Electronic Supplementary Material (ESI) for Nanoscale Advances.

SUPPLEMENTARY INFORMATION

Starting a Subnanoscale Tank Tread: Dynamic Fluxionality of a Boron-Based $B_{10}Ca$ Alloy Cluster

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Supplementary Information – Part I

Table S1. Cartesian coordinates for the global-minimum (GM) structures of $B_{10}Ca$ (C_2, ^1A) and B_{10} (C_{2h}, ^1A_g) clusters at the PBE0/6-311+G* level.

Figure S1. Alternative optimized structures of $B_{10}Ca$ cluster at PBE0/6-311+G* level. Relative energies are shown in eV with corrections for zero-point energies (ZPEs). Shown in square brackets for top two structures are the relative energies using single-point CCSD(T) calculations, that is, at CCSD(T)/6-311+G* //PBE0/6-311+G* level.

Figure S2. Optimized key structures of $B_{10}Ca$ and B_{10} clusters at PBE0/6-311+G* level, with bond distances being labelled in Å. (a) B_{10} GM (C_{2h}, ^1A_g) and TS (C_s, $^1A'$). (b) $B_{10}Ca$ GM (C_2, ^1A), TS_1 (C_{2v}, $^1A_1$), and TS_2 (C_{2v}, $^1A_1$).

Figure S3. Natural atomic charges (in |e|) from natural bond orbital (NBO) analyses at PBE0/6-311G* level. (a) B_{10} GM (C_{2h}, ^1A_g) and TS (C_s, $^1A'$). (b) $B_{10}Ca$ GM (C_2, ^1A), TS_1 (C_{2v}, $^1A_1$), and TS_2 (C_{2v}, $^1A_1$).

Figure S4. Pictures of occupied canonical molecular orbitals (CMOs) of $B_{10}Ca$ TS_1 (C_{2v}, $^1A_1$) cluster, calculated at PBE0/6-311+G* level. The CMOs are sorted to three subsets according to their constituent atomic orbitals (AOs).

Figure S5. Pictures of occupied CMOs of $B_{10}Ca$ TS_2 (C_{2v}, $^1A_1$) cluster, calculated at PBE0/6-311+G* level. The CMOs are sorted to three subsets according to their constituent AOs.

Figure S6. (a) Electron localization functions, ELF_σ and ELF_π, of $B_{10}Ca$ TS_2 (C_{2v}, $^1A_1$) cluster. (b) Chemical bonding pattern of $B_{10}Ca$ TS_2 (C_{2v}, $^1A_1$) cluster on the basis of adaptive natural density partitioning (AdNDP) analysis, wherein the global 10σ framework is approximated to "island" σ bonds. Occupation numbers (ONs) are indicated.

Figure S7. Pictures of occupied CMOs of B_{10} GM (C_{2h}, ^1A_g) cluster, calculated at PBE0/6-311+G* level. The CMOs are sorted to three subsets according to their constituent AOs.

Figure S8. Pictures of occupied CMOs of B_{10} TS (C_s, $^1A'$) cluster, calculated at PBE0/6-311+G* level. The CMOs are sorted to three subsets according to their constituent AOs.

Figure S9. (a) ELF_σ and ELF_π of B_{10} TS (C_s, $^1A'$) cluster. (b) AdNDP bonding pattern of B_{10} TS (C_s, $^1A'$) cluster, wherein the global 8σ framework is approximated to island σ bonds. ONs are indicated.

Supplementary Information – Part II

A short movie extracted from the BOMD simulation for $B_{10}Ca$ cluster. Each frame of the snapshot is reoriented horizontally. The simulation was performed at 900 K for 50 ps. The movie roughly covers a time span of 2.5 ps. Similar BOMD properties were revealed at 600 K (not shown), albeit with slower rotation.

