Structural Diversity in $B_7O_7^{+/0/-}$ Clusters: Emergence of Seven-Membered Ring and Inverted Heart-like Ring Stabilized By *3c-2e* Localized-Bond

Wen-Juan Tian,* Zi-Yan Guo,[a] Jing-Jing Wang,[a] Hui-Qing Sun, Feng-Li Yang, Rui Bao, Hong-Xin Lv

Institute of Molecular Science, Shanxi University, Taiyuan 030006, China

a Z.-Y. Guo and J.-J. Wang contributed equally to this work

Figures S1-S3 Alternative low-lying isomeric structures of $B_7O_7^{+/0/-}$ cluster at the B3LYP/6-311+G(d,p) level. Relative energies with zero-point energy (ZPE) corrections are presented in kcal mol^{-1}, at the B3LYP/6-311+G(d,p), PBE0/6-311+G(d,p) (in *italic*), and single-point CCSD(T)//B3LYP/ 6-311+G(d,p) (in **bold**) levels, respectively. Red color represents the O atoms.

Figure S4 Calculated Wiberg bond indices (left) and natural atomic charges (in |e|, right) for B_7O_7 (**3**) and $B_7O_7^-$ (**5**) clusters based on NBO analyses at the B3LYP/6-311+G(d,p) level.

Figure S5 Pictures of CMOs for $B_7O_7^{+/0/-}$ cluster (a-e).

Figure S6 Electron localization function (ELF) maps, (a) $B_7O_7^+$(**1**), (b) B_7O_7(**2**) and (c) $B_7O_7^-$(**4**).

Figure S7 Investigating σ or π electrons separately, (a) the ELF-σ of $B_7O_7^+$(**1**), (b) the ELF-π of $B_7O_7^+$(**1**), (c) the ELF-π of B_7O_7(**2**) and (d) the ELF-π of $B_7O_7^-$(**4**).

Figure S8 Chemical bonding scheme of LM B_7O_7 (**3**) cluster according to AdNDP analysis. Occupation numbers (ONs) are shown.

Figure S9 TDOS and PDOS for GM $B_7O_7^+$ (**1**, a), GM B_7O_7 (**2**, b) and GM $B_7O_7^-$ (**4**, c).

Figure S10 Chemical bonding scheme of LM $B_7O_7^-$ (**5**) cluster according to AdNDP analysis. Occupation numbers (ONs) are shown.

Figure S11 Born-Oppenheimer molecular dynamics simulations of $B_7O_7^+$ (**1**, a), B_7O_7 (**2**, b) and $B_7O_7^-$ (**4**, c) at 900K for 30 ps. The maximum bond length deviation (MAXD) values (on average) are indicated in Å.

Figure S12 Calculated infrared (IR) absorption spectra (in cm^{-1}) for the GM structures of $B_7O_7^{+/0/-}$ (**1**, **2**, **4**).

Table S1 The relative energies (in kcal/mol) of the GM $B_7O_7^{+/0/-}$ clusters (**1**, **2**, **4**) with different multiplicities at the B3LYP/6-311++g(d,p) level.

Table S2 Cartesian coordinates (in Å) at the B3LYP/ 6-311+G(d,p) level for $B_7O_7^{+/0/-}$ (**1-5**) clusters.

Figure S1 Alternative low-lying isomeric structures of $B_7O_7^+$ cation cluster at the B3LYP/6-311+G(d,p) level. Relative energies with zero-point energy (ZPE) corrections are presented in kcal mol^{-1}, at the B3LYP/6-311+G(d,p), PBE0/6-311+G(d,p) (in *italic*), and single-point CCSD(T)//B3LYP/ 6-311+G(d,p) (in **bold**) levels, respectively. Red color represents the O atoms.

