SUPPORTING INFORMATION

Be$_3$B$_{11}^-$ cluster: A dynamically fluxional beryllo-borospherene†

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Supplementary Information – Part I

Table S1. Cartesian coordinates for (a) the global-minimum (GM) (C_{2v}, $^1A_1$), (b) the local minimum (LM) (C_s, $^1A'$), and (c) the transition state (TS) (C_1, ^1A) structures of Be$_3$B$_{11}^-$ cluster at the PBE0/6-311+G* level.

Figure S1. Alternative optimized structures of Be$_3$B$_{11}^-$ cluster at the PBE0/6-311+G* level, the relative energies (in eV) are shown in square bracket with the corrections of zero-point energies (ZPEs), as well as for top four isomers at the single-point CCSD(T)/6-311+G*//PBE0/6-311+G* level.

Figure S2. The bond distances (in Å) obtained at the PBE0/6-311+G(d) level for (a) the GM (C_{2v}, $^1A_1$) and (b) the LM (C_s, $^1A'$) structures of Be$_3$B$_{11}^-$ cluster.

Figure S3. Calculated Wiberg bond indices (WBIs) in black and natural atomic charges (in |e|) in blue for (a) the GM (C_{2v}, $^1A_1$) and (b) the LM (C_s, $^1A'$) of $Be_3B_{11}^-$ cluster from natural bond orbital (NBO) analyses at the PBE0/6-311+G* level.

Figure S4. The parameters of (a) bond distances, (b) Wiberg bond indices (WBIs) and (c) natural atomic charges in |e| for TS (C_1, ^1A) structure of $Be_3B_{11}^-$ cluster. The WBIs and natural atomics are obtained from the natural bond orbital (NBO) analysis at the PBE0/6-311+G* level.

Figure S5 Born-Oppenheimer molecular dynamic simulations for $Be_3B_{11}^-$ cluster at (a) 300 K, (b) 400 K, and (c) 600 K for 50 ps using the software suite CP2K. Some typical GM structures are picked up during the dynamic simulations. The root-mean-square-deviation (RMSD) and maximum bond length deviation (MAXD) values (on average) are indicated.

Figure S6. The canonical molecular orbitals (CMOs) for the GM (C_{2v}, $^1A_1$) of $Be_3B_{11}^-$ cluster. (a) Thirteen σ CMOs for ten Lewis two-center two-electron (2c-2e) B–B σ bonds in B_{11} skeleton, two three-center two-electron (3c-2e) and one six-center two-electron (6c-2e) delocalized σ bonds on two B_3 triangles. (b) Four radials π CMOs for three delocalized π bonds on waist and one delocalized π bond on two B_3 triangles. (c) Three tangential π CMOs for three delocalized π bonds on waist.

