Supporting Information for

Geometry of hexagonal Boron Nitride clusters in the initial stages of chemical vapor deposition growth on Cu(111) surface

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Table S1. Parameters for Cu(111) substrates. "ch" and "r" in $B_nN_{m\text{-}ch}$ and $B_nN_{m\text{-}r}$ (m=n-1, n, n+1) stand for chain and ring, respectively. A B_nN_m represents an sp^2-network cluster.

Substrate	a (Å)	b (Å)	γ	Energy (eV)	K points	Clusters on the substrate
1	7.668	7.668	2π/3	-115.565	7*7*1	B_1, N_1, $B_1N_{1\text{-}ch}$
2	10.224	10.224	2π/3	-204.984	7*7*1	$B_1N_{2\text{-}ch}$, $B_2N_{1\text{-}ch}$, $B_2N_{2\text{-}ch}$, $B_1N_{2\text{-}r}$, $B_2N_{2\text{-}r}$, $B_2N_{3\text{-}r}$, $B_3N_{3\text{-}r}$,
3	12.780	12.780	2π/3	-321.019	5*5*1	$B_nN_{n\text{-}r}$, $B_nN_{n\text{-}ch}$ (n=3, 4, 5, 6, 7), $B_2N_{3\text{-}ch}$, $B_{(n\text{-}1)}N_n$, $B_{n\text{-}1}N_{n\text{-}r}$ (n=4, 5, 6, 7), $B_3N_{2\text{-}ch}$, $B_nN_{(n\text{-}1)\text{-}r}$, $B_nN_{n\text{-}1}$ (n=4, 5, 6), B_7N_6
4	15.336	15.336	2π/3	-460.712	5*5*1	$B_4N_{4\text{-}ch}$, $B_3N_{4\text{-}ch}$, $B_4N_{3\text{-}ch}$, B_6N_7, B_nN_n, $B_nN_{n\text{-}r}$, (n=7, 8), $B_{(n\text{-}1)}N_n$, $B_{(n\text{-}1)}N_{n\text{-}r}$, (n=8, 9), $B_nN_{(n\text{-}1)}$, $B_nN_{(n\text{-}1)\text{-}r}$, (n=8, 9).
5	10.224	25.560	2π/3	-512.306	7*5*1	$B_6N_{7\text{-}ch}$, $B_7N_{6\text{-}ch}$, $B_7N_{7\text{-}ch}$, $B_7N_{8\text{-}ch}$, $B_8N_{7\text{-}ch}$
6	10.224	28.116	2π/3	-563.984	7*5*1	$B_8N_{8\text{-}ch}$
7	17.892	17.892	2π/3	-628.424	5*5*1	$B_4N_{5\text{-}ch}$, $B_5N_{4\text{-}ch}$, $B_6N_{7\text{-}ch}$, $B_7N_{6\text{-}ch}$, $B_7N_{7\text{-}ch}$,
8	17.708	17.892	π/2	-717.339	3*3*1	$B_{12}N_{12}$, $B_{16}N_{16}$, $B_{19}N_{18}$
9	20.448	20.448	2π/3	-818.053	1*1*1	$B_5N_{5\text{-}ch}$, $B_5N_{6\text{-}ch}$, $B_6N_{5\text{-}ch}$, $B_6N_{6\text{-}ch}$, $B_7N_{8\text{-}ch}$, $B_8N_{7\text{-}ch}$, $B_{23}N_{24}$, $B_{24}N_{23}$
10	20.448	17.708	π/2	-819.640	1*3*1	$B_{20}N_{20}$
11	23.004	23.004	2π/3	-1036.134	1*1*1	$B_{29}N_{30}$, $B_{30}N_{29}$, $B_{32}N_{32}$
12	23.004	22.135	π/2	-1151.770	1*1*1	$B_{21}N_{21}$, $B_{27}N_{27}$

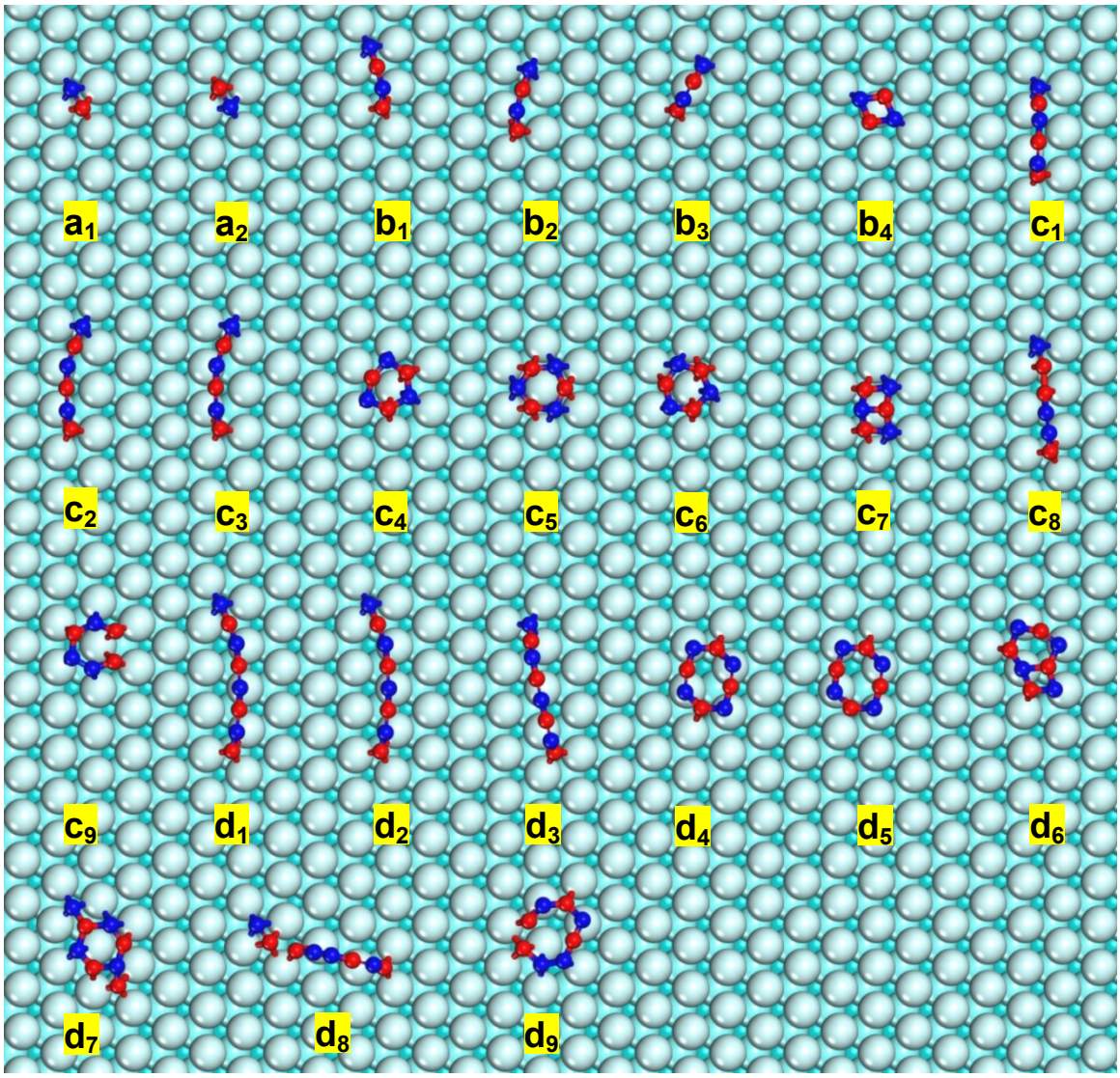

Fig. S1 Structures and formation energies of small B_nN_n ($1 \leq n \leq 4$) clusters on a Cu (111) surface. (a_1) $B_1N_{1\text{-ch}\_1}$, 3.079 eV; (a_2) $B_1N_{1\text{-ch}\_2}$, 3.117 eV; (b_1) $B_2N_{2\text{-ch}\_1}$, 4.519 eV; (b_2) $B_2N_{2\text{-ch}\_2}$, 4.562 eV; (b_3) $B_2N_{2\text{-ch}\_3}$, 4.735 eV; (b_4) $B_2N_{2\text{-r}\_1}$, 5.999 eV; (c_1) $B_3N_{3\text{-ch}\_1}$, 6.157 eV; (c_2) $B_3N_{3\text{-ch}\_2}$, 6.285 eV; (c_3) $B_3N_{3\text{-ch}\_3}$, 6.286 eV; (c_4) $B_3N_{3\text{-r}\_1}$, 7.327 eV; (c_5) $B_3N_{3\text{-r}\_2}$, 7.329 eV; (c_6) $B_3N_{3\text{-r}\_3}$, 7.349 eV; (c_7) $B_3N_{3\text{-r}\_4}$, 7.936 eV; (c_8) $B_3N_{3\text{-ch}\_4}$, 9.086 eV; (c_9) $B_3N_{3\text{-r}\_5}$, 9.715 eV; (d_1) $B_4N_{4\text{-ch}\_1}$, 7.396 eV; (d_2) $B_4N_{4\text{-ch}\_2}$, 7.468 eV; (d_3) $B_4N_{4\text{-ch}\_3}$, 7.699 eV; (d_4) $B_4N_{4\_r\_1}$, 8.978 eV; (d_5) $B_4N_{4\_r\_2}$, 8.979 eV; (d_6) $B_4N_{4\_1}$, 9.002 eV; (d_7) $B_4N_{4\_2}$, 9.443 eV; (d_8) $B_4N_{4\text{-ch}\_4}$, 10.714 eV; (d_9) $B_4N_{4\_r\_3}$, 11.510 eV. “ch” and “r” in $B_nN_{n\text{-ch}}$ and $B_nN_{n\text{-r}}$ stand for chain and ring, respectively. The same-sized clusters are arranged in ascending order of the values of their formation energies. The B and N atoms are in red and blue, respectively. The Cu atoms are shown from celeste to aqua according to their depth from the top surface.

