

## Supporting Information

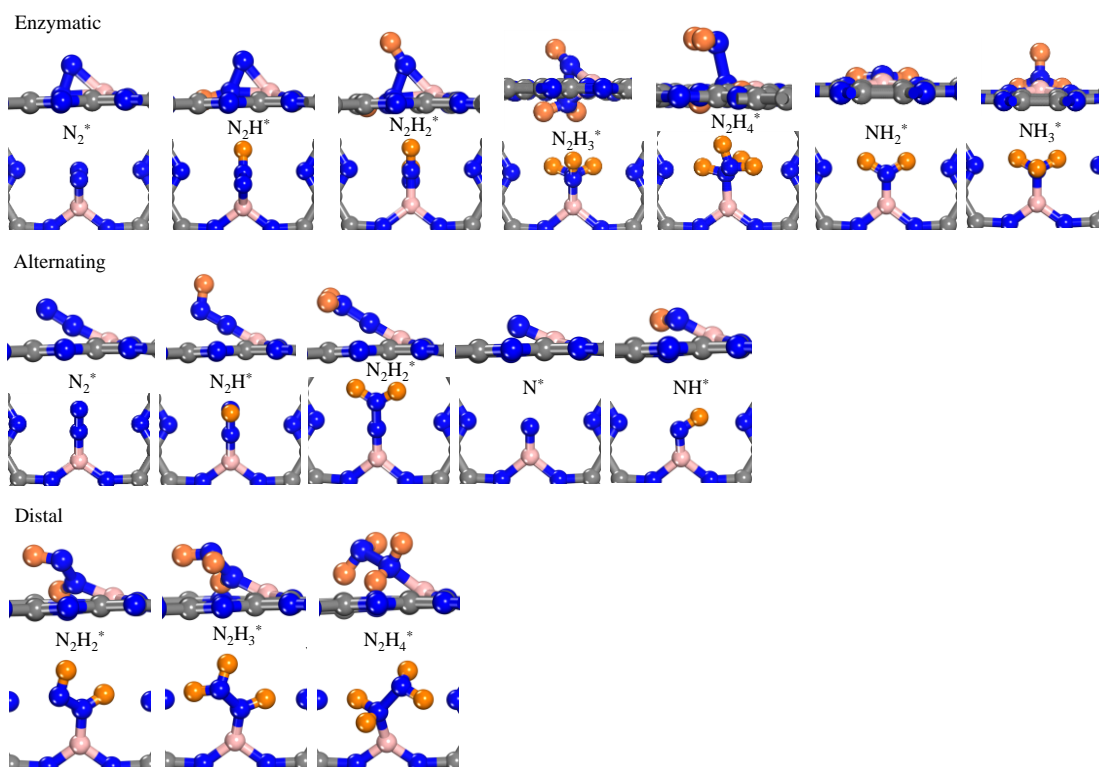
### **Boron-Interstitial Doped C<sub>2</sub>N Layer as a Metal-Free Electrocatalyst for N<sub>2</sub>**

