SUPPLEMENTARY INFORMATION

Boron-based tubular BeB$_{12}^{+}$ and quasi-planar BeB$_{12}^{0/-}$ clusters: structural transformation and chemical bonding†

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Table S1. Cartesian coordinates for the global-minimum (GM) structures of BeB$_{12}^{-/0/+}$ clusters at the PBE0/6-311+G (d) level.
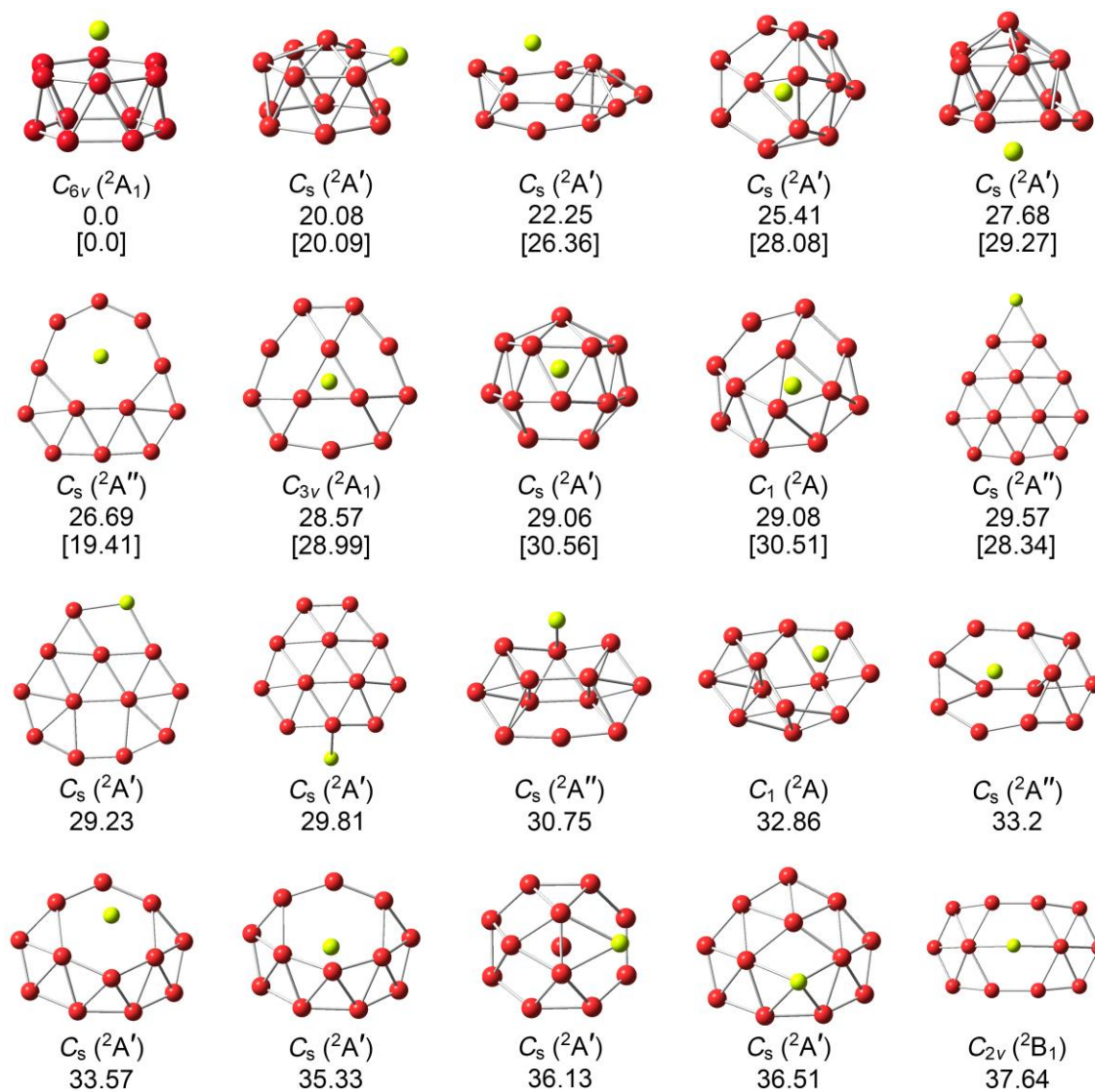
Figure S1. Alternative low-lying structures of BeB$_{12}^{+}$ cluster at the PBE0-D3/6-311+G(d) level. Relative energies are shown with corrections for zero-point energies (ZPEs). Also shown are energies for top ten low-lying isomers at the single-point CCSD(T)/6-311+G(d) level in square brackets. All energies are in kcal mol^{-1}.

