

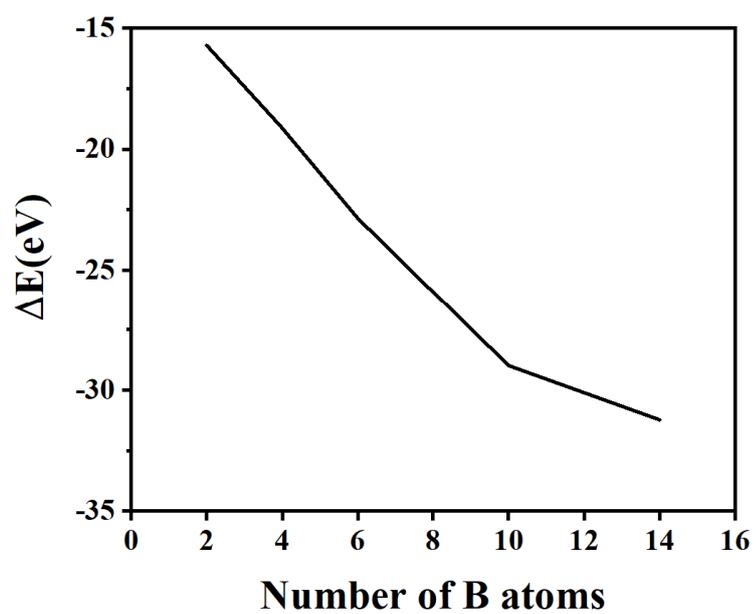
# Restructuring and Hydrogen Evolution on Sub-nanosized Pd<sub>x</sub>B<sub>y</sub> Clusters

## Supplementary Materials

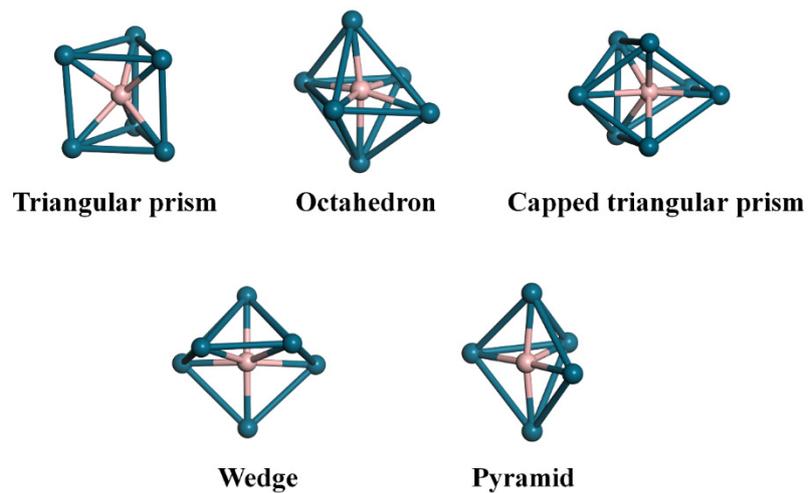
De Zhang, Ruijing Wang, Sijia Luo and Guangfeng Wei \*

Shanghai Key Laboratory of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China.