#### **Fixation: A Computational Study**

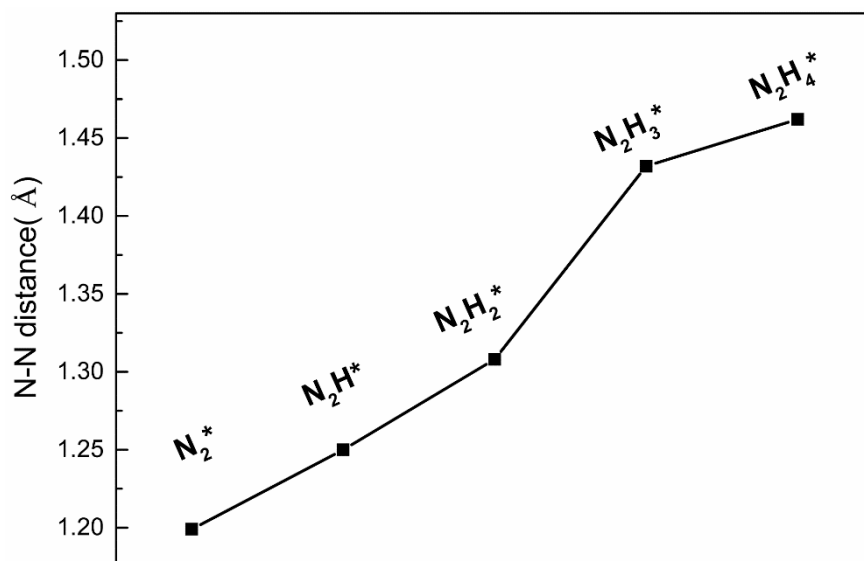
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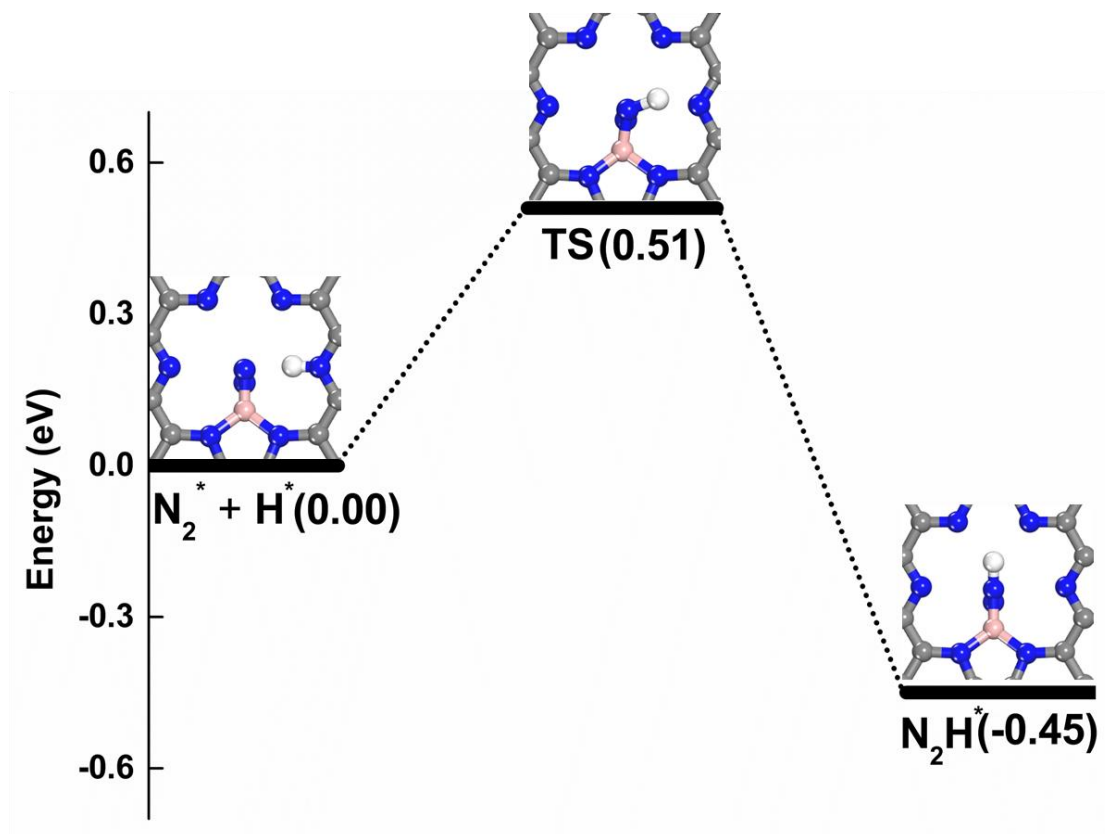
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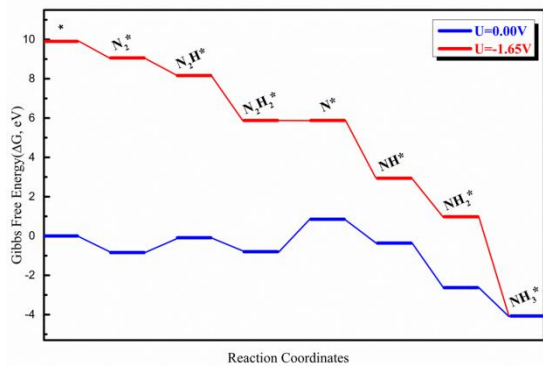
**Figure S1.** The side and top views of the involved NRR intermediates on B<sub>int</sub> surface along the enzymatic, alternating, and distal pathways.