Figure S7. The CMOs for the LM (C_s, $^1A'$) of $Be_3B_{11}^-$ cluster. (a) Thirteen σ CMOs for eleven Lewis 2c-2e B–B σ bonds in B_{11} skeleton, one 3c-2e σ bond on bottom B_3 triangle and one 7c-2e delocalized σ bond on the top B_4 pyramid and bottom B_3 triangle. (b) Four radials π CMOs for three delocalized π bonds on waist and one delocalized π bond on top B_4 pyramid and bottom B_3 triangle. (c) Three tangential π CMOs for three delocalized π bonds on waist.
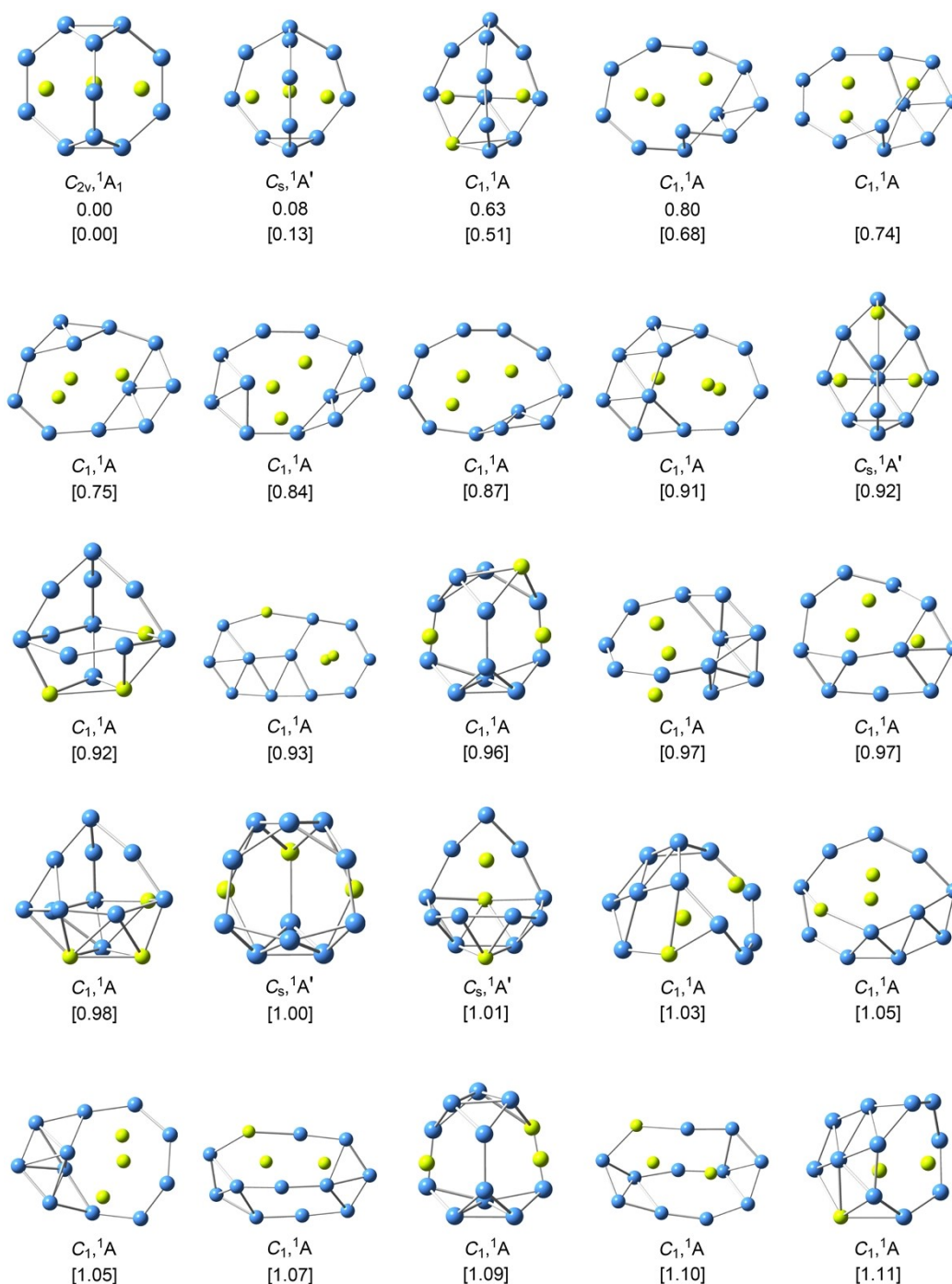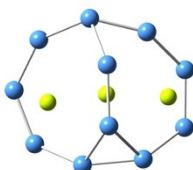
Figure S8. Electron localization functions (ELFs) for (a) the GM (C_{2v}, $^1A_1$), (b) the LM (C_s, $^1A'$) and (c) the TS (C_1, ^1A) structures.

Figure S9. The CMOs for the TS (C_1, ^1A) of $Be_3B_{11}^-$ cluster. (a) Thirteen σ CMOs for eleven 2c-2e B–B σ bonds in B_{11} skeleton, one 3c-2e σ bonds on bottom B_3 triangle and

one 7c-2e delocalized σ bond on top B_4 pyramid bottom B_3 triangle. (b) Four radials π CMOs for three delocalized π bonds on waist and one delocalized π bond on top B_4 pyramid and bottom B_3 triangle. (c) Three tangential π CMOs for three delocalized π bonds on waist.

Figure S10. The adaptive natural density partitioning (AdNDP) bonding pattern for the TS (C_1, ^1A) structure of $Be_3B_{11}^-$ cluster. The occupation numbers (ONs) are indicated.

Figure S11. The evolution process of the delocalized (a) 6c-2e σ bond and (b) 6c-2e π bond on two B_3 triangles during the interconversion between the GM and LM.

Supplementary Information – Part II

A short movie extracted from the BOMD simulation for $Be_3B_{11}^-$ cluster. The simulation was performed at the temperature of 600 K for 50 ps, starting from the equilibrium GM structure with random atom velocities. The movie roughly covers a time span of 12 ps.

