Electronic Supplementary Information for

Metal-free spin and spin-gapless semiconducting heterobilayers: Monolayer boron carbonitrides on hexagonal boron nitride

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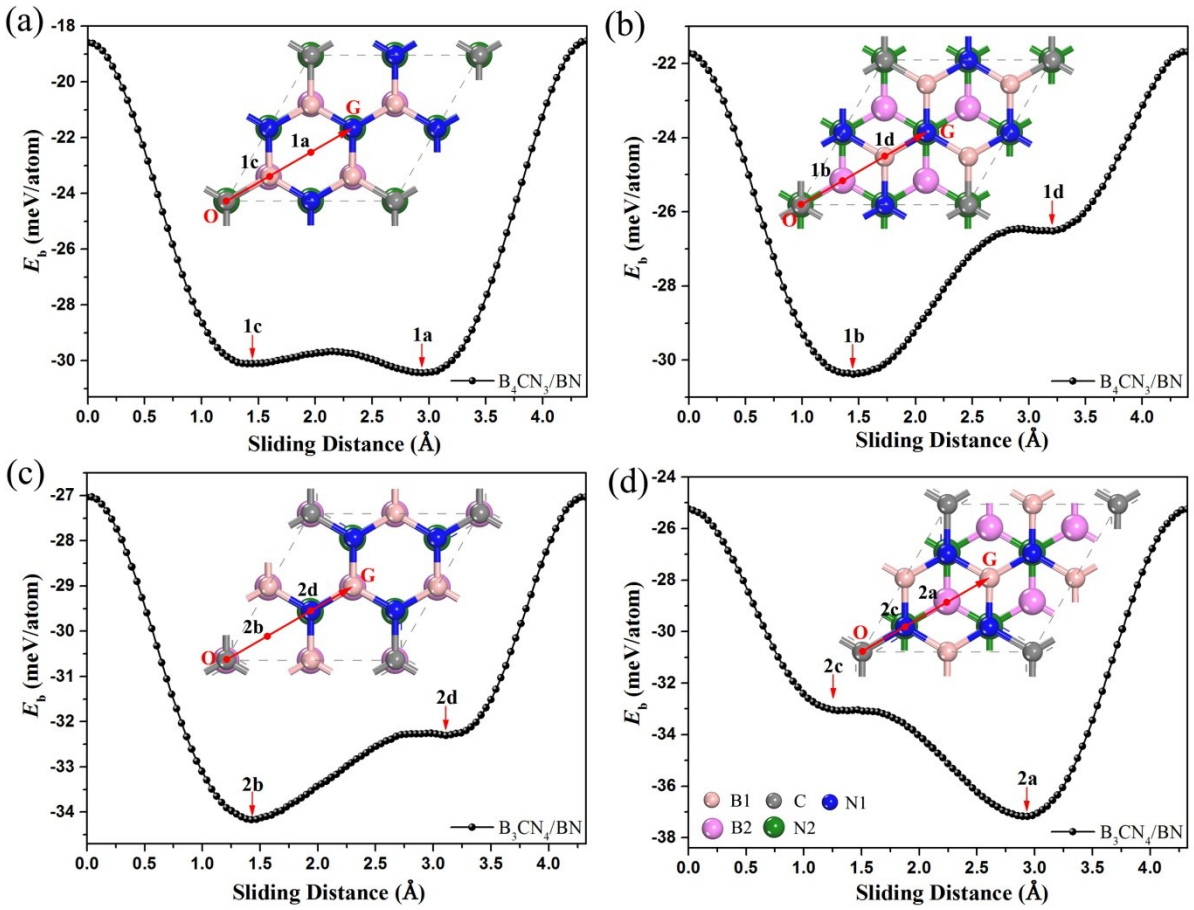

Fig. S1 The binding energies of B_4CN_3 and B_3CN_4 sliding on *h*-BN monolayer along the O–G direction. Insets are the top views of corresponding initial configurations. (a) AA and (b) AB′ stacking modes of B_4CN_3 on *h*-BN monolayer; (c) AA and (d) AB′ stacking modes of B_3CN_4 on *h*-BN monolayer. The red lines with arrows indicate the high symmetry sliding path O–G. 1a–1d and 2a–2d in the path correspond to the stacking modes shown in Figs. 1 and 2. The interlayer distance is fixed to 3.10 Å.