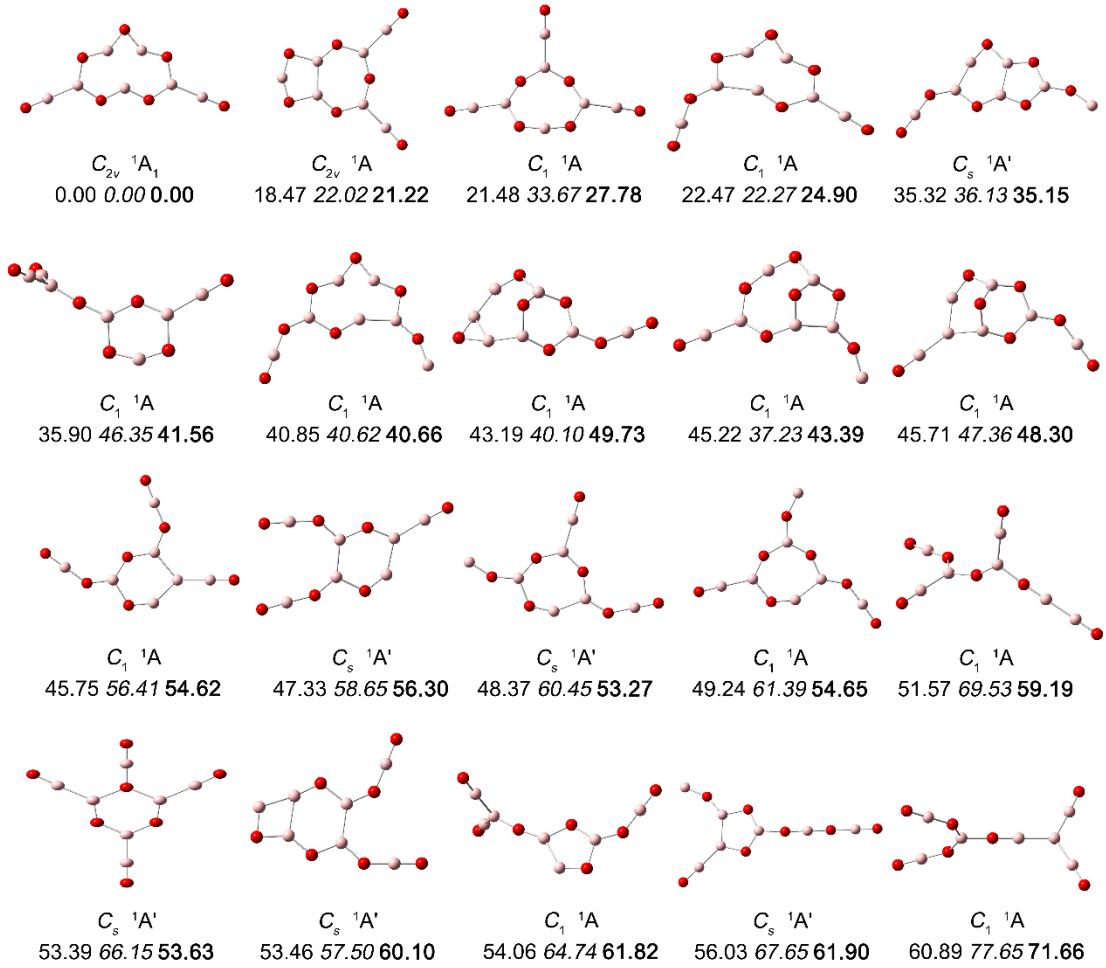


Figure S2 Alternative low-lying isomeric structures of B_7O_7 cluster at the B3LYP/6-311+G(d,p) level. Relative energies with zero-point energy (ZPE) corrections are presented in kcal mol^{-1}, at the B3LYP/6-311+G(d,p), PBE0/6-311+G(d,p) (in *italic*), and single-point CCSD(T)//B3LYP/ 6-311+G(d,p) (in **bold**) levels, respectively. Red color represents the O atoms.

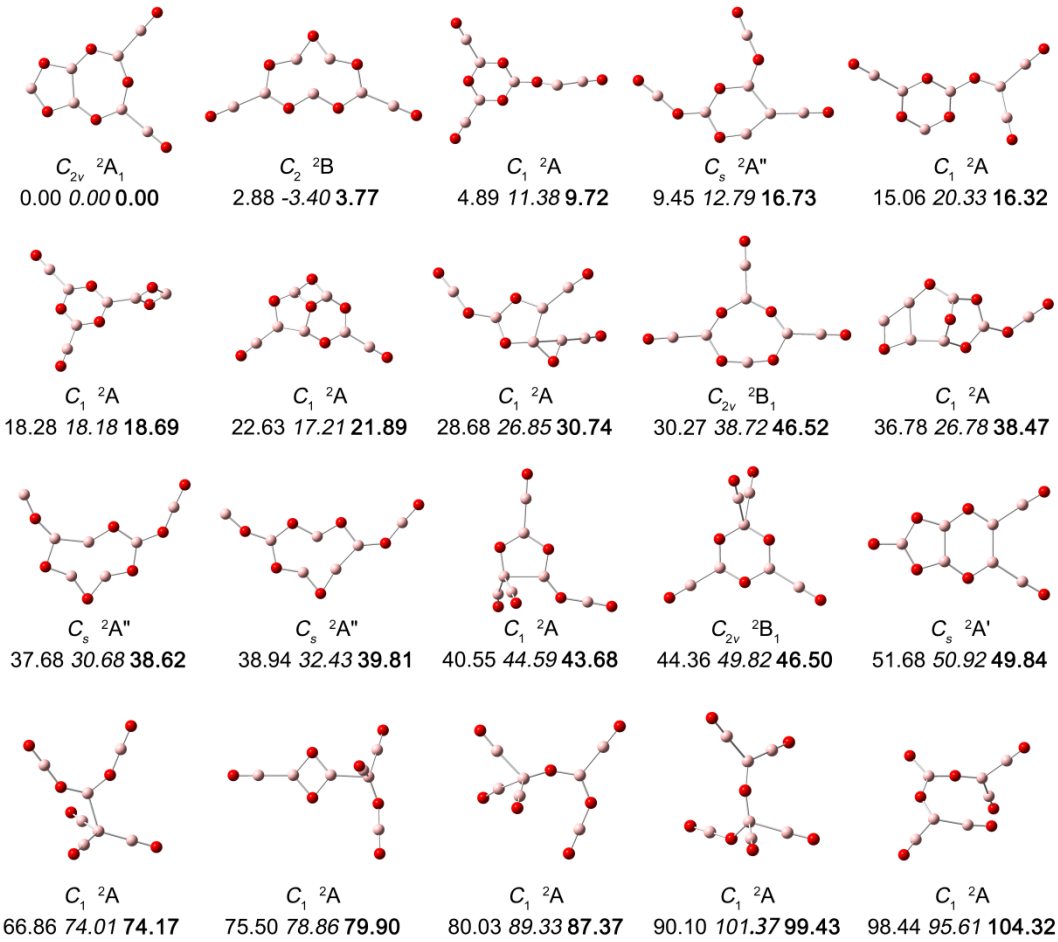


Figure S3 Alternative low-lying isomeric structures of $B_7O_7^-$ anion cluster at the B3LYP/6-311+G(d,p) level. Relative energies with zero-point energy (ZPE) corrections are presented in kcal mol^{-1}, at the B3LYP/6-311+G(d,p), PBE0/6-311+G(d,p) (in *italic*), and single-point CCSD(T)//B3LYP/ 6-311+G(d,p) (in **bold**) levels, respectively. Red color represents the O atoms.