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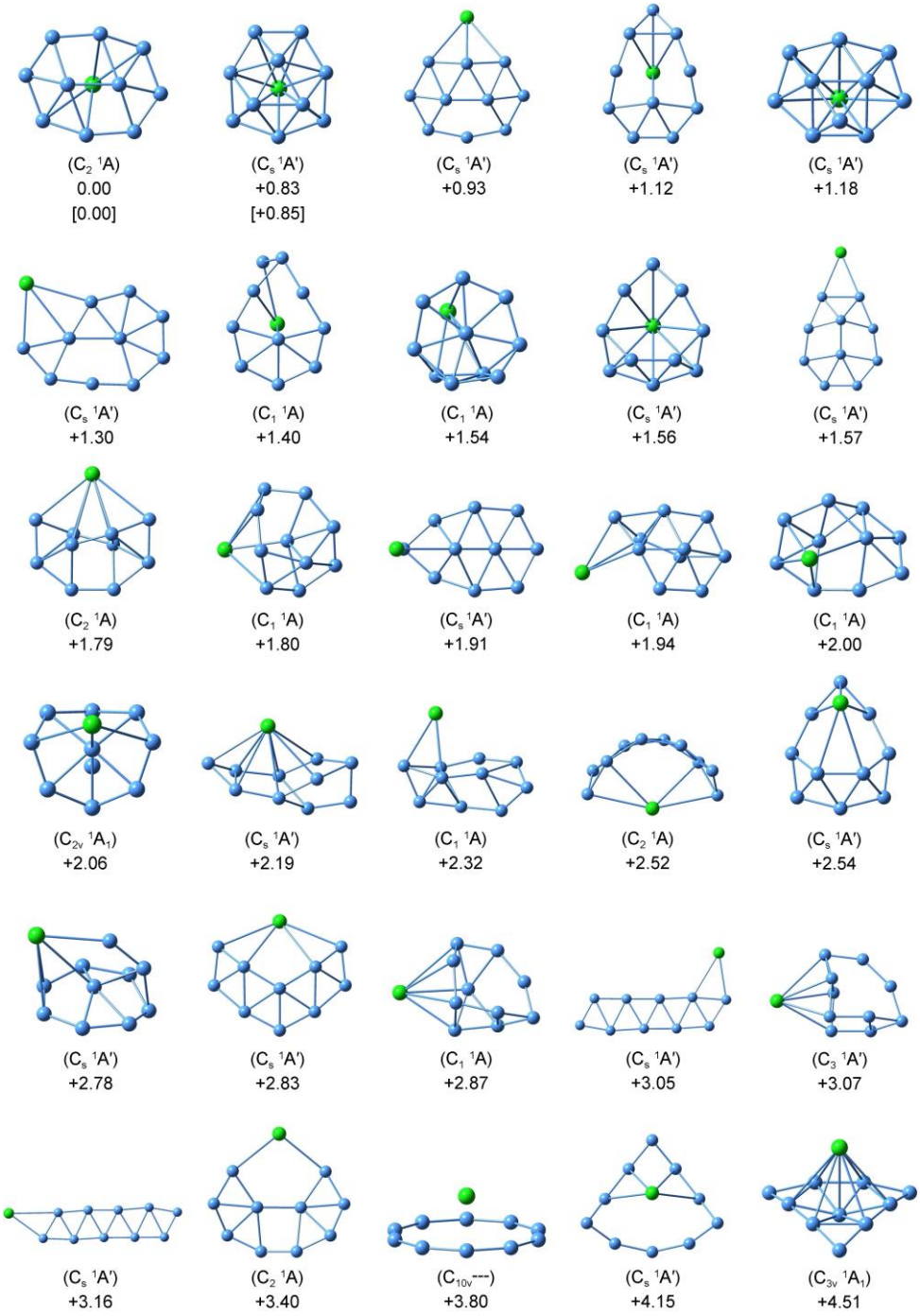

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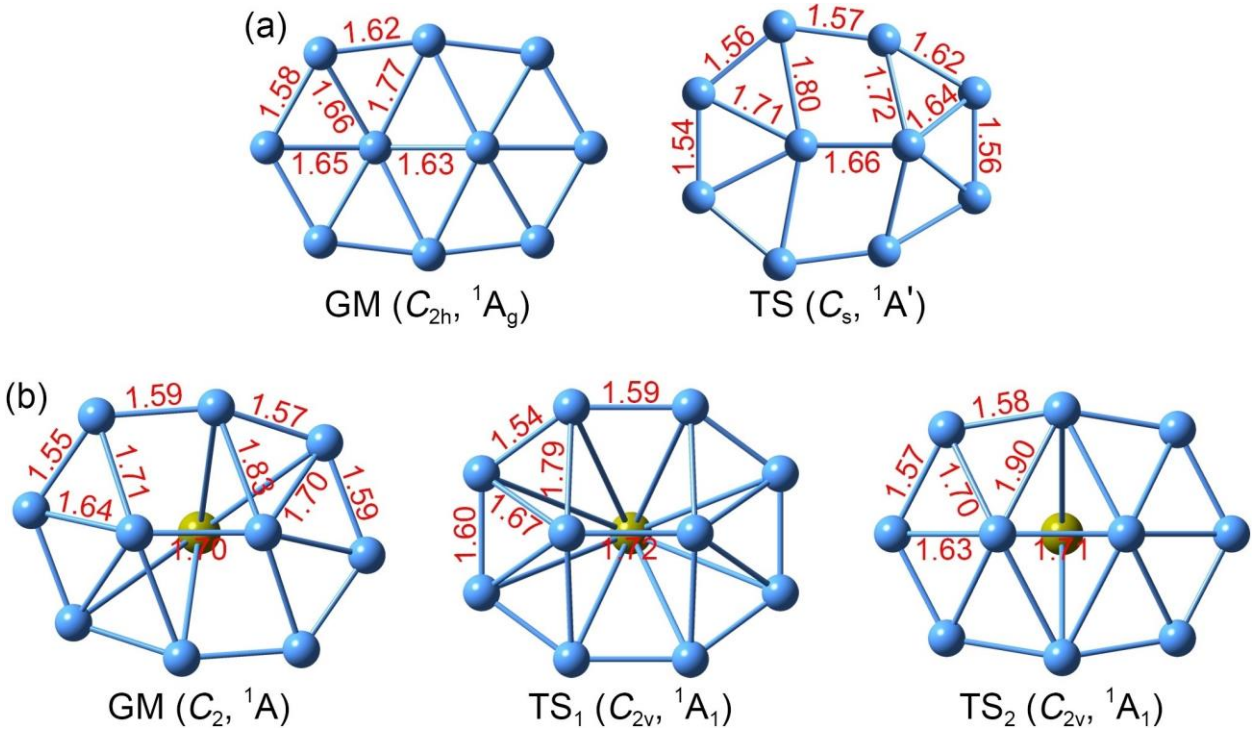