Figure S2. Alternative low-lying structures of BeB$_{12}$ cluster at the PBE0-D3/6-311+G(d) level. Relative energies are shown with corrections for zero-point energies (ZPEs). Also shown are energies for top low-lying isomers at the single-point CCSD(T)/6-311+G(d) level in square brackets. All energies are in kcal mol^{-1}.

Figure S3. Alternative low-lying structures of BeB$_{12}^{-}$ cluster at the PBE0-D3/6-311+G(d) level. Relative energies are shown with corrections for zero-point energies (ZPEs). Also shown are energies for top low-lying isomers at the single-point CCSD(T)/6-311+G(d) level in square brackets. All energies are in kcal mol^{-1}.
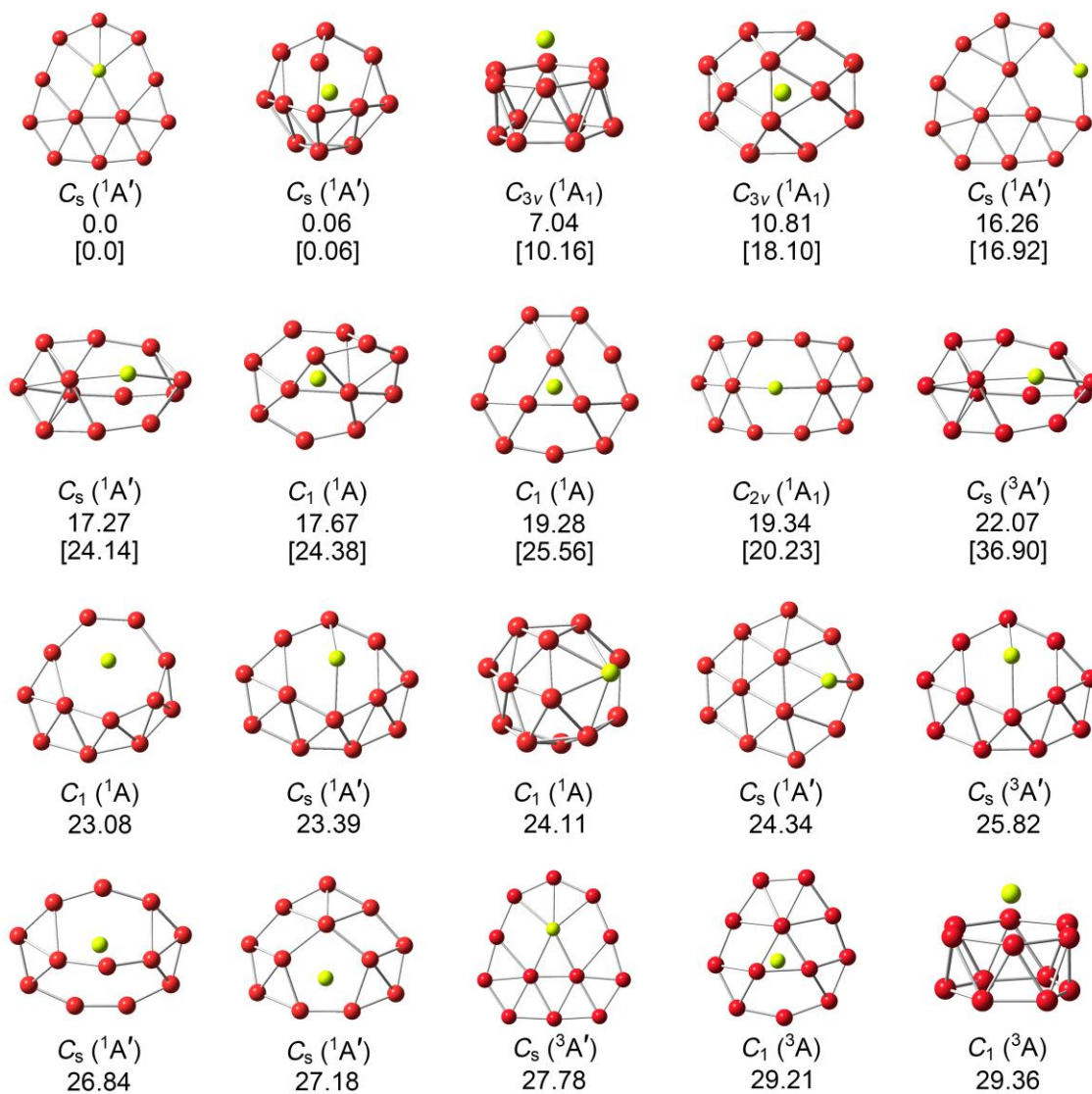
Figure S1. Alternative low-lying structures of BeB_{12}^{+} cluster at the PBE0-D3/6-311+G(d) level. Relative energies are shown with corrections for zero-point energies (ZPEs). Also shown are energies for top ten low-lying isomers at the single-point CCSD(T)/6-311+G(d) level in square brackets. All energies are in kcal mol^{-1}.