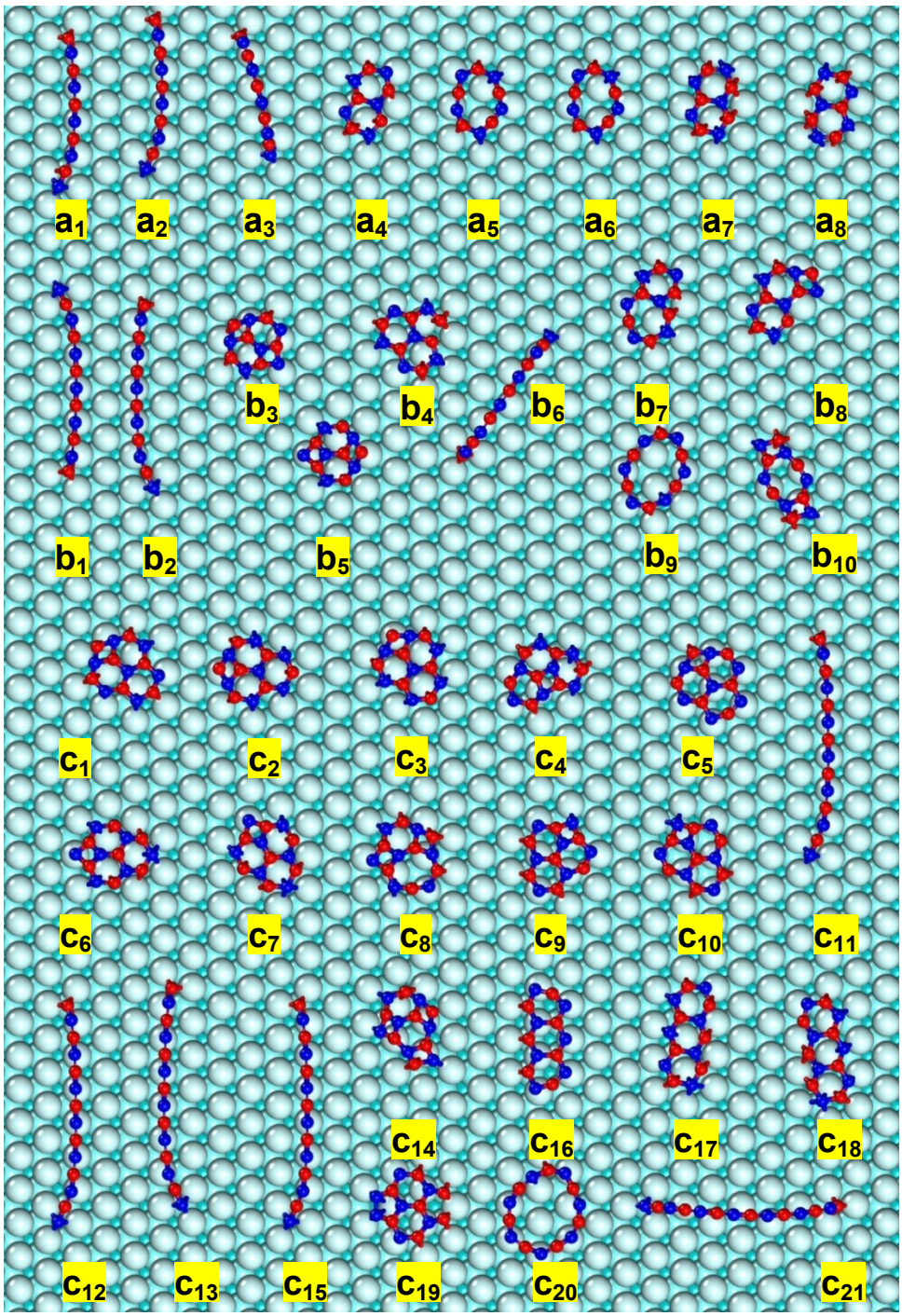

Fig. S2 Structures and formation energies of medium-sized B_nN_n ($5 \leq n \leq 7$) clusters on a Cu (111) surface. (a_1) $B_5N_{5\text{-}ch\_1}$, 8.960 eV; (a_2) $B_5N_{5\text{-}ch\_2}$, 9.040 eV; (a_3) $B_5N_{5\text{-}ch\_3}$, 9.837 eV; (a_4) $B_5N_{5\_1}$, 10.224 eV; (a_5) $B_5N_{5\text{-}r\_1}$, 10.246 eV; (a_6) $B_5N_{5\text{-}r\_2}$, 10.246 eV; (a_7) $B_5N_{5\_2}$, 10.254 eV; (a_8) $B_5N_{5\_3}$, 10.295 eV; (b_1) $B_6N_{6\text{-}ch\_1}$, 10.451 eV; (b_2) $B_6N_{6\text{-}ch\_2}$, 10.542 eV; (b_3) $B_6N_{6\_1}$, 10.555 eV ; (b_4) $B_6N_{6\_2}$, 10.674 eV; (b_5) $B_6N_{6\_3}$, 11.008 eV; (b_6) $B_6N_{6\text{-}ch\_3}$, 11.443 eV; (b_7) $B_6N_{6\_4}$, 11.447 eV; (b_8) $B_6N_{6\_5}$, 11.537 eV; (b_9) $B_6N_{6\text{-}r\_1}$, 11.749 eV; (b_{10}) $B_6N_{6\_6}$, 11.916 eV; (c_1) $B_7N_{7\_1}$,10.884 eV; (c_2) $B_7N_{7\_2}$,11.320 eV; (c_3) $B_7N_{7\_3}$,11.320 eV ; (c_4) $B_7N_{7\_4}$,11.321 eV; (c_5) $B_7N_{7\_5}$,11.344 eV; (c_6) $B_7N_{7\_6}$,11.463 eV; (c_7) $B_7N_{7\_7}$,11.463 eV; (c_8) $B_7N_{7\_8}$,11.658 eV; (c_9) $B_7N_{7\_9}$,11.704 eV; (c_{10}) $B_7N_{7\_10}$,11.713 eV; (c_{11}) $B_7N_{7\text{-}ch\_1}$,12.077 eV; (c_{12}) $B_7N_{7\text{-}ch\_2}$,12.078 eV; (c_{13}) $B_7N_{7\text{-}ch\_3}$,12.163 eV ; (c_{14}) $B_7N_{7\_11}$,12.175 eV; (c_{15}) $B_7N_{7\text{-}ch\_4}$,12.280 eV; (c_{16}) $B_7N_{7\_12}$,12.315 eV; (c_{17}) $B_7N_{7\_13}$,12.413 eV; (c_{18}) $B_7N_{7\_14}$,12.448 eV; (c_{19}) $B_7N_{7\_15}$,12.891 eV; (c_{20}) $B_7N_{7\text{-}r\_1}$, 13.270 eV; (c_{21}) $B_7N_{7\text{-}ch\_5}$,13.394 eV. "ch" and "r" in $B_nN_{n\text{-}ch}$ and $B_nN_{n\text{-}r}$ stand for chain and ring, respectively. The same-sized clusters are arranged in ascending order of the values of their formation energies.