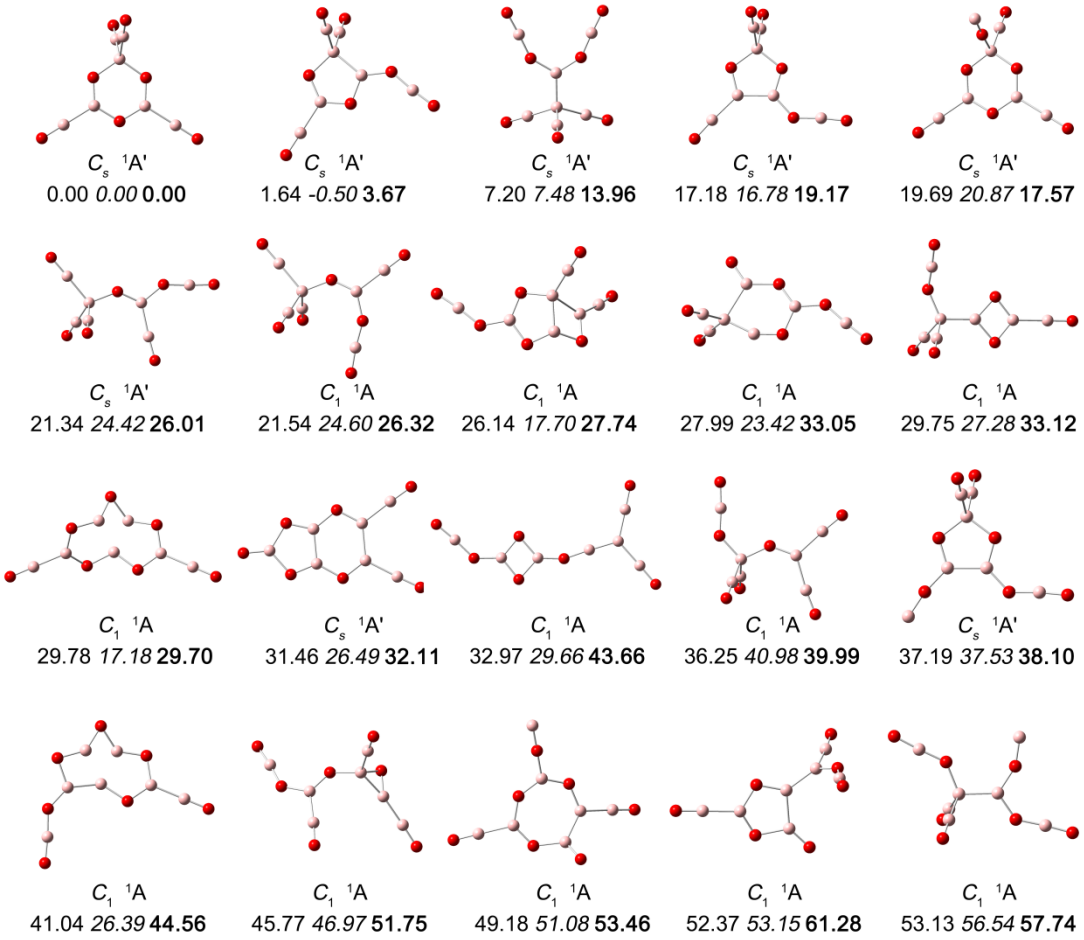
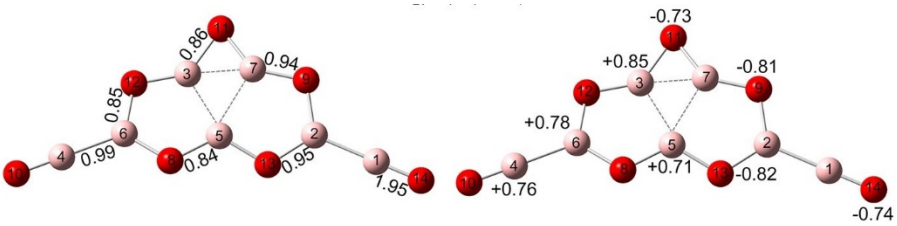
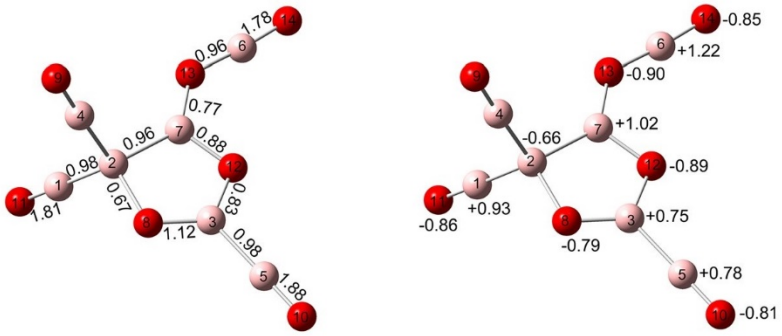


Figure S4 Calculated Wiberg bond indices (left) and natural atomic charges (in |e|, right) for B_7O_7 (**3**) and $B_7O_7^-$ (**5**) clusters from NBO analyses at the B3LYP/6-311+G(d,p) level.

