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

SUPPLEMENTARY INFORMATION

Chemical bonding and dynamic fluxionality of B_{15}^+ cluster: a nanoscale double-axle tank tread†

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SUPPLEMENTARY INFORMATION – PART I

Table S1. Cartesian coordinates for the global-minimum structure of B_{15}^+ C_{2v} ($^1A_1$) and its corresponding C_{2v} transition state at the PBE0/6-311+G* level.

Figure S1. Canonical molecular orbitals (CMOs) for the subset of eleven peripheral σ bonds in the C_{2v} ($^1A_1$) global minimum of B_{15}^+ cluster. These CMOs are readily localized as two-center two-electron (2c-2e) σ bonds.

Figure S2. Canonical molecular orbitals (CMOs) of the C_{2v} ($^1A_1$) transition state of B_{15}^+ cluster. (a) Eleven peripheral σ bonds, which can be localized as 2c-2e bonds. (b) Five delocalized σ bonds. (c) Two delocalized σ bonds associated with the inner rhombic B_4 core. (d) Four delocalized π bonds. The CMOs for the (a), (b), and (d) subsets show one-to-one correspondence to each other, from bottom up.

Figure S3. Chemical bonding in the C_{2v} transition state of B_{15}^{+}. (a) The electron localization functions (ELFs). (b) Bonding elements as revealed from the adaptive natural density partitioning (AdNDP) analysis. The occupation numbers (ONs) are shown.

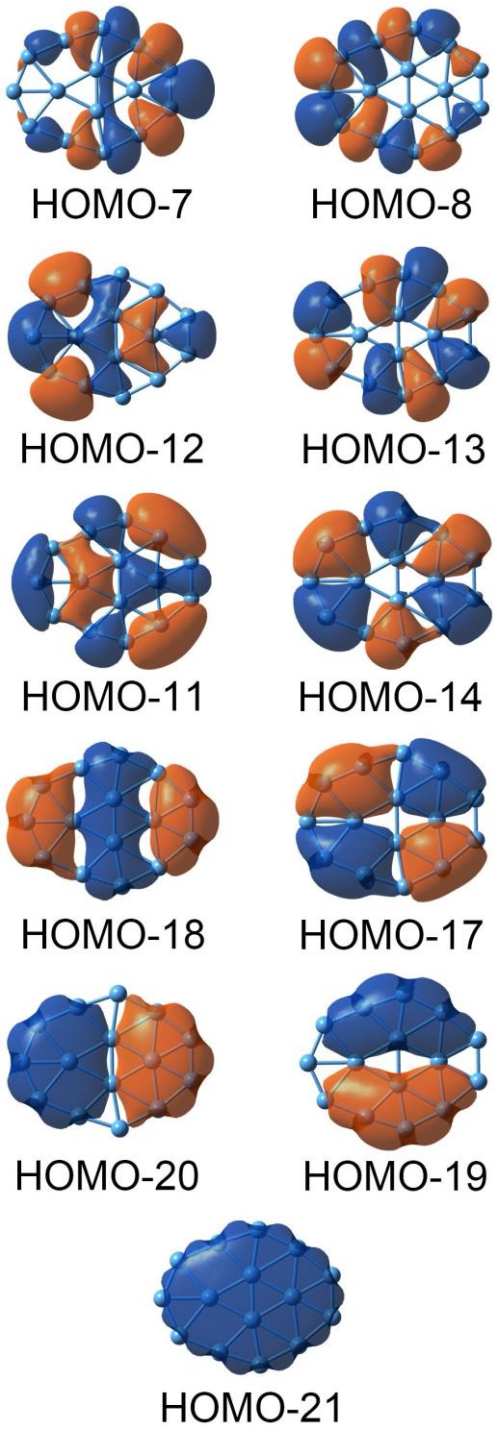
Figure S4. Optimized structure of the C_{2v} global minimum of B_{14}^{-} cluster at the PBE0/6-311+G* level.

Figure S5. Evolution of electron localization function, ELF_{σ}, against the bifurcation value for the C_{2v} global minimum of B_{15}^{+} cluster. Note that for the rhombic B1B2B12B11 unit, the ELF_{σ} data is consistent with one four-center island only, rather than two three-center islands (B1B2B12 and B11B1B12), supporting the AdNDP scheme presented in Fig. 5(b).

SUPPLEMENTARY INFORMATION – PART II

A short movie extracted from the BOMD simulation for B_{15}^{+}. Each frame of the snapshot is reoriented horizontally. The simulation is performed at 500 K for over 60 ps and the movie roughly covers a time span of 30 ps.

Figure S1. Canonical molecular orbitals (CMOs) for the subset of eleven peripheral σ bonds in the C_{2v} ($^1A_1$) global minimum of B_{15}^+ cluster. These CMOs are readily localized as two-center two-electron (2c-2e) σ bonds.