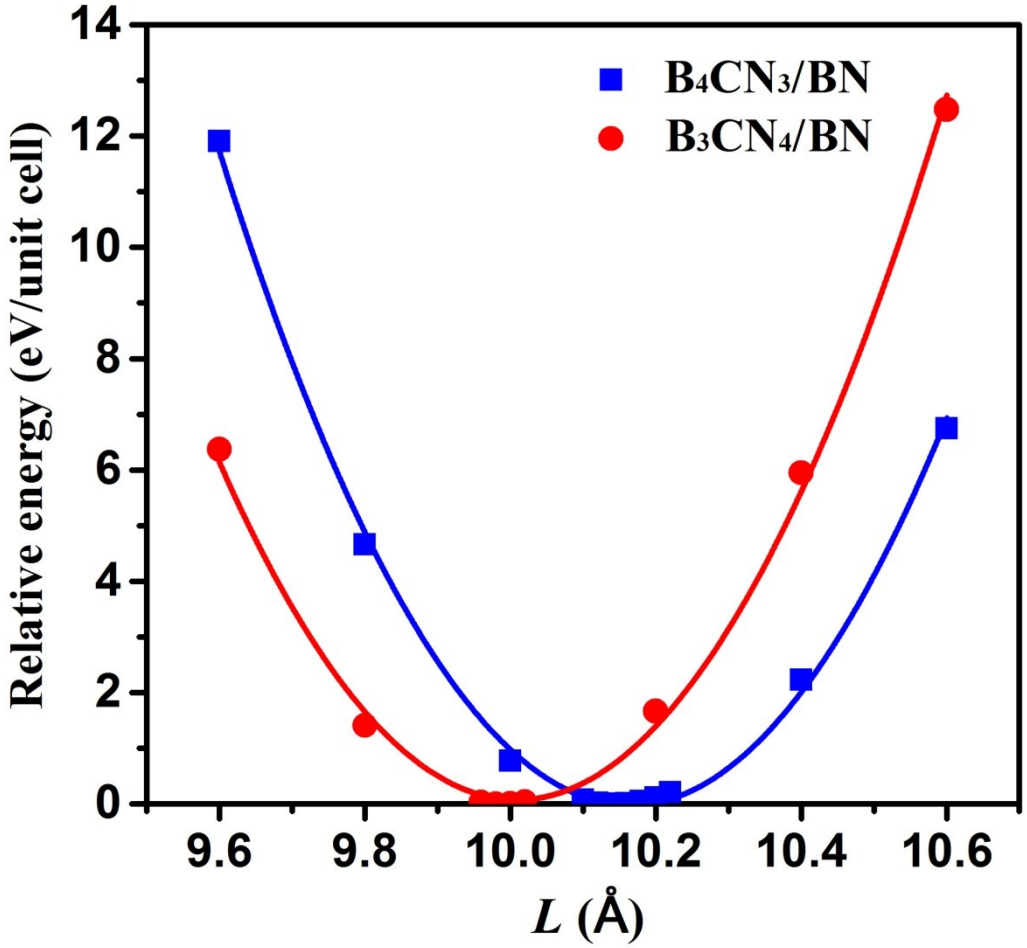

Fig. S2 The calculated relative lattice energies as a function of lattice constants of B_4CN_3/BN (blue line with squares) and B_3CN_4/BN (red line with circles) structures.

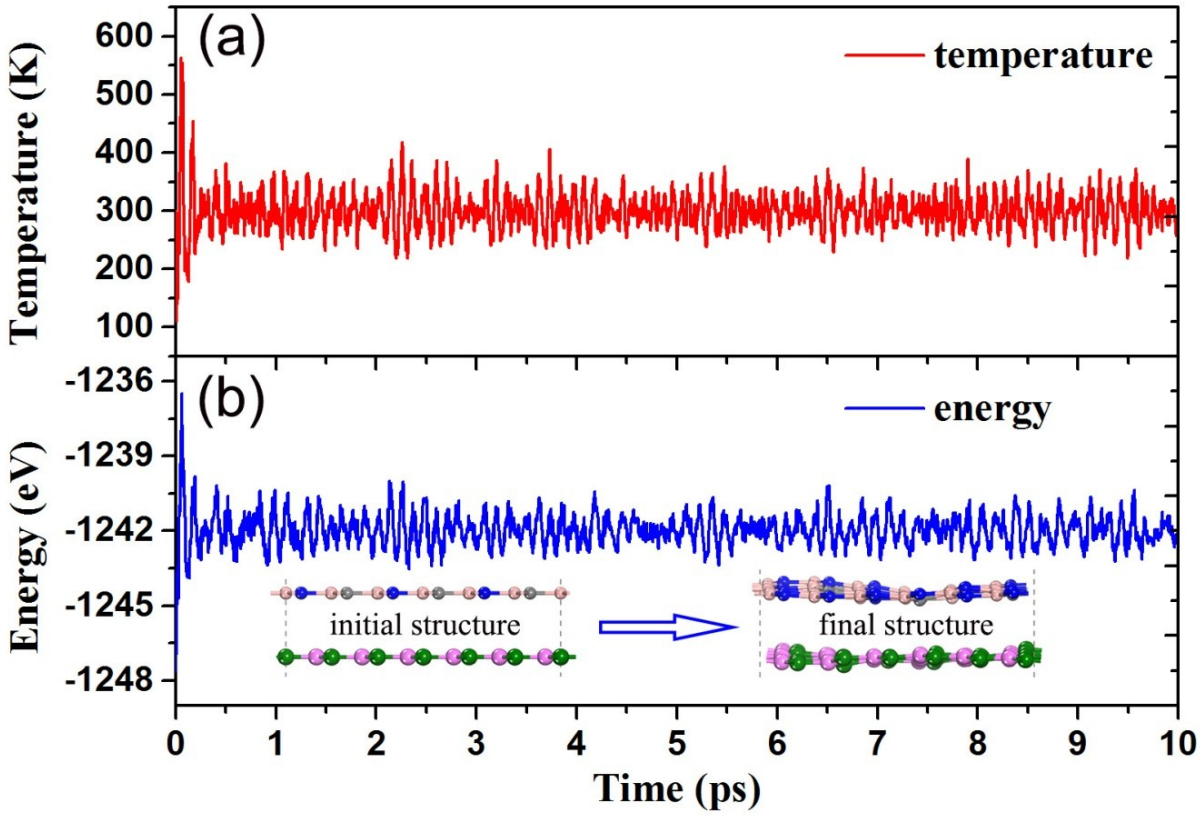

Fig. S3 The fluctuations of (a) temperature and (b) energy with respect to MD steps at 300K for B_4CN_3/BN system.