C_{6v} ($^2A_1$)
0.0
[0.0]

C_s ($^2A'$)
20.08
[20.09]

C_s ($^2A'$)
22.25
[26.36]

C_s ($^2A'$)
25.41
[28.08]

C_s ($^2A'$)
27.68
[29.27]

C_s ($^2A''$)
26.69
[19.41]

C_{3v} ($^2A_1$)
28.57
[28.99]

C_s ($^2A'$)
29.06
[30.56]

C_1 (^2A)
29.08
[30.51]

C_s ($^2A''$)
29.57
[28.34]

C_s ($^2A'$)
29.23

C_s ($^2A'$)
29.81

C_s ($^2A''$)
30.75

C_1 (^2A)
32.86

C_s ($^2A''$)
33.2

C_s ($^2A'$)
33.57

C_s ($^2A'$)
35.33

C_s ($^2A'$)
36.13

C_s ($^2A'$)
36.51

C_{2v} ($^2B_1$)
37.64

Figure S2. Alternative low-lying structures of BeB_{12} cluster at the PBE0-D3/6-311+G(d) level. Relative energies are shown with corrections for zero-point energies (ZPEs). Also shown are energies for top low-lying isomers at the single-point CCSD(T)/6-311+G(d) level in square brackets. All energies are in kcal mol^{-1}.

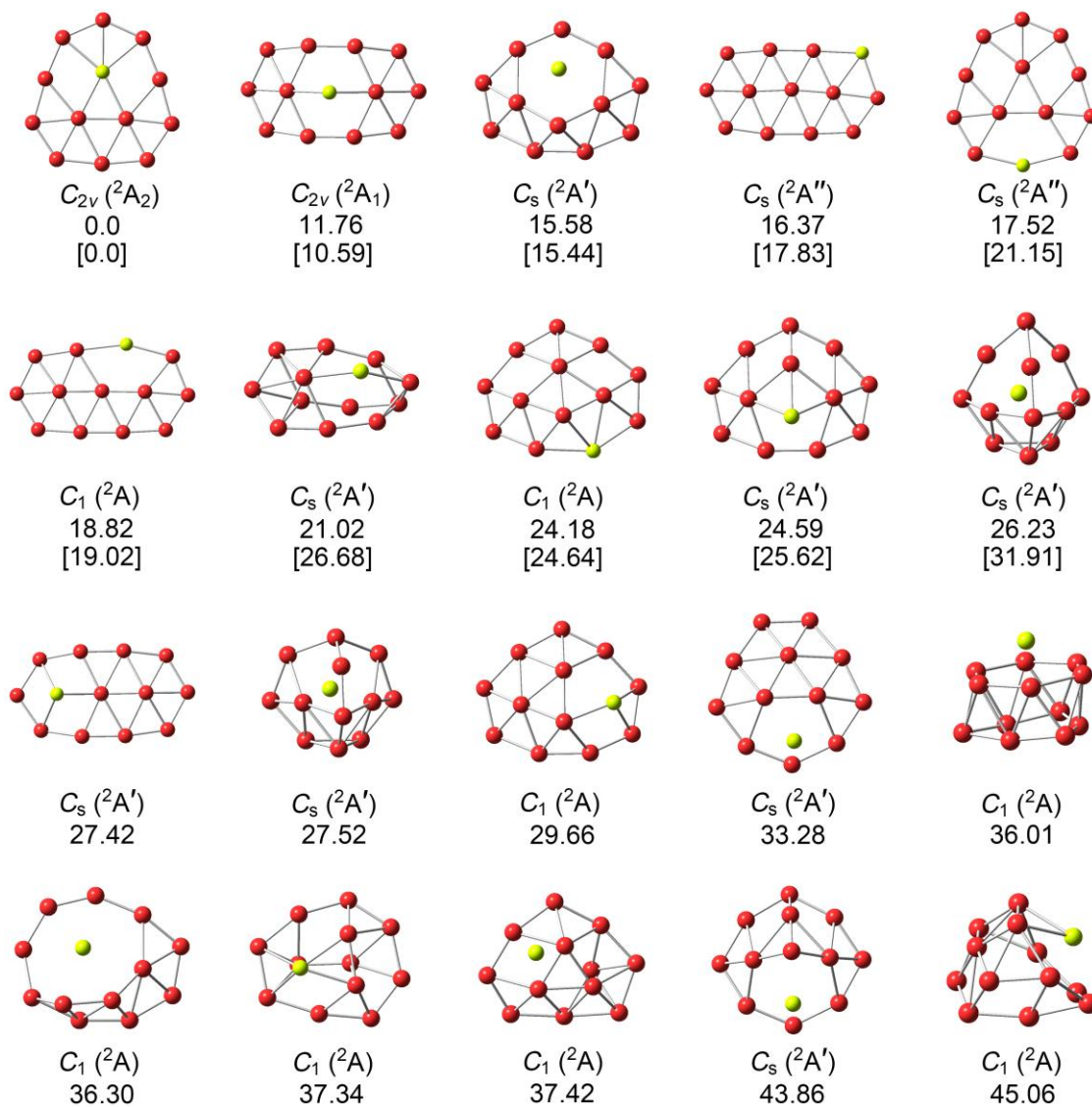|				
C_s ($^1A'$)	C_s ($^1A'$)	C_{3v} ($^1A_1$)	C_{3v} ($^1A_1$)	C_s ($^1A'$)
0.0	0.06	7.04	10.81	16.26
[0.0]	[0.06]	[10.16]	[18.10]	[16.92]
C_s ($^1A'$)	C_1 (^1A)	C_1 (^1A)	C_{2v} ($^1A_1$)	C_s ($^3A'$)
17.27	17.67	19.28	19.34	22.07
[24.14]	[24.38]	[25.56]	[20.23]	[36.90]
C_1 (^1A)	C_s ($^1A'$)	C_1 (^1A)	C_s ($^1A'$)	C_s ($^3A'$)
23.08	23.39	24.11	24.34	25.82
C_s ($^1A'$)	C_s ($^1A'$)	C_s ($^3A'$)	C_1 (^3A)	C_1 (^3A)
26.84	27.18	27.78	29.21	29.36

