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

SUPPLEMENTARY INFORMATION

Boron-based binary $Be_6B_{10}^{2-}$ cluster: three-layered aromatic sandwich, electronic transmutation, and dynamic structural fluxionality

Lin-Yan Feng,[a] Jin-Chang Guo,[ab] Peng-Fei Li,[a] and Hua-Jin Zhai*[a]

[a]*Nanocluster Laboratory, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China*

[b]*Department of Chemistry, Xinzhou Teachers University, Xinzhou 034000, Shanxi, China*

E-mail: hj.zhai@sxu.edu.cn

Supplementary Information – Part I

Table S1. Calculated orbital compositions for canonical molecular orbitals (CMOs) of the global-minimum (GM) structure of $Be_6B_{10}^{2-}$ (**1**, C_{2v}, $^1A_1$) cluster. Main components are marked in red color.

Figure S1. Optimized geometries at PBE0/6-311+G(d) level of (a) salt complex cluster $Be_6B_{10}Na_2$, a local-minimum (LM) structure, and (b) re-optimized GM of $Be_6B_{11}^-$ cluster (ref 11). Bond distances are in Å. B atoms are in red color, Be in yellow, and Na in purple.

Figure S2. An alternative AdNDP scheme for delocalized π and σ frameworks of $Be_6B_{10}^{2-}$ (**1**) cluster, in which Be centers are excluded. The occupation numbers (ONs) are only slightly reduced with respect to those in the 16c-2e π/σ AdNDP scheme (see Fig. 7).

Figure S3. AdNDP bonding pattern for D_{10h} C_{10} cluster.

Figure S4. Canonical molecular orbitals (CMOs) of the TS structure of $Be_6B_{10}^{2-}$ cluster (see Fig. 2(c)).

Figure S5. AdNDP bonding pattern for the TS structure of $Be_6B_{10}^{2-}$ cluster (Fig. 2(c)). ONs are shown.

Figure S6. Displacement vectors of (a) selected vibrational frequencies of GM $Be_6B_{10}^{2-}$ (**1**) cluster and (b) those of two TS structures (**TS1** and **TS2**).

Supplementary Information – Part II

Three short movies extracted from the molecular dynamics simulations for $Be_6B_{10}^{2-}$ cluster at temperatures of 300, 600, and 1500 K.

Table S1. Calculated orbital compositions for canonical molecular orbitals (CMOs) of the global-minimum (GM) structure of $Be_6B_{10}^{2-}$ (**1**, C_{2v}, $^1A_1$). Main components are marked in red color.