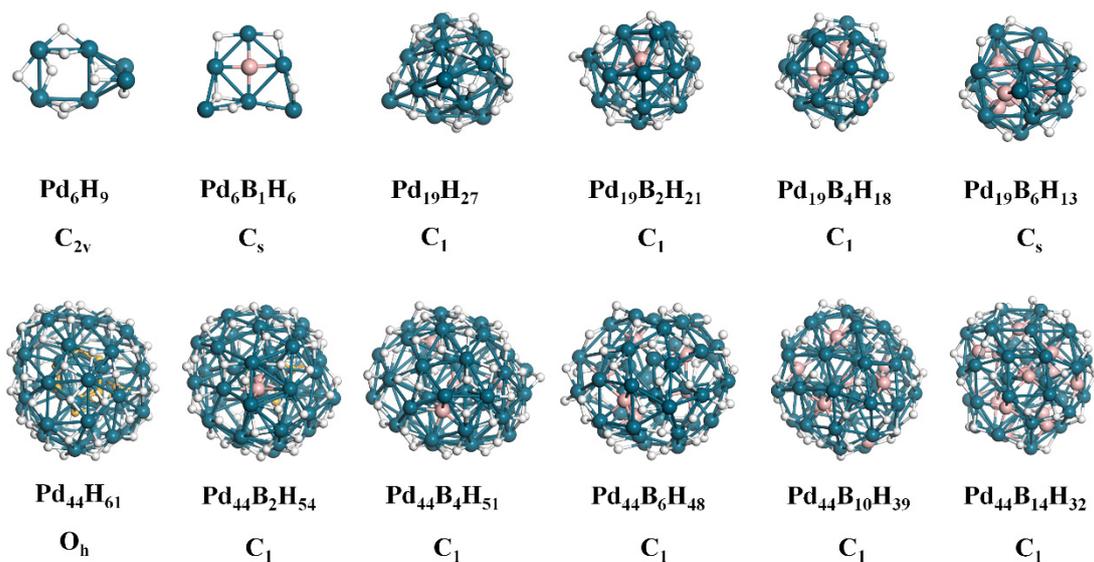
\* Correspondence: weigf@tongji.edu.cn



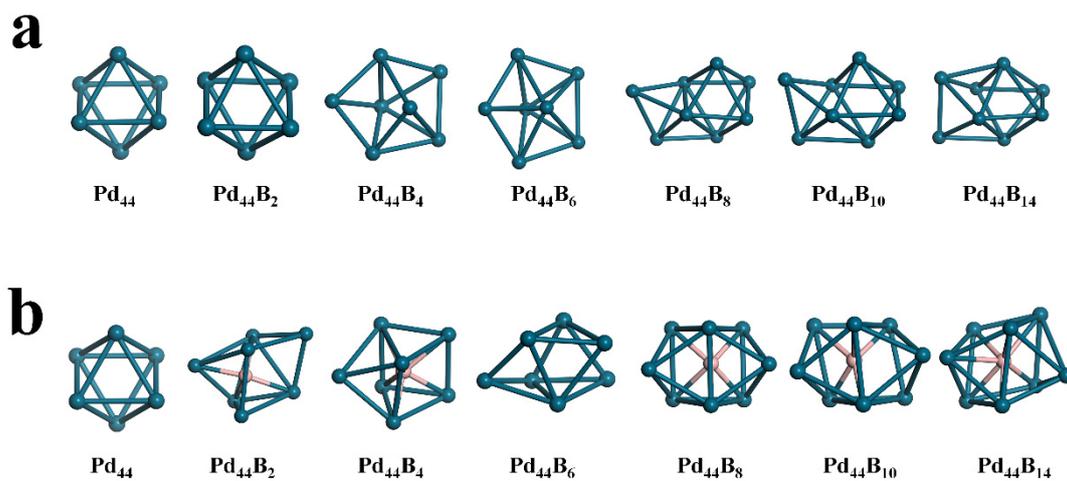
**Figure S1.** The decrease of GM energy ( $\Delta E$ ) of the most stable cluster varies with the number of B atoms.



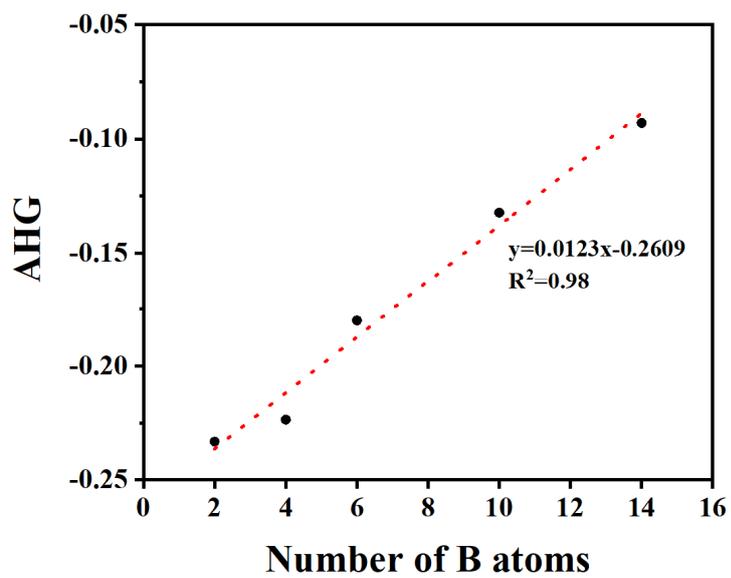
**Figure S2.** Coordination geometry of B atoms in Pd<sub>x</sub>B<sub>y</sub> GM clusters (deep-blue ball presents Pd atom, pink ball presents B atom).



**Figure S3.** GM structures of Pd<sub>x</sub>B<sub>y</sub>H<sub>z</sub> clusters under HER conditions with their symmetry of Pd sub-structure (deep-blue ball presents Pd atom, pink ball presents B atom, white ball presents H atom on cluster surface, and orange ball presents H atom siting inner of the cluster).