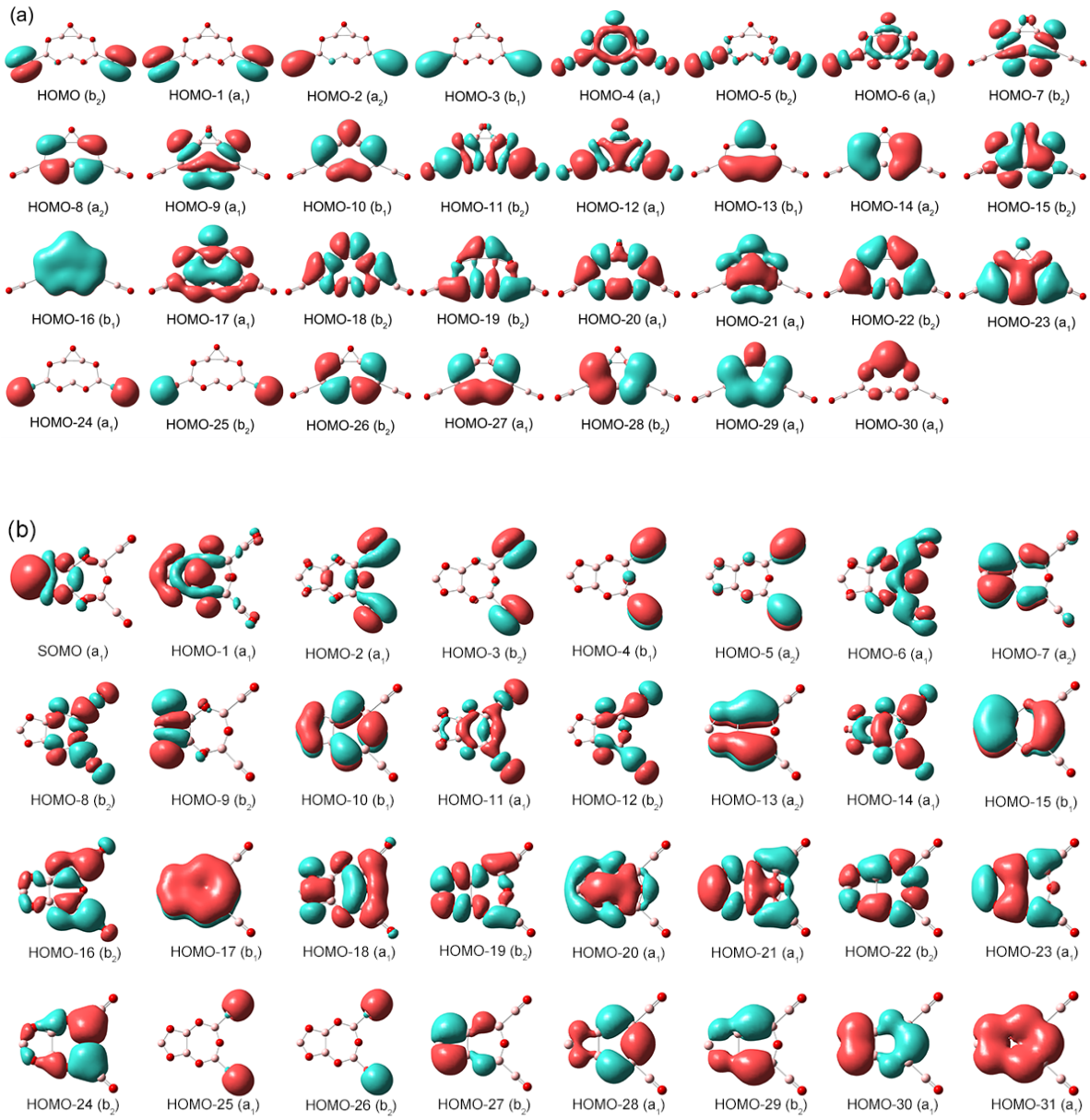


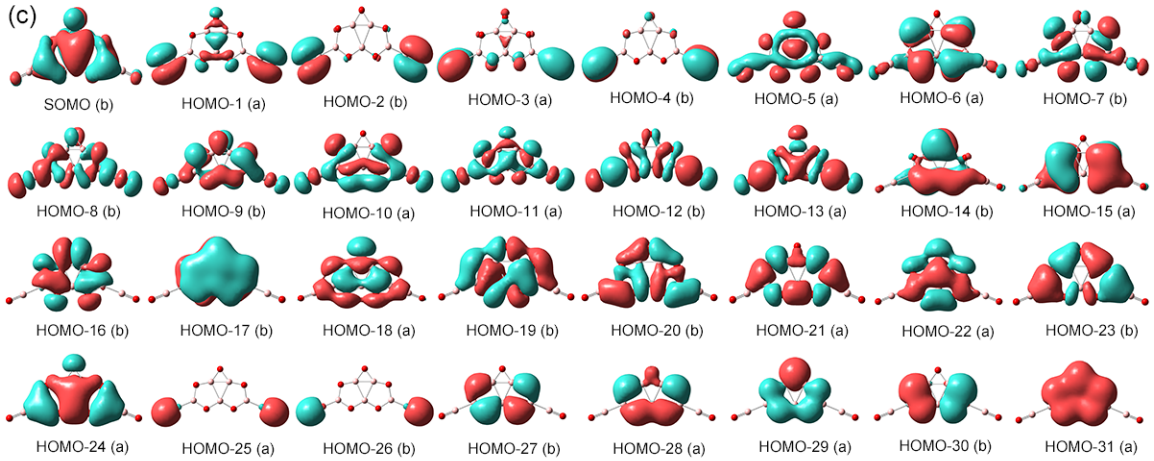
3 C_2 B_7O_7 (^{2}B)

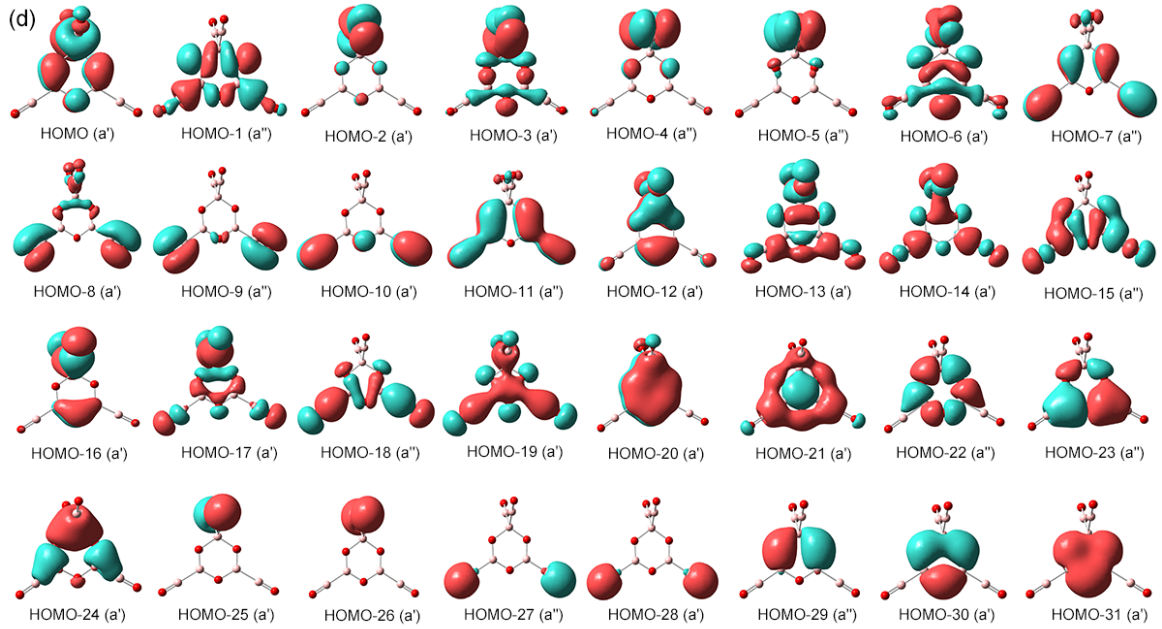


5 C_s $B_7O_7^-$ (^{1}A')

Figure S5 Pictures of CMOs for $B_7O_7^{+/0/-}$ (**1-5**) cluster, (a) for $B_7O_7^{+}$(**1**), (b) for B_7O_7(**2**), (c) for B_7O_7(**3**), (d) for $B_7O_7^{-}$(**4**) and (e) for $B_7O_7^{-}$(**5**).