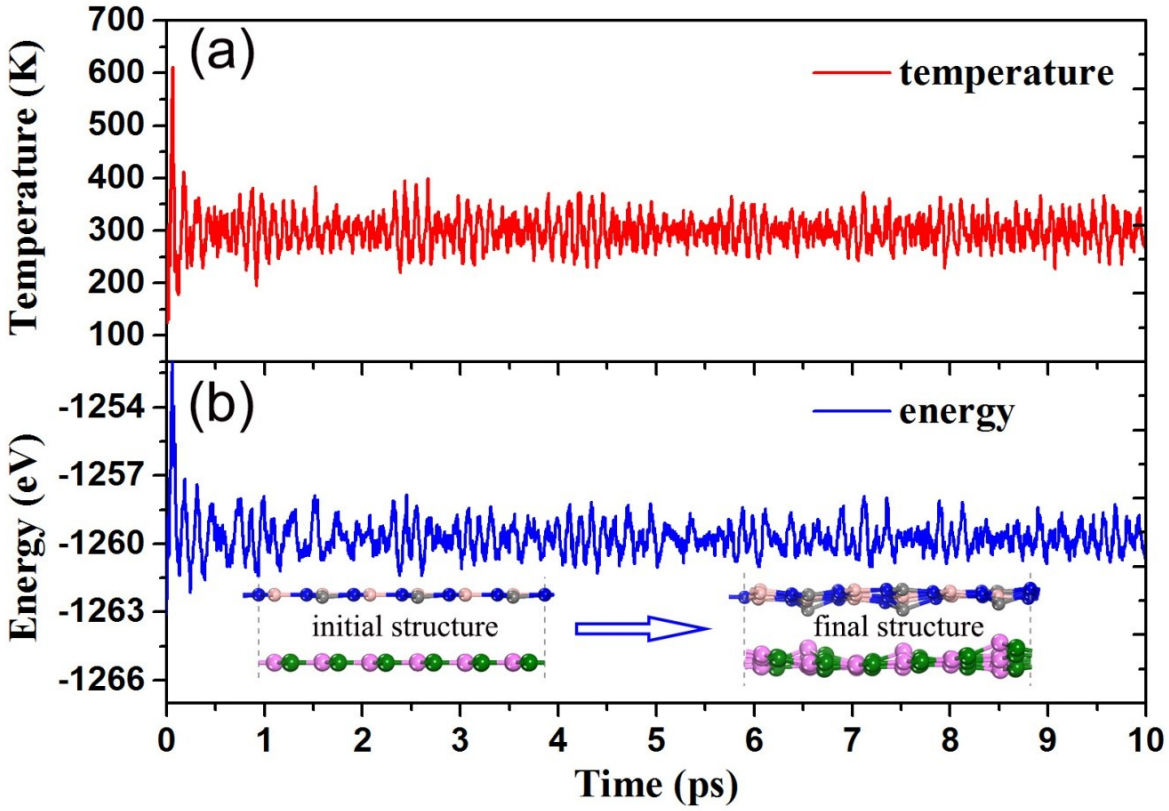

Fig. S4 The fluctuations of (a) temperature and (b) energy with respect to MD steps at 300K for B_3CN_4/BN system.

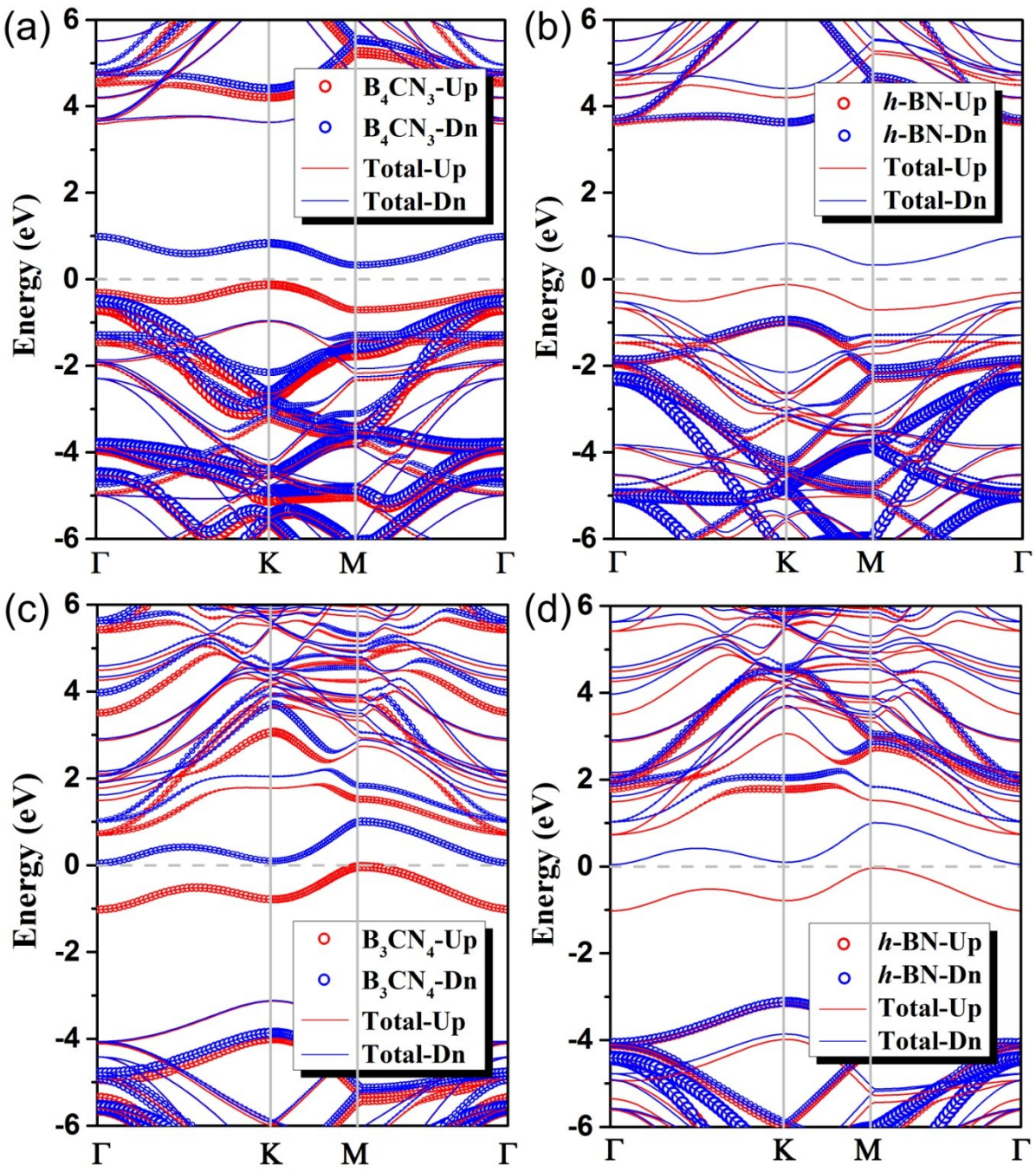

Fig. S5 Spin-resolved total and projected band structures of B_4CN_3/BN and B_3CN_4/BN. The red and blue lines in each figure indicate the total spin-up and spin-down bands of the corresponding systems, respectively. (a) The red and blue circles denote the projected spin-up and spin-down bands of B_4CN_3 layer in B_4CN_3/BN bilayer. (b) The red and blue circles denote the projected spin-up and spin-down bands of *h*-BN layer in B_4CN_3/BN bilayer. (c) The red and blue circles denote the projected spin-up and spin-down bands of B_3CN_4 layer in B_3CN_4/BN bilayer. (d) The red and blue circles denote the projected spin-up and spin-down bands of *h*-BN layer in B_3CN_4/BN bilayer. The Fermi energy is set to zero and marked by grey dashed line.