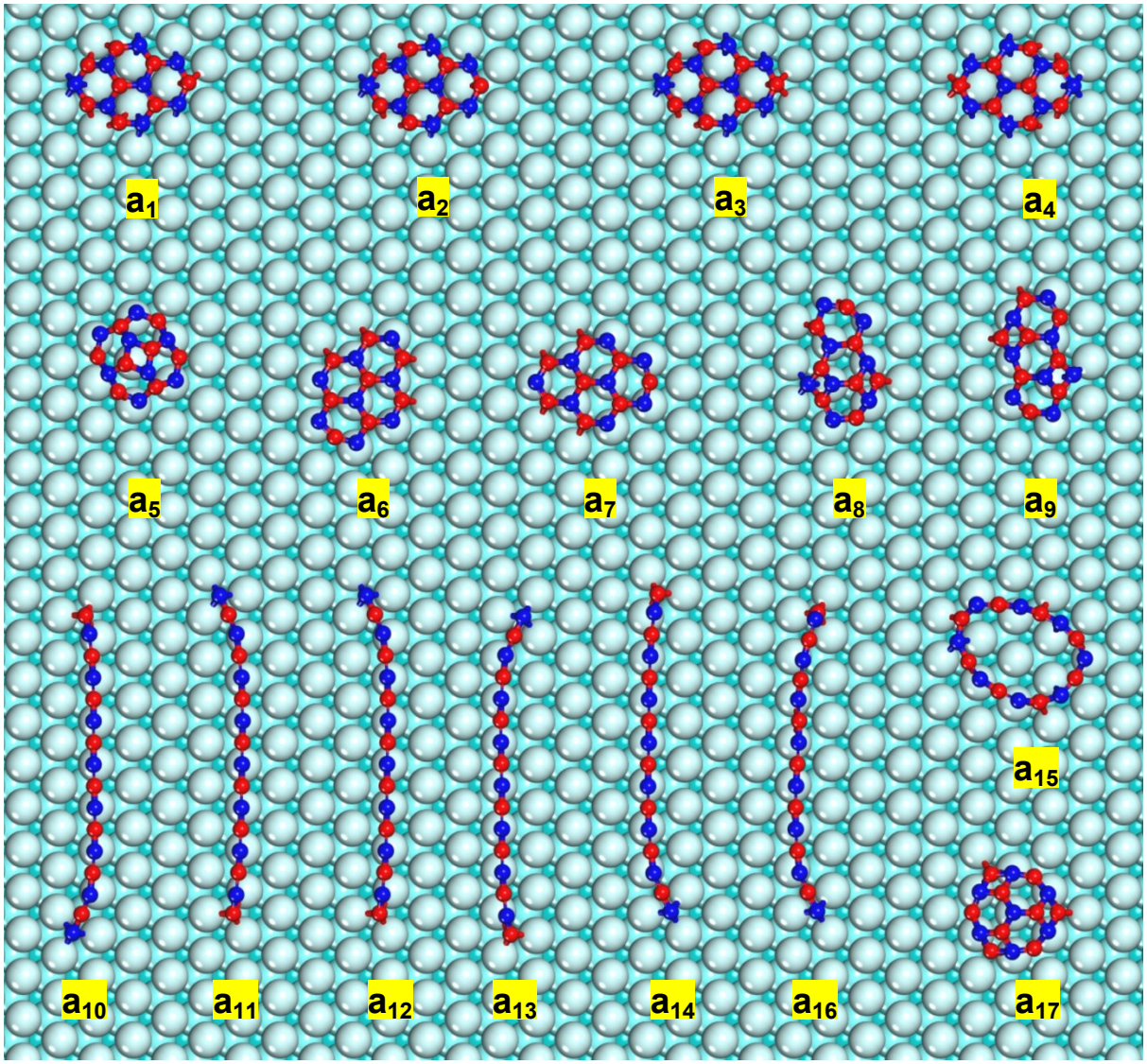

Fig. S3 Structures and formation energies of B_8N_8 clusters on a Cu (111) surface. (a_1) $B_8N_{8\_1}$, 11.583 eV; (a_2) $B_8N_{8\_2}$, 11.589 eV; (a_3) $B_8N_{8\_3}$, 11.603 eV; (a_4) $B_8N_{8\_4}$, 11.605 eV; (a_5) $B_8N_{8\_5}$, 11.982 eV; (a_6) $B_8N_{8\_6}$, 12.024 eV; (a_7) $B_8N_{8\_7}$, 12.050 eV; (a_8) $B_8N_{8\_8}$, 12.884 eV; (a_9) $B_8N_{8\_9}$, 12.928 eV; (a_{10}) $B_8N_{8\text{-}ch\_1}$, 13.955 eV; (a_{11}) $B_8N_{8\text{-}ch\_2}$, 13.984 eV; (a_{12}) $B_8N_{8\text{-}ch\_3}$, 13.987 eV; (a_{13}) $B_8N_{8\text{-}ch\_4}$, 14.007 eV; (a_{14}) $B_8N_{8\text{-}ch\_5}$, 14.051 eV; (a_{15}) $B_8N_{8\text{-}r\_1}$, 14.132 eV; (a_{16}) B8N8-ch_6, 14.291 eV; (a_{17}) $B_8N_{8\_10}$, 14.319 eV. "ch" and "r" in $B_nN_{n\text{-}ch}$ and $B_nN_{n\text{-}r}$ stand for chain and ring, respectively. The same-sized clusters are arranged in ascending order of the values of their formation energies.