**Figure S4.** Changes of core structures in  $\text{Pd}_{44}\text{B}_y$  clusters. (a) The core structures in  $\text{Pd}_x\text{B}_y$  clusters. (b) The core structures in  $\text{Pd}_x\text{B}_y\text{H}_z$  clusters under HER conditions.



**Figure S5.** The change of average H adsorption free energy (AHG) of Pd<sub>44</sub>B<sub>y</sub>H<sub>z</sub> GM structures with the number of B atoms, and red line is its linear fitting.

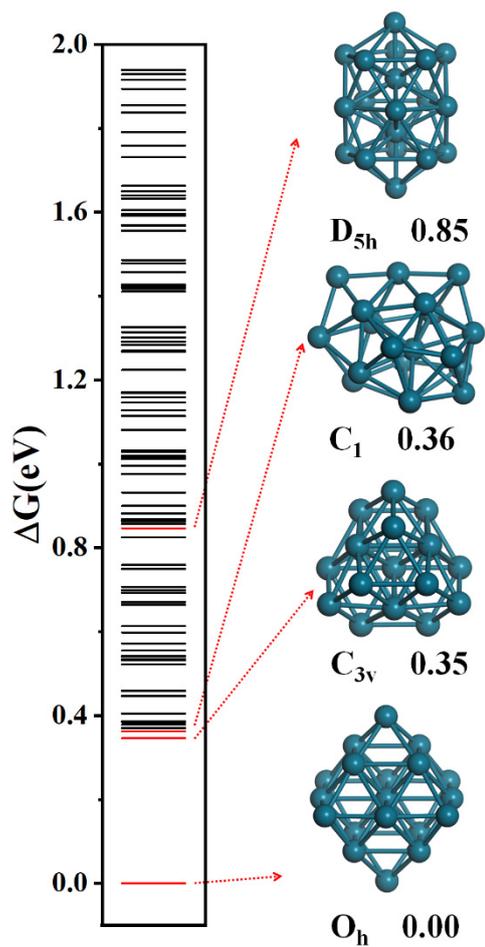


Figure S6. Low-lying isomers diagram of Pd<sub>19</sub> clusters.

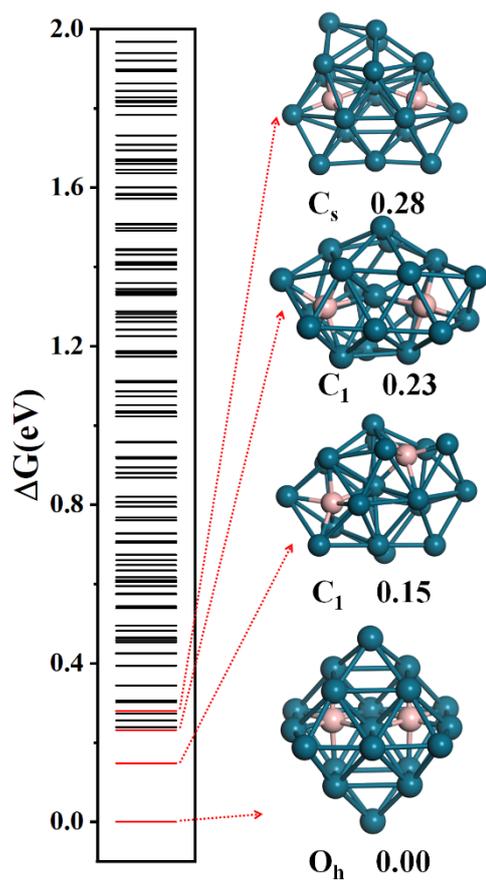


Figure S7. Low-lying isomers diagram of Pd<sub>19</sub>B<sub>2</sub> clusters.

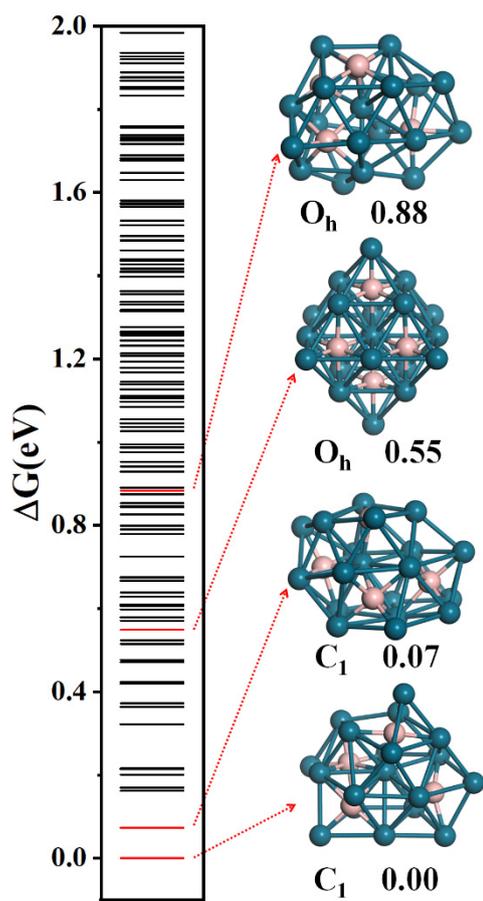


Figure S8. Low-lying isomers diagram of Pd<sub>19</sub>B<sub>4</sub> clusters.

