Adsorption of nucleobase pairs on hexagonal boron nitride sheet: hydrogen bonding versus stacking

Supporting Information

Adsorption of single nucleobase molecules on the *h*-BN surface

Among the five nucleobase molecules, the purines, i.e., guanine and adenine all have a similar six- and a five- member ring structure. Different from the other four molecules, thymine has a methyl group which breaks the six-member ring plane of the molecule. Here, in order to discuses the H-bonded and stacked nucleobase pair adsorption systems, five single nuclebase molecule adsorption systems were constructed first. For each of the five adsorption systems, a particular nuclobase molecule was put on top of the *h*-BN surface and parallel to the surface. The initial interlayer distance between nucleobase and *h*-BN was set as 4 Å. Then, geometry optimizations on the five adsorption systems with all of the nucleobase molecules and *h*-BN being relaxed were carried out. To give a further confirmation about the optimized geometries, the potential energy surface (PES) of the five adsorption systems was also explored. Fig.S1(a) shows the interaction energies as a function of the interlayer distance for the five adsorption systems. Fig.S1(b) plots the interaction energy landscapes of adenine on the position plane in one lattice. The final stable configurations of the five adsorption systems are shown in Fig.S1(c).

According to the geometry optimization results, all the nucleobase molecule planes were nearly parallel to the *h*-BN surface except thymine which contained a methyl group leading to a 5° dip. The interplanar distances were found to be about 3.0 Å, and are presented in Table S1. As shown in Fig.S1(c), no obvious changes occurred for the structures of nucleobases and *h*-BN. The nucleobase molecules oriented on the *h*-BN with a clear AB-stacking phenomenon. A basic rule is the centre of the hexagonal ring of the nucleobases prefers to stay on top of the nitrogen atom of *h*-BN (named: $\mathrm{Top}^{\mathrm{N}}$ site). And the N atom of the hexagonal ring of nucleobase favors to stay on top of the B atom on *h*-BN surface. These stable configurations basically agreed with the main plane position of nucleobases on *h*-BN surface in the previous work which focused on the adsorption of single nucleobase molecules with an additional methyl group.[36] The interaction energies of the five adsorption systems were calculated and presented in Table S1. The range of the interaction energy changed from -1.10eV to -0.66eV. The trend of the interaction energy can be easily observed to be G>A>T>C>U.

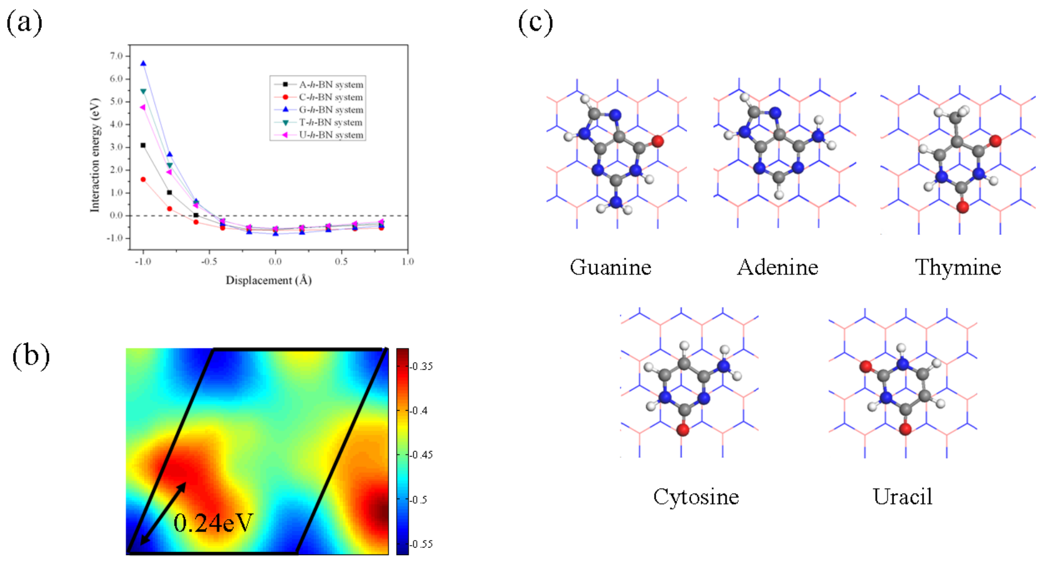

Fig.S1(a) Potential energy variation of nucleobases adsorbing on the *h*-BN surface as a function of displacement with respect to the equilibrium position obtained initially; (b) The interaction energy landscapes for adenine adsorbing on the *h*-BN surface. The highest energy difference is 0.24 eV; (c) Optimized geometries of nucleobases adsorbing on the *h*-BN surface.

Table S1 Calculated parameters of single nucleobase molecule adsorption systems including the distance between the nucleobase molecule and *h*-BN *d*; the interaction energy ΔE .

Systems	d (Å)	Interaction energy ΔE (eV)
G-*h*-BN	3.09	-1.10
A-*h*-BN	3.06	-0.87
T-*h*-BN	3.08	-0.77
C-*h*-BN	3.05	-0.75
U-*h*-BN	3.05	-0.66