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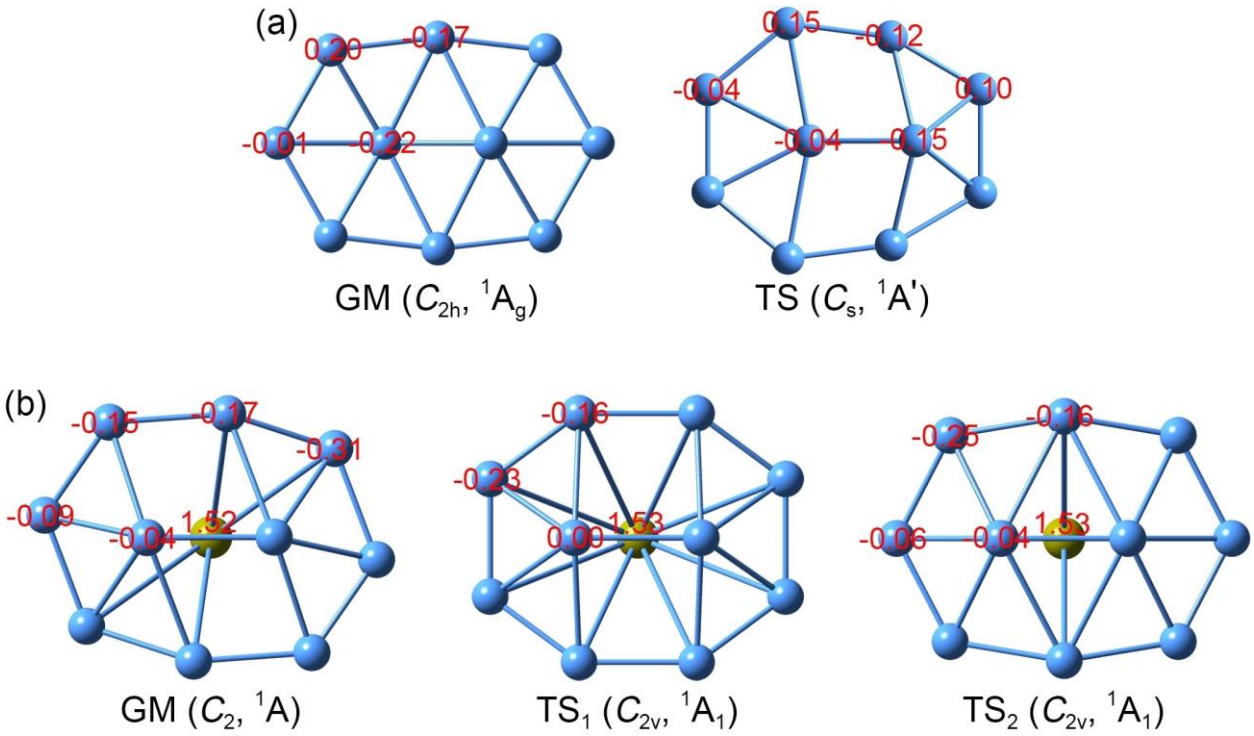