Figure S3. Alternative low-lying structures of BeB_{12}^- cluster at the PBE0-D3/6-311+G(d) level. Relative energies are shown with corrections for zero-point energies (ZPEs). Also shown are energies for top low-lying isomers at the single-point CCSD(T)/6-311+G(d) level in square brackets. All energies are in kcal mol^{-1}.

C_{2v} ($^2A_2$)
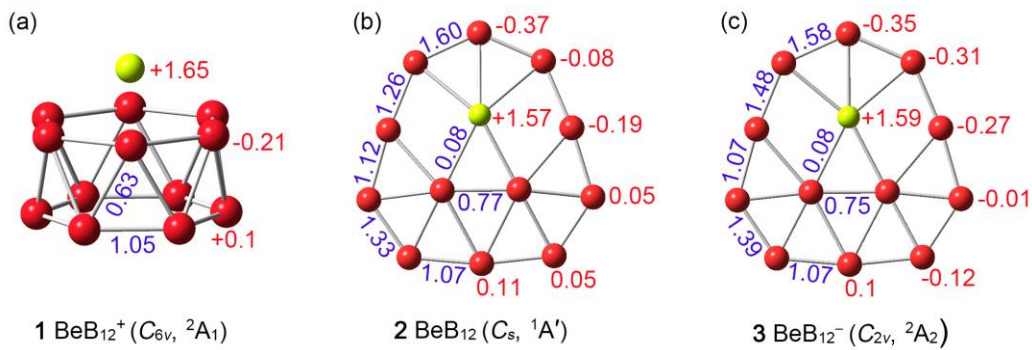0.0
[0.0]

C_{2v} ($^2A_1$)
11.76
[10.59]

C_s ($^2A'$)
15.58
[15.44]

C_s ($^2A''$)
16.37
[17.83]

C_s ($^2A''$)
17.52
[21.15]

C_1 (^2A)
18.82
[19.02]

C_s ($^2A'$)
21.02
[26.68]

C_1 (^2A)
24.18
[24.64]

C_s ($^2A'$)
24.59
[25.62]

C_s ($^2A'$)
26.23
[31.91]

C_s ($^2A'$)
27.42

C_s ($^2A'$)
27.52

C_1 (^2A)
29.66

C_s ($^2A'$)
33.28

C_1 (^2A)
36.01

C_1 (^2A)
36.30

C_1 (^2A)
37.34

C_1 (^2A)
37.42

C_s ($^2A'$)
43.86

C_1 (^2A)
45.06

Figure S4. Calculated Wiberg bond indices (WBIs; in bule color) and natural atomic charges (in |e|; red color) at the PBE0/6-311+G(d) level. (a) Cationic BeB_{12}^{+} (**1**, C_{2v}, $^2A_1$) cluster. (b) Neutral BeB_{12} (**2**, C_s, $^1A'$) cluster. (c) Anionic BeB_{12}^{-} (**3**, C_{2v}, $^2A_2$) cluster.

