Supporting Information

Crossover from Linear Chains to a Honeycomb Network for the Nucleation of Hexagonal Boron Nitride Grown on the Ni(111) Surface

Hongxia Zhu,[†] Jianping Zhu,[†] Zhuhua Zhang[‡] and Ruiqi Zhao*[†]

[†]Henan Key Laboratory of Materials on Deep-Earth Engineering, School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo, Henan 454003, China

[‡]Key Laboratory for Intelligent Nano Materials and Devices of Ministry of Education, State Key Laboratory of Mechanics and Control of Mechanical Structures, and Institute for Frontier Science, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

*Author to whom correspondence should be addressed: *zhaoruiqi@hpu.edu.cn.*

Contents:

1. Adsorption sites, tests of stable configurations of BN film on the Ni(111) surface and relative energy calculated with PBE and vdw-D3 functionals.

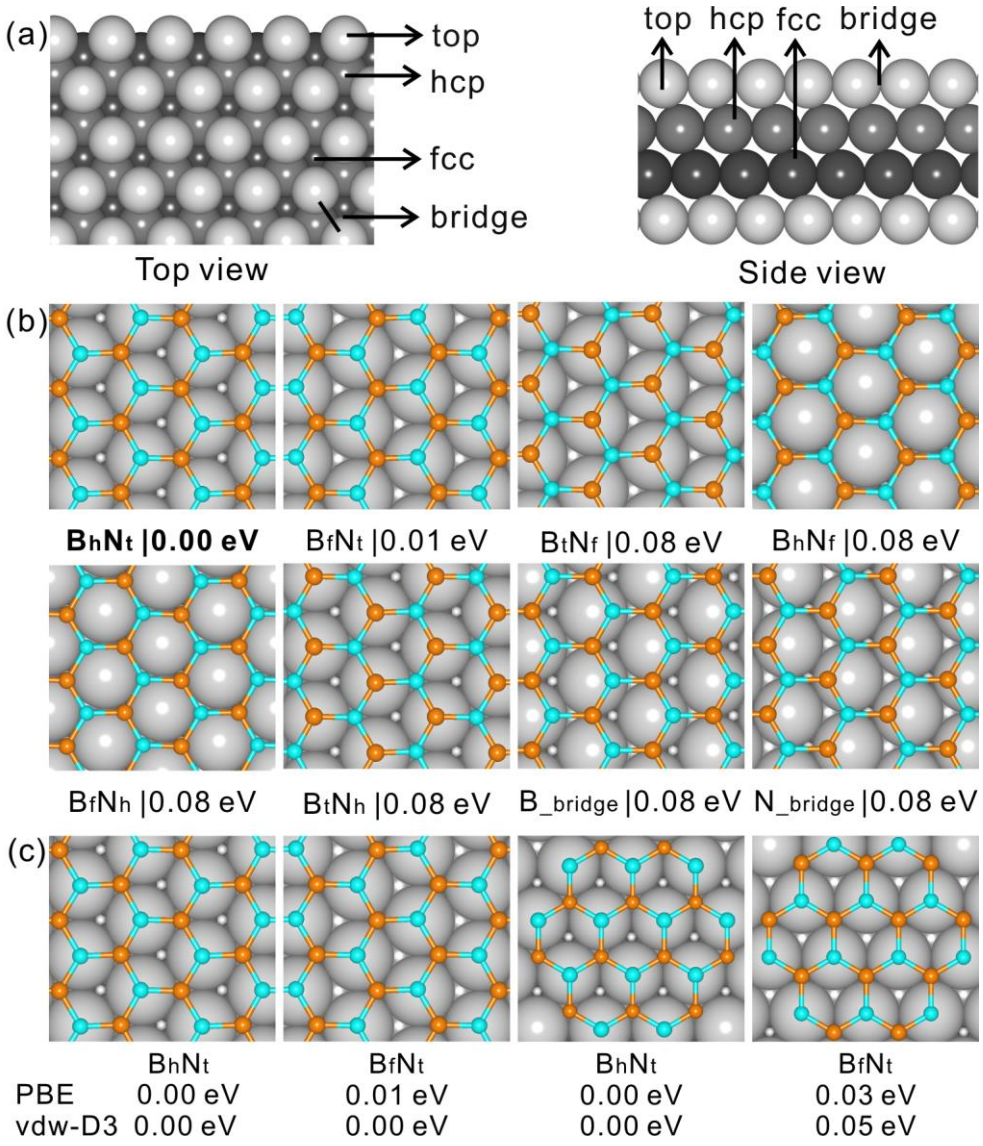

Figure S1: (Color on line) (a) Adsorption sites of top, hcp, fcc and bridge seen from top (left) and side (right) views, the configurations are named with composed elements and abbreviations of adsorption sites. (b) Eight configurations of BN film on Ni(111) surface and their relative energies calculated with PBE functional. The configurations B_hN_t and B_fN_t are the most stable ones. (c) Relative energies (eV) between two stable configurations of BN film and honeycombed $(BN)_{12}$ cluster calculated with PBE and vdw-D3 functionals, respectively.