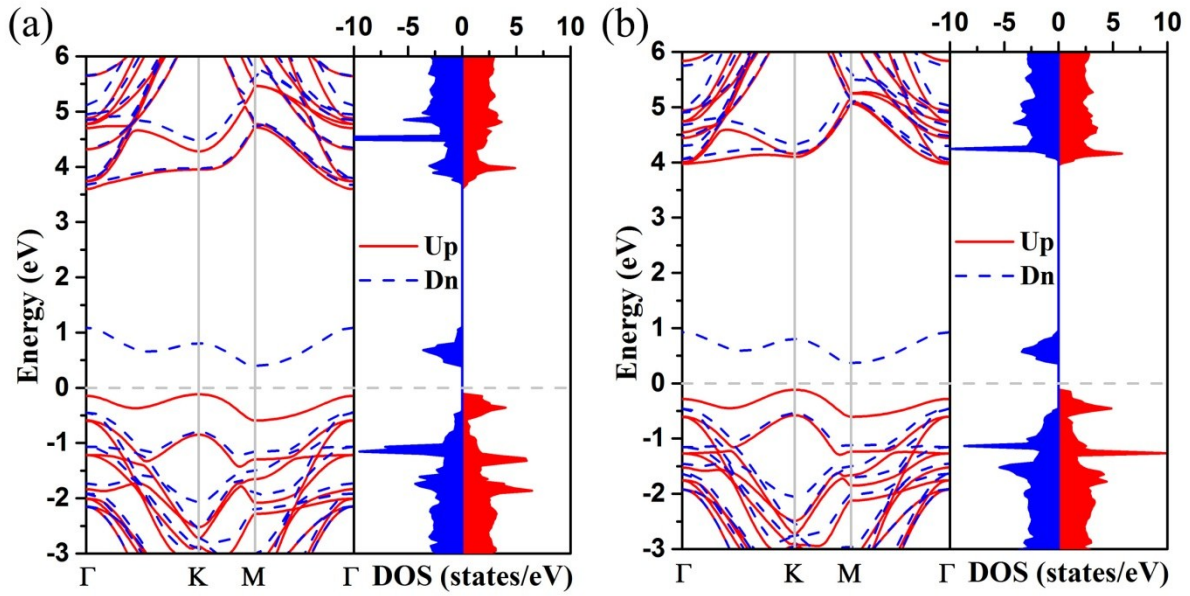

Fig. S6 Band structures (left) and total DOS (right) of (a) 1b and (b) 1c configurations. The Fermi energy is set to zero and marked by grey dashed line.

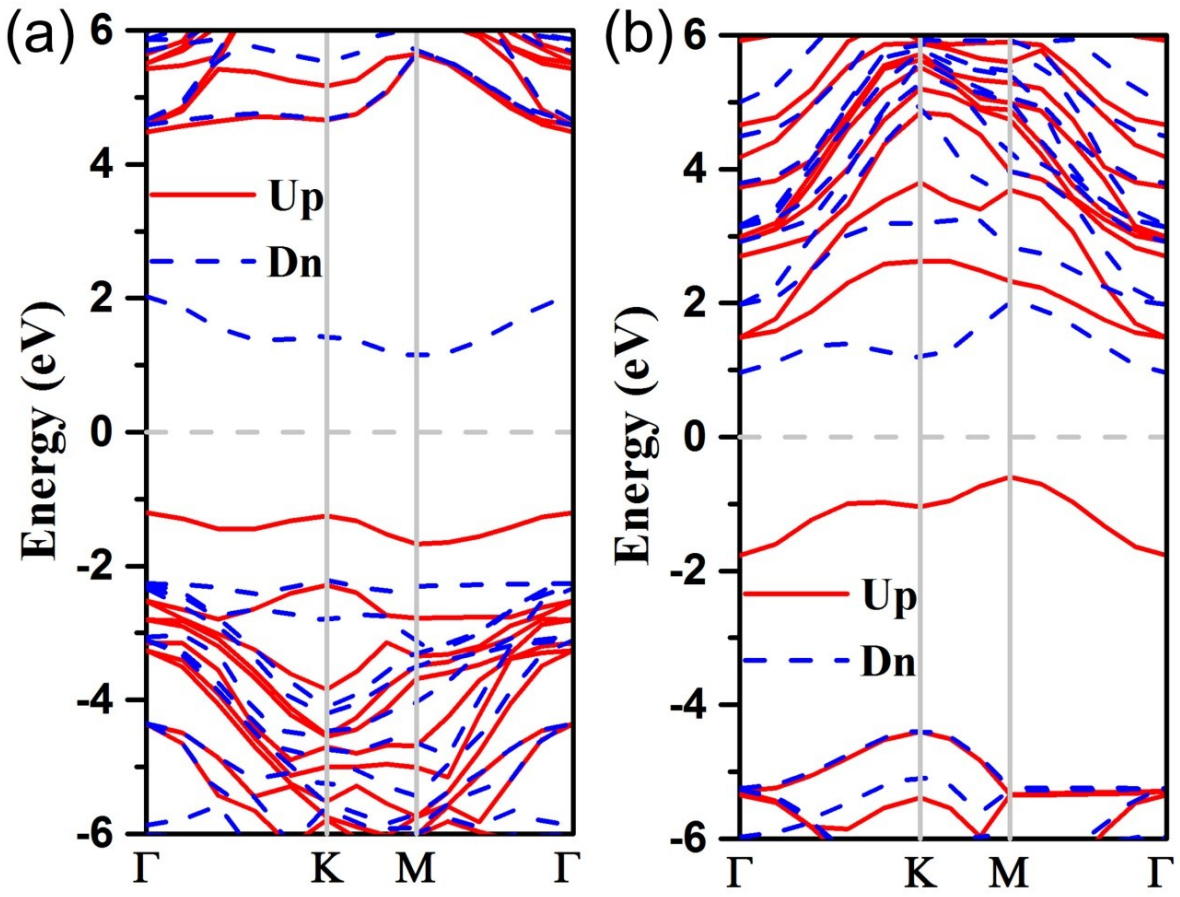

Fig. S7 Spin-resolved band structures within hybrid HSE06 functional for the most stable structures of (a) B_4CN_3/BN and (b) B_3CN_4/BN primitive cell. The Fermi energy is set to zero and marked by grey dashed line.