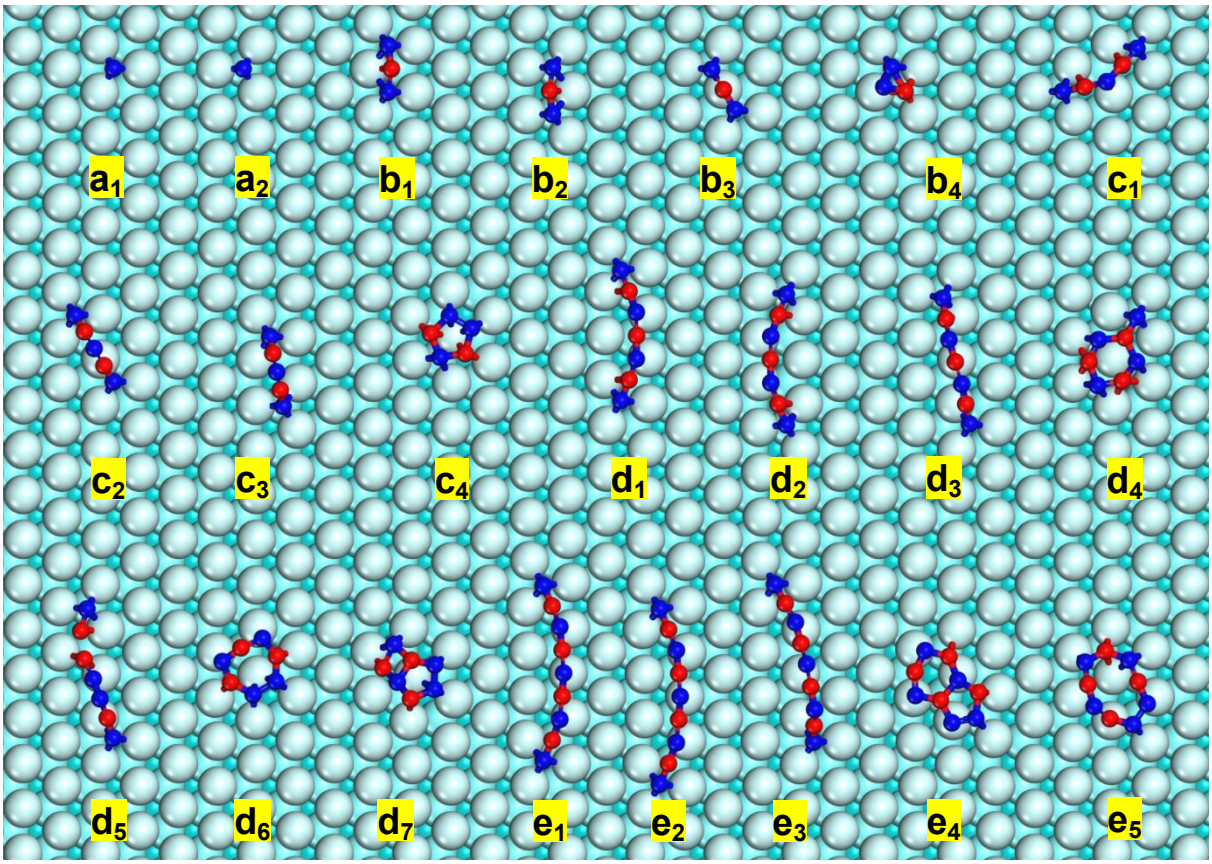

Fig. S4 Structures and formation energies of small $B_{n-1}N_n$ ($1 \leq n \leq 5$) clusters on a Cu (111) surface. (a_1) N_{1_1}, 0.924 eV; (a_2) N_{1_2}, 1.027 eV; (b_1) $B_1N_{2\text{-}ch\_1}$, 1.963 eV; (b_2) $B_1N_{2\text{-}ch\_2}$, 2.083 eV ; (b_3) $B_1N_{2\text{-}ch\_3}$, 2.423 eV; (b_4) $B_1N_{2\text{-}r\_1}$, 4.541 eV; (c_1) $B_2N_{3\text{-}ch\_1}$, 3.066 eV; (c_2) $B_2N_{3\text{-}ch\_2}$, 3.143 eV; (c_3) $B_2N_{3\text{-}ch\_3}$, 3.250 eV; (c_4) $B_2N_{3\text{-}r\_1}$, 5.826 eV; (d_1) $B_3N_{4\text{-}ch\_1}$, 4.192 eV ; (d_2) $B_3N_{4\text{-}ch\_2}$, 4.192 eV; (d_3) $B_3N_{4\text{-}ch\_3}$, 4.856 eV; (d_4) $B_3N_{4\_1}$, 6.304 eV; (d_5) $B_3N_{4\text{-}ch\_4}$, 7.620 eV; (d_6) $B_3N_{4\text{-}r\_1}$, 7.901 eV; (d_7) $B_3N_{4\_2}$, 7.907 eV; (e_1) $B_4N_{5\text{-}ch\_1}$, 5.872 eV; (e_2) $B_4N_{5\text{-}ch\_2}$, 5.978 eV; (e_3) $B_4N_{5\text{-}ch\_3}$, 6.075 eV; (e_4) $B_4N_{5\_1}$, 9.119 eV; (e_5) $B_4N_{5\text{-}r\_1}$, 9.786 eV. “ch” and “r” in $B_{n-1}N_{n\text{-}ch}$ and $B_{n-1}N_{n\text{-}r}$ stand for chain and ring, respectively. The same-sized clusters are arranged in ascending order of the values of their formation energies.

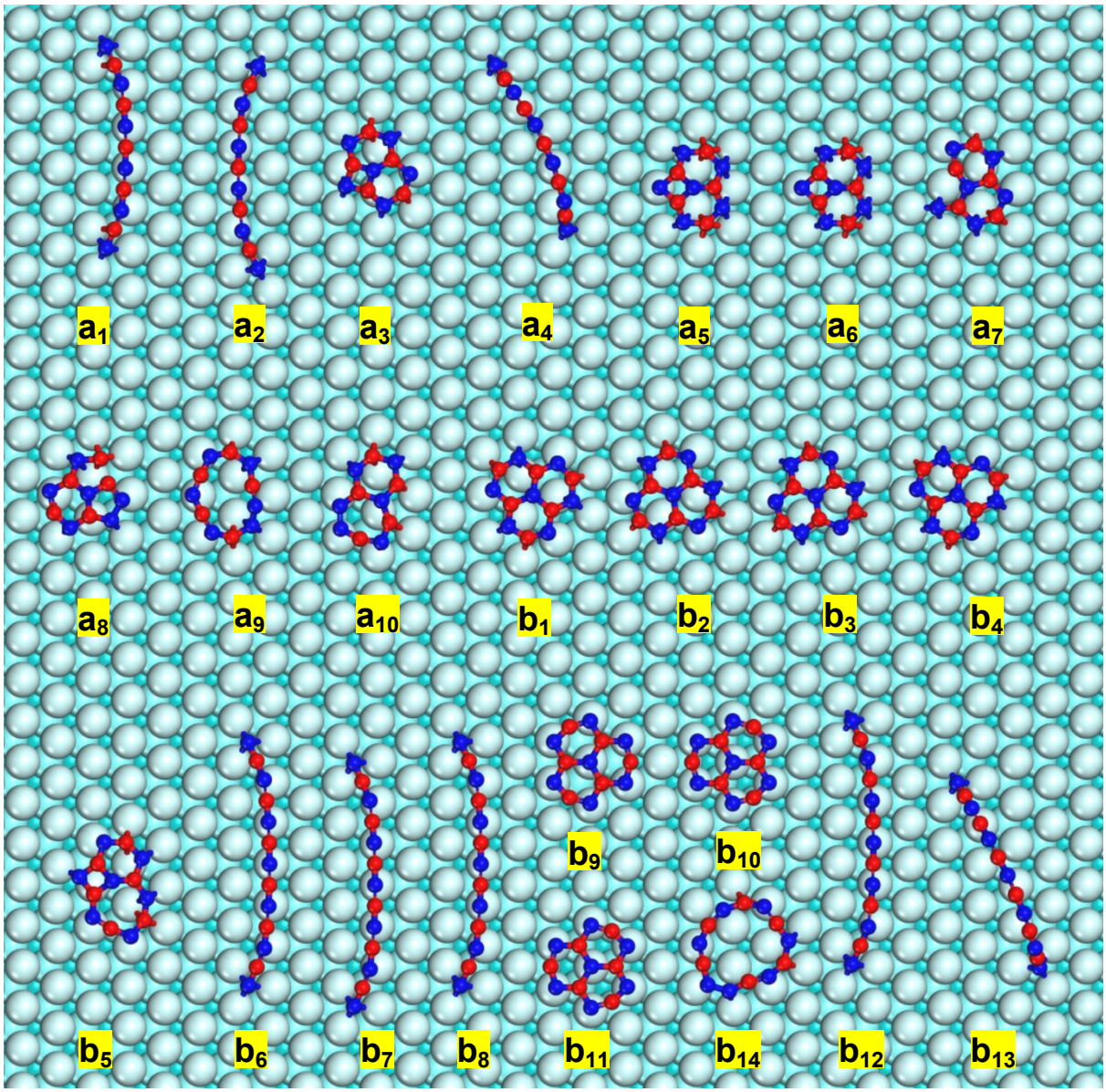

Fig. S5 Structures and formation energies of medium-sized $B_{n-1}N_n$ ($n = 6, 7$) clusters on a Cu (111) surface. (a_1) $B_5N_{6\text{-}ch\_1}$, 7.328 eV; (a_2) $B_5N_{6\text{-}ch\_2}$, 7.486 eV; (a_3) $B_5N_{6\_1}$, 7.902 eV; (a_4) $B_5N_{6\text{-}ch\_3}$, 8.017 eV; (a_5) $B_5N_{6\_2}$, 8.121 eV; (a_6) $B_5N_{6\_3}$, 8.141 eV; (a_7) $B_5N_{6\_4}$, 8.746 eV; (a_8) $B_5N_{6\_5}$, 10.042 eV; (a_9) $B_5N_{6\text{-}r\_1}$, 11.081 eV; (a_{10}) $B_5N_{6\_6}$, 11.751 eV; (b_1) $B_6N_{7\_1}$, 8.456 eV; (b_2) $B_6N_{7\_2}$, 8.477 eV; (b_3) $B_6N_{7\_3}$, 8.491 eV; (b_4) $B_6N_{7\_4}$, 8.494 eV; (b_5) $B_6N_{7\_5}$, 8.872 eV; (b_6) $B_6N_{7\text{-}ch\_1}$, 8.910 eV; (b_7) $B_6N_{7\text{-}ch\_2}$, 8.911 eV; (b_8) $B_6N_{7\text{-}ch\_3}$, 8.913 eV; (b_9) $B_6N_{7\_6}$, 9.006 eV; (b_{10}) $B_6N_{7\_7}$, 9.008 eV; (b_{11}) $B_6N_{7\_8}$, 9.009 eV; (b_{12}) $B_6N_{7\text{-}ch\_4}$, 9.664 eV; (b_{13}) $B_6N_{7\text{-}ch\_5}$, 10.217 eV; (b_{14}) $B_6N_{7\text{-}r\_1}$, 12.714 eV. “ch” and “r” in $B_{n-1}N_{n\text{-}ch}$ and $B_{n-1}N_{n\text{-}r}$ stand for chain and ring, respectively. The same-sized clusters are arranged in ascending order of the values of their formation energies.