(c)
SOMO (b)
HOMO-1 (a)
HOMO-2 (b)
HOMO-3 (a)
HOMO-4 (b)
HOMO-5 (a)
HOMO-6 (a)
HOMO-7 (b)
HOMO-8 (b)
HOMO-9 (b)
HOMO-10 (a)
HOMO-11 (a)
HOMO-12 (b)
HOMO-13 (a)
HOMO-14 (b)
HOMO-15 (a)
HOMO-16 (b)
HOMO-17 (b)
HOMO-18 (a)
HOMO-19 (b)
HOMO-20 (b)
HOMO-21 (a)
HOMO-22 (a)
HOMO-23 (b)
HOMO-24 (a)
HOMO-25 (a)
HOMO-26 (b)
HOMO-27 (b)
HOMO-28 (a)
HOMO-29 (a)
HOMO-30 (b)
HOMO-31 (a)


(d)
HOMO (a')
HOMO-1 (a'')
HOMO-2 (a')
HOMO-3 (a')
HOMO-4 (a'')
HOMO-5 (a'')
HOMO-6 (a')
HOMO-7 (a'')
HOMO-8 (a')
HOMO-9 (a'')
HOMO-10 (a')
HOMO-11 (a'')
HOMO-12 (a')
HOMO-13 (a')
HOMO-14 (a')
HOMO-15 (a'')
HOMO-16 (a')
HOMO-17 (a')
HOMO-18 (a'')
HOMO-19 (a')
HOMO-20 (a')
HOMO-21 (a')
HOMO-22 (a'')
HOMO-23 (a'')
HOMO-24 (a')
HOMO-25 (a')
HOMO-26 (a')
HOMO-27 (a'')
HOMO-28 (a')
HOMO-29 (a'')
HOMO-30 (a')
HOMO-31 (a')

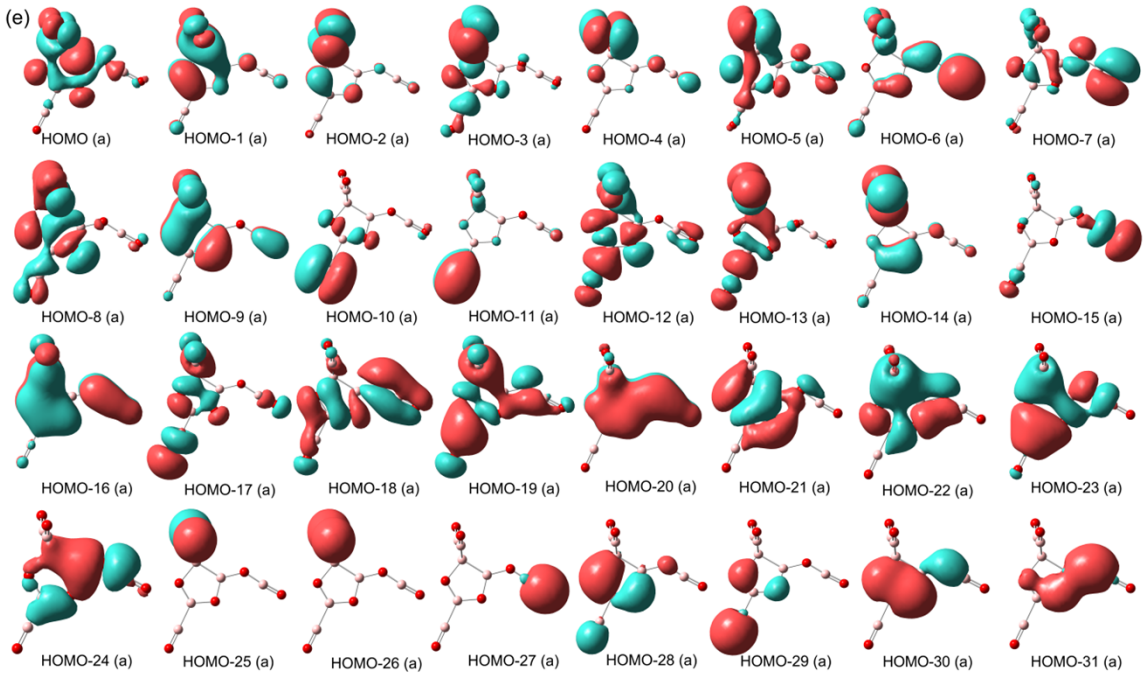


Figure S6 Electron localization function (ELF) maps, (a) $B_7O_7^+$(**1**), (b) B_7O_7(**2**) and (c) $B_7O_7^-$(**4**).

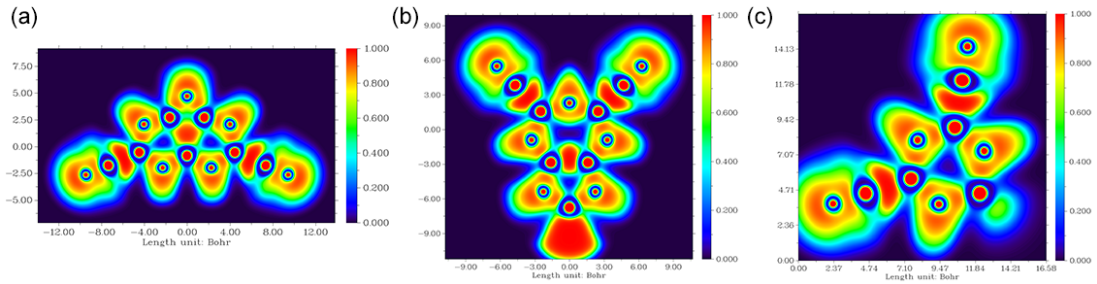


Figure S7 Investigating σ or π electrons separately, (a) the ELF-σ of $B_7O_7^+$ (**1**), (b) the ELF-π of $B_7O_7^+$ (**1**), (c) the ELF-π of B_7O_7 (**2**) and (d) the ELF-π of $B_7O_7^-$ (**4**).