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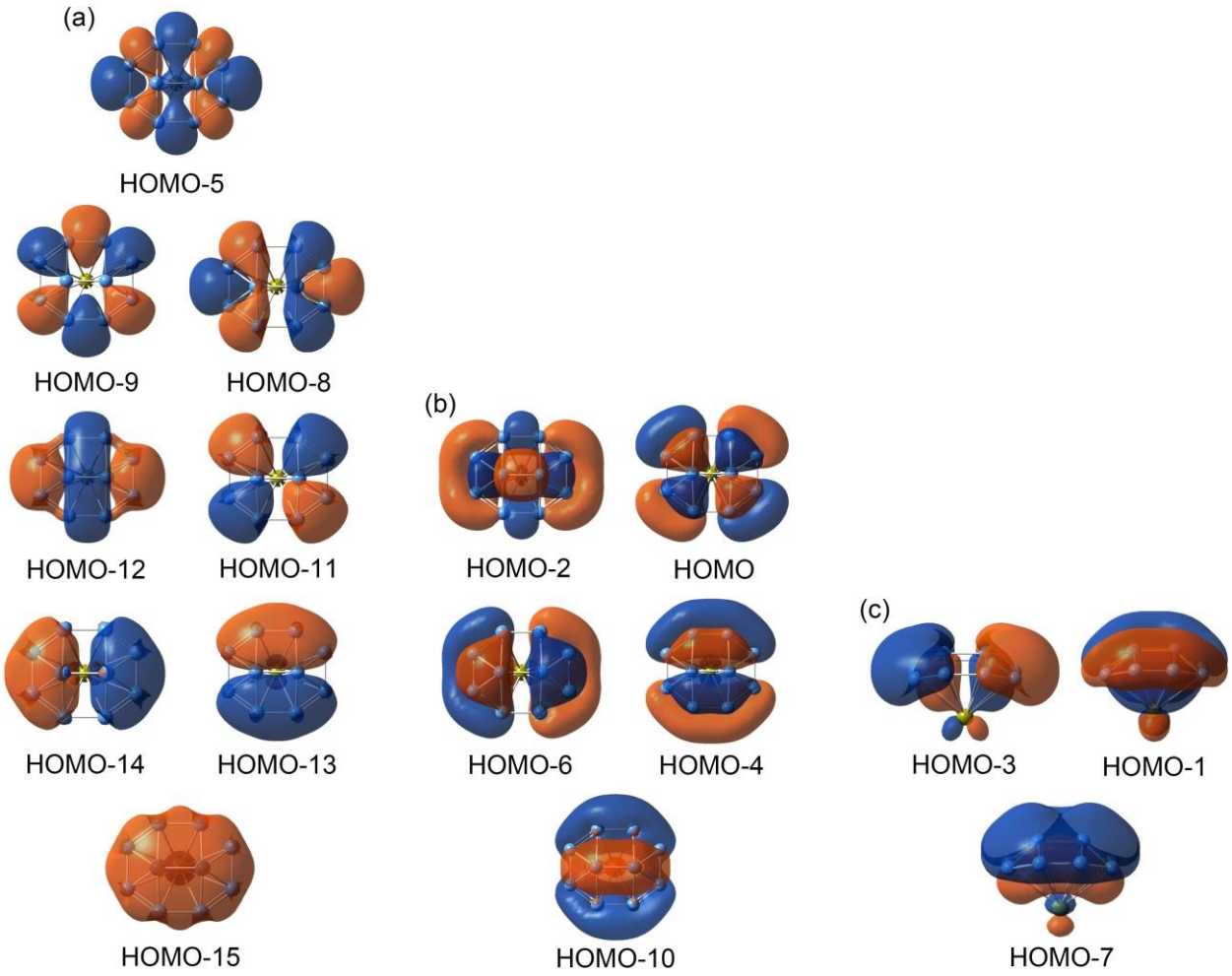
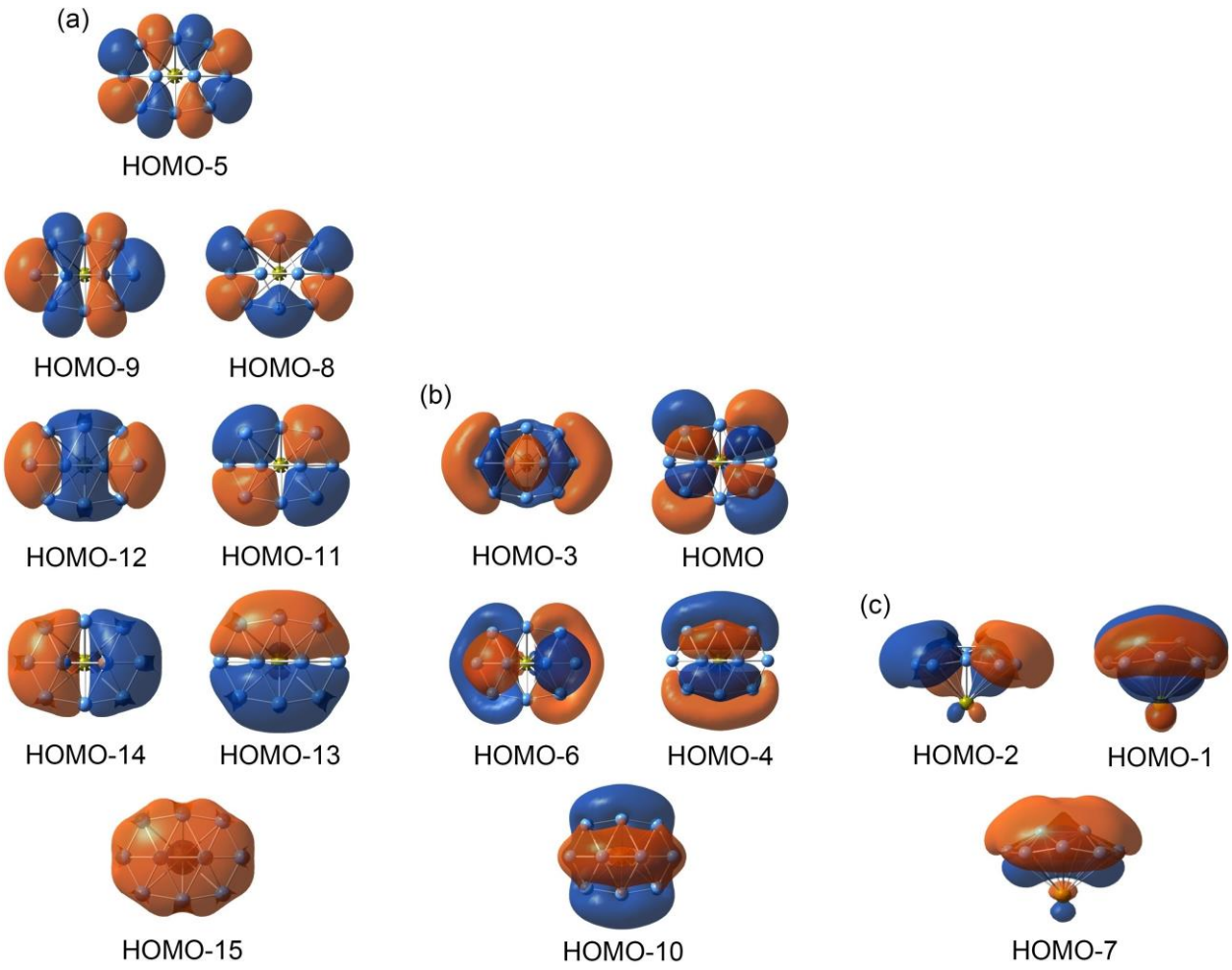