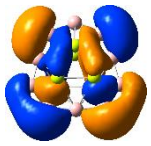
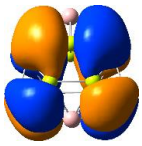
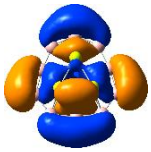
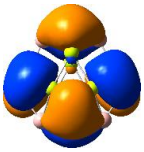
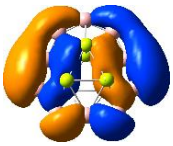
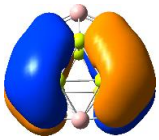
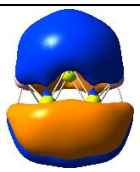
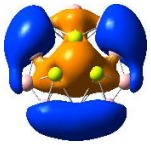
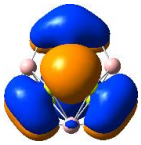
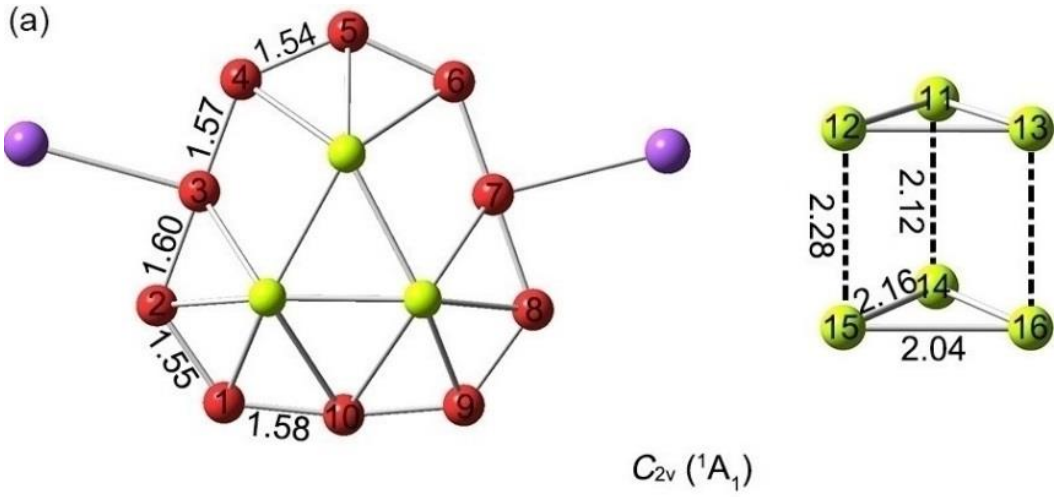
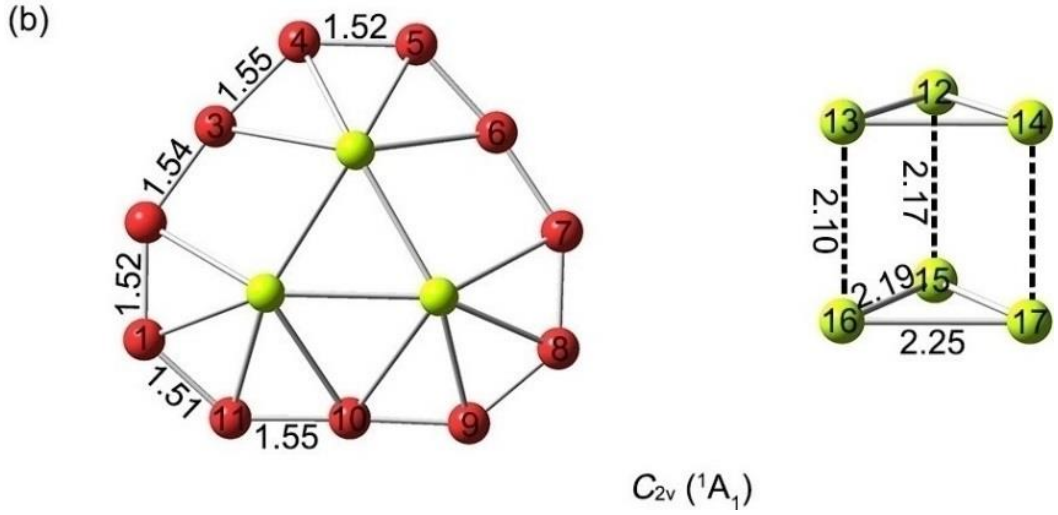
CMO	B 2s/2p (%)	Be 2s/2p (%)	CMO	B 2s/2p (%)	Be 2s/2p (%)
 HOMO	**89.0**	8.2	 HOMO–2	**65.3**	26.5
 HOMO–1	**85.7**	12.0	 HOMO–3	**70.2**	28.6
 HOMO–6	**93.3**	5.7	 HOMO–10	**76.9**	22.1
 HOMO–7	**91.1**	8.0	 HOMO–9	**75.4**	23.4
 HOMO–13	**78.7**	20.6	 HOMO–14	**60.0**	38.1
 HOMO–5	39.3	**58.9**	 HOMO–4	32.8	**66.1**

Figure S1. Optimized geometries at PBE0/6-311+G(d) level of (a) salt complex cluster $Be_6B_{10}Na_2$, a local-minimum (LM) structure, and (b) re-optimized GM of $Be_6B_{11}^-$ cluster (ref 11). Bond distances are in Å. B atoms are in red color, Be in yellow, and Na in purple.