Figure S1. Alternative optimized structures of $Be_3B_{11}^-$ cluster at the PBE0/6-311+G* level, the relative energies (in eV) are shown in square bracket with the corrections of zero-point energies (ZPEs), as well as for top four isomers at the single-point CCSD(T)/6-311+G*//PBE0/6-311+G* level.
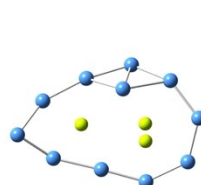

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0.00
[0.00]

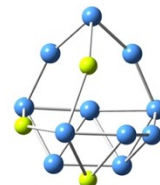C_s, $^1A'$
0.08
[0.13]

C_1, ^1A
0.63
[0.51]

C_1, ^1A
0.80
[0.68]

C_1, ^1A
[0.74]

C_1, ^1A
[0.75]

C_1, ^1A
[0.84]

C_1, ^1A
[0.87]

C_1, ^1A
[0.91]

C_s, $^1A'$
[0.92]

C_1, ^1A
[0.92]

C_1, ^1A
[0.93]

C_1, ^1A
[0.96]

C_1, ^1A
[0.97]

C_1, ^1A
[0.97]

C_1, ^1A
[0.98]

C_s, $^1A'$
[1.00]

C_s, $^1A'$
[1.01]

C_1, ^1A
[1.03]

C_1, ^1A
[1.05]

C_1, ^1A
[1.05]

C_1, ^1A
[1.07]

C_1, ^1A
[1.09]

C_1, ^1A
[1.10]
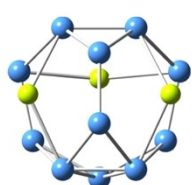
C_1, ^1A
[1.11]
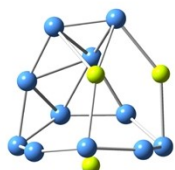
(continued …)

$C_s, {}^1A'$
[1.12]

$C_1, {}^1A$
[1.13]

$C_1, {}^1A$
[1.17]

$C_1, {}^1A$
[1.17]

$C_1, {}^1A$
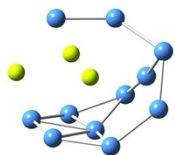[1.17]
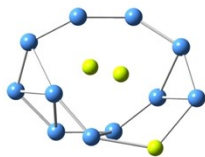
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[1.18]
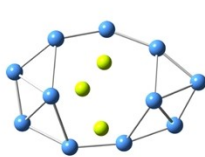
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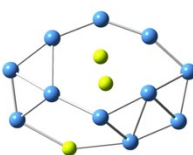[1.19]
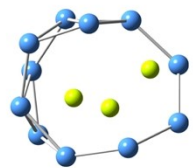
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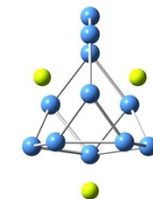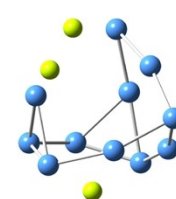[1.20]
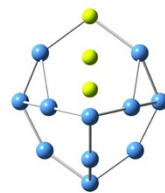
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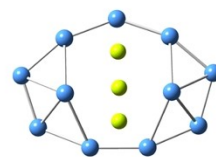
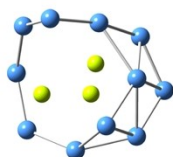$C_s, {}^1A'$
[1.22]
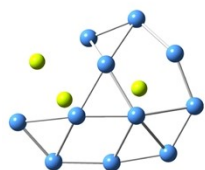
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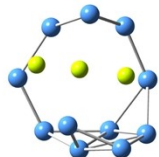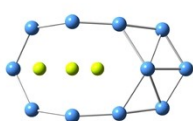[1.22]

$C_1, {}^1A$
[1.22]

$C_1, {}^1A$
[1.22]
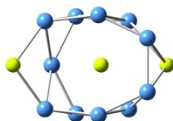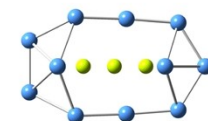
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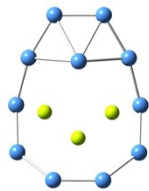[1.23]

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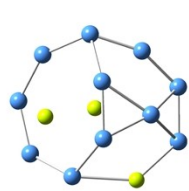[1.25]