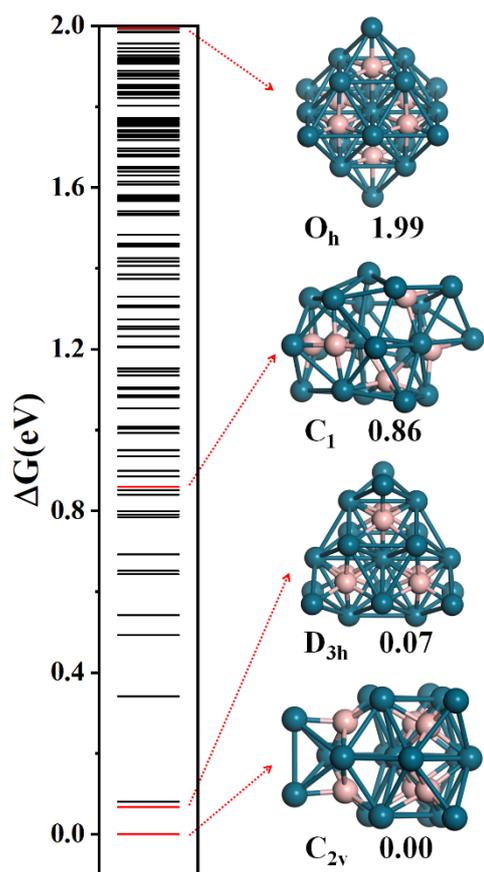


Figure S9. Low-lying isomers diagram of Pd<sub>19</sub>B<sub>6</sub> clusters.

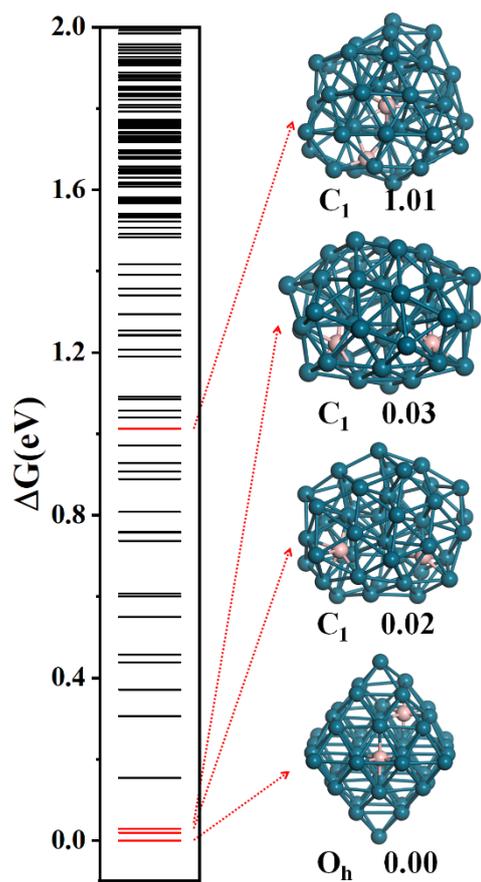


Figure S10. Low-lying isomers diagram of  $\text{Pd}_{44}\text{B}_2$  clusters.