(a)

+1.65

−0.21

0.63

1.05 +0.1

1 BeB_{12}^{+} (C_{6v}, $^2A_1$)

(b)

1.60 −0.37

−0.08

1.26

1.12

0.08 +1.57 −0.19

1.33

0.77 0.05

1.07 0.11 0.05

2 BeB_{12} (C_s, $^1A'$)

(c)

1.58 −0.35

−0.31

1.48

1.07

0.08 +1.59 −0.27

1.39

0.75 −0.01

1.07 0.1 −0.12

3 BeB_{12}^{-} (C_{2v}, $^2A_2$)

Figure S5. Calculated (a) bond distances (in Å; black color), (b) Wiberg bond indices (WBIs; blue color), and (c) natural atomic charges (in |e|; red color) of a local minimum (LM) structure for BeB$_{12}$ cluster.

(a)

1.63 — 1.64 1.93 1.55 1.73 1.55 1.59 1.74 1.71 1.60 1.67

(b)

1.01 — 1.10 0.37 1.20 0.60 1.45 1.01 0.51 0.67 1.19 0.96

LM (C_s, $^1A'$)

(c)

−0.29 0.17 — −0.11 −0.27 +1.65 −0.42 −0.10 −0.28
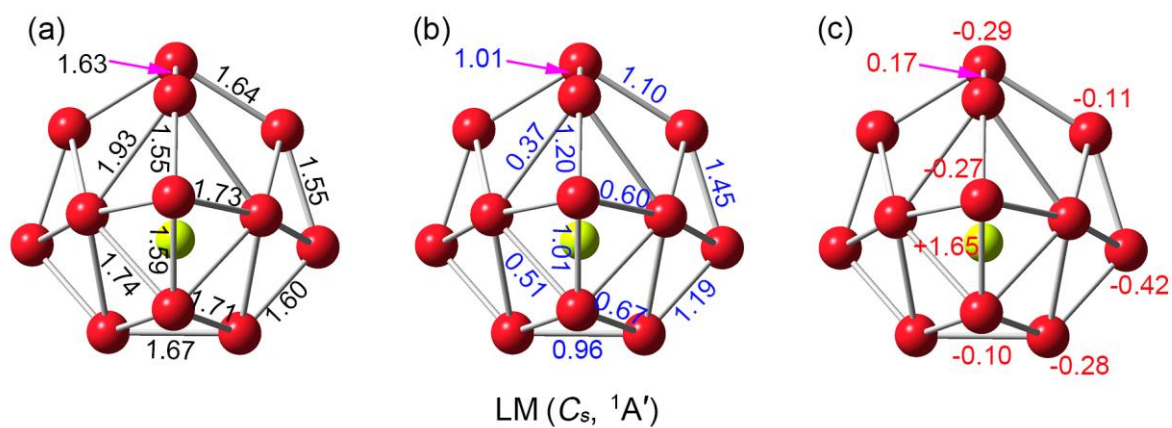
**Figure S6.** An alternative AdNDP bonding scheme of tubular BeB_{12}^{+} cluster, in which the contribution of third B atom is excluded. The occupation numbers (ONs) are slightly less than those in delocalized 3c-2e σ scheme (in Fig. 3).

(a)

12×2c-2e σ bonds
ON = 1.75 |e|

(b)

3×12c-2e σ + σ bonds
ON = 2.00 |e|

(c)

12c-2e σ - σ bond
ON = 1.82 |e|

(d)