Figure S5. Pictures of occupied CMOs of $B_{10}Ca$ TS_2 (C_{2v}, $^1A_1$) cluster, calculated at PBE0/6-311+G* level. The CMOs are sorted to three subsets according to their constituent AOs.



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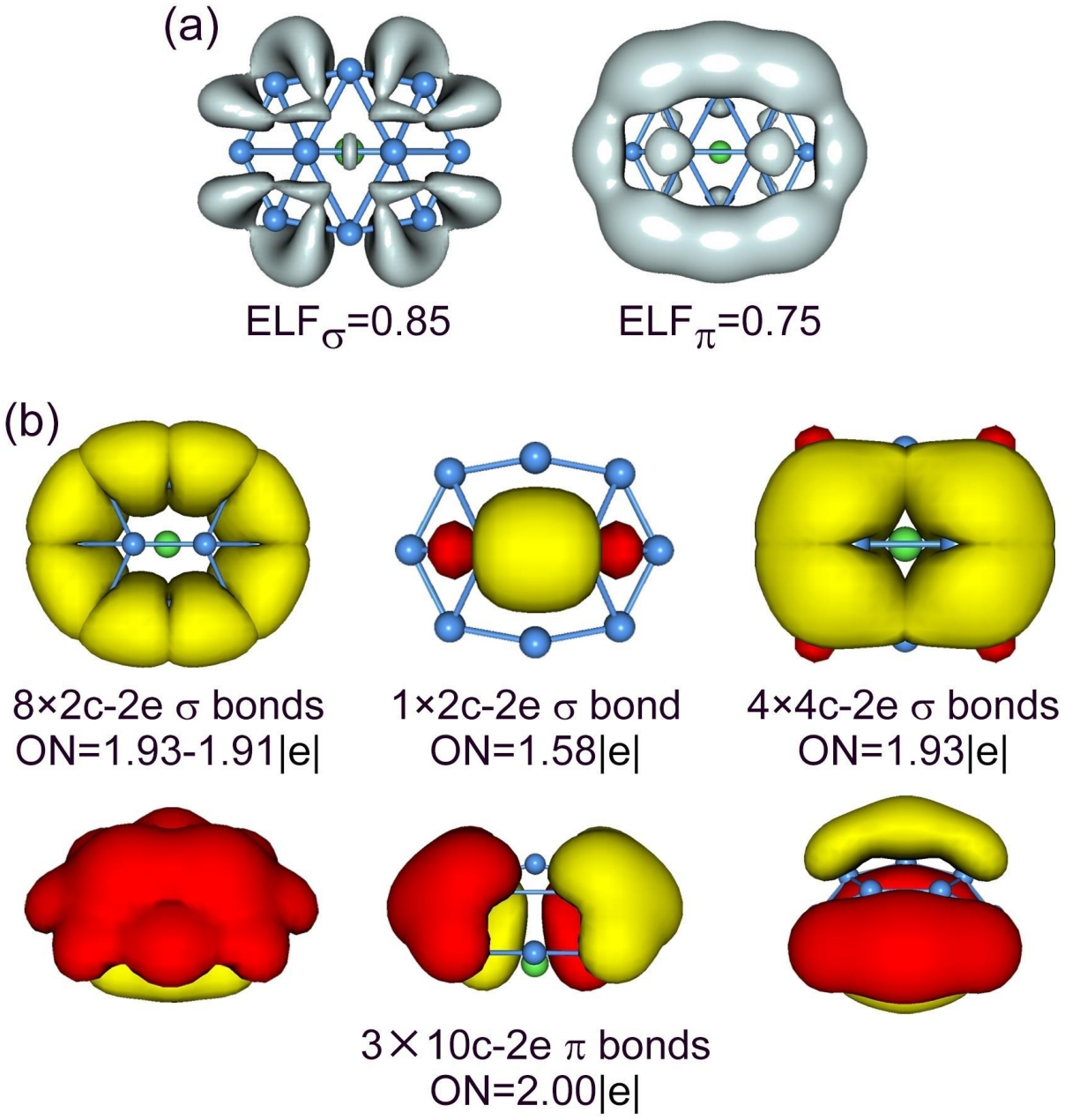