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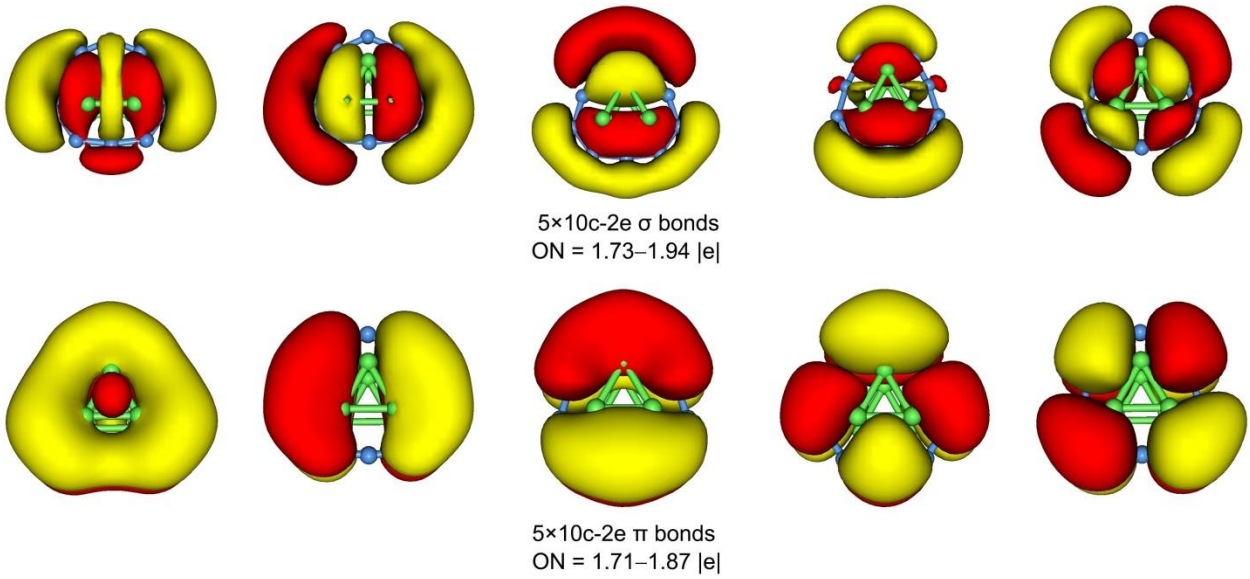

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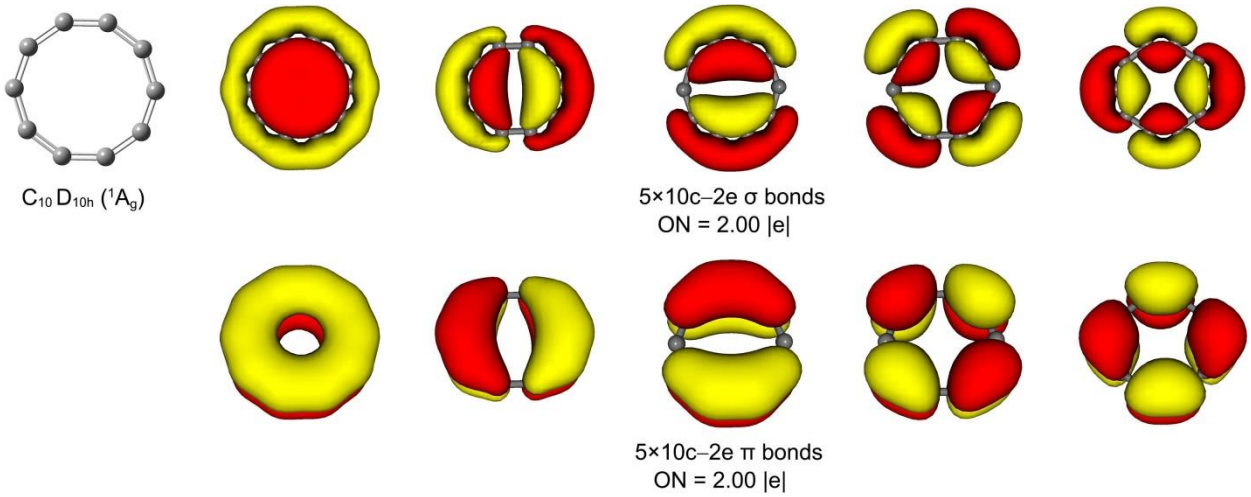