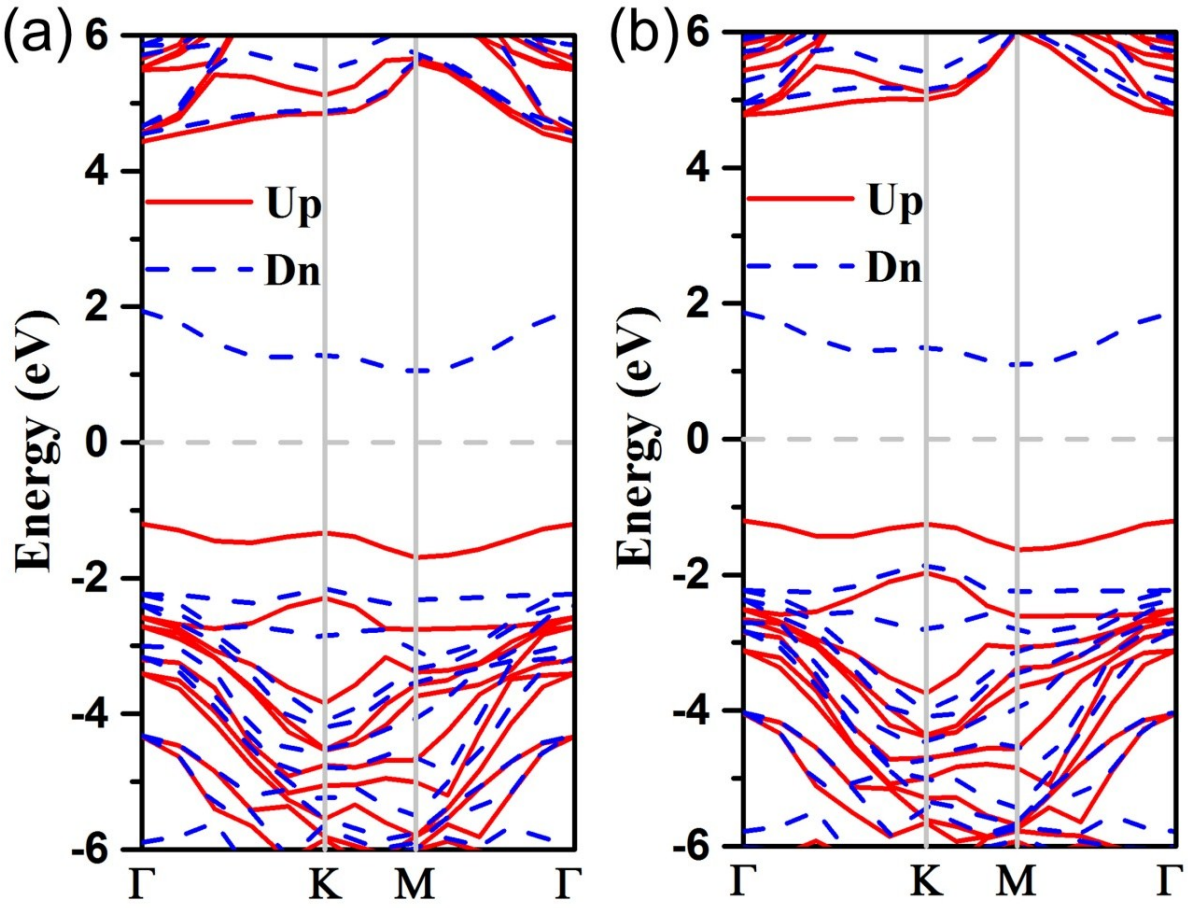

Fig. S8 Spin-resolved band structures within hybrid HSE06 functional for (a) 1b and (b) 1c configurations. The Fermi energy is set to zero and marked by grey dashed line.

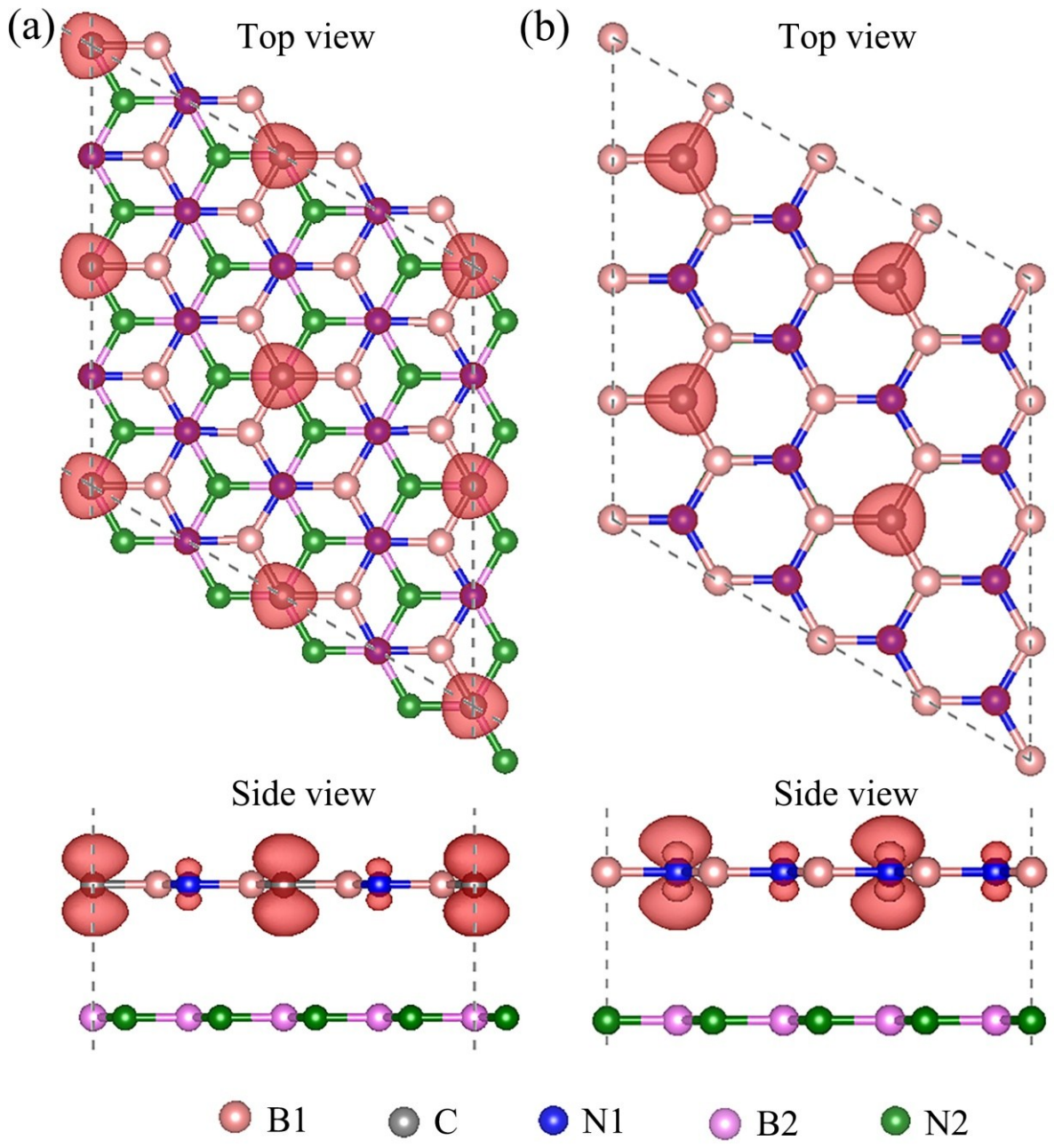

Fig. S9 Calculated PDOS of (a) B1, C and N1 atoms in B_4CN_3 layer, (b) B2 and N2 atoms in *h*-BN layer of 1b configuration, (c) B1, C and N1 atoms in B_3CN_4 layer, and (d) B2 and N2 atoms in *h*-BN layer of 1c configuration. The Fermi energy is set to zero and marked by dashed line.