3×12c-2e π + π bonds
ON = 1.98-1.99 |e|
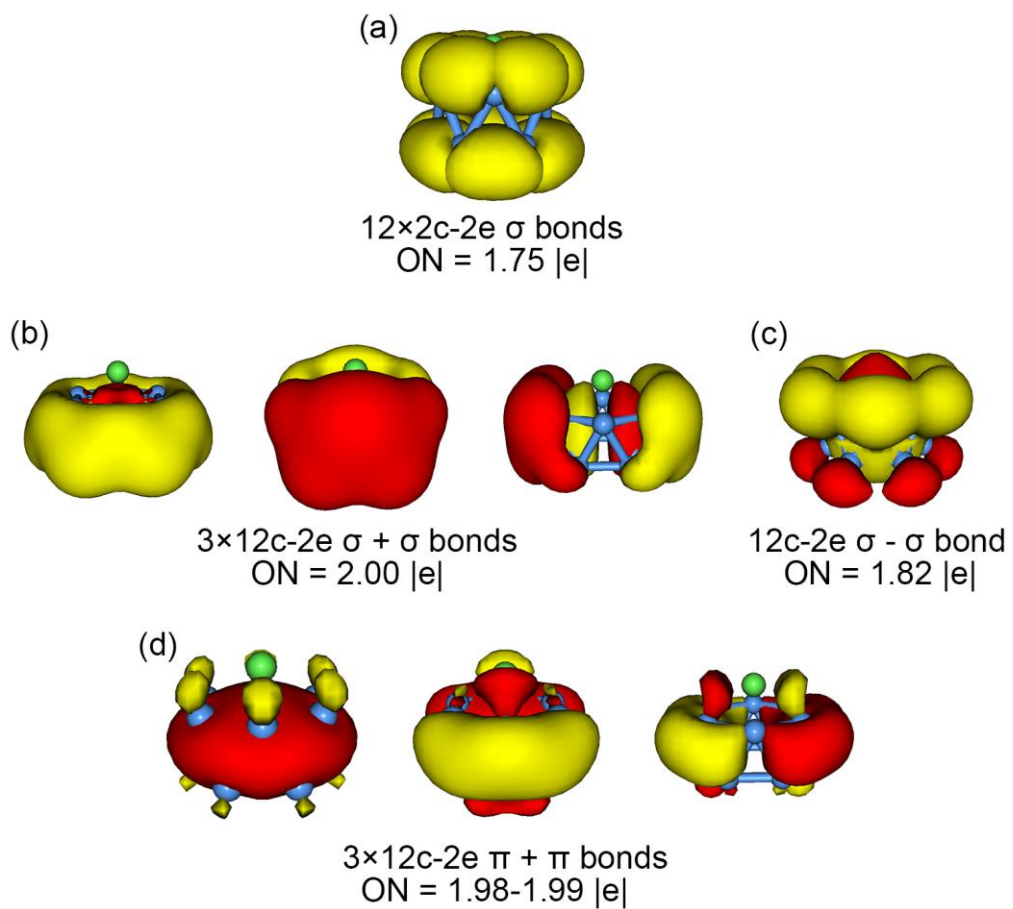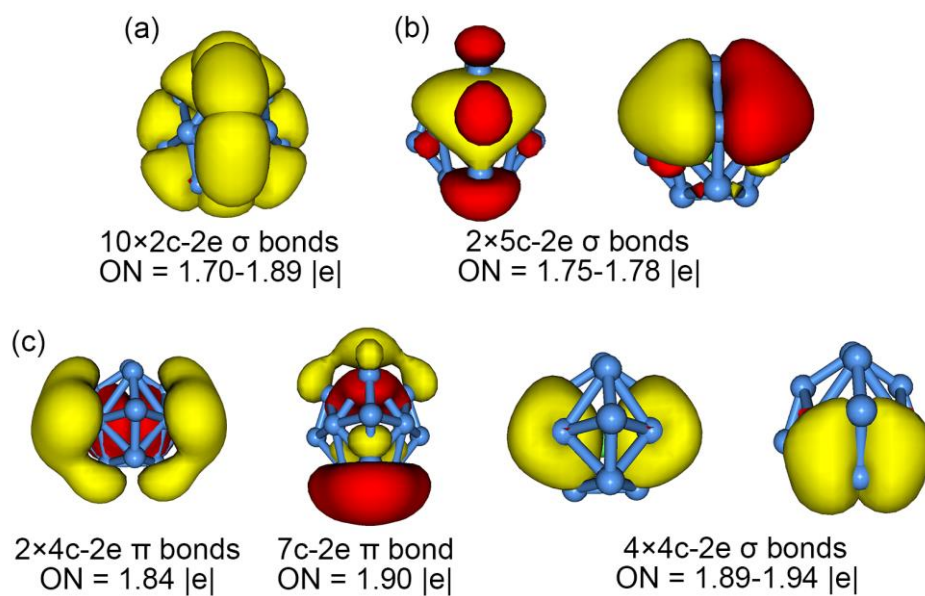
Figure S7. The occupied canonical molecular orbital (CMOs) of neutral BeB$_{12}$ (**2**, C_s, ^{1}A′). (a) Three delocalized π bonds. (b) Five delocalized σ bonds. (c) One