On a Ni(1111) surface, there are four special adsorption sites, top, hcp, fcc and bridge docked by B and N atoms (see Figure S1a), which result in eight different configurations because of the binary composition of h-BN. Eight configurations of BN film on a Ni(111) surface are obtained, which are presented in Figure S1b along with their relative energies calculated with PBE functional. The

configurations B_hN_t and B_fN_t are the most stable ones. The energy of the most stable configuration, B_hN_t, is set as zero and the relative energies of other configurations are calculated compared to B_hN_t. Besides, the relative energies of $(BN)_{12}$ cluster on Ni(111) are calculated with PBE and vdw-D3 functionals, as shown in Figure S1c. The results from both functionals present that B_hN_t is the most stable one in BN film and $(BN)_{12}$ cluster. The energy difference from both functionals are close, indicating the influence from van der Waals force can be neglected in studying the stabilities of BN clusters. Therefore, PBE is used in all simulations in this work.

2. Relaxed configurations, formation energies and relative energies of honeycomb structures of $(BN)_8$ on the Ni(111) surface.

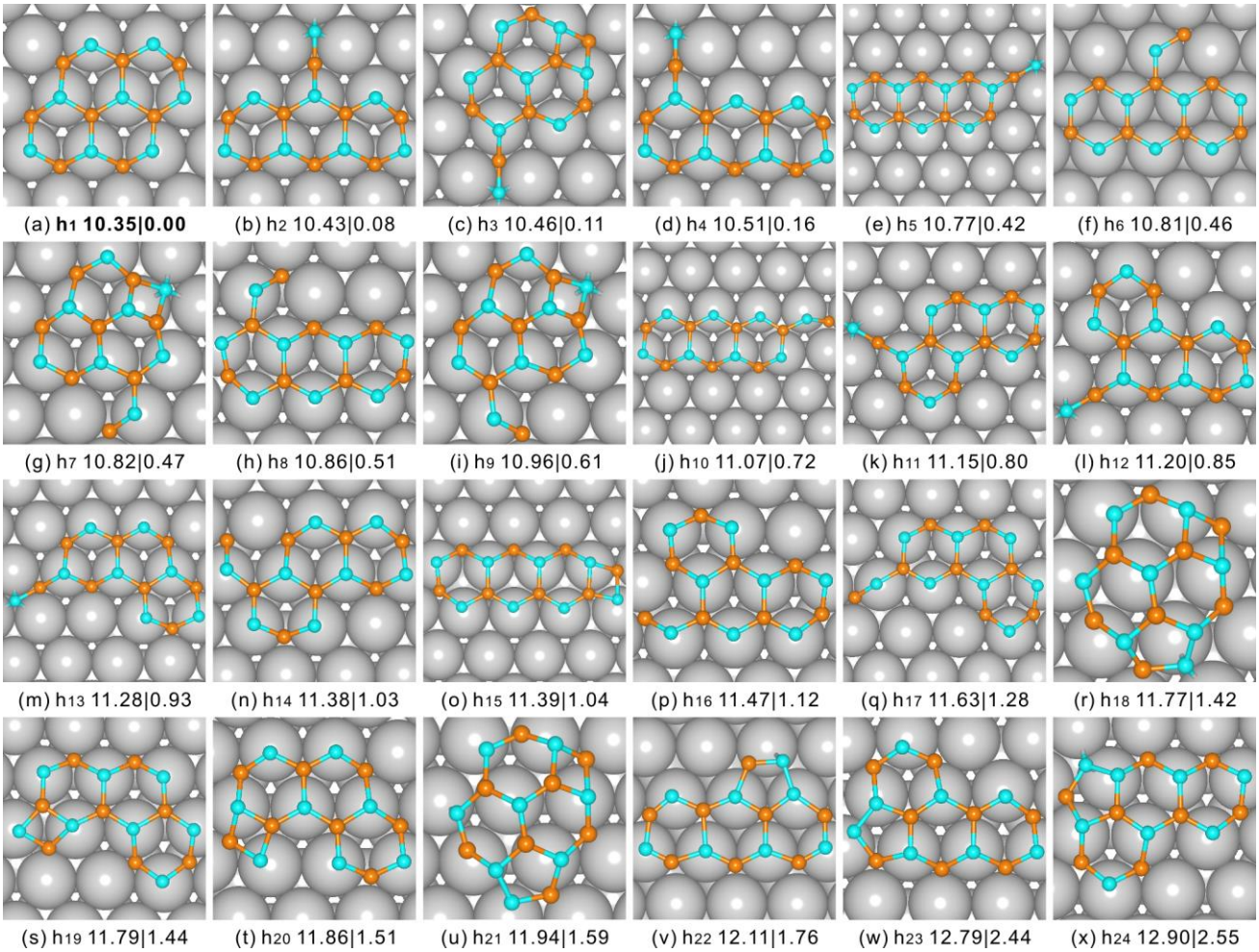

Figure S2: (Color on line) Relaxed configurations, formation energies and relative energies of $(BN)_n$ (n = 8) on Ni(111) surface. The relative energy (ΔE/eV) of each configuration is calculated based on geometry shown in panel a. The ground-state is highlighted in bold.

3. Relaxed configurations, formation energies and relative energies of honeycomb structures of $(BN)_{11}$ on the Ni(111) surface.

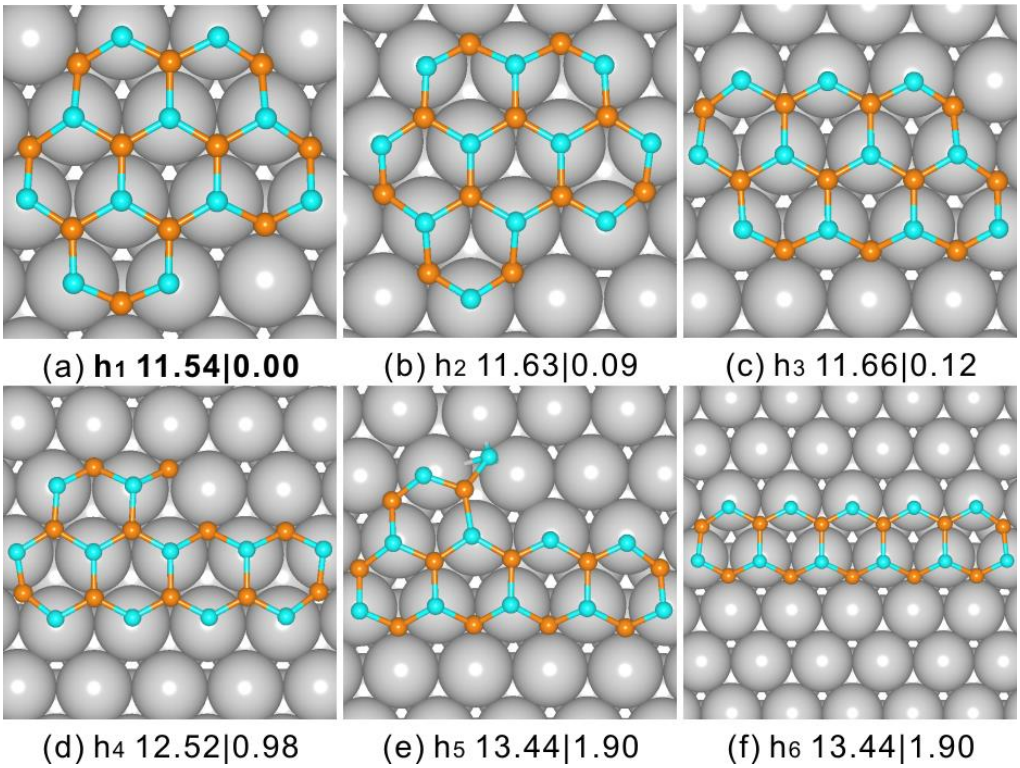

Figure S3: (Color on line) Relaxed configurations, formation energies and relative energies of $(BN)_n$ (n = 11) on Ni(111) surface. The relative energy (ΔE/eV) of each configuration is calculated based on geometry shown in panel a. The ground-state is highlighted in bold.

4. Relaxed configurations and relative energies of chain-like and ring-shaped geometries of $(BN)_6$ on the Ni(111) surface.