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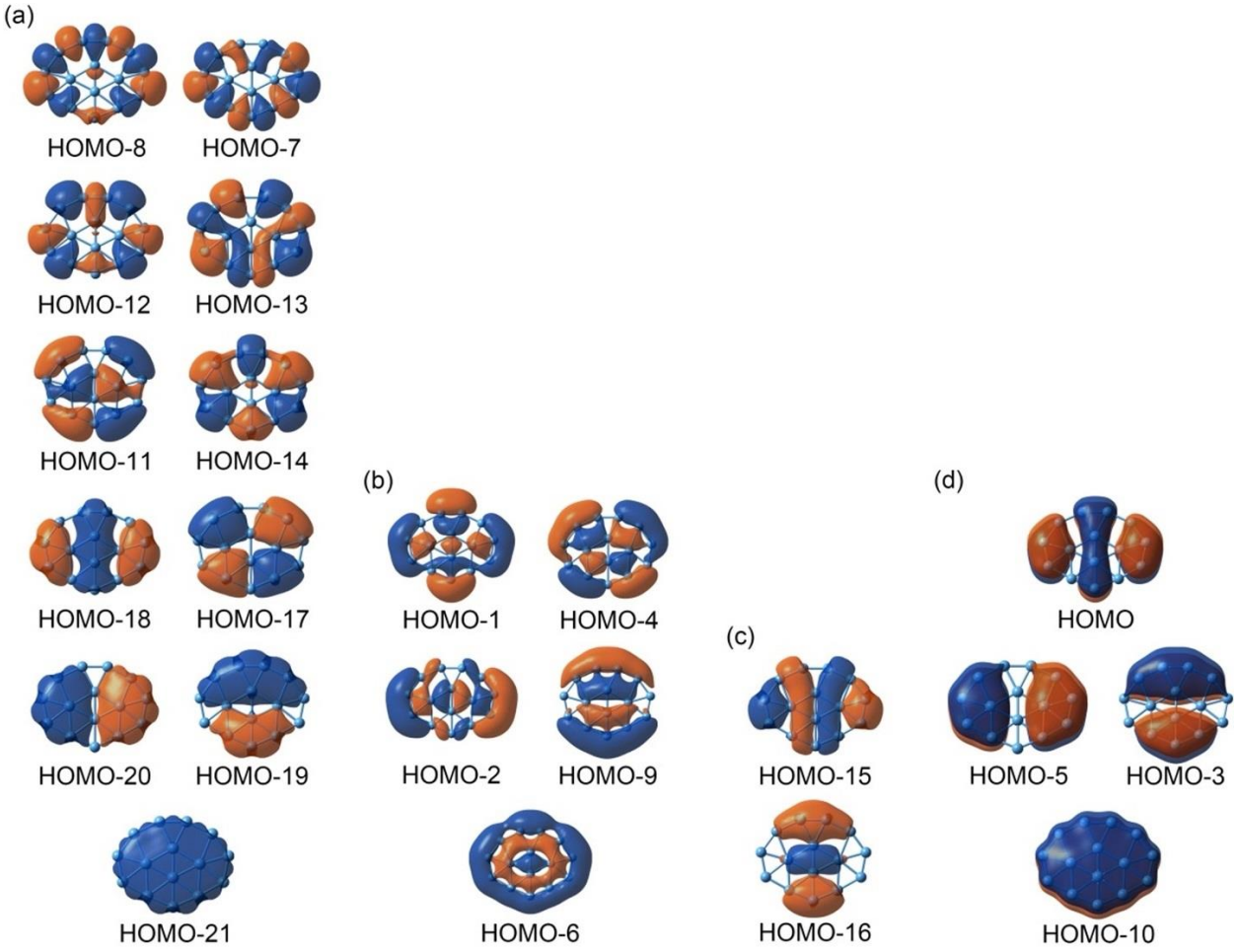


Figure S3. Chemical bonding in the C_{2v} transition state of B_{15}^{+}. (a) The electron localization functions (ELFs). (b) Bonding elements as revealed from the adaptive natural density partitioning (AdNDP) analysis. The occupation numbers (ONs) are shown.