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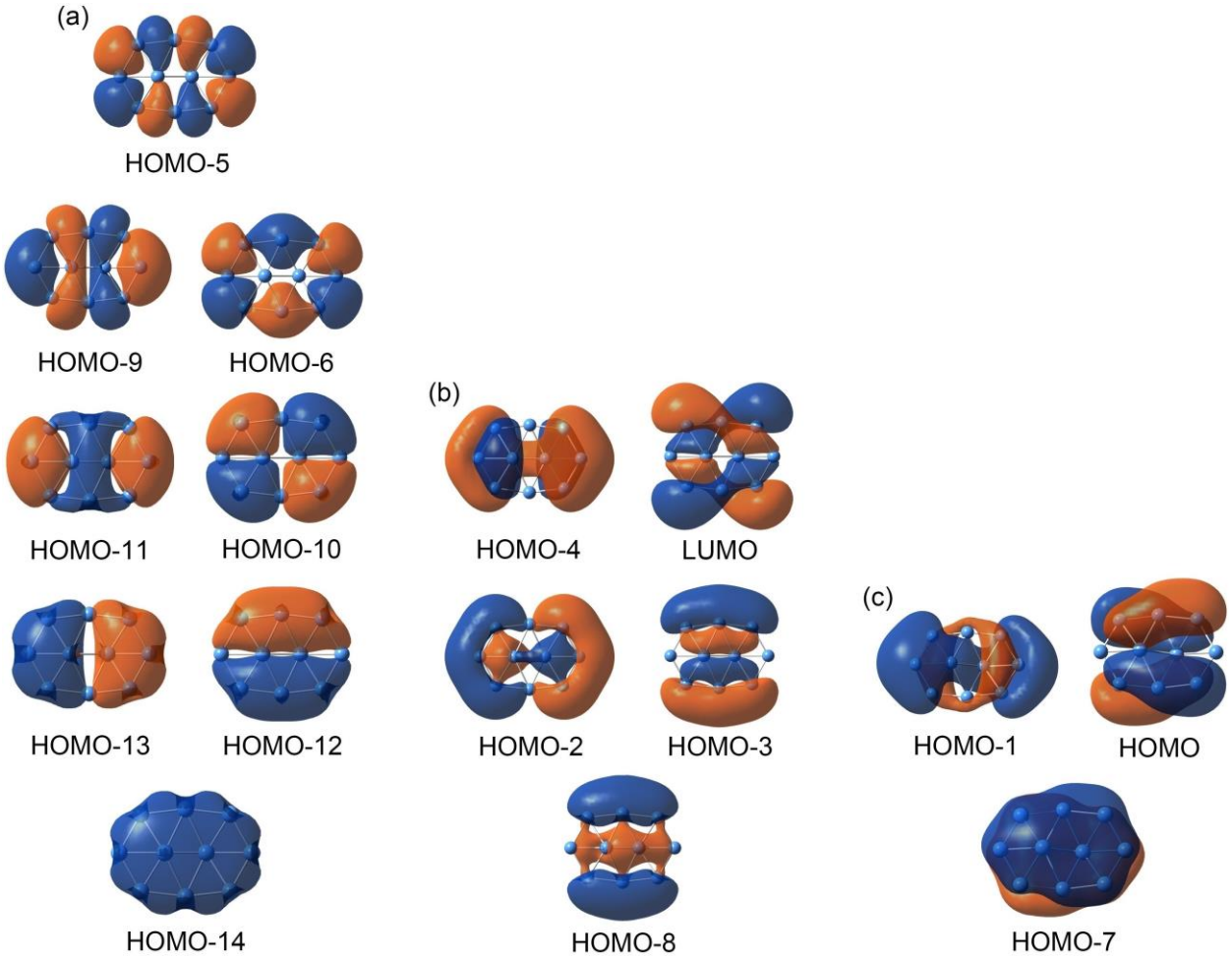