$C_1, {}^1A$
[1.25]

$C_1, {}^1A$
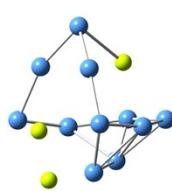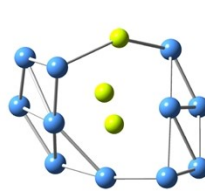[1.31]

$C_1, {}^1A$
[1.33]

$C_s, {}^1A'$
[1.37]

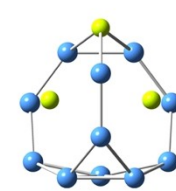$C_s, {}^1A'$
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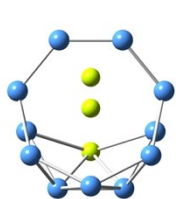
$C_s, {}^1A'$
[1.40]

$C_1, {}^1A$
[1.41]

$C_1, {}^1A$
[1.41]

$C_1, {}^1A$
[1.43]

$C_s, {}^1A'$
[1.44]

(continued …)

$C_s, {}^1A'$
[1.44]
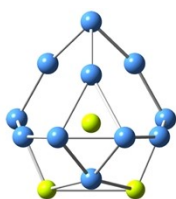
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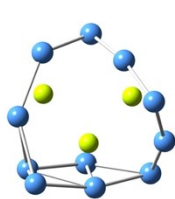
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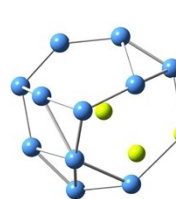
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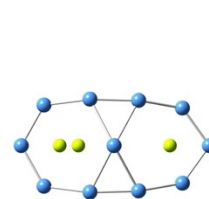
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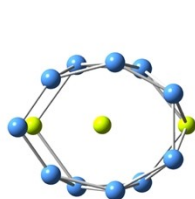
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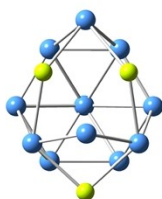
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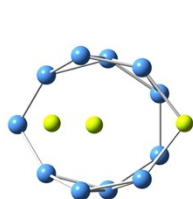
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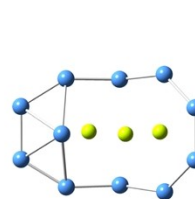
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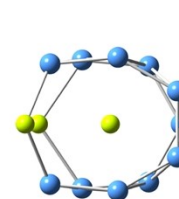
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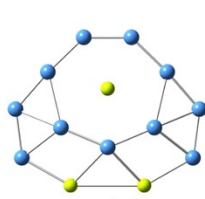
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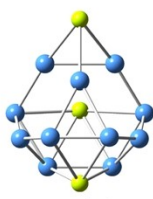
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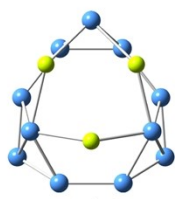
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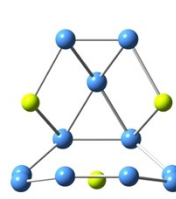
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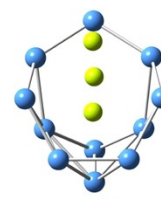
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[1.32]
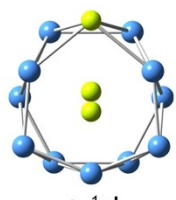
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[2.40]
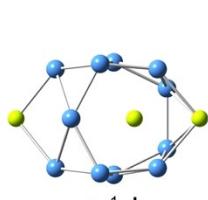
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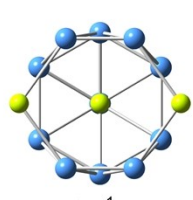
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[2.76]
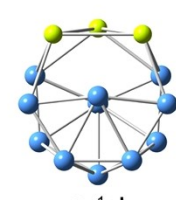
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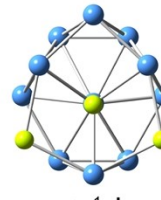
$C_s, {}^1A'$
[3.15]

$C_s, {}^1A'$
[3.31]

Figure S2. The bond distances (in Å) obtained at the PBE0/6-311+G(d) level for (a) the GM (C_{2v}, $^1A_1$) and (b) the LM (C_s, $^1A'$) structures of $Be_3B_{11}^-$ cluster.