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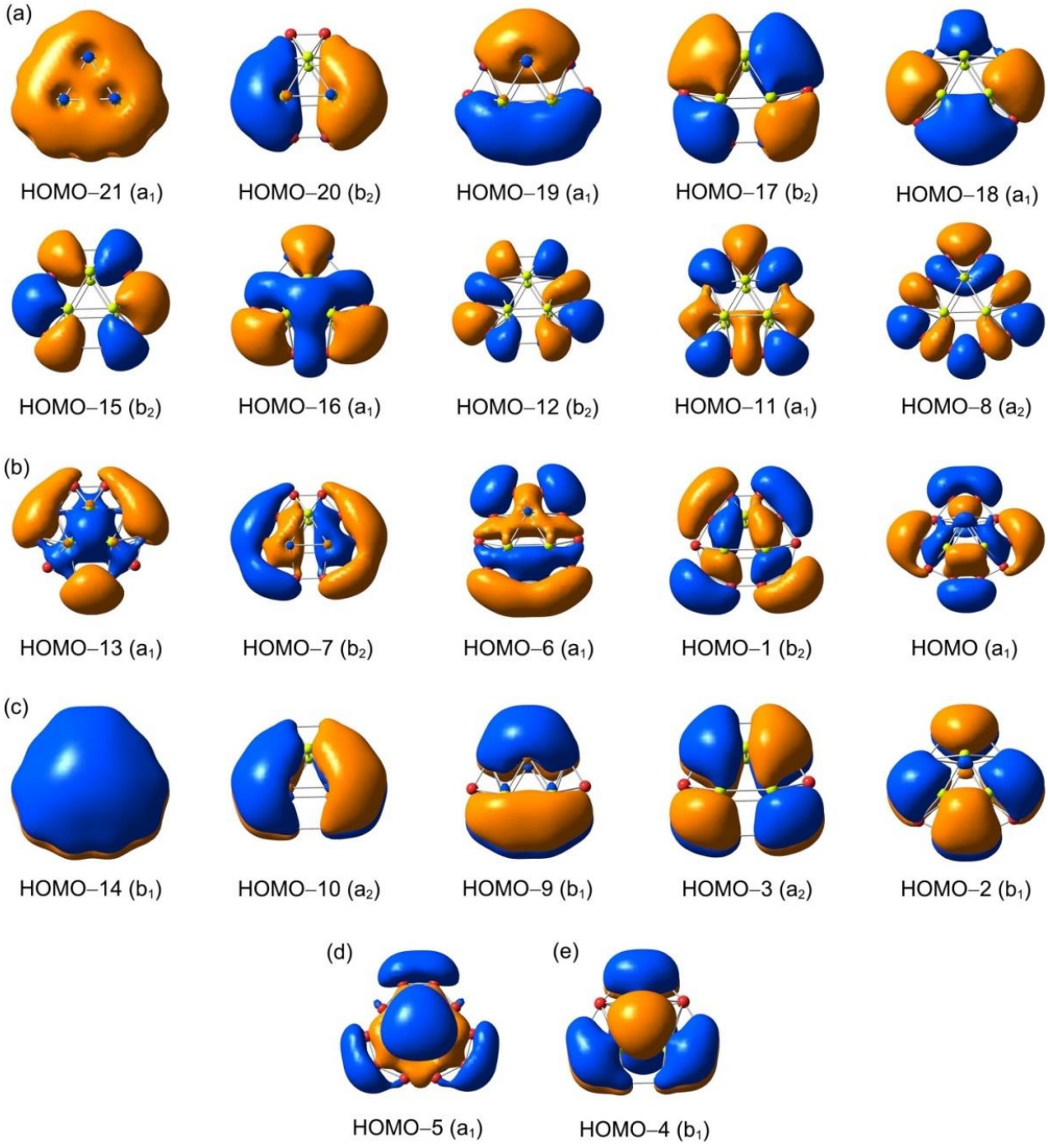

