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Armchair shaped polymeric nitrogen N_8 chains confined in h-BN matrix at ambient conditions: stability and vibration analysis

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As shown in Fig.S1, in order to evaluate the energetic stability of armchair form relative to the zigzag N_8 confined inside h-BN matrix, we performed the geometry optimization for both the zigzag and armchair N_8@h-BN structures. After the relaxation, we found that the zigzag N_8 chain relaxed into the twisty armchair N_8 chain, indicating that the confined zigzag N_8 chain is unstable. For comparison, we found that the armchair N_8@h-BN structure (c) is more stable than the twisty armchair N_8@h-BN structure (b), due to the lower energy of the former. Thus, the armchair N_8@h-BN structure is more stable than the zigzag N_8@h-BN structure.

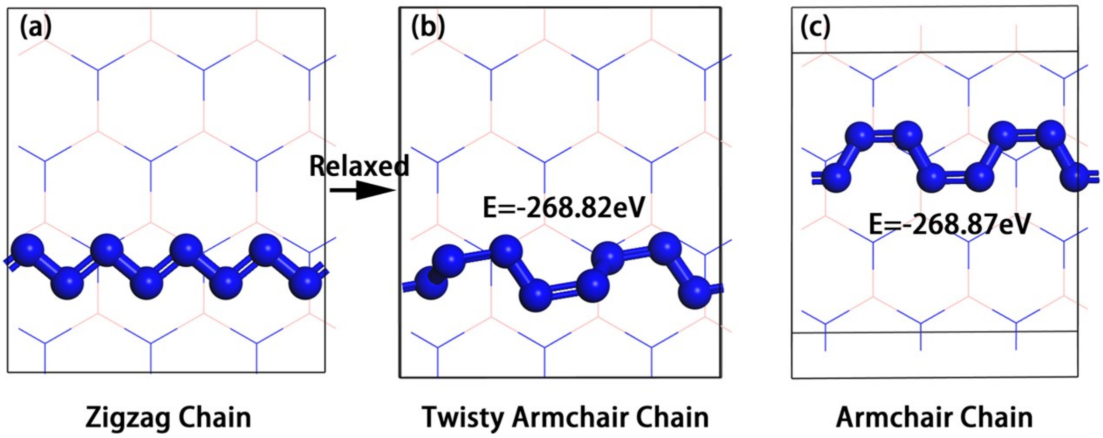

Fig.S1. (a) Unit cell of zigzag N_8@h-BN crystal structure. (b) Unit cell of twisty armchair N_8@h-BN crystal structure after the relaxation. (c) Unit cell of armchair N_8@h-BN crystal structure.

In order to obtain the optimal arrangement of N_8@h-BN structure, we construct the 1×2×2 supercell structure of h-BN matrix and put the single N_8 molecule in the different directions. As shown in Fig.S2 (a), the N_8 molecule of figures 1, 2, and 3 laying on the *oxy* plane with its stretching direction point to the *oz*, *oyz* and *oy* directions, respectively. For the figures 4 and 5, the titled (45°) and perpendicular directions are selected with the stretching direction of N_8 molecule point to the *oz* direction (Shown in *oxy* plane). As the built five typical models, the DFT total energy calculation is performed by self-consistent calculation method. As shown in Fig.S2 (b), the energy differences (ΔE) of different molecular orientation of N_8 molecule are presented. It can be seen that the N_8 molecule in *oz* direction is more suitable than that in *oyz* and *oy* directions [$(\Delta E_1<\Delta E_5<\Delta E_4) <\Delta E_2<\Delta E_3$], while the laying N_8 molecule is more suitable than the tilted and standing N_8 molecule ($\Delta E_1<\Delta E_5<\Delta E_4$). Thus, the optimal arrangement of N_8@h-BN structure is the laying N_8 molecule in the *oz* direction.

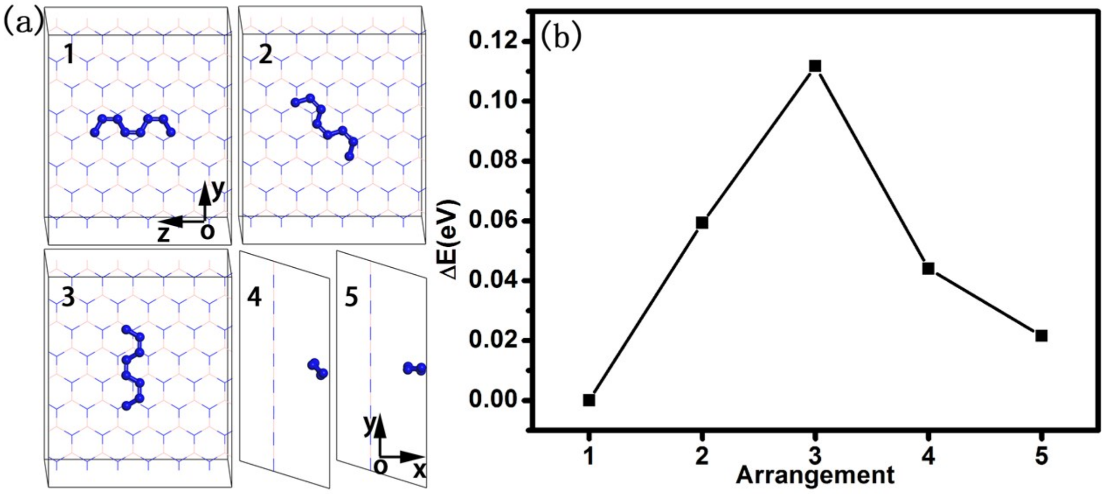

Fig.S2. (a) Images of five typical arrangements of N_8 molecule between h-BN matrix are presented. (b) The energy difference (ΔE) of different molecular arrangements.

For the N_8@h-BN periodic structure, the N_8 composes of two unit cells of nitrogen chain (4 atoms); while the h-BN composes of 1×4×3 unit cell structure. The N_8 lying on the *oc* direction. The details of the lattice constants are as follows.

For h-BN: *oa*=6.661 Å, *ob*=*oc*=2.504 Å.

For N_4: *oa*=4.635 Å, *ob*=5.165 Å, *oc*=3.927 Å.

The lattice mismatch $\delta= |(3*L_{BN}-2*L_{N4})/2*L_{N4}|=0.0435$; L refers to lattice constants *oc* (N_8 chain is in the oc direction). According to the reports, if $|\delta| < 5\%$, the lattice matches well. (A. Zur, and T. C. McGill, Journal of Applied Physics 1984, 55, 378 and He, Z., Zhang, M et.al, Journal of Nanchang University (Natural Science), 2006,vol 30). The result of lattice mismatch ensures that the system size at computationally affordable level.