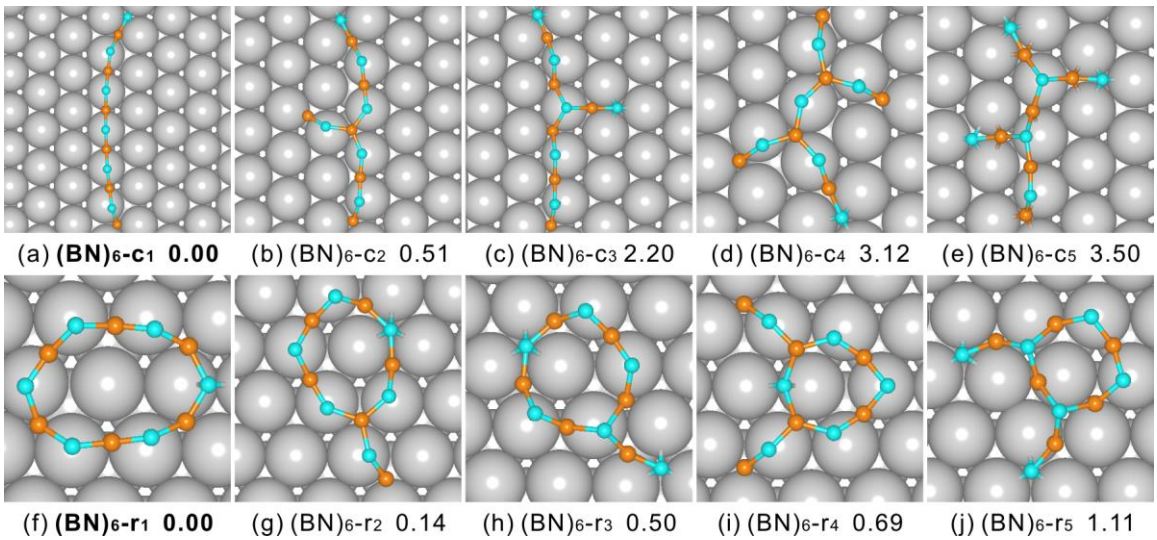

Figure S4: (Color on line) Relaxed configurations and relative energies (eV) of chain-like (a-e) and ring-shaped (f-j) geometries of $(BN)_6$ on Ni(111) surface. Here, only the geometries containing side chains are considered. The relative energies are calculated with pristine chain-like and ring-shaped as reference. It clearly presents the pristine geometry in both cases is the stable one. The pristine geometries are highlighted in bold.

5. Relaxed configurations, formation energies and relative energies of honeycomb structures of $(BN)_9$ on the Ni(111) surface.

