Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A Boron-decorated Melon-based Carbon Nitride as a Metal-free Photocatalyst for N_2 Fixation: a DFT Study

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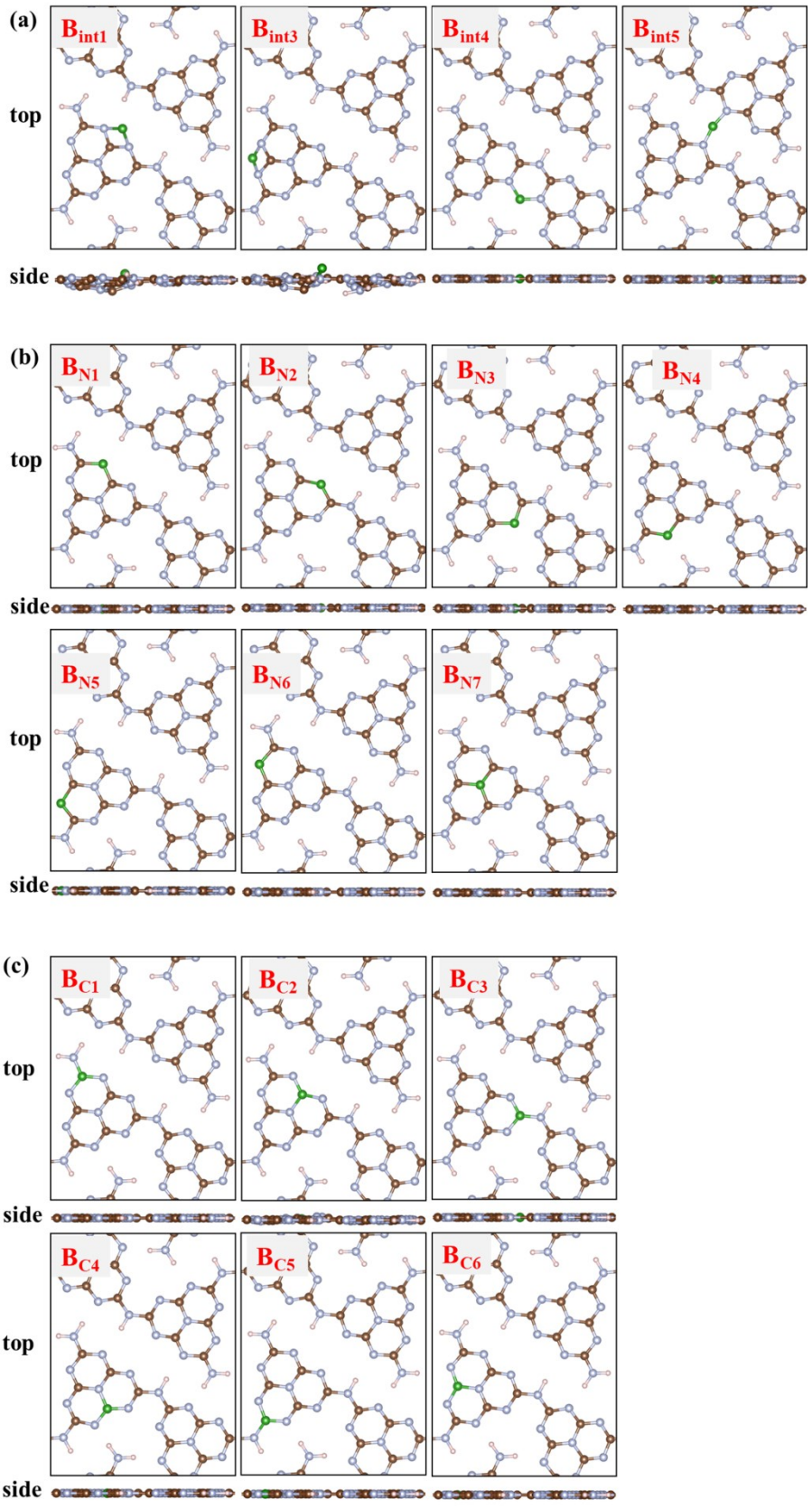

Fig. S1 The top and side views of optimized structures of B-decorated melon-based CNs with (a) B_{int}, (b) B_N, and (c) B_C configurations.

Table S1 Binding energy (E_b) and formation energies (E_{form}) of B-decorated melon-based CNs with B_{int}, B_N and B_C, in which B_{int} represents a B atom adsorption on melon-based CN, while the B_N and B_C are doping of single B atom to N and C atom respectively.