GM (C_{2v}, $^1A_1$)

LM (C_s, $^1A'$)

Figure S3. Calculated Wiberg bond indices (WBIs) in black and natural atomic charges (in |e|) in blue for (a) the GM (C_{2v}, $^1A_1$) and (b) the LM (C_s, $^1A'$) of $Be_3B_{11}^-$ cluster from natural bond orbital (NBO) analyses at the PBE0/6-311+G* level.

GM (C_{2v}, $^1A_1$)

LM (C_s, $^1A'$)

Figure S4. The parameters of (a) bond distances, (b) Wiberg bond indices (WBIs) and (c) natural atomic charges in |e| for TS (C_1, ^{1}A) structure of $Be_3B_{11}{}^-$ cluster. The WBIs and natural atomics are obtained from the natural bond orbital (NBO) analysis at the PBE0/6-311+G* level.

LM (C_s, ^{1}A')

Figure S5   Born-Oppenheimer molecular dynamic simulations for $Be_3B_{11}^-$ cluster at (a) 300 K, (b) 400 K, and (c) 600 K for 50 ps using the software suite CP2K. Some typical GM structures are picked up during the dynamic simulations. The root-mean-square-deviation (RMSD) and maximum bond length deviation (MAXD) values (on average) are indicated.

Figure S6. The canonical molecular orbitals (CMOs) for the GM (C_{2v}, $^1A_1$) of $Be_3B_{11}^-$ cluster. (a) Thirteen σ CMOs for ten Lewis two-center two-electron (2c-2e) B–B σ bonds in B_{11} skeleton, two three-center two-electron (3c-2e) and one six-center two-electron (6c-2e) delocalized σ bonds on two B_3 triangles. (b) Four radials π CMOs for three delocalized π bonds on waist and one delocalized π bond on two B_3 triangles. (c) Three tangential π CMOs for three delocalized π bonds on waist.

(a)

HOMO-19   HOMO-18   HOMO-17   HOMO-16   HOMO-15   HOMO-14   HOMO-13

HOMO-11   HOMO-8   HOMO-7   HOMO-6   HOMO-3   HOMO

(b)

HOMO-9   HOMO-2   HOMO-1   HOMO-4

(c)

HOMO-5   HOMO-10   HOMO-12

Figure S7. The CMOs for the LM (C_s, $^1A'$) of $Be_3B_{11}^-$ cluster. (a) Thirteen σ CMOs for eleven Lewis 2c-2e B–B σ bonds in B_{11} skeleton, one 3c-2e σ bond on bottom B_3 triangle and one 7c-2e delocalized σ bond on the top B_4 pyramid and bottom B_3 triangle. (b) Four radials π CMOs for three delocalized π bonds on waist and one delocalized π bond on top B_4 pyramid and bottom B_3 triangle. (c) Three tangential π CMOs for three delocalized π bonds on waist.

Figure S8. Electron localization functions (ELFs) for (a) the GM (C_{2v}, $^1A_1$), (b) the LM (C_s, $^1A'$) and (c) the TS (C_1, ^1A) structures.

(a)

$ELF_\sigma = 0.83$　　$ELF_\pi = 0.83$　　$ELF_\pi = 0.83$

GM (C_{2v}, $^1A_1$)

(b)

$ELF_\sigma = 0.83$　　$ELF_\pi = 0.83$　　$ELF_\pi = 0.83$

LM (C_s, $^1A'$)

(c)

$ELF_\sigma = 0.83$　　$ELF_\pi = 0.83$　　$ELF_\pi = 0.83$

TS (C_1, ^1A)

Figure S9. The CMOs for the TS (C_1, ^1A) of $Be_3B_{11}^-$ cluster. (a) Thirteen σ CMOs for eleven 2c-2e B−B σ bonds in B_{11} skeleton, one 3c-2e σ bonds on bottom B_3 triangle and one 7c-2e delocalized σ bond on top B_4 pyramid bottom B_3 triangle. (b) Four radials π CMOs for three delocalized π bonds on waist and one delocalized π bond on top B_4 pyramid and bottom B_3 triangle. (c) Three tangential π CMOs for three delocalized π bonds on waist.