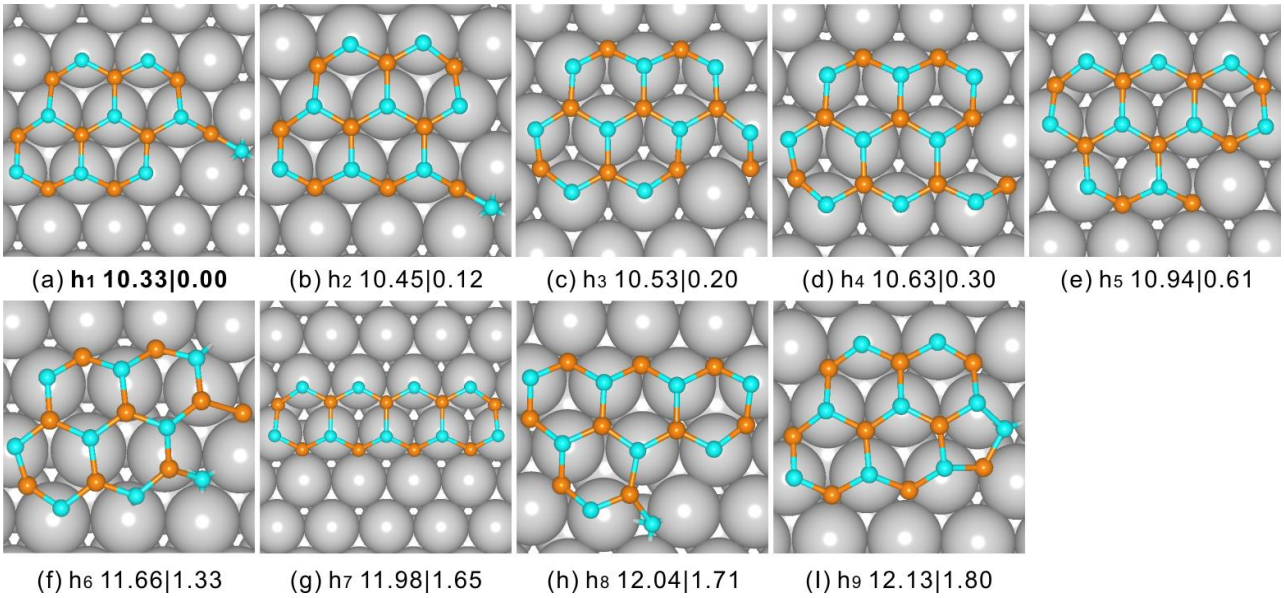

Figure S5: (Color on line) Relaxed configurations, formation energies and relative energies of $(BN)_9$ on Ni(111) surface. The relative energy (ΔE/eV) of each configuration is calculated based on geometry shown in panel a. The ground-state is highlighted in bold.

6. Relaxed configurations, formation energies and relative energies of honeycomb structures of $(BN)_{10}$ on the Ni(111) surface..