	B_{int1}	B_{int3}	B_{int4}	B_{int5}			
E_b (eV)	-1.93	-1.92	-3.42	-2.96			
	B_{N1}	B_{N2}	B_{N3}	B_{N4}	B_{N5}	B_{N6}	B_{N7}
E_{form} (eV)	1.92	1.31	0.52	2.23	0.97	2.21	1.63
	B_{C1}	B_{C2}	B_{C3}	B_{C4}	B_{C5}	B_{C6}	
E_{form} (eV)	1.62	0.96	0.70	0.74	0.83	1.04	

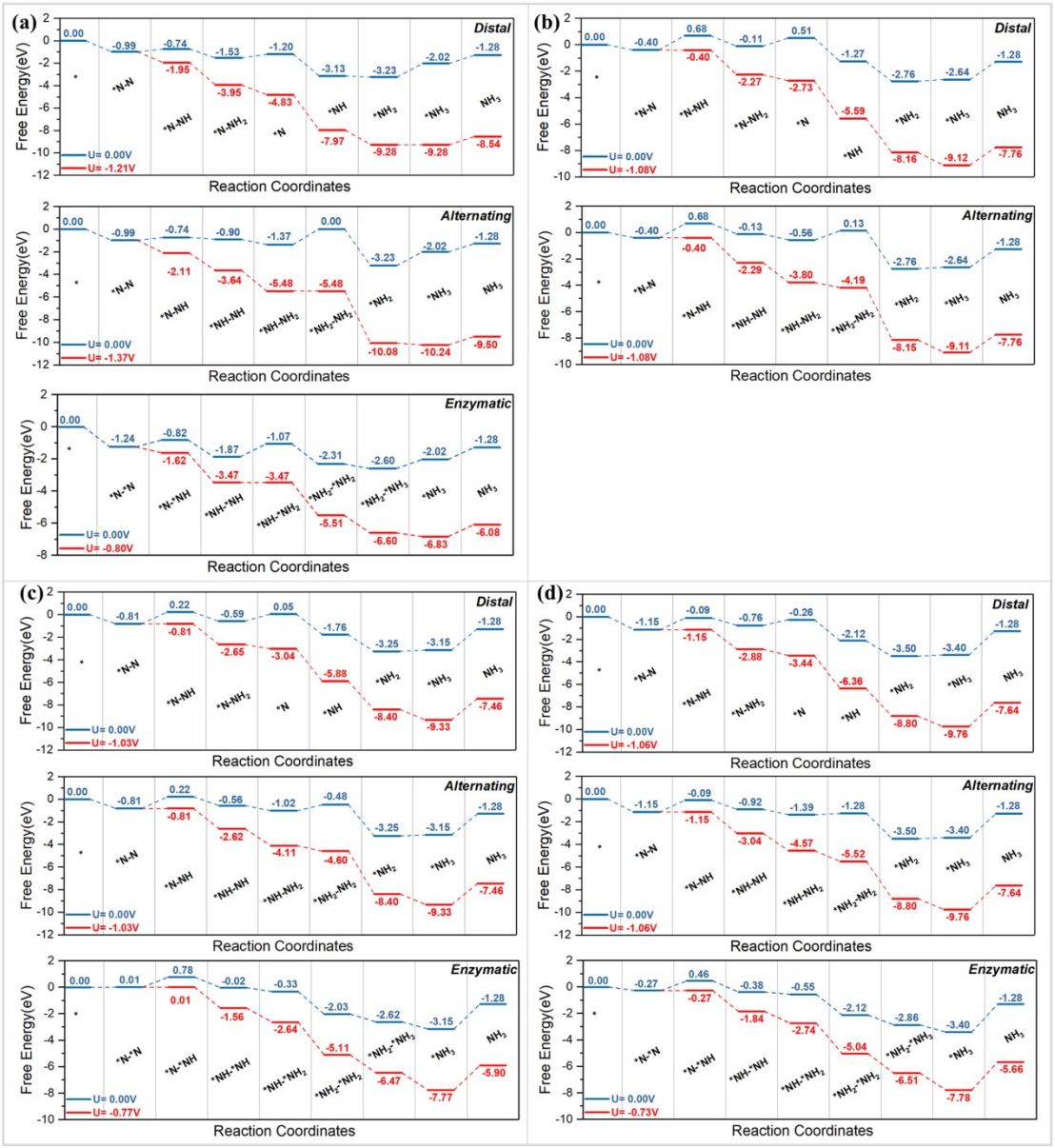

Fig. S2 Free energy diagrams for N_2 reduction through distal, alternating and enzymatic mechanisms on the (a) B_{int5}, (b) B_{N3}, (c) B_{N5} and (d) B_{N2}.