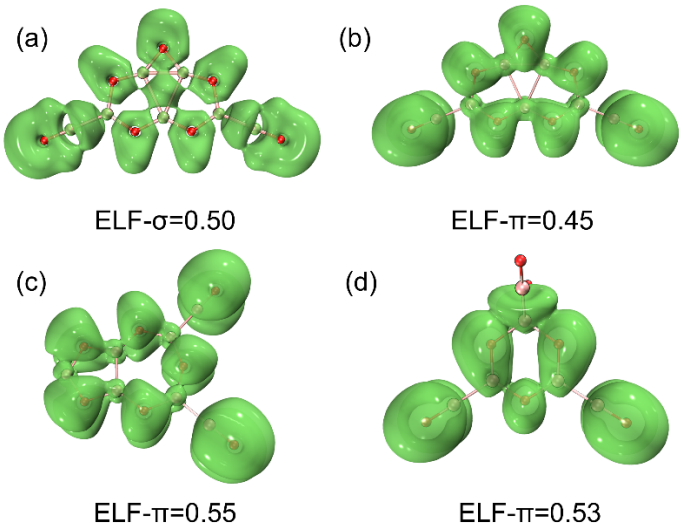


Figure S8 Chemical bonding scheme of LM B_7O_7 (**3**) cluster according to AdNDP analysis. Occupation numbers (ONs) are shown.

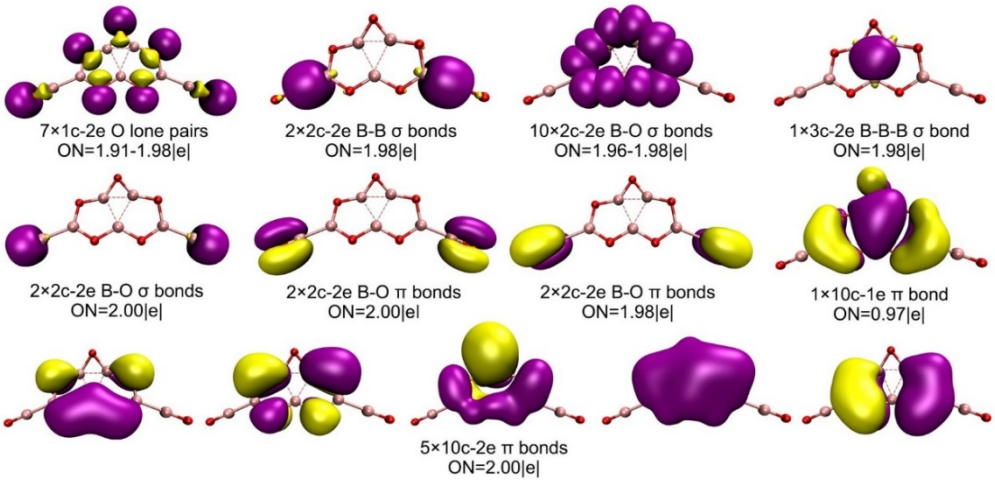


Figure S9 TDOS and PDOS for GM $B_7O_7^+$ (a), GM B_7O_7 (b) and GM $B_7O_7^-$ (c).

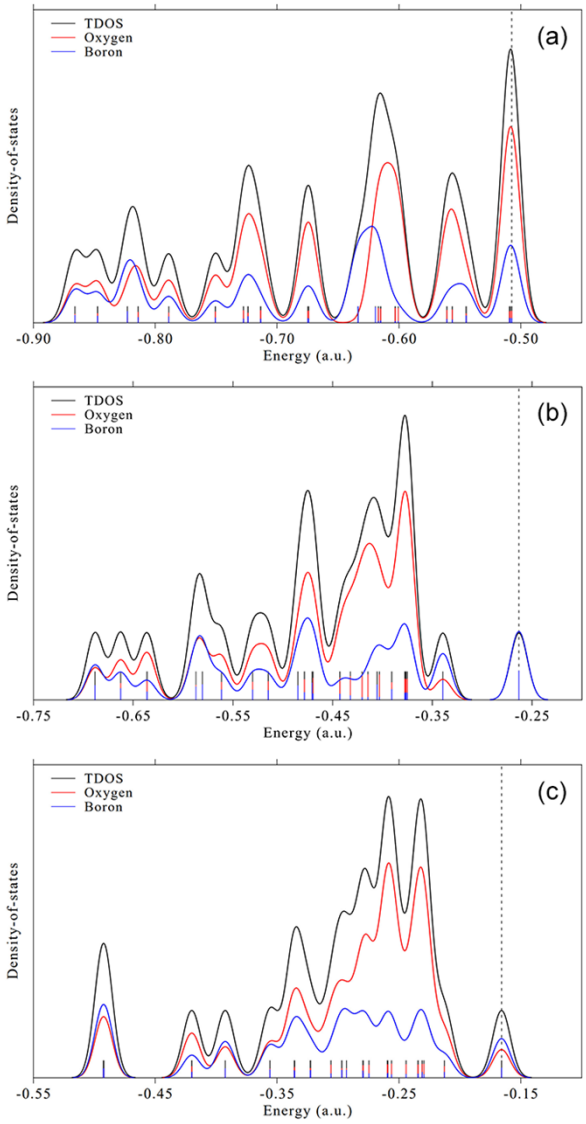


Figure S10 Chemical bonding scheme of LM $B_7O_7^-$ (**5**) cluster according to AdNDP analysis. Occupation numbers (ONs) are shown.