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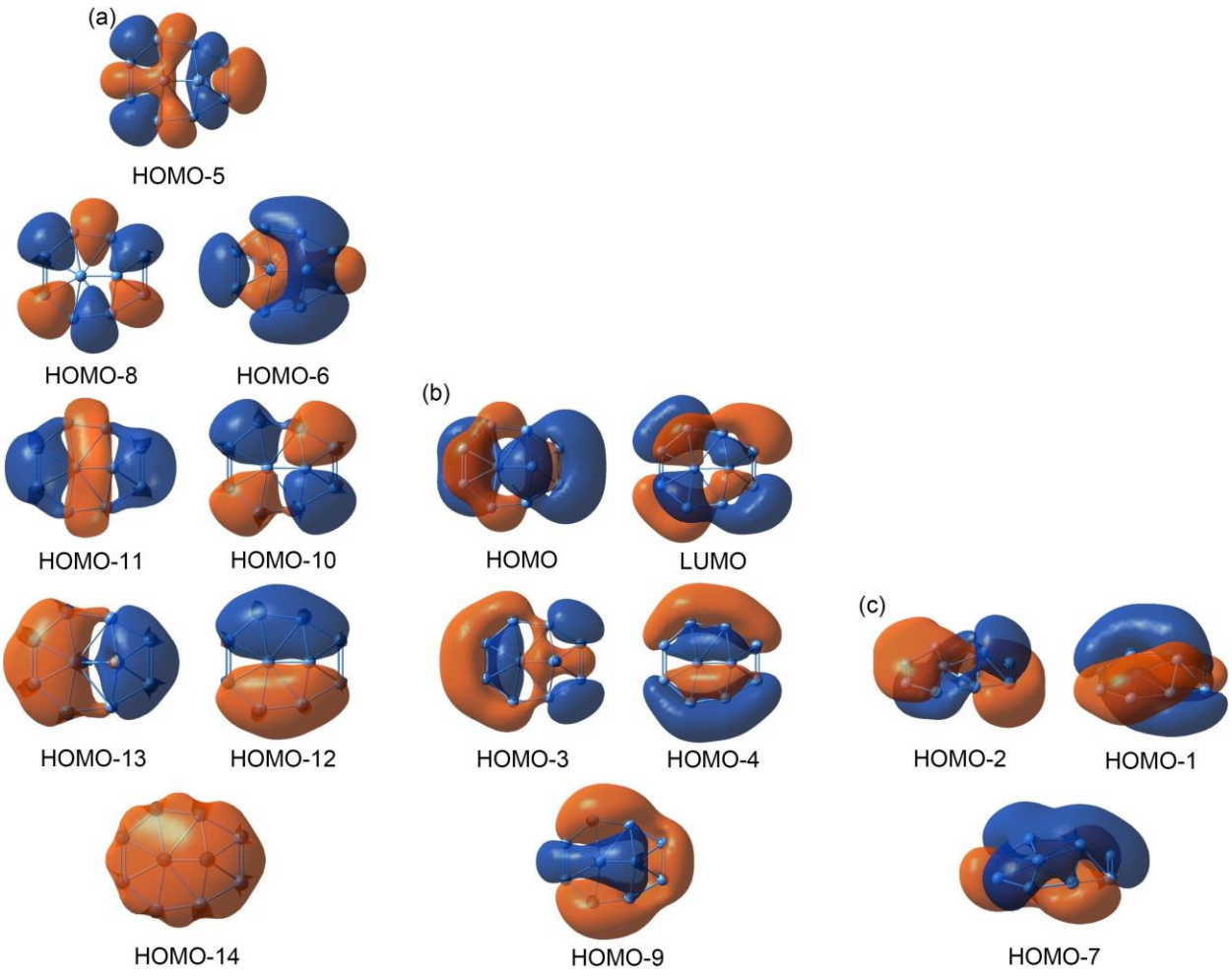

Figure S9. (a) ELF_{σ} and ELF_{π} of B_{10} TS (C_s, $^1A'$) cluster. (b) AdNDP bonding pattern of B_{10} TS (C_s, $^1A'$) cluster, wherein the global 8σ framework is approximated to island σ bonds. ONs are indicated.