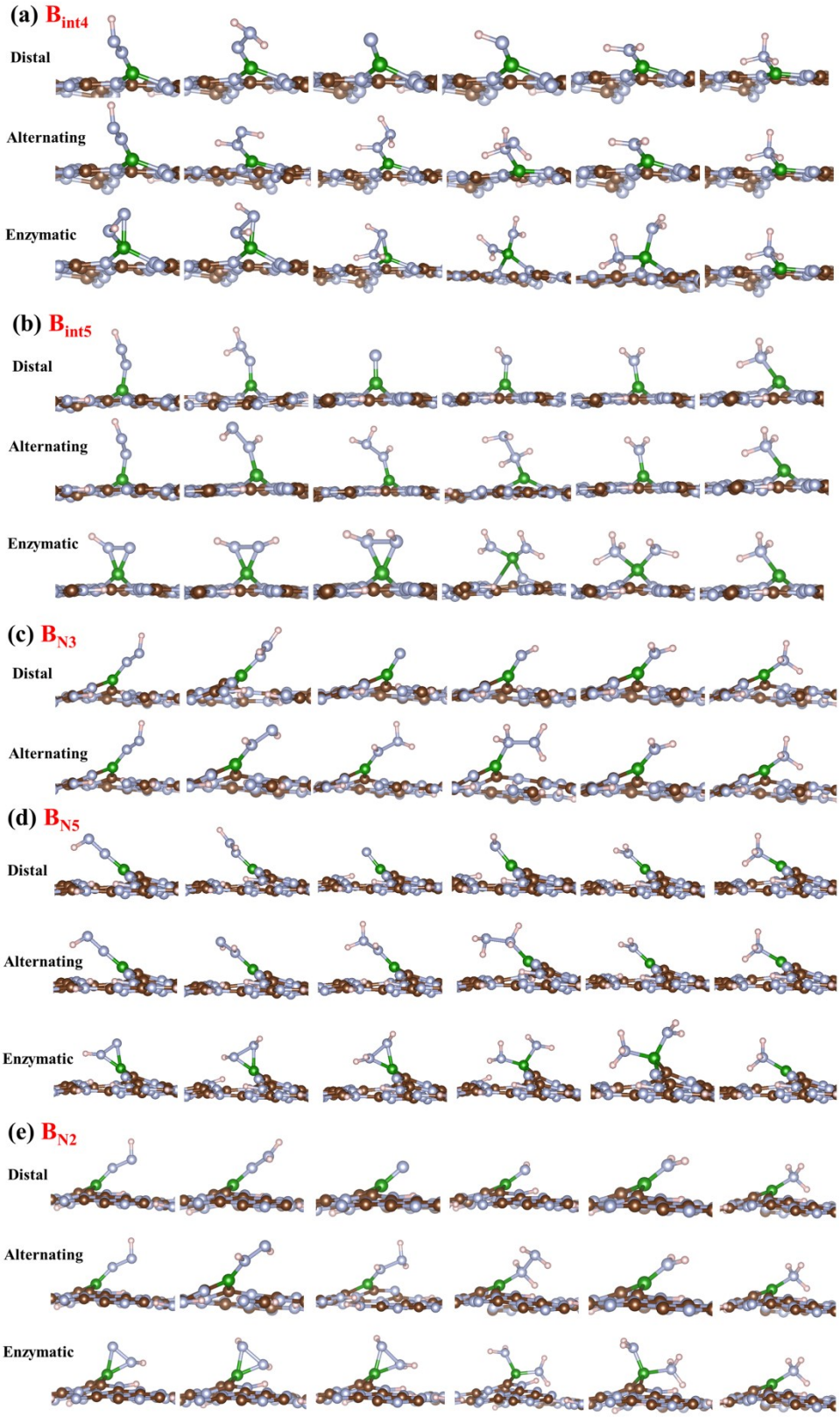

Fig. S3 The various intermediates for N_2 reduction through distal, alternating and enzymatic mechanisms on the (a) B_{int4}, (b) B_{int5}, (c) B_{N3}, (d) B_{N5} and (e) B_{N2}.