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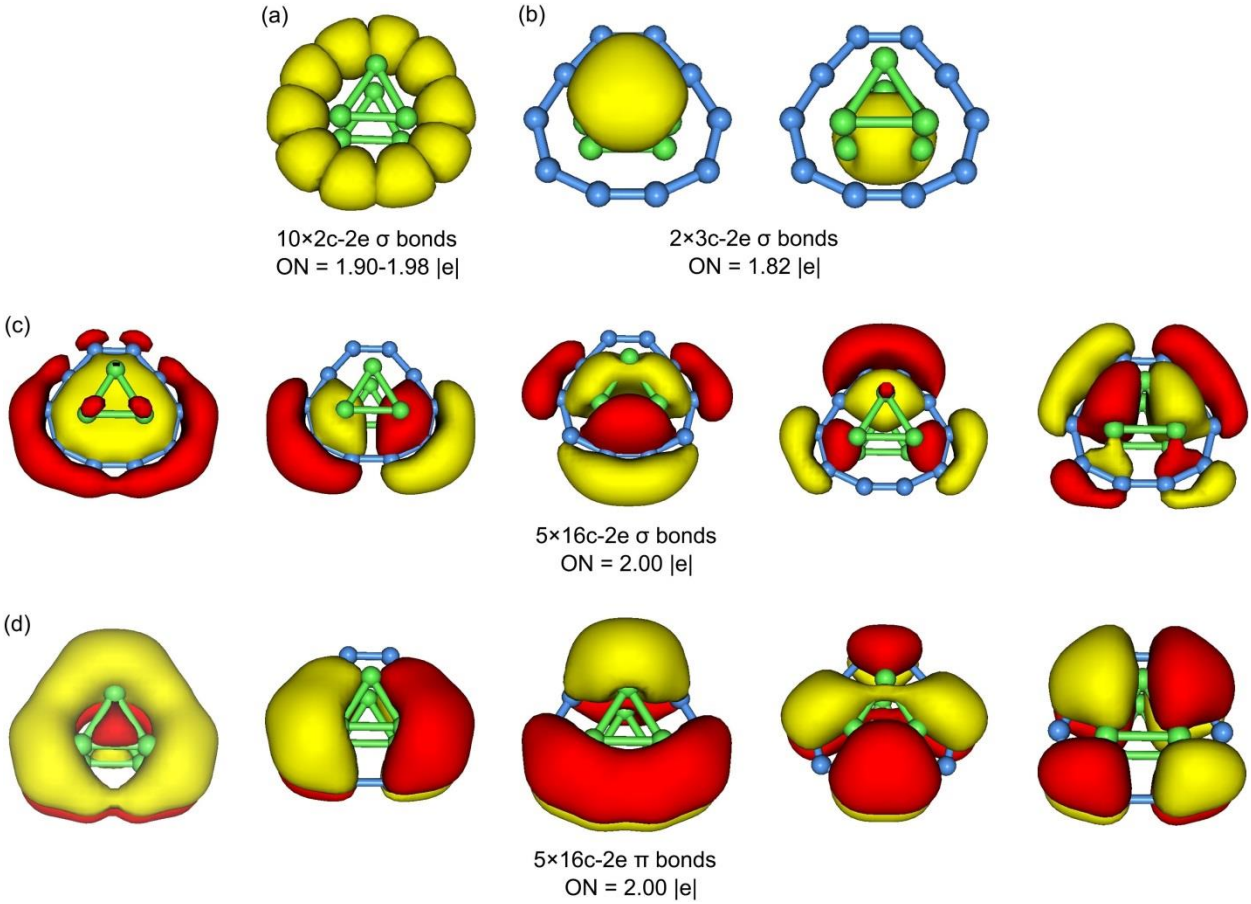

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