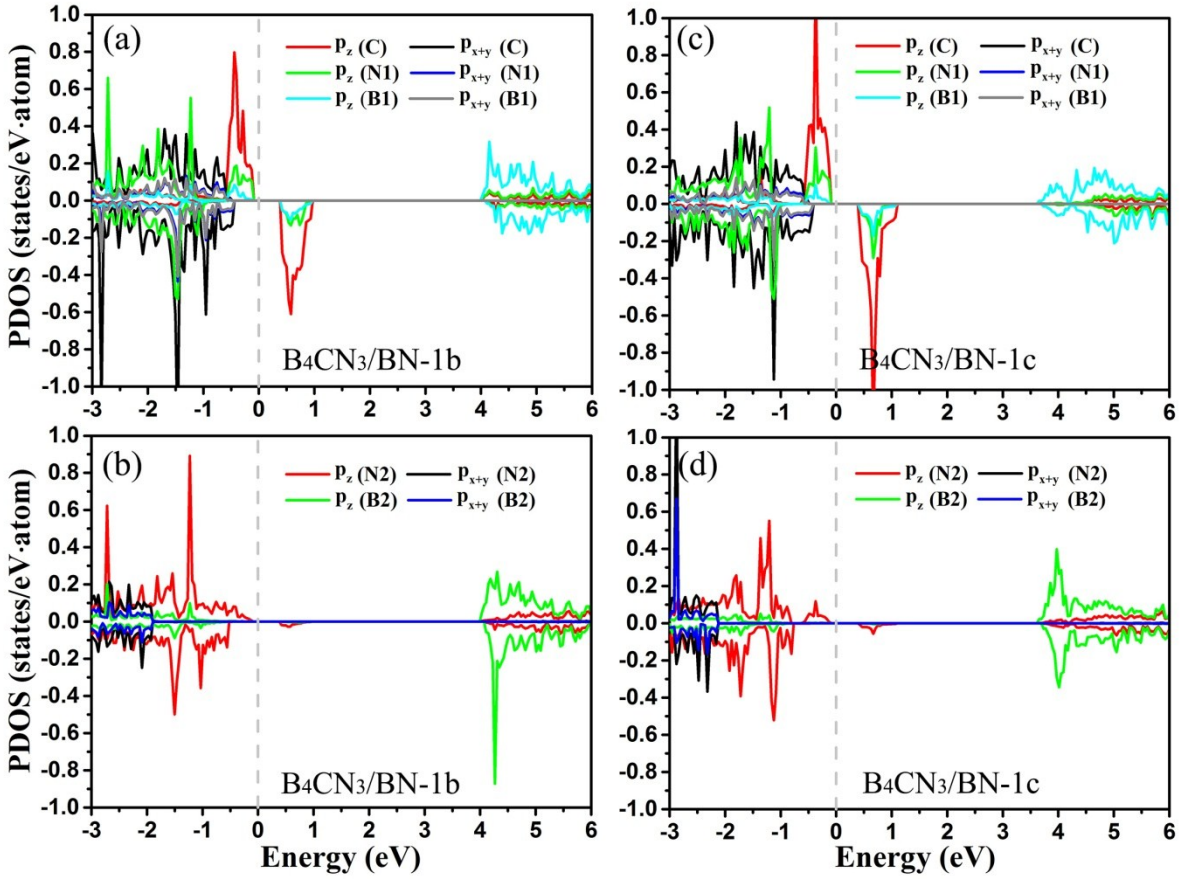

Fig. S10 Schematic illustrations of top and side views for spin density distributions ($\Delta\rho = \rho_{\uparrow} - \rho_{\downarrow}$) of (a) 1b and (b) 1c configurations. The isosurface value of spin-polarized electron density is set to be 0.06 e/Å^3. Red color indicates the positive (spin-up) value.