delocalized σ bond in the BeB$_2$ core. (d) Ten delocalized σ bonds for peripheral two-center two-electron (2c-2e) B−B single bonds.
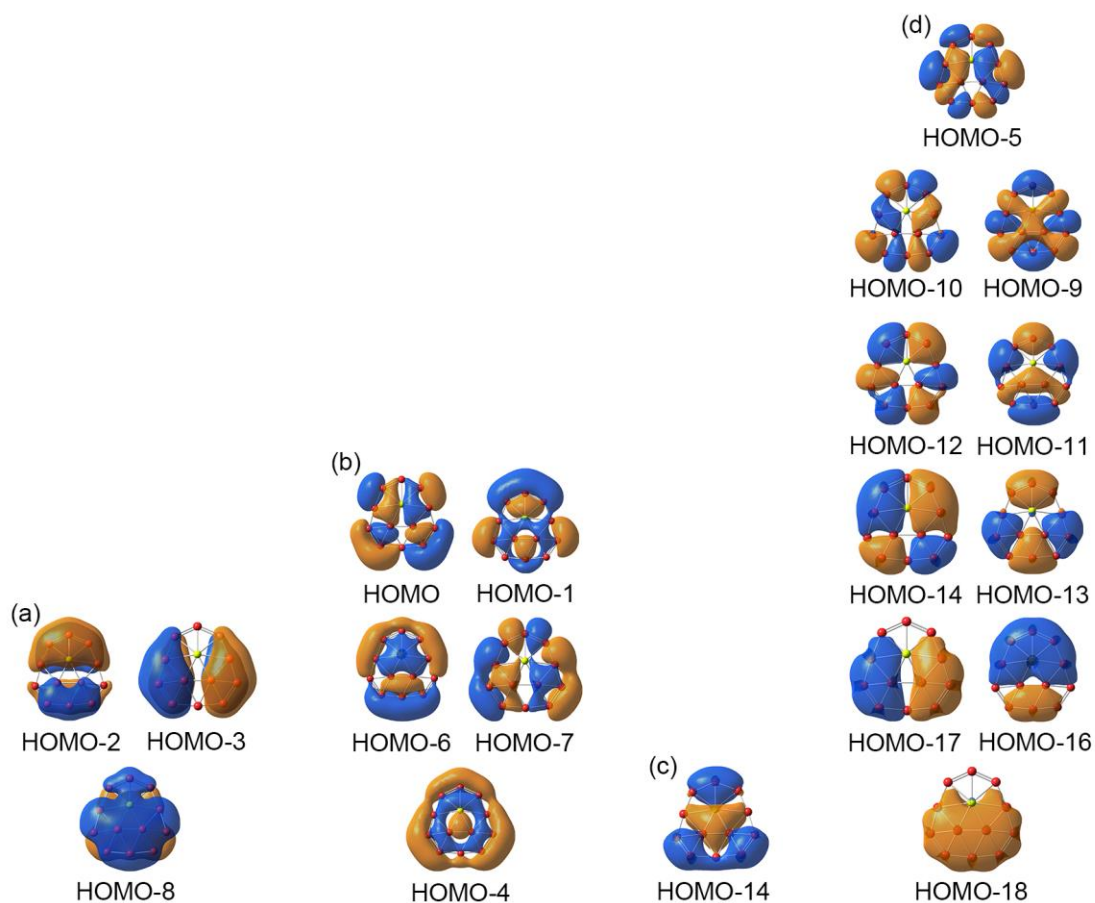
Figure S8. AdNDP bonding analysis of LM (C_s, $^1A'$) structure for neutral BeB_{12}. The ON are indicated.