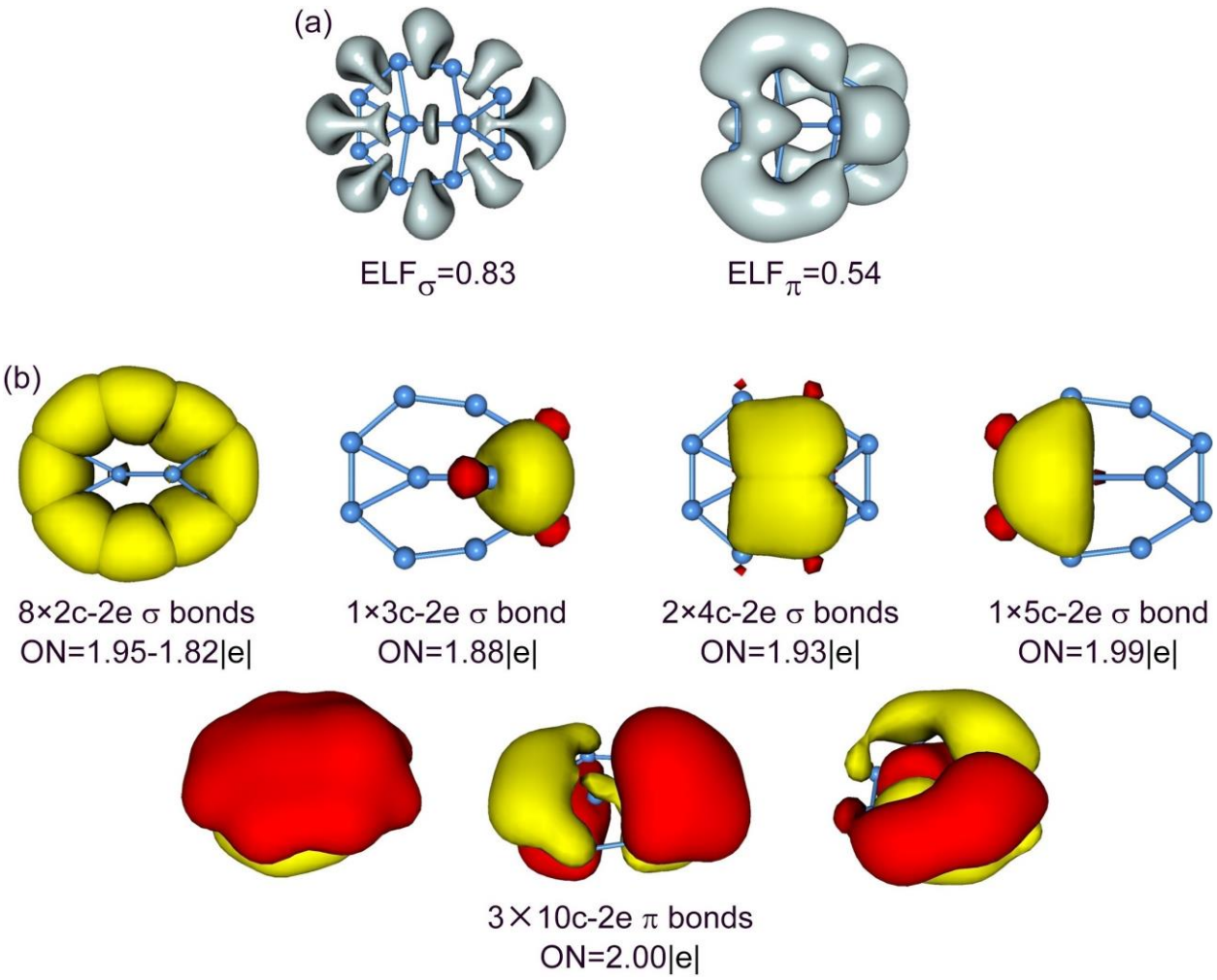

Table S1. Cartesian coordinates for the global-minimum (GM) structures of $B_{10}Ca$ (C_2, ^1A) and B_{10} (C_{2h}, ^1A_g) clusters at the PBE0/6-311+G* level.

(a) GM, $B_{10}Ca$ (C_2, ^1A)

B	-1.53445900	1.62978100	-0.29715800
B	-2.04334400	0.20120700	-0.60295700
B	-1.21353100	-1.15130300	-0.65893800
B	0.00000000	-2.04266500	-0.23094800
B	1.53445900	-1.62978100	-0.29715800
B	2.04334400	-0.20120700	-0.60295700
B	1.21353100	1.15130300	-0.65893800
B	0.00000000	2.04266500	-0.23094800
B	-0.49317500	0.69315900	-1.14667700
B	0.49317500	-0.69315900	-1.14667700
Ca	0.00000000	0.00000000	1.46833900

(b) GM, B_{10} (C_{2h}, ^1A_g)

B	-0.12423000	2.37427600	0.00000000
B	0.00000000	1.60510800	-1.37798000
B	0.00000000	0.00000000	-1.56571100
B	0.00000000	-1.60510800	-1.37798000
B	0.12423000	-2.37427600	0.00000000
B	0.00000000	-1.60510800	1.37798000
B	0.00000000	0.00000000	1.56571100
B	0.00000000	1.60510800	1.37798000
B	-0.34294400	0.73905800	0.00000000
B	0.34294400	-0.73905800	0.00000000