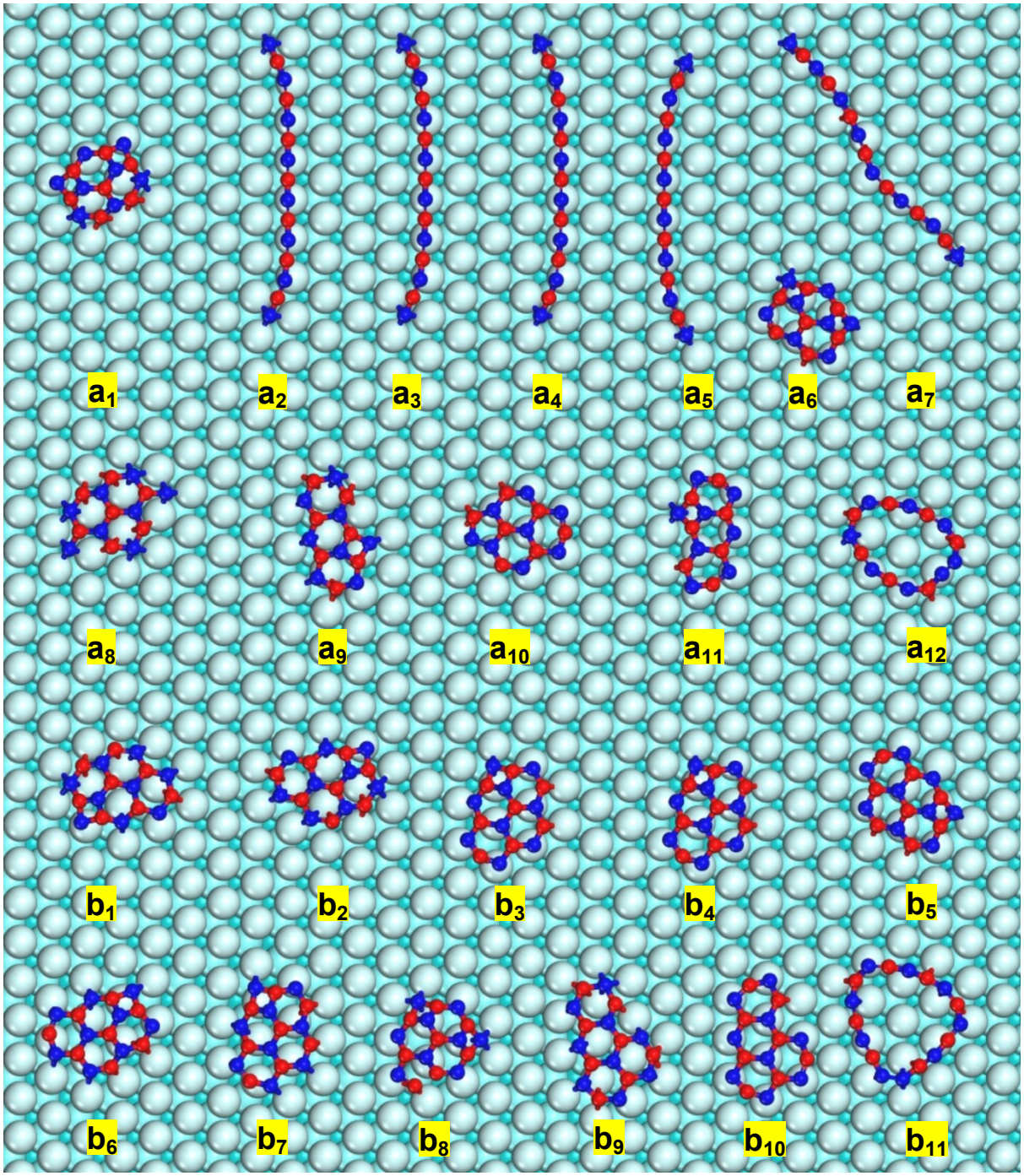

Fig. S6 Structures and formation energies of medium-sized $B_{n-1}N_n$ ($n = 8, 9$) clusters on a Cu (111) surface. (a_1) $B_7N_{8\_1}$, 9.237 eV; (a_2) $B_7N_{8\text{-}ch\_1}$, 10.462 eV; (a_3) $B_7N_{8\text{-}ch\_2}$, 10.511 eV; (a_4) $B_7N_{8\text{-}ch\_3}$, 10.511 eV; (a_5) $B_7N_{8\text{-}ch\_4}$, 10.641 eV; (a_6) $B_7N_{8\_2}$, 11.166 eV; (a_7) $B_7N_{8\text{-}ch\_5}$, 11.425 eV; (a_8) $B_7N_{8\_3}$, 12.338 eV; (a_9) $B_7N_{8\_4}$, 12.457 eV; (a_{10}) $B_7N_{8\_5}$, 13.098 eV; (a_{11}) $B_7N_{8\_6}$, 13.238 eV; (a_{12}) $B_7N_{8\text{-}r\_1}$, 16.331 eV; (b_1) $B_8N_{9\_1}$, 9.589 eV; (b_2) $B_8N_{9\_2}$, 9.609 eV; (b_3) $B_8N_{9\_3}$, 9.905 eV; (b_4) $B_8N_{9\_4}$, 9.908 eV; (b_5) $B_8N_{9\_5}$, 9.908 eV; (b_6) $B_8N_{9\_6}$, 9.963 eV; (b_7) $B_8N_{9\_7}$, 9.975 eV; (b_8) $B_8N_{9\_8}$, 10.072 eV; (b_9) $B_8N_{9\_9}$, 10.837 eV; (b_{10}) $B_8N_{9\_10}$, 11.274 eV; (b_{11}) $B_8N_{9\text{-}r\_1}$, 15.546 eV. “ch” and “r” in $B_{n-1}N_{n\text{-}ch}$ and $B_{n-1}N_{n\text{-}r}$ stand for chain and ring, respectively. The same-sized clusters are arranged in ascending order of the values of their formation energies.

