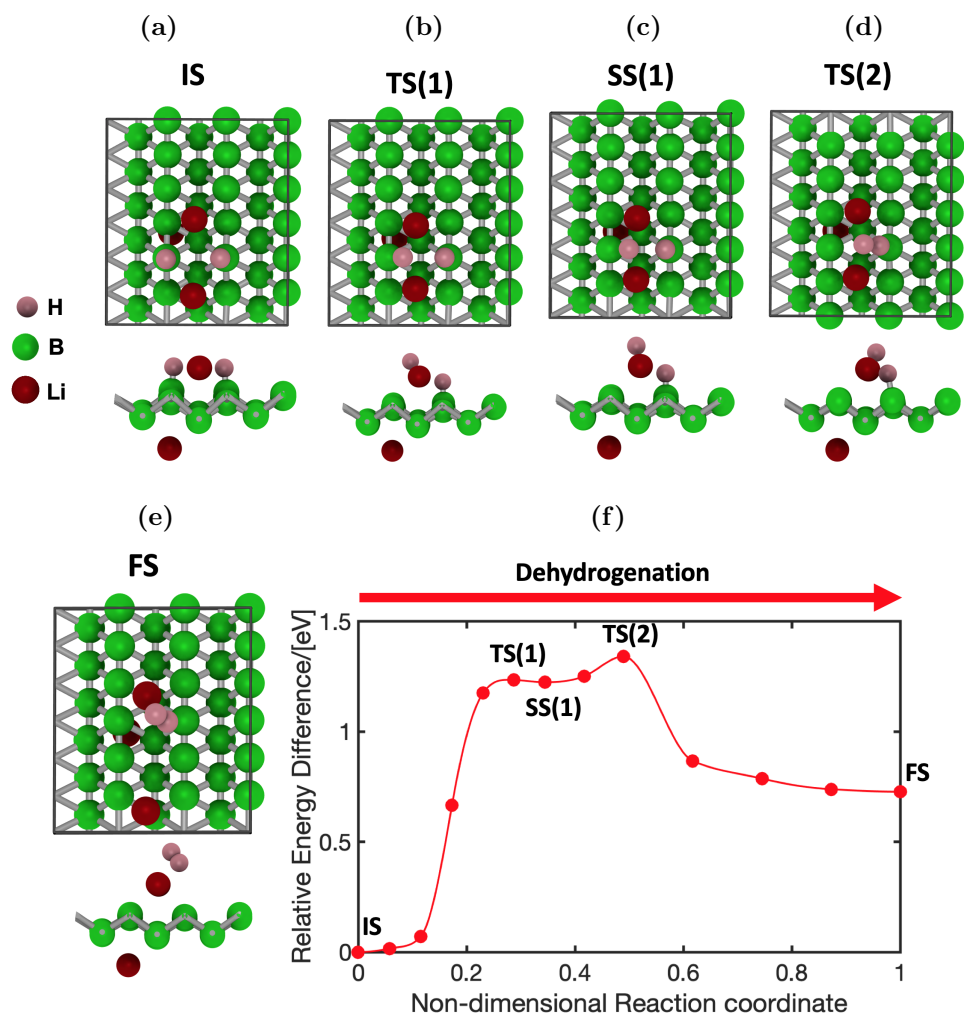


Figure S10: All the stationary states (SS) and transition states (TS) for H-dissociation on hydrogenated 3 Li doped striped borophene are shown in (b)-(d), along with the corresponding initial state (IS), and final state (FS) shown in (a), and (e), respectively. The corresponding minimum energy pathway is shown in subfigure (f). The H-atoms that are undergoing dehydrogenations are colored pink, while the rest of H-atoms are colored grey.