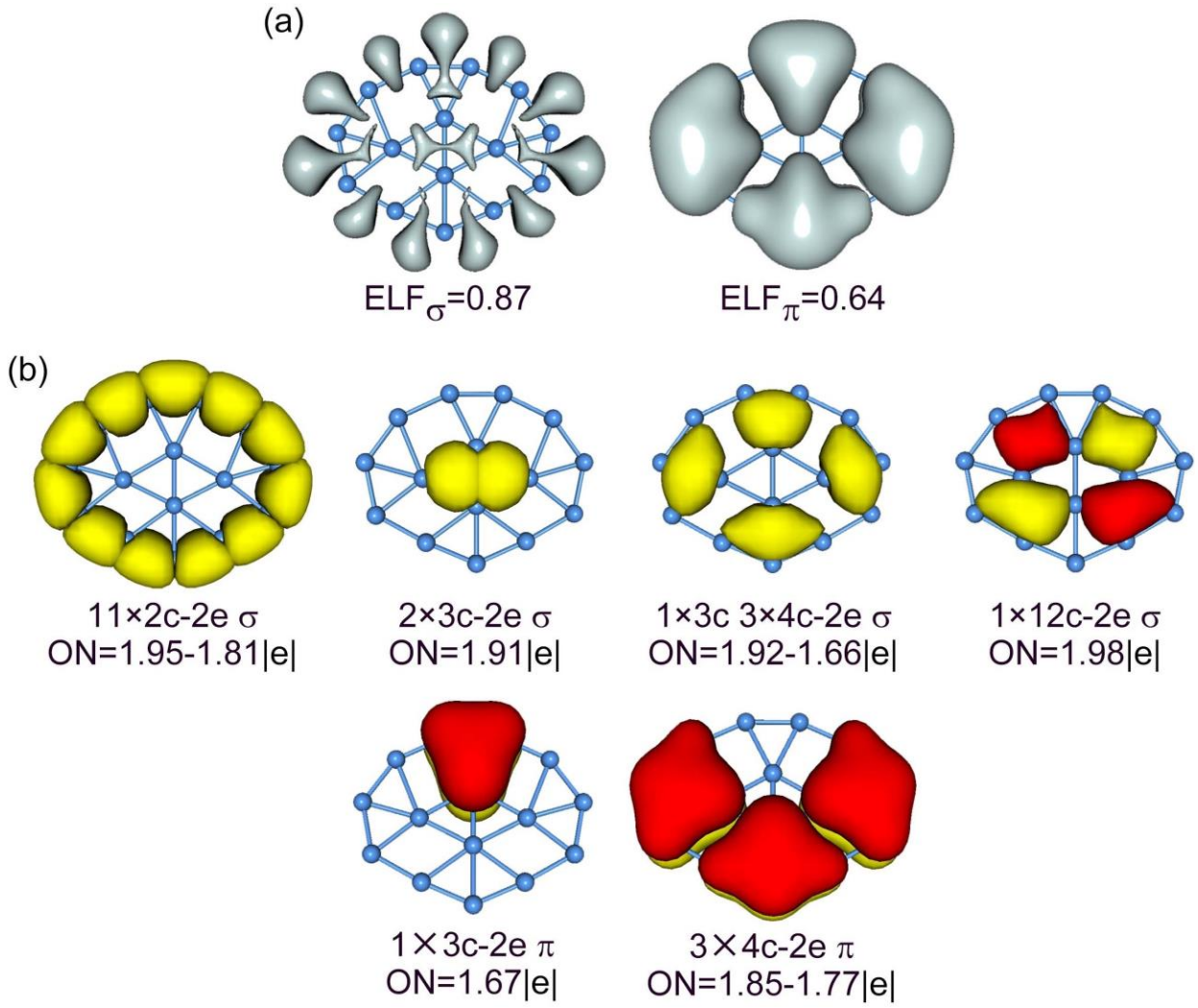
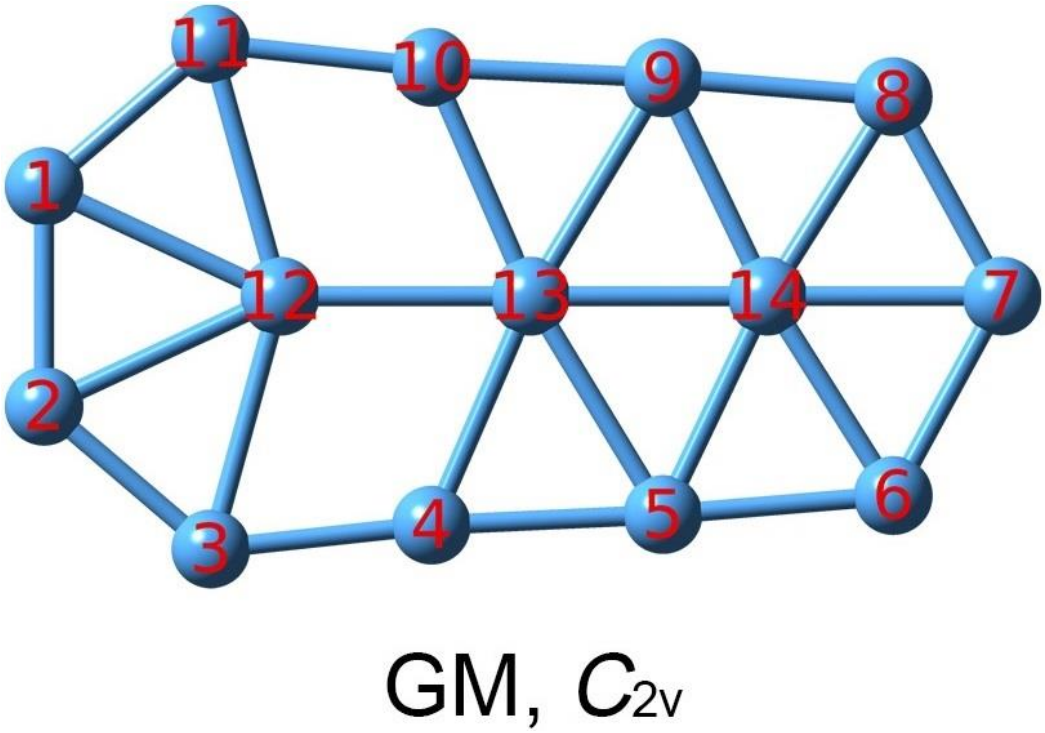