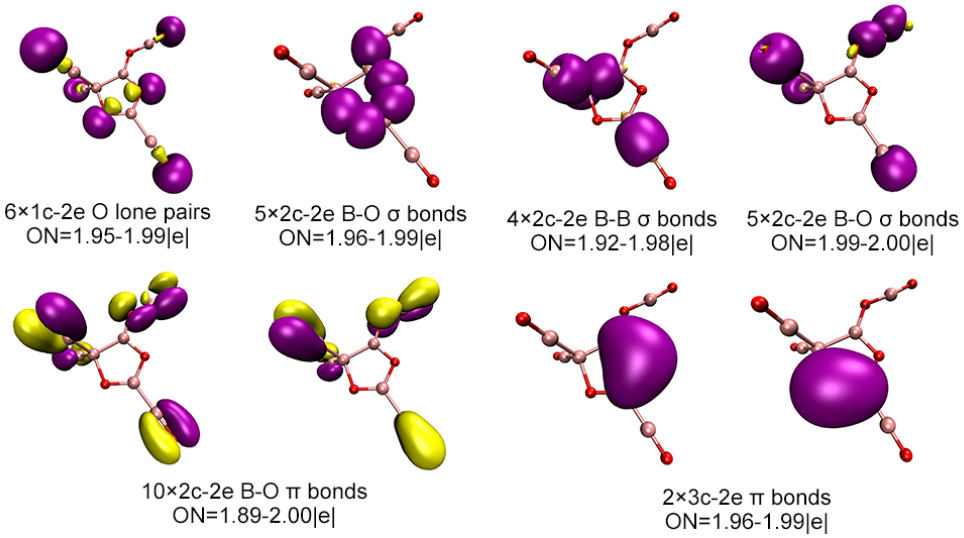


Figure S11 MAXD (in Å) versus simulation time (in ps) for the BOMD simulations of GM structures of $B_7O_7^{+/0/-}$ at the PBE/DZVP level and 900 K.

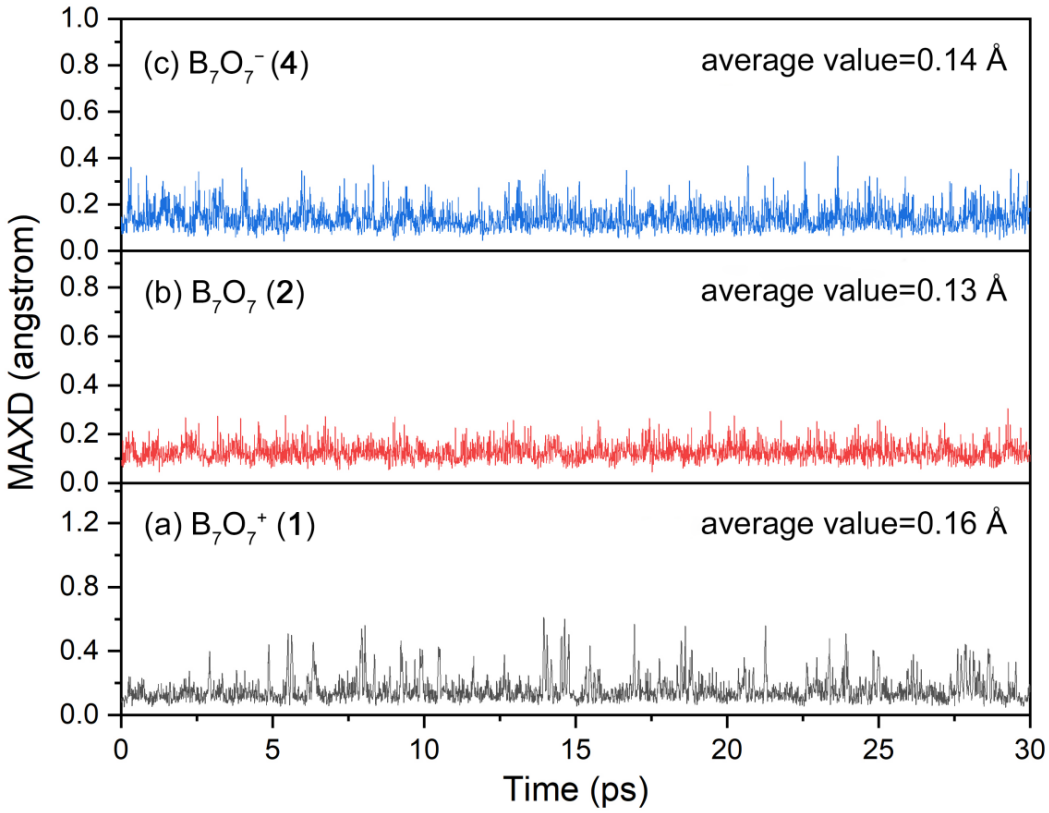


Figure S12 Calculated infrared (IR) absorption spectra (in cm^{-1}) for the GM structures of $B_7O_7^{+/0/-}$.