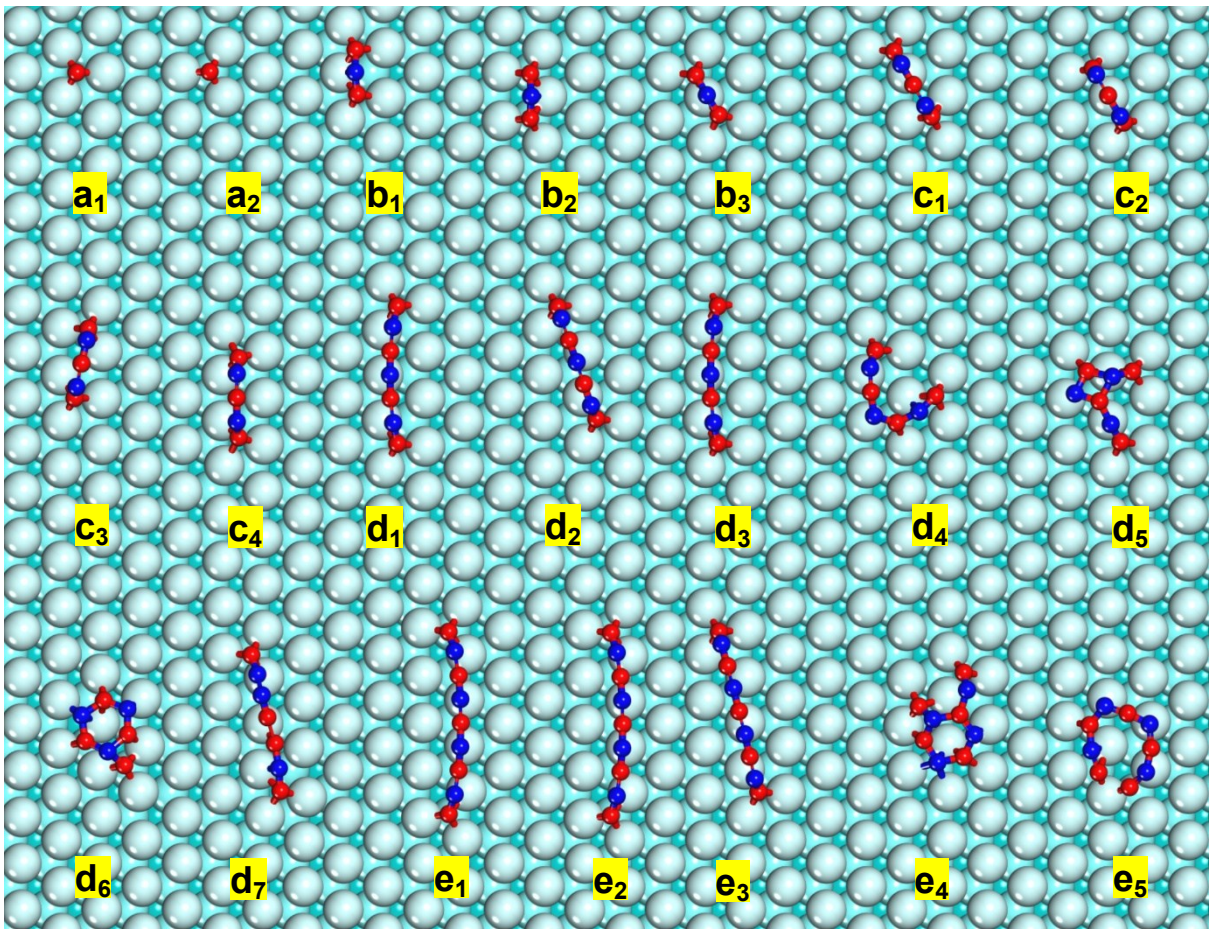

Fig. S7 Structures and formation energies of small B_nN_{n-1} ($1 \leq n \leq 5$) clusters on a Cu (111) surface. (a_1) B_{1_1}, 5.249 eV; (a_2) B_{1_2}, 5.255 eV; (b_1) $B_2N_{1\text{-}ch\_1}$, 6.208 eV; (b_2) $B_2N_{1\text{-}ch\_2}$, 6.215 eV; (b_3) $B_2N_{1\text{-}ch\_3}$, 6.352 eV; (c_1) $B_3N_{2\text{-}ch\_1}$, 7.508 eV; (c_2) $B_3N_{2\text{-}ch\_2}$, 7.612 eV; (c_3) $B_3N_{2\text{-}ch\_3}$, 7.629 eV; (c_4) $B_3N_{2\text{-}ch\_4}$, 7.890 eV; (d_1) $B_4N_{3\text{-}ch\_1}$, 9.048 eV; (d_2) $B_4N_{3\text{-}ch\_2}$, 9.052 eV; (d_3) $B_4N_{3\text{-}ch\_3}$, 9.064 eV; (d_4) $B_4N_{3\text{-}r\_1}$, 10.218 eV; (d_5) $B_4N_{3\_1}$, 10.300 eV; (d_6) $B_4N_{3\_2}$, 10.667 eV; (d_7) $B_4N_{3\text{-}ch\_4}$, 11.999 eV; (e_1) $B_5N_{4\text{-}ch\_1}$, 10.671 eV; (e_2) $B_5N_{4\text{-}ch\_2}$, 10.720 eV; (e_3) $B_5N_{4\text{-}ch\_3}$, 10.877 eV; (e_4) $B_5N_{4\_1}$, 11.874 eV; (e_5) $B_5N_{4\text{-}r\_1}$, 12.150 eV. “ch” and “r” in $B_nN_{(n-1)\text{-}ch}$ and $B_nN_{(n-1)\text{-}r}$ stand for chain and ring, respectively. The same-sized clusters are arranged in ascending order of the values of their formation energies.

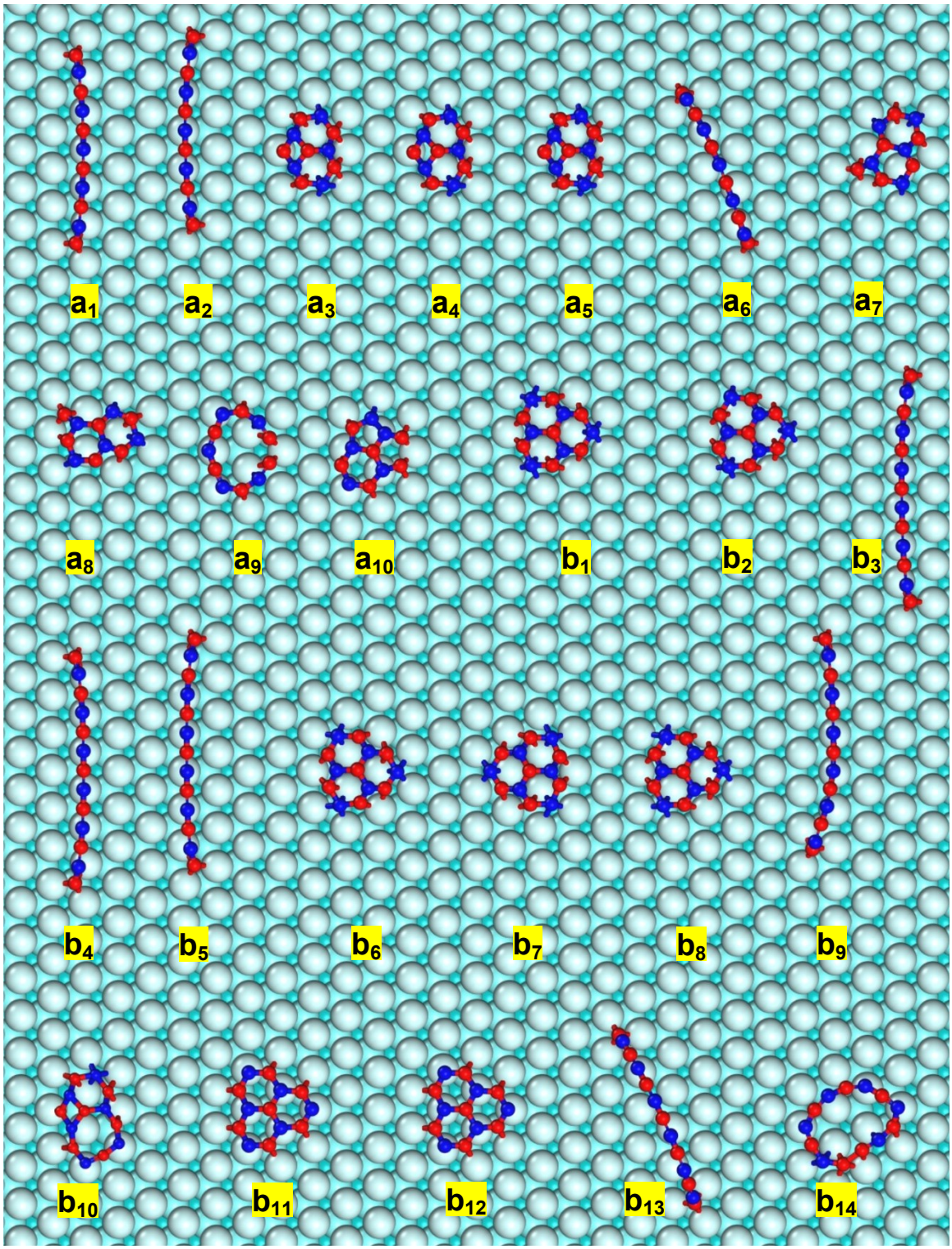

Fig. S8 Structures and formation energies of medium-sized B_nN_{n-1} ($n = 6, 7$) clusters on a Cu (111) surface. (a_1) $B_6N_{5\text{-}ch\_1}$, 12.089 eV; (a_2) $B_6N_{5\text{-}ch\_2}$, 12.103 eV; (a_3) $B_6N_{5\_1}$, 12.548 eV; (a_4) $B_6N_{5\_2}$, 12.549 eV; (a_5) $B_6N_{5\_3}$, 12.569 eV; (a_6) $B_6N_{5\text{-}ch\_3}$, 12.580 eV; (a_7) $B_6N_{5\_4}$, 13.061 eV; (a_8) $B_6N_{5\_5}$, 13.197 eV; (a_9) $B_6N_{5\text{-}r\_1}$, 13.686 eV; (a_{10}) $B_6N_{5\_6}$, 14.826 eV; (b_1) $B_7N_{6\_1}$, 13.624 eV ; (b_2) $B_7N_{6\_2}$, 13.624 eV; (b_3) $B_7N_{6\text{-}ch\_1}$, 13.643 eV; (b_4) $B_7N_{6\text{-}ch\_2}$, 13.645 eV; (b_5) $B_7N_{6\text{-}ch\_3}$, 13.647 eV; (b_6) $B_7N_{6\_3}$, 13.681 eV; (b_7) $B_7N_{6\_4}$, 13.681 eV; (b_8) $B_7N_{6\_5}$, 13.682 eV; (b_9) $B_7N_{6\text{-}ch\_4}$, 13.870 eV; (b_{10}) $B_7N_{6\_6}$, 13.880 eV; (b_{11}) $B_7N_{6\_7}$, 14.183 eV; (b_{12}) $B_7N_{6\_8}$, 14.248 eV; (b_{13}) $B_7N_{6\text{-}ch\_5}$, 14.564 eV; (b_{14}) $B_7N_{6\text{-}r\_1}$, 15.532 eV. “ch” and “r” in $B_nN_{(n-1)\text{-}ch}$ and $B_nN_{(n-1)\text{-}r}$ stand for chain and ring, respectively. The same-sized clusters are arranged in ascending order of the values of their formation energies.