(a)

10×2c-2e σ bonds
ON = 1.70-1.89 |e|

(b)

2×5c-2e σ bonds
ON = 1.75-1.78 |e|

(c)

2×4c-2e π bonds
ON = 1.84 |e|

7c-2e π bond
ON = 1.90 |e|

4×4c-2e σ bonds
ON = 1.89-1.94 |e|

Figure S9. Selected optimized structures at PBE0-D3/6-311+G(d) level for (a) GM BeB_{12}^+ (**1**, C_{6v}, $^2A_1$); (b) LM LiB_{12} (C_{2v}, $^2A'$), and (c) GM Li_2B_{12} (D_{6d}, $^1A_1$). Bond distances (in Å) are shown.

(a)

(b)

(c)

1.71

1.72

1.74

1.62

1.62

1.60

BeB_{12}^+ (C_{6v}, $^2A_1$)

LiB_{12} (C_{2v}, $^2A'$)

Li_2B_{12} (D_{6d}, $^1A_1$)
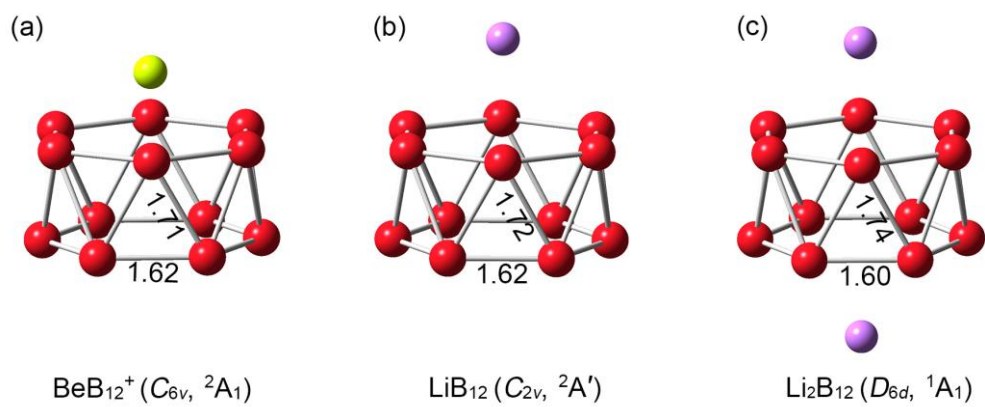
Figure S10. The displacement vectors of soft vibrational modes of neutral BeB_{12} cluster (a) global-minimum (GM) and (b) transition state (TS) structure at PBE0-D3/6-311+G(d) level, which relevant to the rotation between the peripheral B_{10} and inner BeB_2 core.
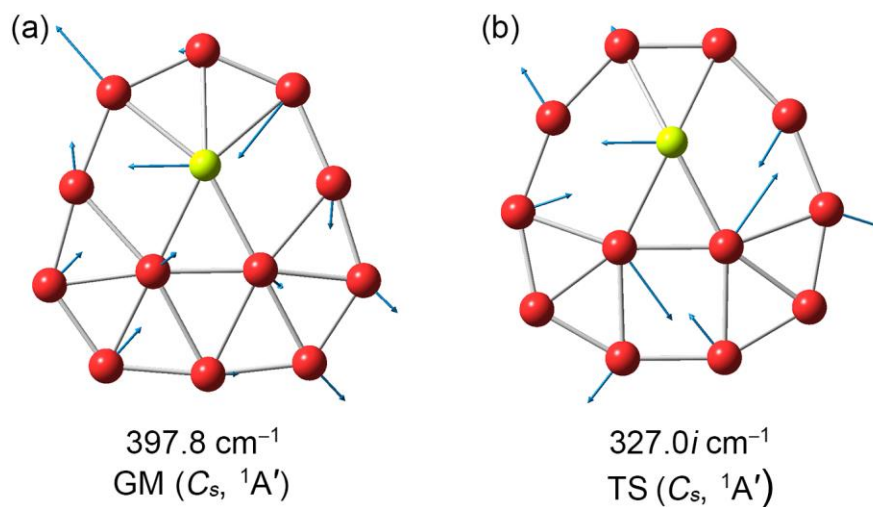
(a)

397.8 cm^{-1}
GM (C_s, $^1A'$)

(b)

327.0i cm^{-1}
TS (C_s, $^1A'$)

Table S1. Cartesian coordinates for the global-minimum (GM) structures of $BeB_{12}^{-/0/+}$ clusters at the PBE0/6-311+G (d) level.

(a) BeB_{12}^+ (**1**, C_{6v}, $^2A_1$)

B	0.00000000	1.61887800	0.63578400
B	-1.61599500	0.00000000	-0.85526500
B	0.80794900	1.39950200	-0.85517100
B	0.00000000	-1.61887800	0.63578400
B	1.40171300	-0.80928300	0.63574100
B	-1.40171300	-0.80928300	0.63574100
B	-0.80794900	1.39950200	-0.85517100
Be	0.00000000	0.00000000	1.64585000
B	-1.40171300	0.80928300	0.63574100
B	-0.80794900	-1.39950200	-0.85517100
B	0.80794900	-1.39950200	-0.85517100
B	1.40171300	0.80928300	0.63574100
B	1.61599500	0.00000000	-0.85526500

(b) BeB_{12} (**2**, C_s, $^1A'$)

B	-0.09892000	-2.10072200	1.59815500
B	0.00847200	0.70463100	2.02077600
B	-0.09949000	2.81892400	0.00000000
B	0.00847200	0.70463100	-2.02077600

B	-0.09892000	-2.10072200	-1.59815500
B	-0.06286900	-0.82152300	-2.46756800
B	-0.05718900	-2.25625300	0.00000000
B	-0.06286900	-0.82152300	2.46756800
B	-0.08228900	2.18191100	1.40791900
B	0.19697200	-0.64598400	-0.84437800
B	0.19697200	-0.64598400	0.84437800
B	-0.08228900	2.18191100	-1.40791900
Be	0.29243400	1.00087800	0.00000000

(c) BeB$_{12}^{-}$ (**3**, C_{2v}, $^{2}A_{2}$)

B	0.00000000	1.60891400	-2.11192300
B	0.00000000	0.00000000	-2.26160400
B	0.00000000	1.42677500	2.18750700
B	0.00000000	-1.60891400	-2.11192300
B	0.00000000	2.46807400	-0.82713700
B	0.00000000	-2.46807400	-0.82713700
B	0.00000000	2.03265900	0.73446100
B	0.00000000	-0.84383500	-0.66035900
B	0.00000000	0.84383500	-0.66035900
B	0.00000000	-2.03265900	0.73446100
B	0.00000000	-1.42677500	2.18750700
B	0.00000000	0.00000000	2.82480200
B	0.00000000	0.00000000	0.98963100