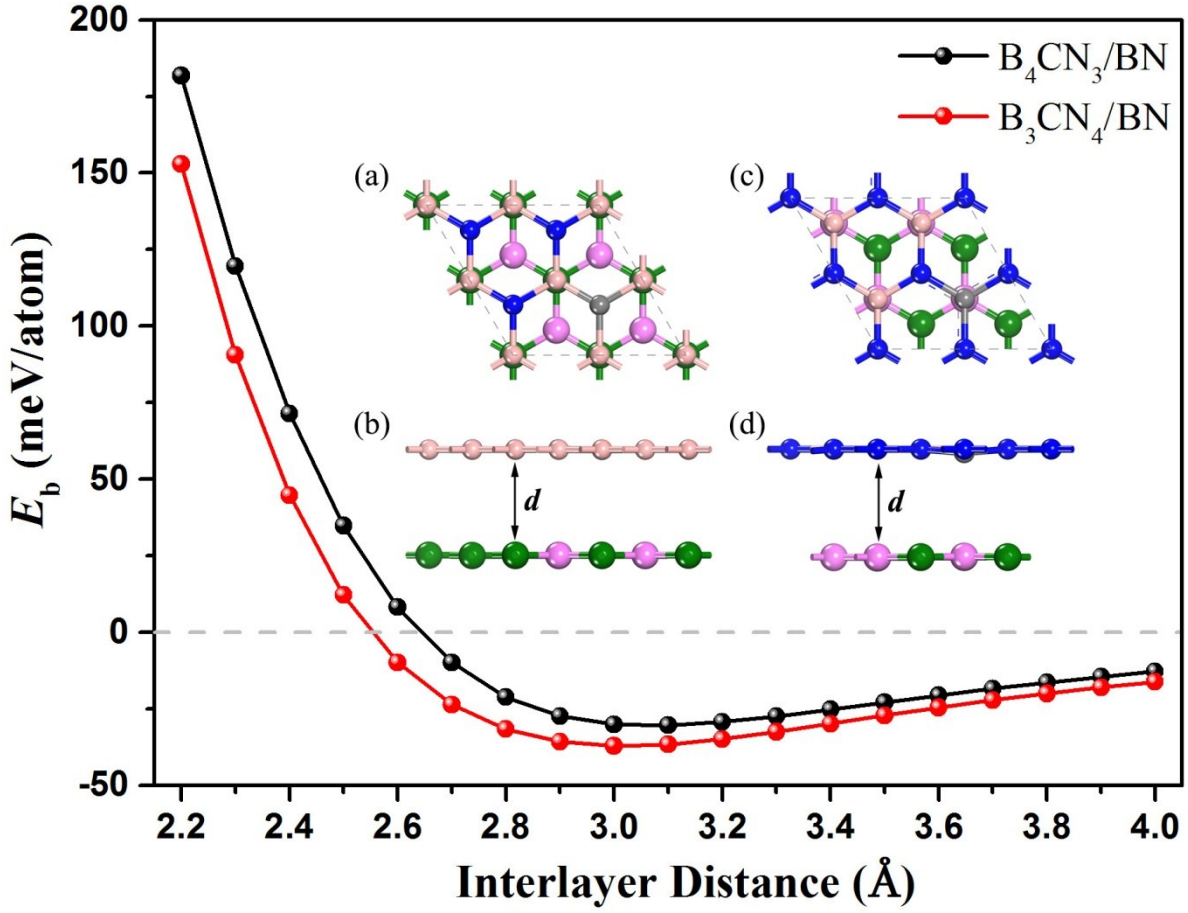

Fig. S11 Binding energies per atom of the B_4CN_3/BN and B_3CN_4/BN bilayers with the most stable structures as a function of interlayer distances. (a), (c) top and (b), (d) side views for the primitive cells of B_4CN_3/BN and B_3CN_4/BN bilayers, respectively.

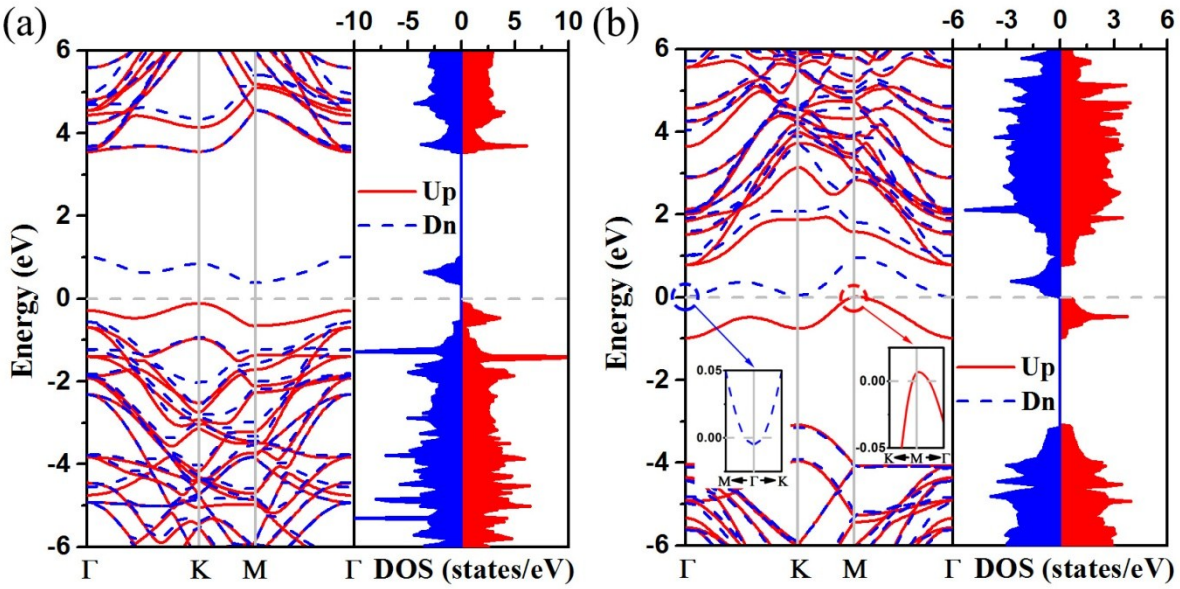

Fig. S12 Spin-resolved band structures (left) and total DOSs (right) of the most stable structures of (a) B_4CN_3/BN and (b) B_3CN_4/BN primitive cells with the same lattice constants as B_4CN_3 and B_3CN_4 monolayers, respectively. The Fermi energy is set to zero and marked by grey dashed line.