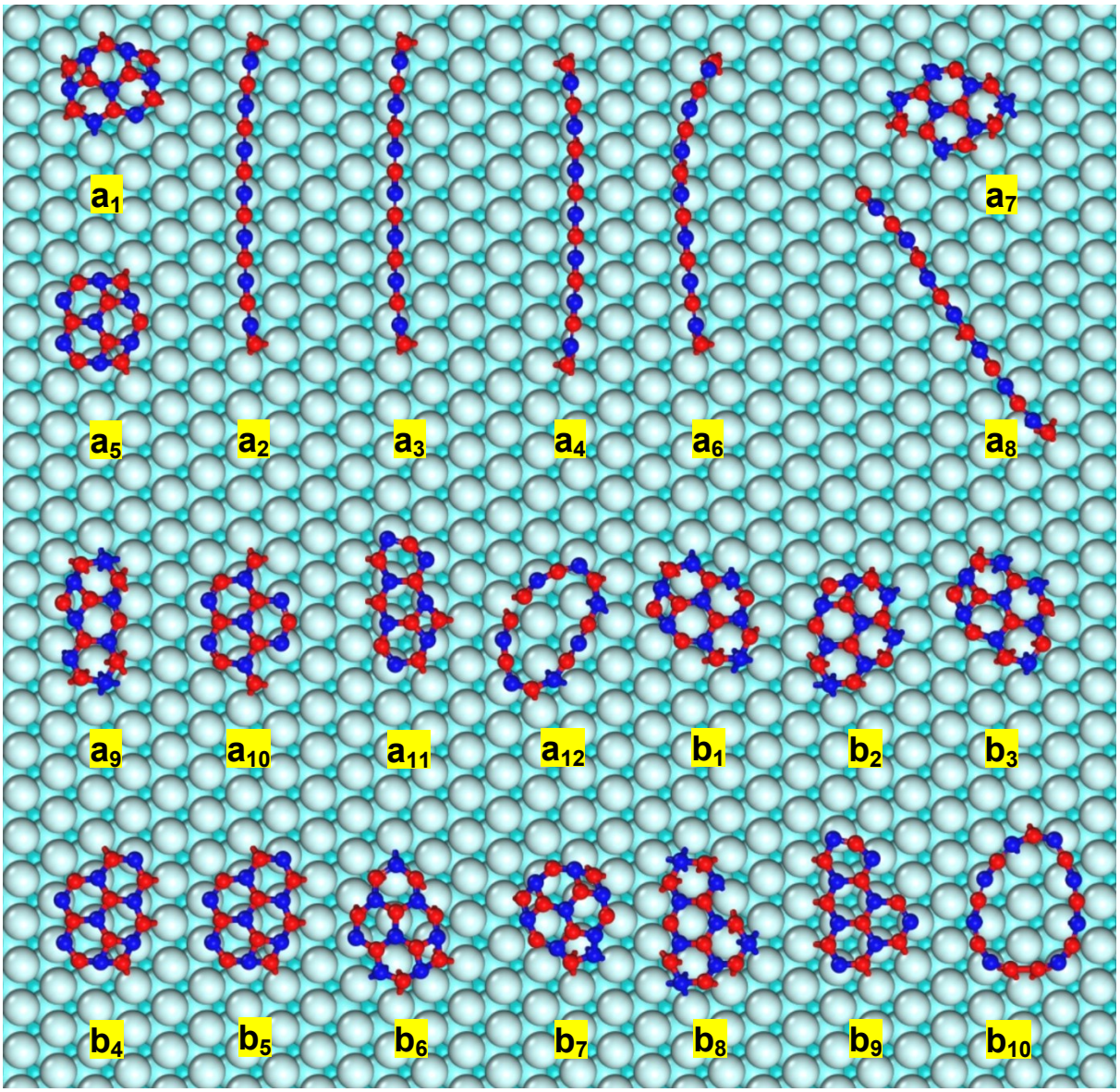

Fig. S9 Structures and formation energies of medium-sized B_nN_{n-1} ($n = 8, 9$) clusters on a Cu (111) surface. (a_1) $B_8N_{7\_1}$, 12.992 eV; (a_2) $B_8N_{7\text{-}ch\_1}$, 15.256 eV; (a_3) $B_8N_{7\text{-}ch\_2}$, 15.262 eV; (a_4) $B_8N_{7\text{-}ch\_3}$, 15.264 eV; (a_5) $B_8N_{7\_2}$, 15.449 eV; (a_6) $B_8N_{7\text{-}ch\_4}$, 15.466 eV; (a_7) $B_8N_{7\_3}$, 15.791 eV; (a_8) $B_8N_{7\text{-}ch\_5}$, 16.203 eV; (a_9) $B_8N_{7\_4}$, 16.460 eV; (a_{10}) $B_8N_{7\_5}$, 16.698 eV; (a_{11}) $B_8N_{7\_6}$, 16.891 eV; (a_{12}) $B_8N_{7\text{-}r\_1}$, 18.535 eV; (b_1) $B_9N_{8\_1}$, 14.138 eV; (b_2) $B_9N_{8\_2}$, 14.180 eV; (b_3) $B_9N_{8\_3}$, 14.276 eV; (b_4) $B_9N_{8\_4}$, 14.411 eV; (b_5) $B_9N_{8\_5}$, 14.413 eV; (b_6) $B_9N_{8\_6}$, 14.512 eV; (b_7) $B_9N_{8\_7}$, 15.392 eV; (b_8) $B_9N_{8\_8}$, 15.453 eV; (b_9) $B_9N_{8\_9}$, 15.897 eV; (b_{10}) $B_9N_{8\text{-}r\_1}$, 17.465 eV. “ch” and “r” in $B_nN_{(n\text{-}1)\text{-}ch}$ and $B_nN_{(n\text{-}1)\text{-}r}$ stand for chain and ring, respectively. The same-sized clusters are arranged in ascending order of the values of their formation energies.

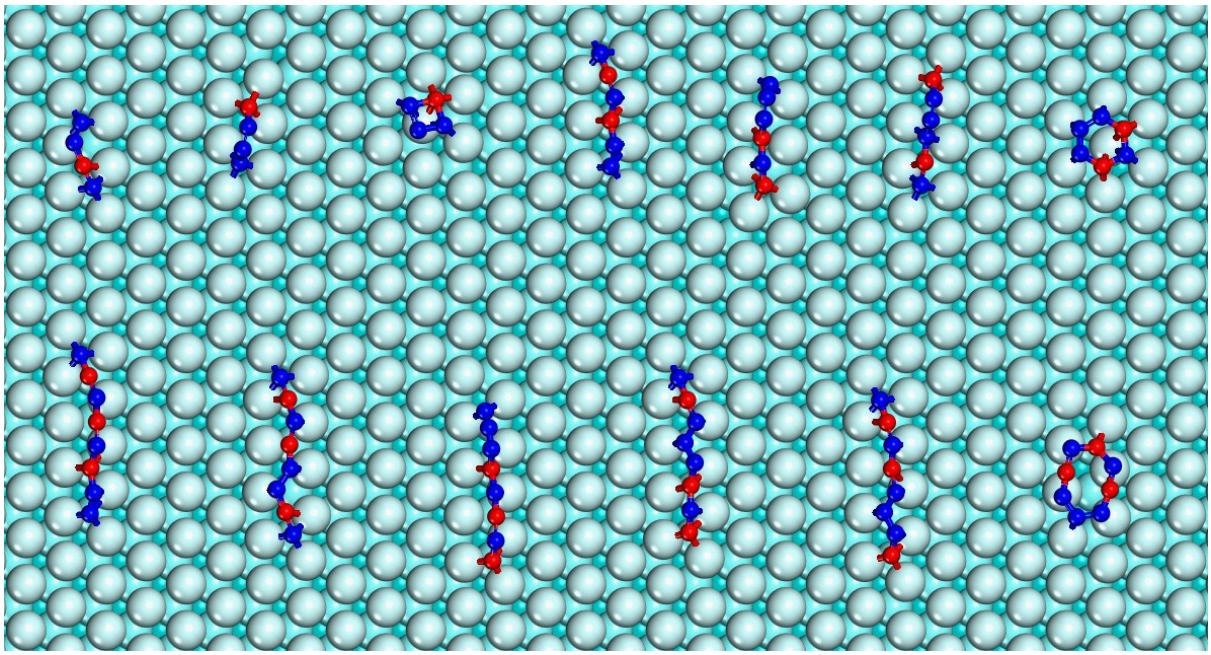

Fig. S11 Structures and formation energies of some chains and rings of $B_{n-2}N_n$ (n=3,4,5) on a Cu (111) surface. (a_1) $B_1N_{3\text{-ch\_1}}$, 2.850 eV; (a_2) $B_1N_{3\text{-ch\_2}}$, 4.061 eV; (a_3) $B_1N_{3\text{-r}}$, 4.838 eV; (b_1) $B_2N_{4\text{-ch\_1}}$, 3.566 eV; (b_2) $B_2N_{4\text{-ch\_2}}$, 6.245 eV; (b_3) $B_2N_{4\text{-ch\_3}}$, 6.326 eV; (b_4) $B_2N_{4\text{-r}}$, 5.740 eV; (c_1) $B_3N_{5\text{-ch\_1}}$, 5.035 eV; (c_2) $B_3N_{5\text{-ch\_2}}$, 5.269 eV; (c_3) $B_3N_{5\text{-ch\_3}}$, 6.688 eV; (c_4) $B_3N_{5\text{-ch\_4}}$, 6.787 eV; (c_5) $B_3N_{5\text{-ch\_5}}$, 6.800 eV; (c_6) $B_3N_{5\text{-r}}$, 9.196 eV. Obviously, as (m-n) increases, more N-N bonds appear in chains and rings of B_nN_m. The more the number of the N-N bonds, the more unstable the h-BN clusters containing them.