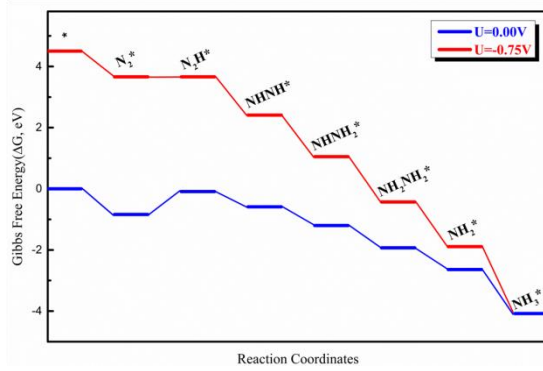
**Figure S2.** The variation of N-N bond lengths of various NRR intermediates on  $B_{int}$  along the enzymatic pathway.



**Figure S3.** The reaction pathway of H-transfer from the N atom around B site to the adsorbed  $N_2$  molecule. TS denotes the transition state.

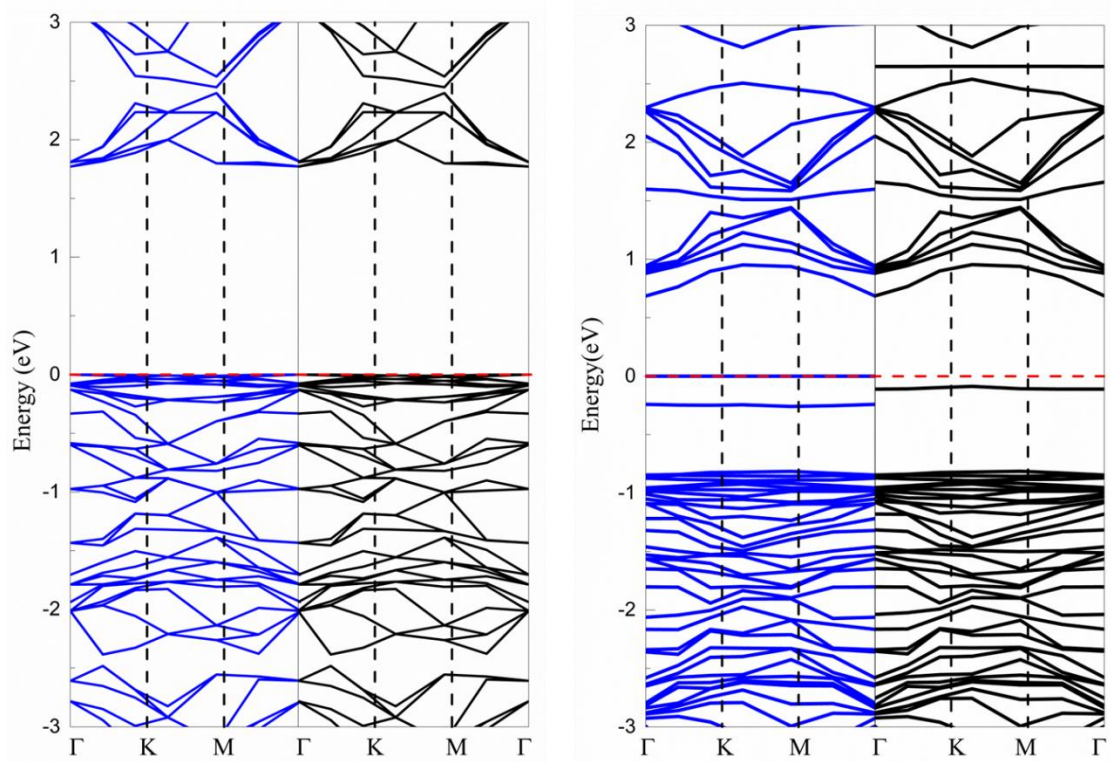


(a)



(b)

**Figure S4.** The free energy profiles of NRR on B<sub>N</sub>-doped C<sub>2</sub>N layer along the (a) distal and (b) alternating pathways.



**Figure S5.** The computed band structures of (a) pure and (b)  $B_{int}$ -doped  $C_2N$  layers.

The Fermi level is set as zero in dotted lines.