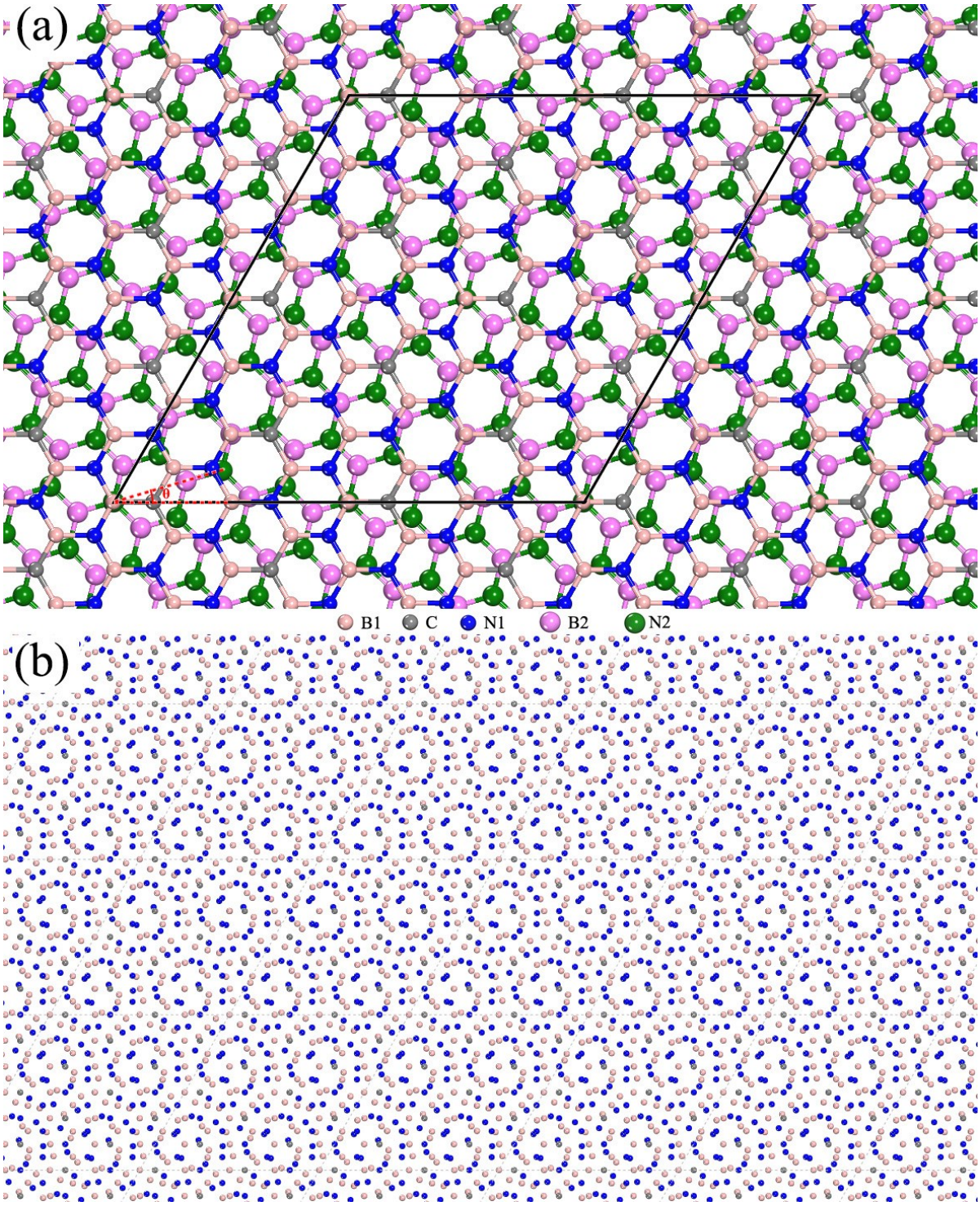

Fig. S13 (a) Top view of B_4CN_3/BN superstructure. The parameters of *n*, *m*, *p*, *q*, θ and N of this superstructure is equal to 3, 1, 2, 2, 16.10° and $N = 200$. (b) The Schematic illustration of the Moiré pattern on the B_4CN_3/BN bilayer.

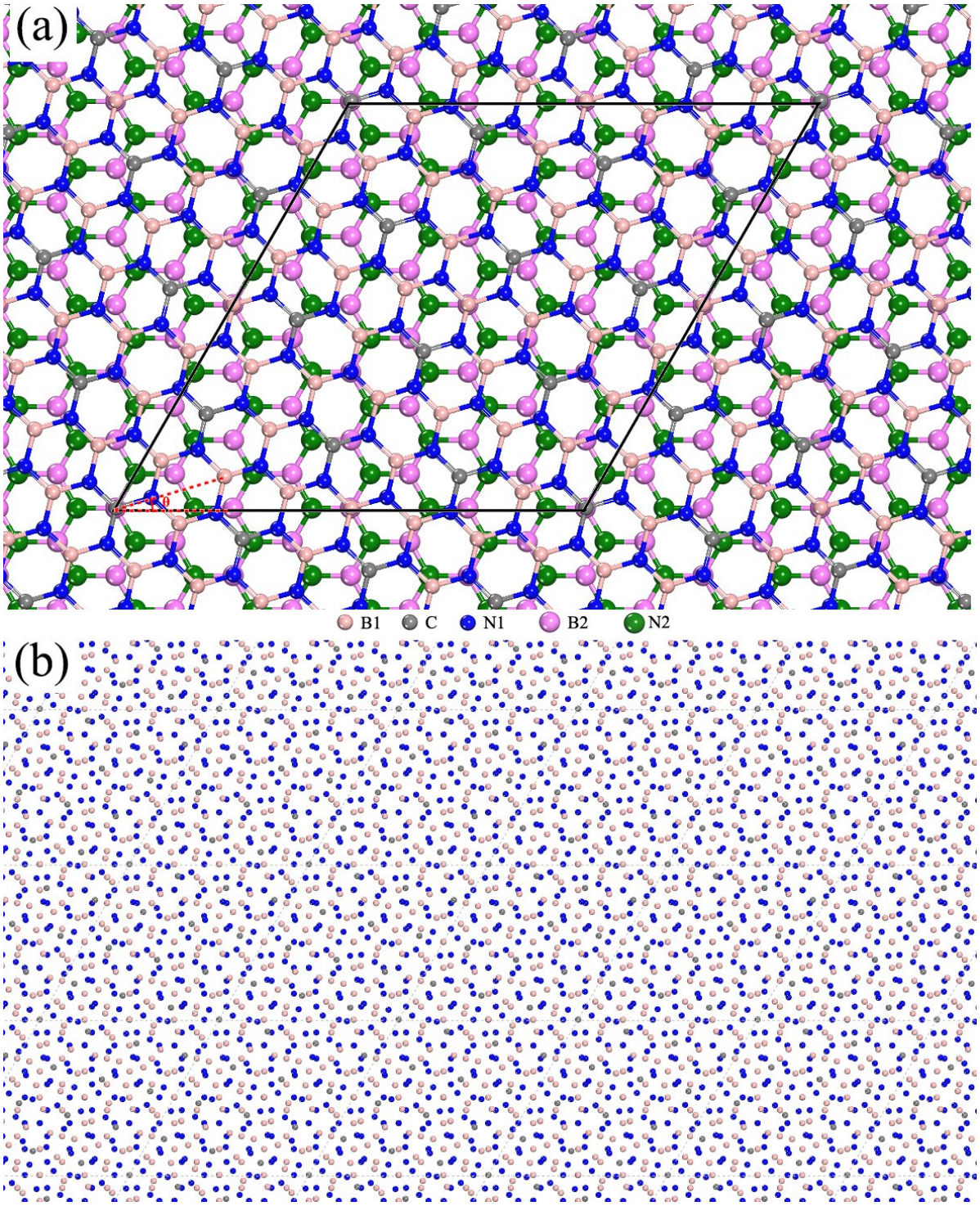

Fig. S14 (a) Top view of B_3CN_4/BN superstructure. The parameters of *n*, *m*, *p*, *q*, θ and N of this superstructure is equal to 2, 2, 3, 1, 16.10° and $N = 200$. (b) The Schematic illustration of the Moiré pattern on the B_3CN_4/BN bilayer.