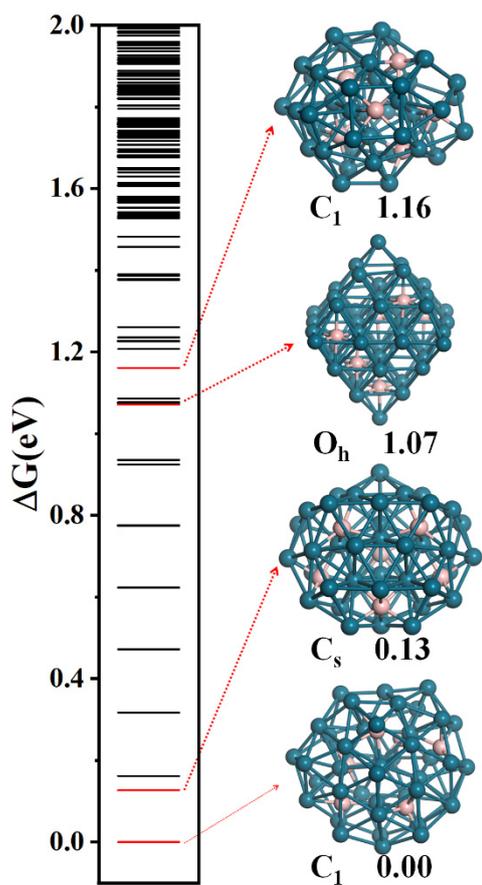


Figure S11. Low-lying isomers diagram of Pd<sub>44</sub>B<sub>6</sub> clusters.

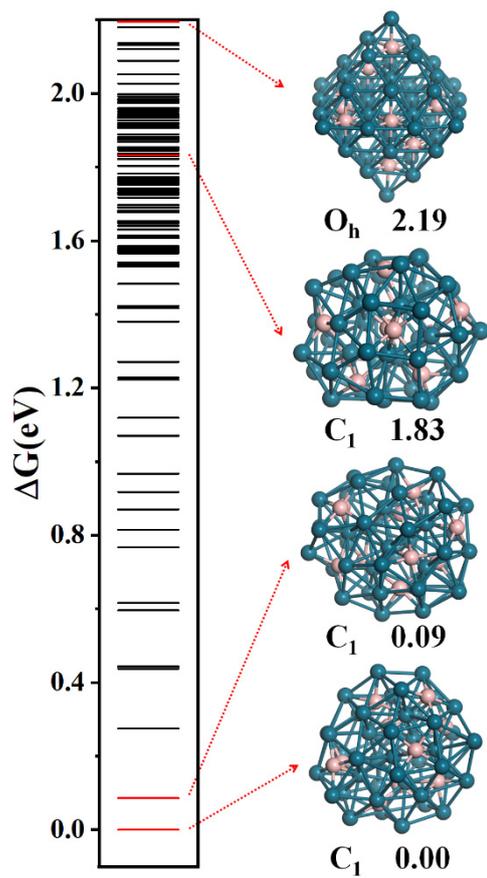


Figure S12. Low-lying isomers diagram of Pd<sub>44</sub>B<sub>10</sub> clusters.

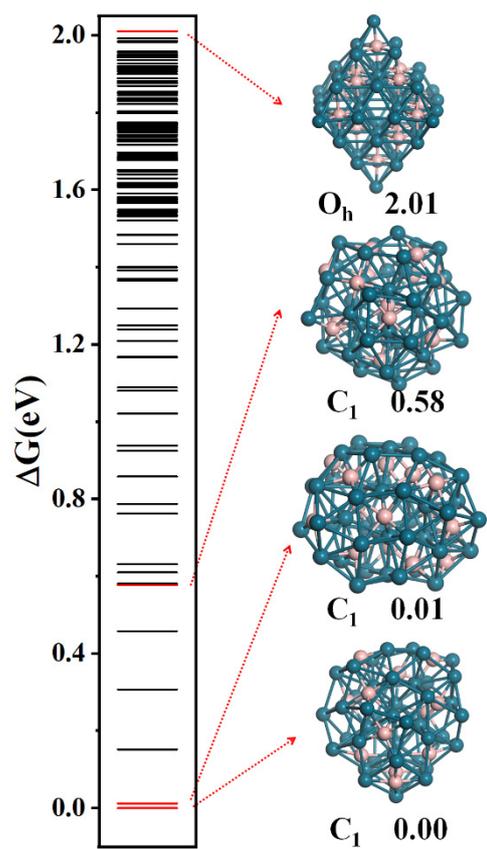
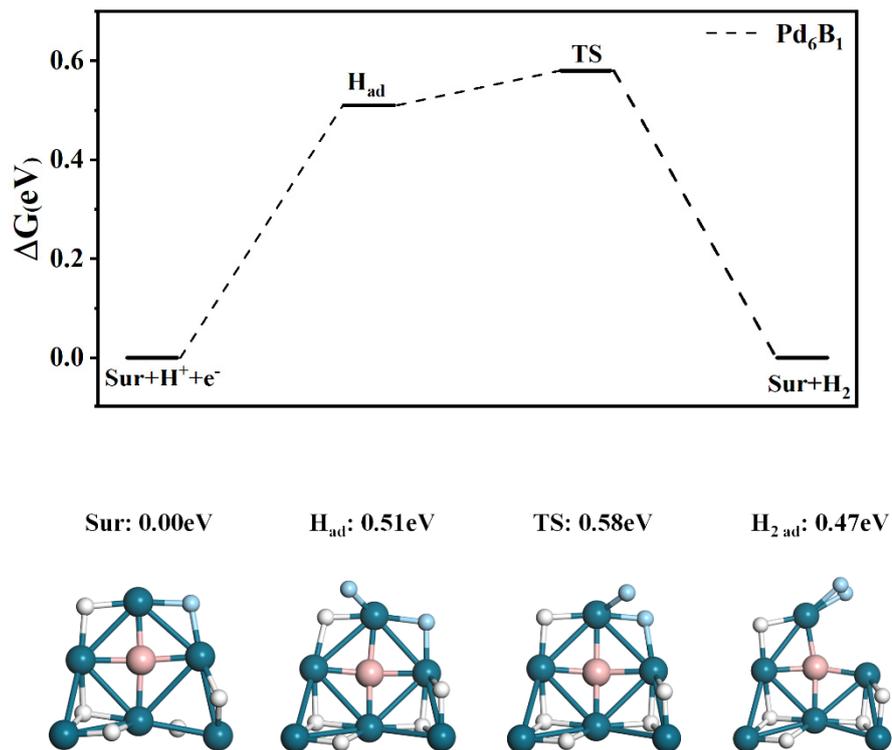