(a)

HOMO-19   HOMO-18   HOMO-17   HOMO-16   HOMO-15   HOMO-14   HOMO-13

HOMO-12   HOMO-11   HOMO-7   HOMO-6   HOMO-2   HOMO

(b)

HOMO-9   HOMO-4   HOMO-1   HOMO-3

(c)

HOMO-5   HOMO-10   HOMO-8

Figure S10. The adaptive natural density partitioning (AdNDP) bonding pattern for the TS (C_1, ^{1}A) structure of $Be_3B_{11}{}^-$ cluster. The occupation numbers (ONs) are indicated.

11×2c-2e σ bonds   1×3c-2e σ bond   1×7c-2e σ bond
ON=1.95-1.76 |e| ON=1.86 |e| ON=1.78 |e|

1×3c-2e π bond   1×3c-2e π bond   1×4c-2e π bond   1×7c-2e π bond
ON=1.73 |e| ON=1.80 |e| ON=1.87 |e| ON=1.90 |e|

1×5c-2e π bond   1×5c-2e π bond   1×6c-2e π bond
ON=1.91 |e| ON=1.90 |e| ON=1.96 |e|

Figure S11. The evolution process of the delocalized (a) 6c-2e σ bond and (b) 6c-2e π bond on two B_3 triangles during the interconversion between the GM and LM.

(a)

LM

GM$_1$

GM$_2$

(b)

LM

GM$_1$

GM$_2$

Table S1. Cartesian coordinates for (a) the global-minimum (GM) (C_{2v}, $^1A_1$), (b) the local minimum (LM) (C_s, $^1A'$), and (c) the transition state (TS) (C_1, ^1A) structures of $Be_3B_{11}^-$ cluster at the PBE0/6-311+G* level.

(a) GM (C_{2v}, $^1A_1$)

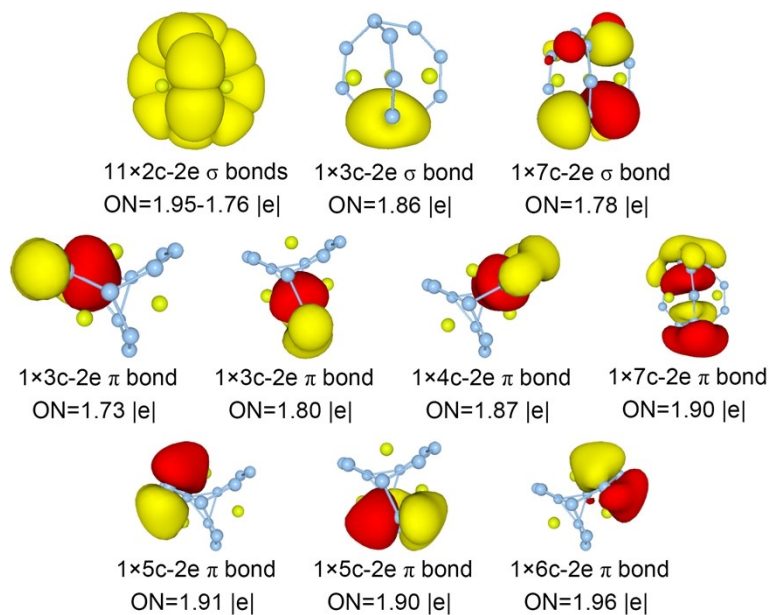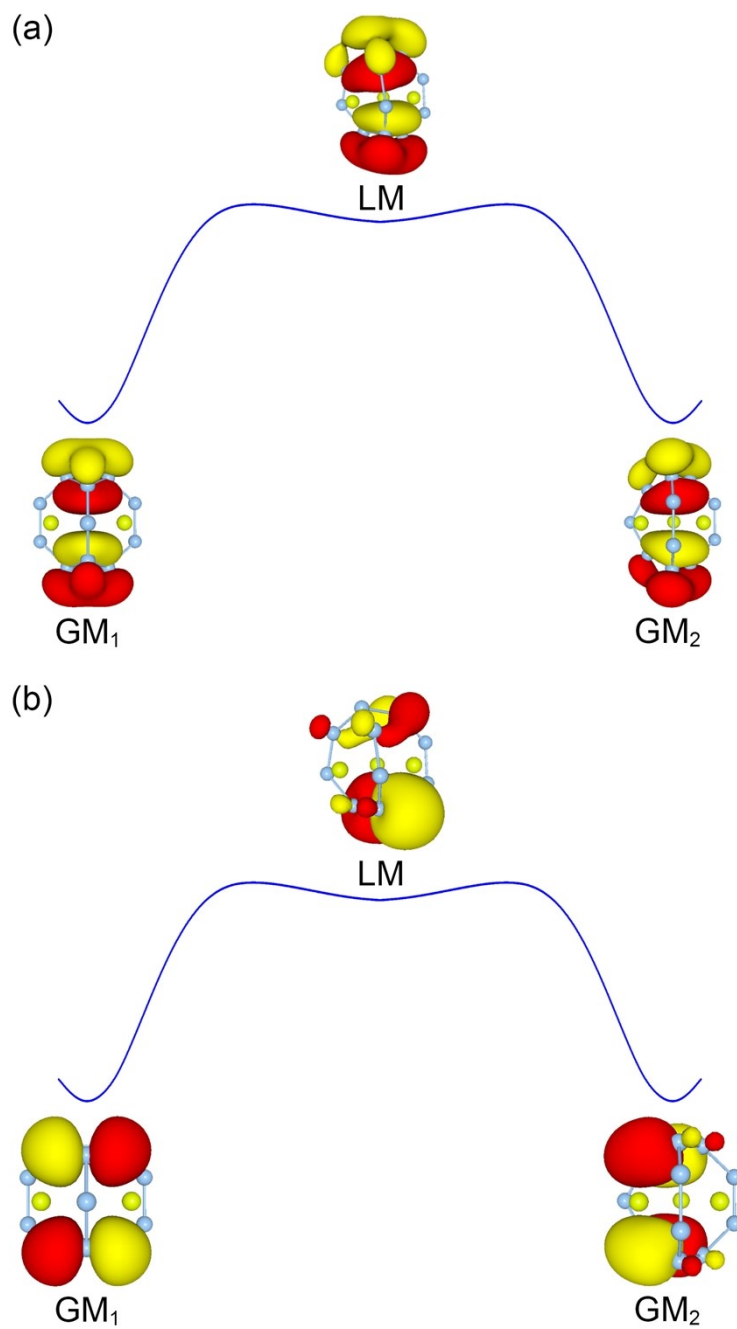|			
B	0.78814700	1.72234800	-0.28463500
B	1.89194400	0.76206000	-0.92078100
B	1.89194400	-0.76206000	-0.92078100
B	0.78814700	-1.72234800	-0.28463500
B	-0.78814700	-1.72234800	-0.28463500
B	-1.89194400	-0.76206000	-0.92078100
B	-1.89194400	0.76206000	-0.92078100
B	-0.78814700	1.72234800	-0.28463500
B	0.00000000	1.32009900	1.25416200
B	0.00000000	0.00000000	2.10125800
B	0.00000000	-1.32009900	1.25416200
Be	-1.33685700	0.00000000	0.74955200
Be	1.33685700	0.00000000	0.74955200
Be	0.00000000	0.00000000	-1.23399800