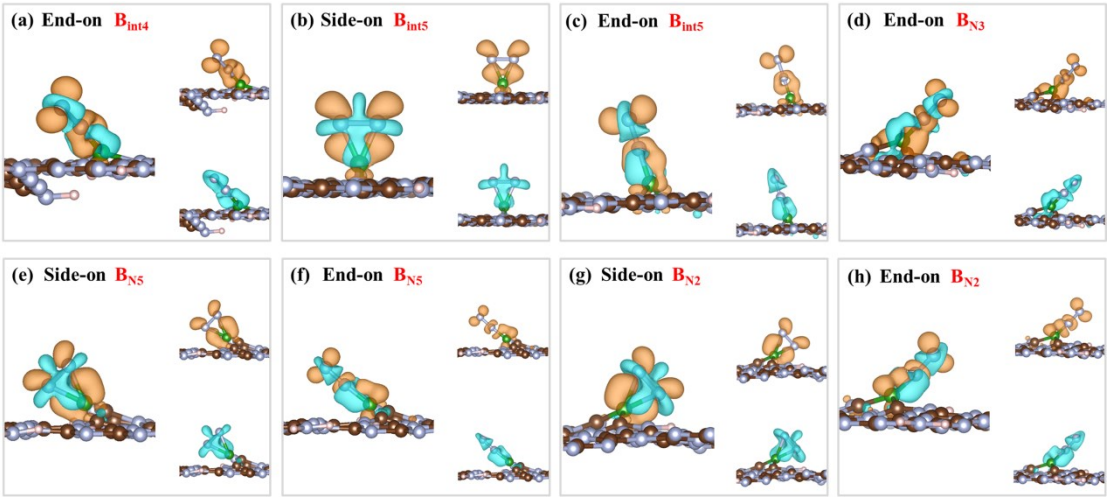

Fig. S4 The charge difference density of adsorbed N_2 on (a) B_{int4} through the end-on pattern, (b-c) B_{int5} through side-on and end-on patterns, (d) B_{N3} through the end-on pattern, (e-f) B_{N5} and (g-h) B_{N2} through the side-on and end-on patterns, respectively. The isosurface value is set to be 0.005 e/Å^3. The orange and cyan regions represent charge accumulation and depletion, respectively.

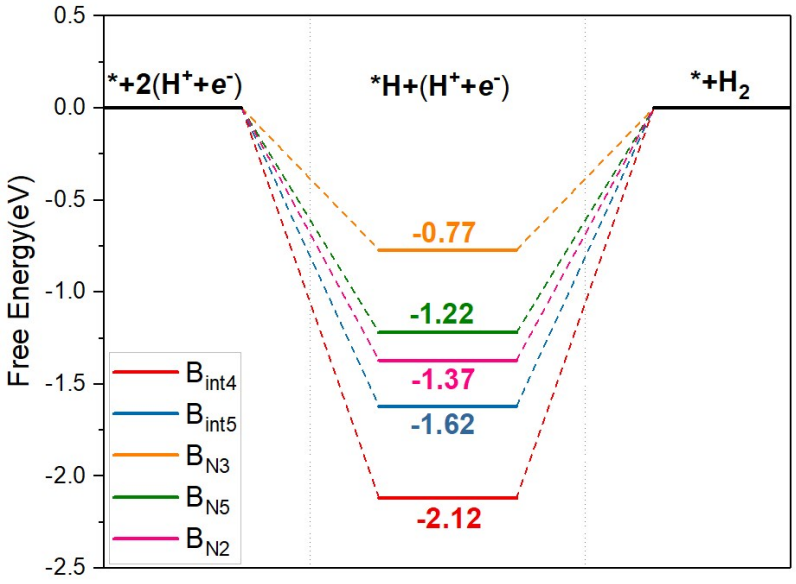

Fig. S5 Free energy diagrams of HER on B_{int4}, B_{int5}, B_{N3}, B_{N5} and B_{N2}.