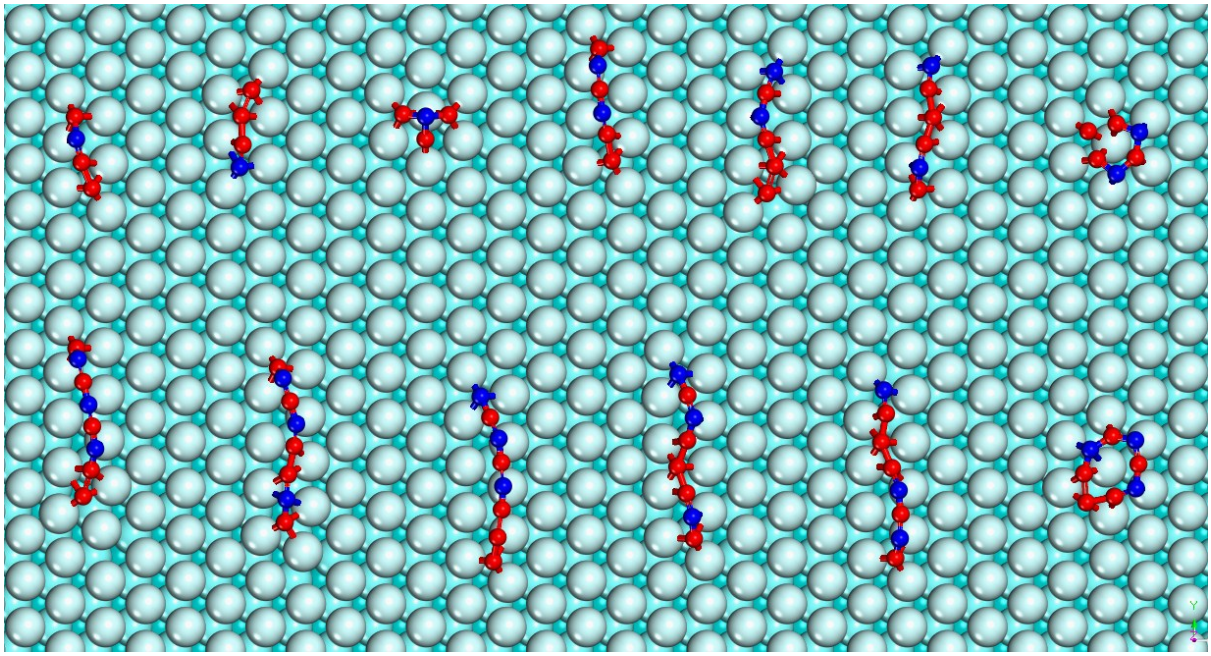

Fig. S12 Structures and formation energies of some chains and rings of B_nN_{n-2} (n=3,4,5) on a Cu (111) surface. (a_1) $B_3N_{1\text{-ch\_1}}$, 9.754 eV; (a_2) $B_3N_{1\text{-ch\_2}}$, 10.278 eV; (a_3) $B_3N_{1\text{-r}}$, 10.502 eV; (b_1) $B_4N_{2\text{-ch\_1}}$, 10.547 eV; (b_2) $B_4N_{2\text{-ch\_2}}$, 12.222 eV; (b_3) $B_4N_{2\text{-ch\_3}}$, 12.186 eV; (b_4) $B_4N_{2\text{-r}}$, 12.422 eV; (c_1) $B_5N_{3\text{-ch\_1}}$, 12.203 eV; (c_2) $B_5N_{3\text{-ch\_2}}$, 12.276 eV; (c_3) $B_5N_{3\text{-ch\_3}}$, 13.261 eV; (c_4) $B_5N_{3\text{-ch\_4}}$, 12.114 eV; (c_5) $B_5N_{3\text{-ch\_5}}$, 12.382 eV; (c_6) $B_5N_{3\text{-r}}$, 14.016 eV. Obviously, as (n-m) increases, more B-B bonds appear in chains and rings of B_nN_m. The more the number of the B-B bonds, the more unstable the h-BN clusters containing them.

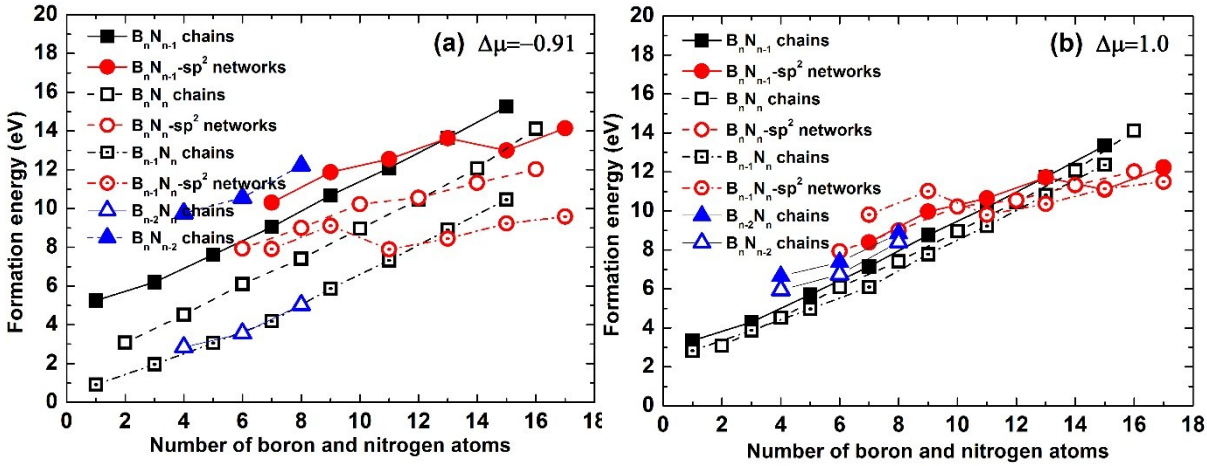

Fig. S13 Formation energies of chains and most-stable sp^2 networks of $B_{n-1}N_n$, B_nN_n, B_nN_{n-1}, $B_{n-2}N_n$ and B_nN_{n-2} on a Cu(111) surface versus the number of atoms in h-BN clusters with chemical potential differences Δμ= (a) -0.91, and (b) 1.0. Blue triangles present that considering B_nN_m chains with more N-N or B-B bonds is not helpful to understand growth of h-BN clusters on a Cu(111) surface.

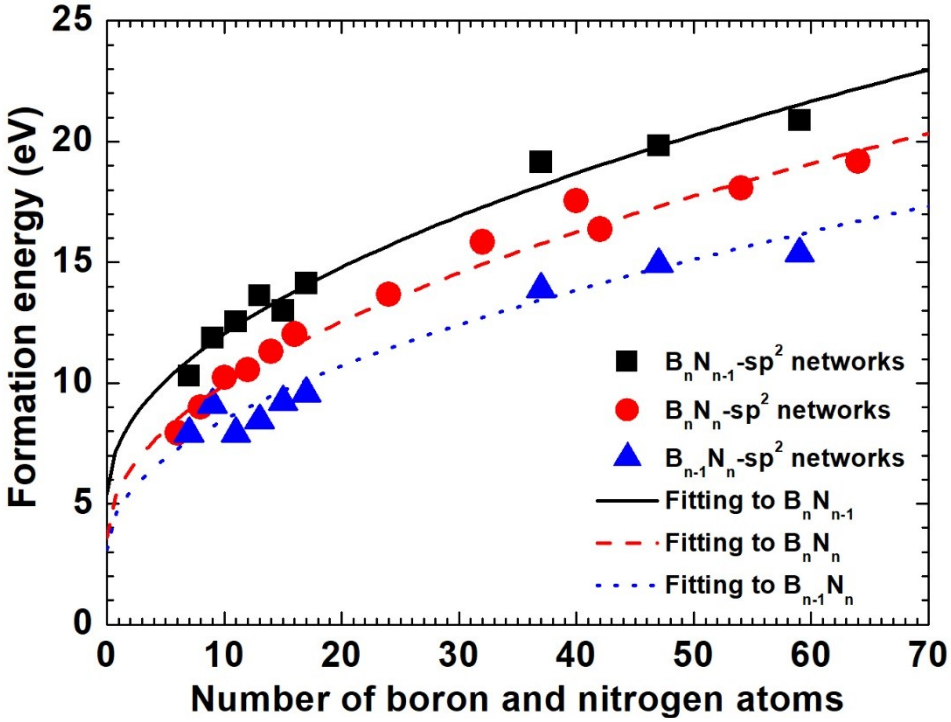

Fig. S14 Formation energies of lowest-energy sp^2 networks of B_nN_m (m=n-1, n, n+1) on a Cu (111) surface versus the number of atoms in h-BN clusters. Fitting curves are obtained by Eq. (5). The values of fitting parameters are presented in Table 1. The fitting curves for sp^2-networks clusters in Fig. 3, 6 and 9 are the same as the corresponding one in this figure, respectively.