Figure S4. Optimized structure of the C_{2v} global minimum of B_{14}^- cluster at the PBE0/6-311+G* level.



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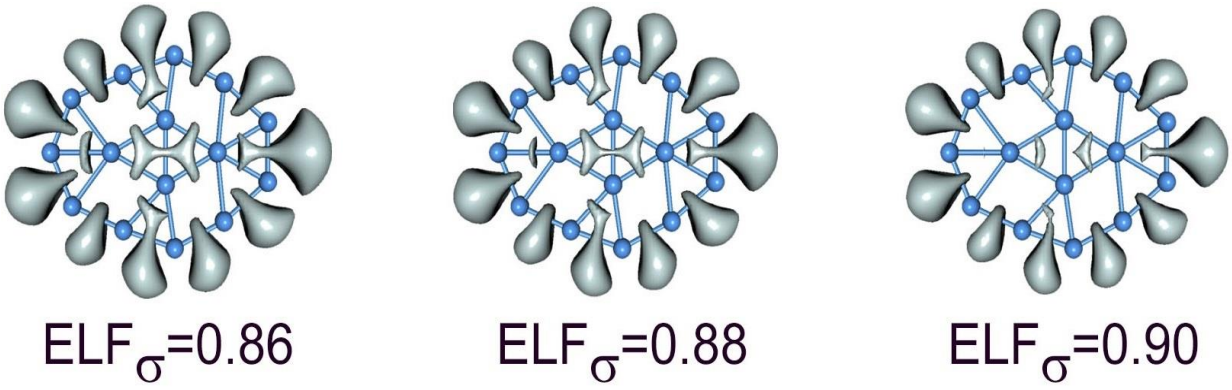

Table S1. Cartesian coordinates for the global-minimum structure of B_{15}^{+} C_{2v} ($^1A_1$) and its corresponding C_{2v} transition state at the PBE0/6-311+G* level.

(a) GM of B_{15}^{+} C_{2v}

B	0.00000000	0.00000000	3.22413600
B	0.00000000	1.38650300	2.60984100
B	0.00000000	2.00601300	1.12463900
B	0.00000000	2.47696800	-0.35955800
B	0.00000000	1.78165400	-1.78525600
B	0.00000000	0.76156000	-3.03970000
B	0.00000000	-0.76156000	-3.03970000
B	0.00000000	-1.78165400	-1.78525600
B	0.00000000	-2.47696800	-0.35955800
B	0.00000000	-2.00601300	1.12463900
B	0.00000000	-1.38650300	2.60984100
B	0.00000000	0.00000000	1.46918600
B	0.00000000	0.82890700	-0.10000900
B	0.00000000	0.00000000	-1.59323600
B	0.00000000	-0.82890700	-0.10000900

(b) TS of B_{15}^{+} C_{2v}

B	0.00000000	3.14286300	-0.38330400
B	0.00000000	2.85508000	1.10302000
B	0.00000000	1.44316400	1.89486400
B	0.00000000	0.00000000	2.51837900

B	0.00000000	-1.44316400	1.89486400
B	0.00000000	-2.85508000	1.10302000
B	0.00000000	-3.14286300	-0.38330400
B	0.00000000	-2.21793000	-1.64214700
B	0.00000000	-0.76617000	-2.32396200
B	0.00000000	0.76617000	-2.32396200
B	0.00000000	2.21793000	-1.64214700
B	0.00000000	1.52931900	0.06796100
B	0.00000000	0.00000000	0.85279500
B	0.00000000	-1.52931900	0.06796100
B	0.00000000	0.00000000	-0.80403700