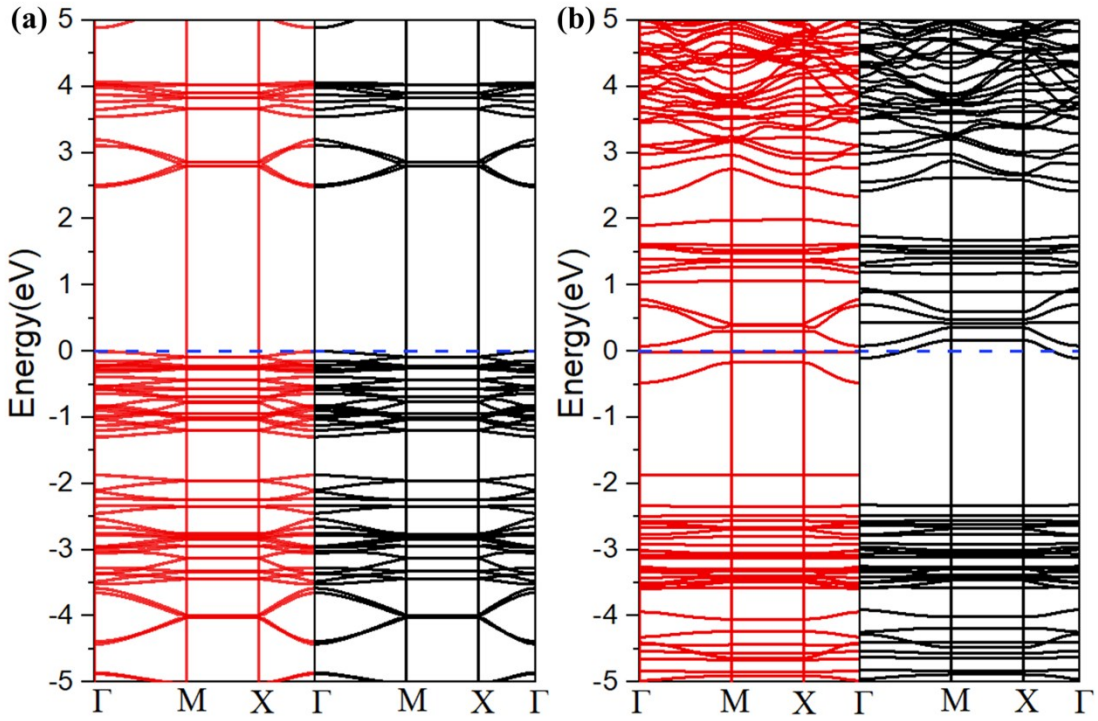

Fig. S6 The computed band structures of (a) pure melon-based CN and (b) B_{int4}. The Fermi level is set as zero in dotted lines.

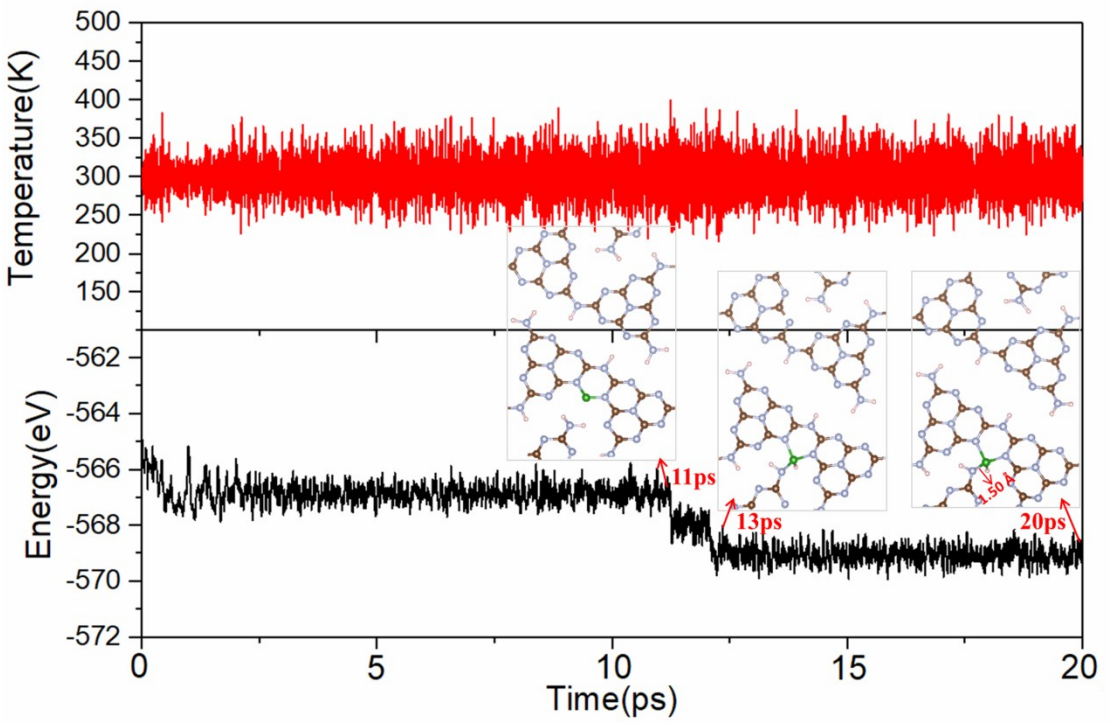

Fig. S7 (a) Variations of energy against the time for AIMD simulation of B_{int4}; the simulation is run under 300 K for 20 ps with a time step of 0.5 fs. (b) The structure of B_{int4} in the dynamic simulation process at about 11, 13 and 20 ps.