Figure S13. Low-lying isomers diagram of  $\text{Pd}_{44}\text{B}_{14}$  clusters.



**Figure S14.** The HER energy diagram of Pd<sub>6</sub>B cluster, and structures of every step during HER pathway.

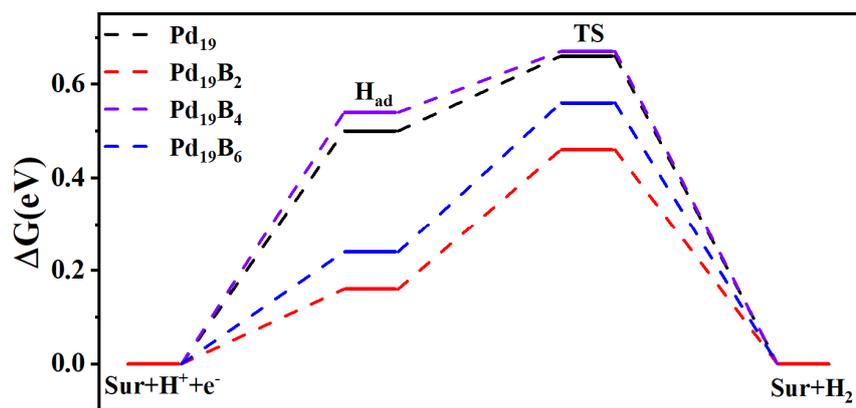
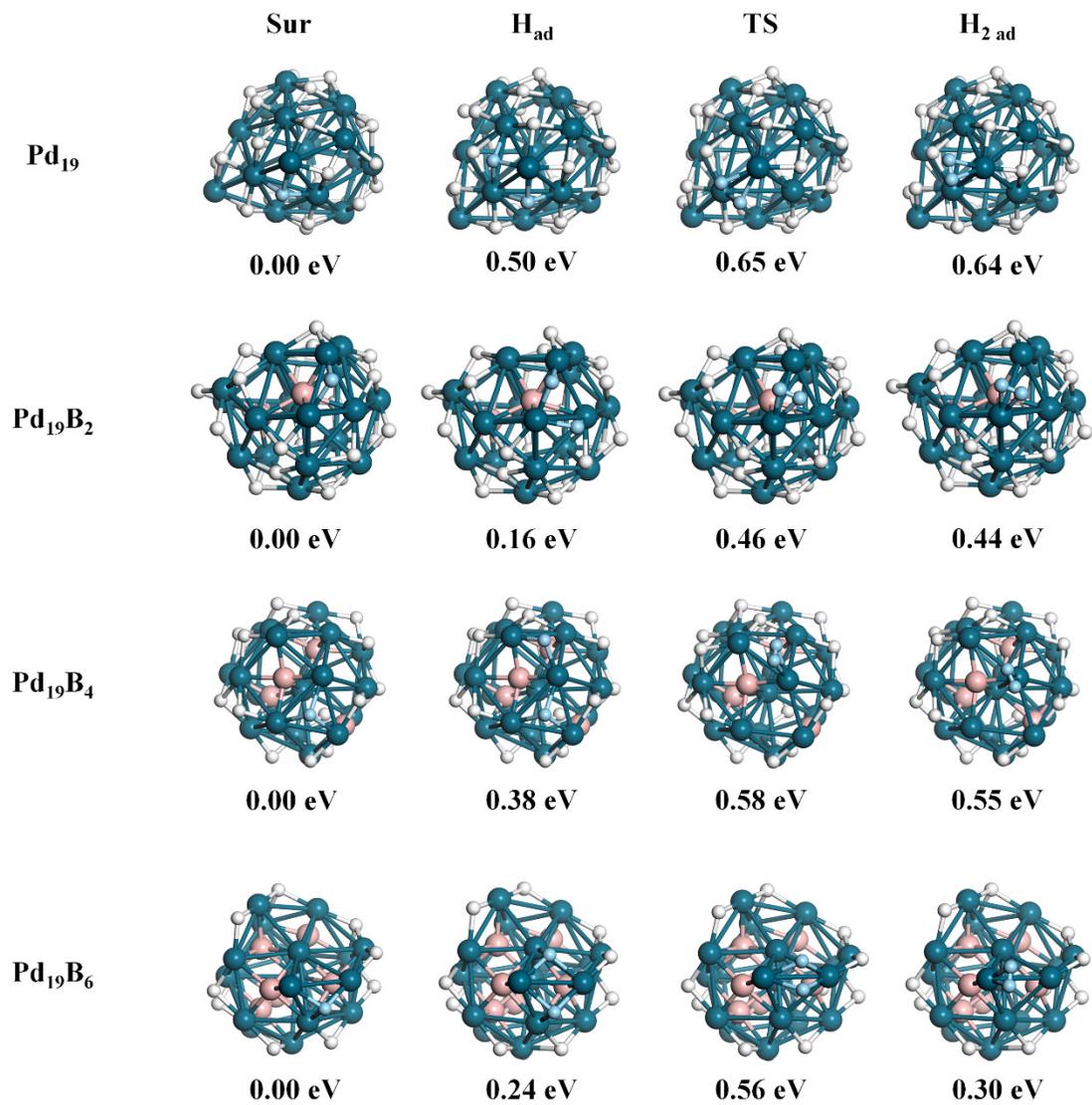