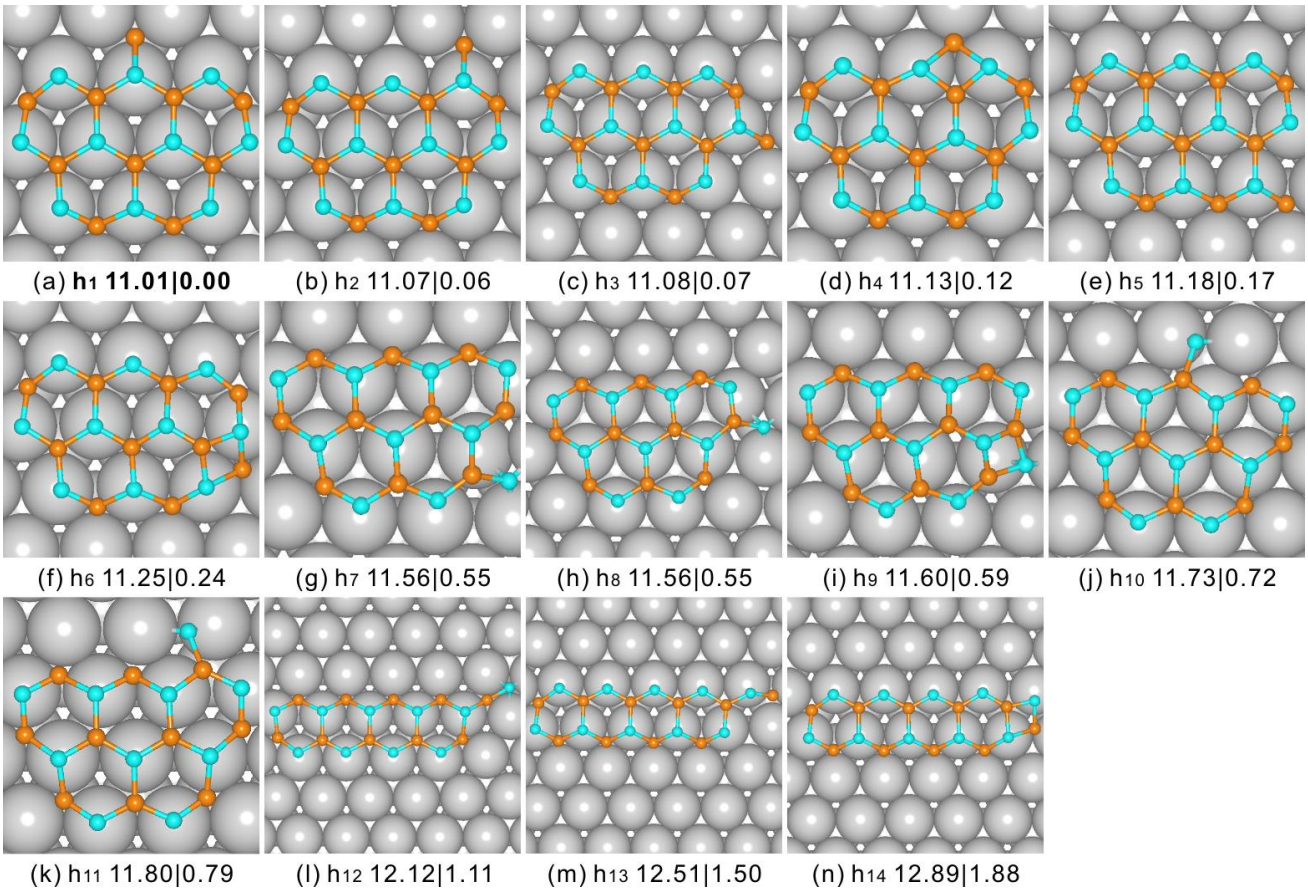

Figure S6: (Color on line) Relaxed configurations, formation energies and relative energies of $(BN)_{10}$ on Ni(111) surface. The relative energy (ΔE/eV) of each configuration is calculated based on geometry shown in panel a. The ground-state is highlighted in bold.

7. Relaxed configurations, formation energies and relative energies of honeycomb structures of $(BN)_{12}$ on the Ni(111) surface.

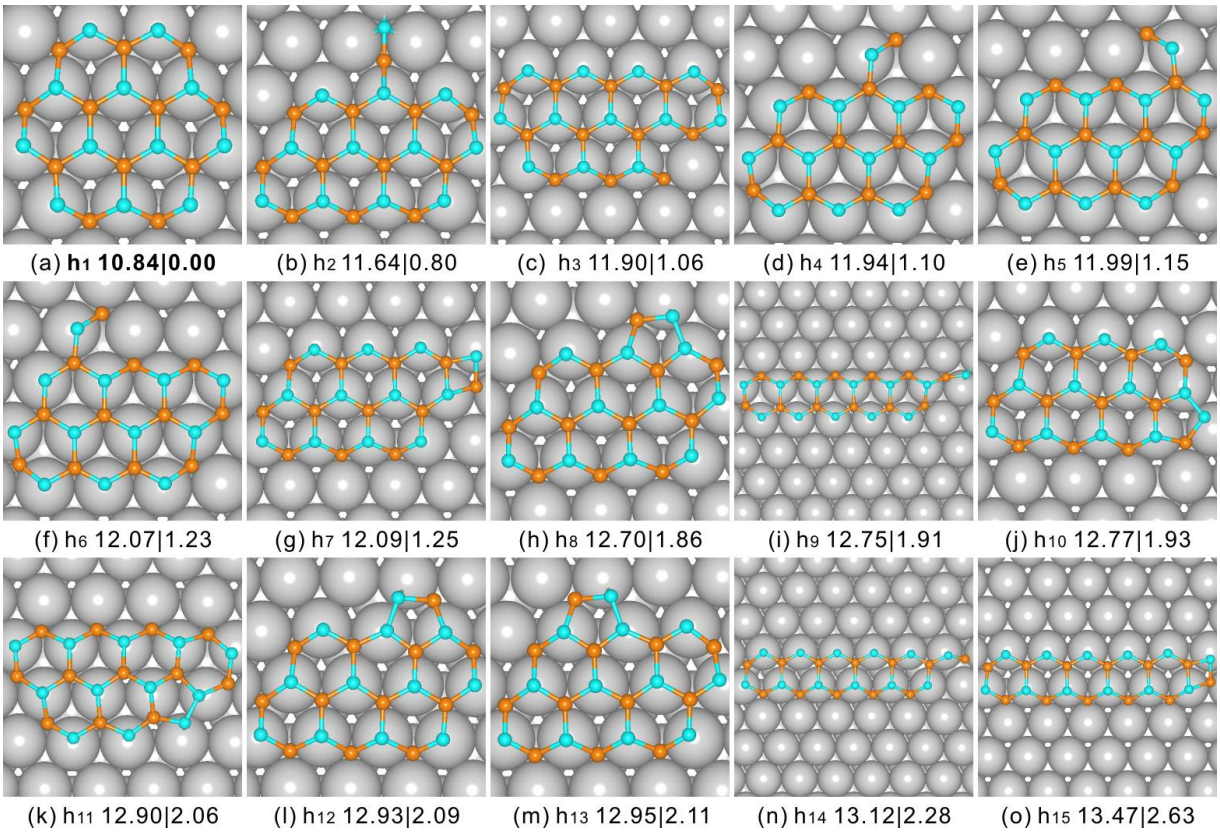

Figure S7: (Color on line) Relaxed configurations, formation energies and relative energies of $(BN)_{12}$ on Ni(111) surface. The relative energy (ΔE/eV) of each configuration is calculated based on geometry shown in panel a. The ground-state is highlighted in bold.