(b) LM (C_s, $^1A'$)

B	1.95382700	0.32161400	0.00000000
B	1.85257700	-1.22519100	0.00000000
B	0.67593300	-2.20138200	0.00000000
B	-0.81980800	-1.75839700	0.00000000
B	-1.54609900	-0.50410300	-0.84801500

B	-0.95895900	0.63557200	-1.80931200
B	0.24898400	1.49356700	-1.37890900
B	1.14715300	1.69340700	0.00000000
B	0.24898400	1.49356700	1.37890900
B	-0.95895900	0.63557200	1.80931200
B	-1.54609900	-0.50410300	0.84801500
Be	-1.10312800	1.11408900	0.00000000
Be	0.36560500	-0.60712100	1.17993400
Be	0.36560500	-0.60712100	-1.17993400

(c) TS (C_1, ^{1}A)

B	-0.04852900	1.95010800	-0.26736200
B	1.45504600	1.62124900	-0.48223900
B	2.21657700	0.29683200	-0.48325400
B	1.58716500	-1.09746500	-0.15207800
B	0.15737700	-1.78208300	-0.52902700
B	-1.09140900	-1.26589800	-1.40623200
B	-1.76025400	0.10104900	-1.20491400
B	-1.50323800	1.33664600	-0.15548300
B	-1.06154000	0.84696900	1.38679200
B	-0.39740000	-0.39050900	2.04179100
B	0.42759900	-1.37271000	1.10522200
Be	-1.24351000	-0.86014500	0.42079500
Be	0.93671500	0.48264200	1.00399400
Be	0.33005300	0.07226600	-1.24130900