Figure S15. The HER energy diagram of Pd<sub>19</sub>B<sub>y</sub> (y=0,2,4,6) clusters.



**Figure S16.** The structures of every step during HER pathway for Pd<sub>19</sub>B<sub>y</sub> (y=0,2,4,6) clusters.

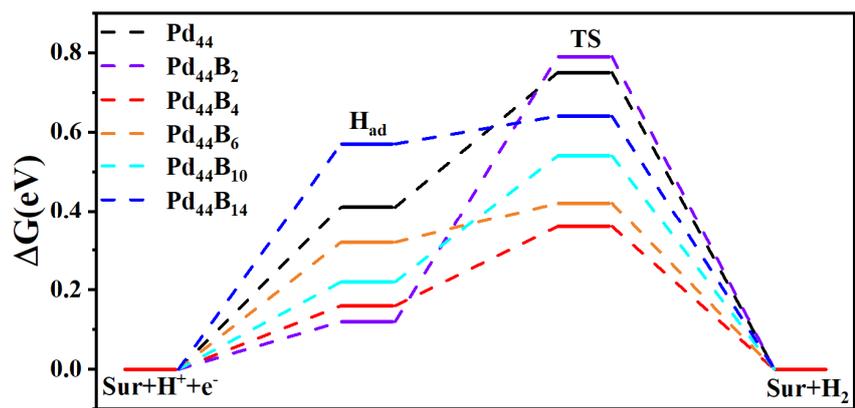
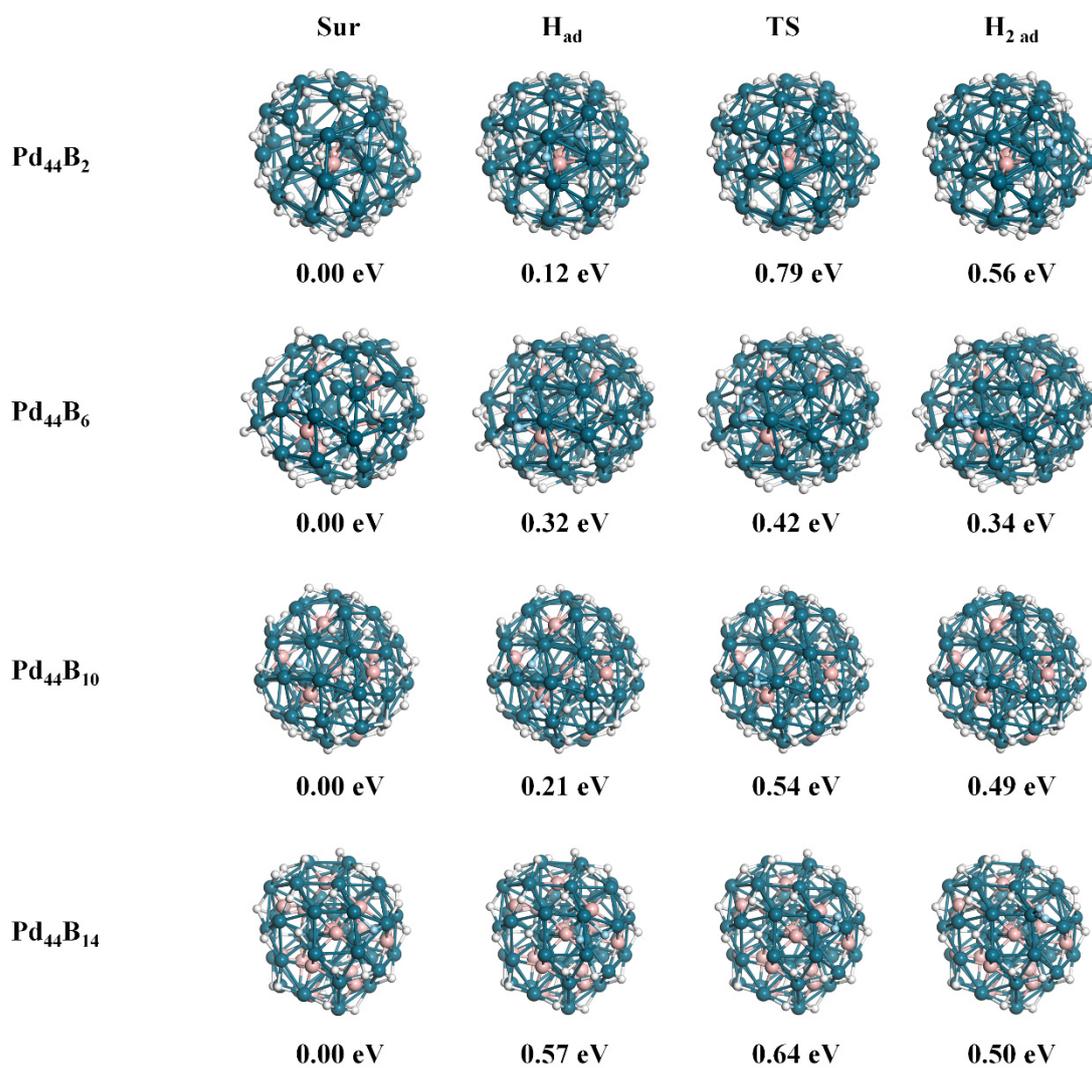
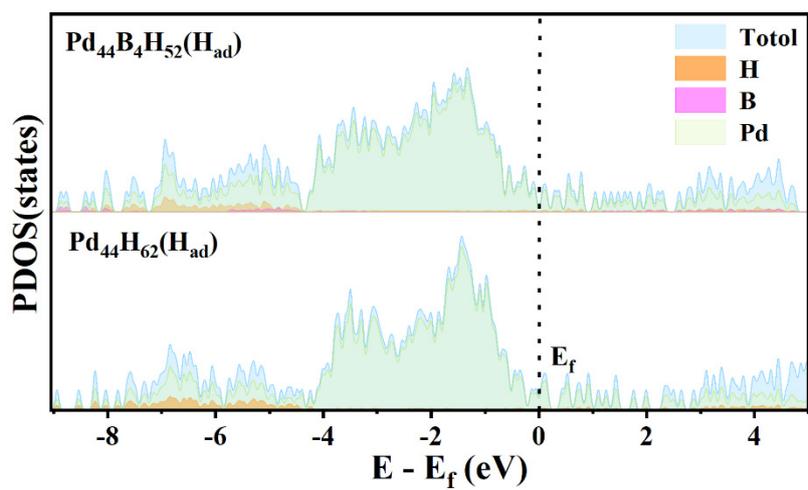


Figure S17. The HER energy diagram of Pd<sub>44</sub>B<sub>y</sub> (y=0,2,4,6,10,14) clusters.



**Figure S18.** The structures of every step during HER pathway for Pd<sub>19</sub>B<sub>y</sub> (y=2,6,10,14) clusters.



**Figure S19.** Partial wave density of state (PDOS) of  $\text{Pd}_{44}\text{B}_4\text{H}_{52}$  and  $\text{Pd}_{44}\text{H}_{62}$  ( $\text{H}_{\text{ad}}$  state for HER).