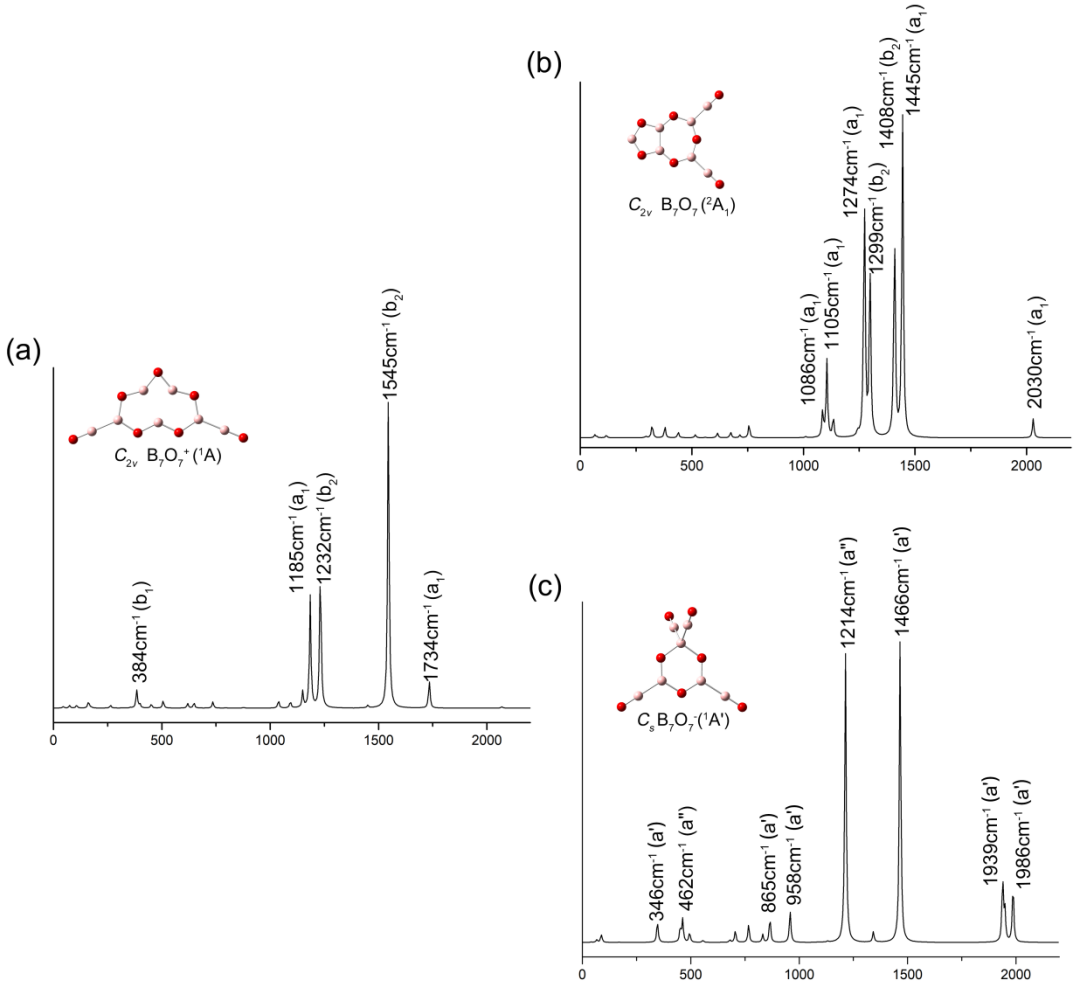


Table S1 The relative energies (in kcal/mol) of $B_7O_7^{+/0/-}$ clusters with different multiplicities at the B3LYP/6-311++g(d,p) level.

	$B_7O_7^+$			B_7O_7			$B_7O_7^-$		
Multiplicity	Singlet	Triplet	Quintet	Doublet	Quartet	Sextet	Singlet	Triplet	Quintet
Relative energies	0.00	75.31	185.26	0.00	78.56	196.17	0.00	83.96	197.07

Table S2 Cartesian coordinates (in Å) at the B3LYP/ 6-311+G(d,p) level for $B_7O_7^{+/0/-}$ (**1-5**) cluster.

1. C_{2v} $B_7O_7^+$ (**1**)

B	0.00000000	3.89520900	-0.91617200
B	0.00000000	2.36391500	-0.27123800
B	0.00000000	-0.85453100	1.45750800
B	0.00000000	-3.89520900	-0.91617200
B	0.00000000	0.00000000	-0.43375100
B	0.00000000	-2.36391500	-0.27123800
B	0.00000000	0.85453100	1.45750800
O	0.00000000	-1.20303600	-1.03117200
O	0.00000000	2.12667600	1.12108100
O	0.00000000	-4.99840400	-1.37792400
O	0.00000000	0.00000000	2.50950200
O	0.00000000	-2.12667600	1.12108100
O	0.00000000	1.20303600	-1.03117200
O	0.00000000	4.99840400	-1.37792400

2. C_{2v} B_7O_7 (**2**)

B	0.00000000	0.00000000	-3.55055900
B	0.00000000	1.31806100	0.84431600
B	0.00000000	0.84570300	-1.49601200
B	0.00000000	-0.84570300	-1.49601200
B	0.00000000	-2.49148500	2.05047400
B	0.00000000	-1.31806100	0.84431600
O	0.00000000	0.00000000	1.23672700
O	0.00000000	1.73954200	-0.46345800
O	0.00000000	1.19191300	-2.83568700
O	0.00000000	-3.32529900	2.91609600
O	0.00000000	-1.73954200	-0.46345800
O	0.00000000	-1.19191300	-2.83568700
B	0.00000000	2.49148500	2.05047400
O	0.00000000	3.32529900	2.91609600

3. $C_2\,B_7O_7$ (**3**)

B	0.00000000	3.87563500	-0.91269700
B	0.04599500	2.34096400	-0.26438800
B	-0.21570900	-0.79809000	1.37860000
B	0.00000000	-3.87563500	-0.91269700
B	0.00000000	0.00000000	-0.30177900
B	-0.04599500	-2.34096400	-0.26438800
B	0.21570900	0.79809000	1.37860000
O	0.09012000	-1.20273700	-1.00247100
O	0.22616800	2.11884000	1.10343100
O	0.03663100	-4.98368700	-1.37703700
O	0.00000000	0.00000000	2.48887400
O	-0.22616800	-2.11884000	1.10343100
O	-0.09012000	1.20273700	-1.00247100
O	-0.03663100	4.98368700	-1.37703700

4. $C_s\,B_7O_7^-$ (**4**)

B	-0.00000300	-0.95752200	1.19415700
B	-0.00001200	1.23219300	0.00000000
B	0.00000500	-1.84814700	-2.63456900
B	-1.40543200	2.22108600	0.00000000
B	0.00000500	-1.84814700	2.63456900
B	-0.00000300	-0.95752200	-1.19415700
O	-0.00000200	0.37113000	1.23964000
O	-0.00000200	-2.48477500	-3.66150700
O	-0.00000200	-1.67648700	0.00000000
O	-2.38748200	2.93220400	0.00000000
O	-0.00000200	0.37113000	-1.23964000
O	-0.00000200	-2.48477500	3.66150700
B	1.40544000	2.22107700	0.00000000
O	2.38749100	2.93218700	0.00000000

5. $C_s\,B_7O_7^-$ (**5**)

B	0.84292800	1.97974900	-1.37454800
B	0.25577100	1.22481700	-0.00020200
B	-1.65401100	-0.15171100	-0.00007900
B	0.84264400	1.97880500	1.37485000
B	-3.26568700	-0.64377800	-0.00011500
B	1.97731900	-2.50778300	-0.00025700
B	0.58175200	-0.44241100	0.00020500
O	-1.29754200	1.13070600	-0.00024800
O	1.29152400	2.48916600	2.38166200

O	-4.42331900	-0.98865900	-0.00025800
O	1.29189100	2.49105000	-2.38083900
O	-0.62996000	-1.11824300	0.00029700
O	1.74858300	-1.21551300	0.00042700
O	2.28087600	-3.68706200	-0.00095100