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

Supplementary Information

Competition between tubular, planar and cage geometries: a complete picture of structural evolution of B_n (n = 31–50) clusters

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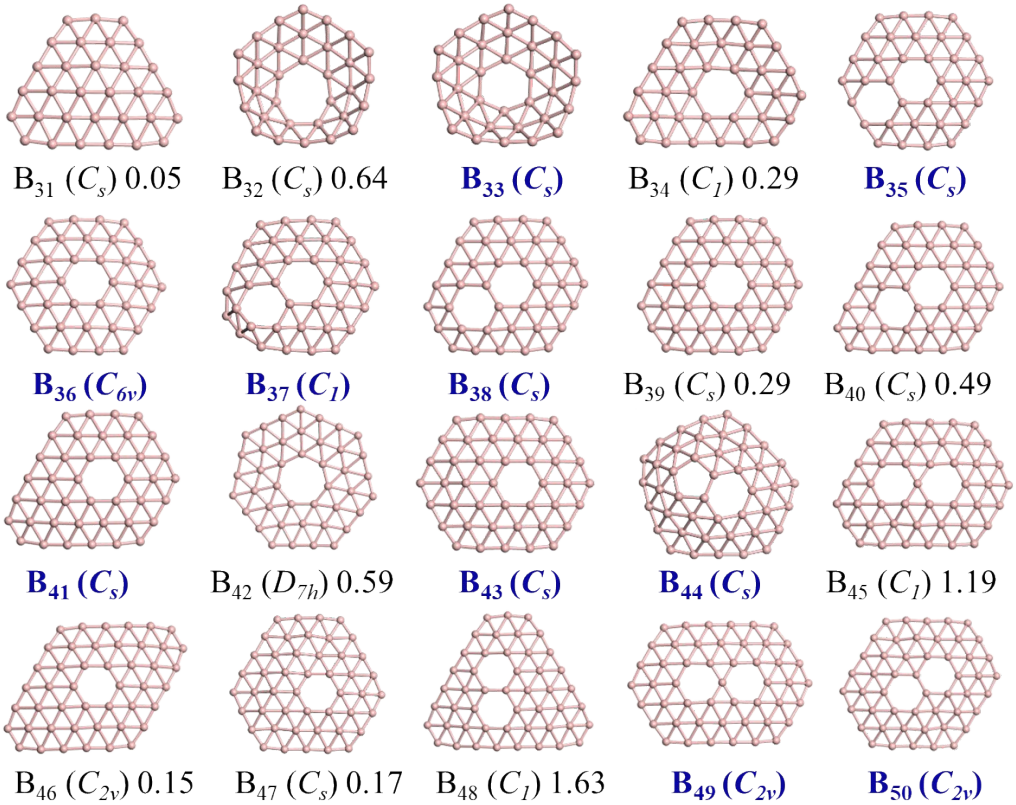

Fig. S1 The quasi-planar structures of neutral B_n (n = 31–50) clusters from TPSSh/6-311+G* calculations. The cluster symmetry and relative energy (in eV) are given at the below each structure. The lowest energy structures are marked in blue.

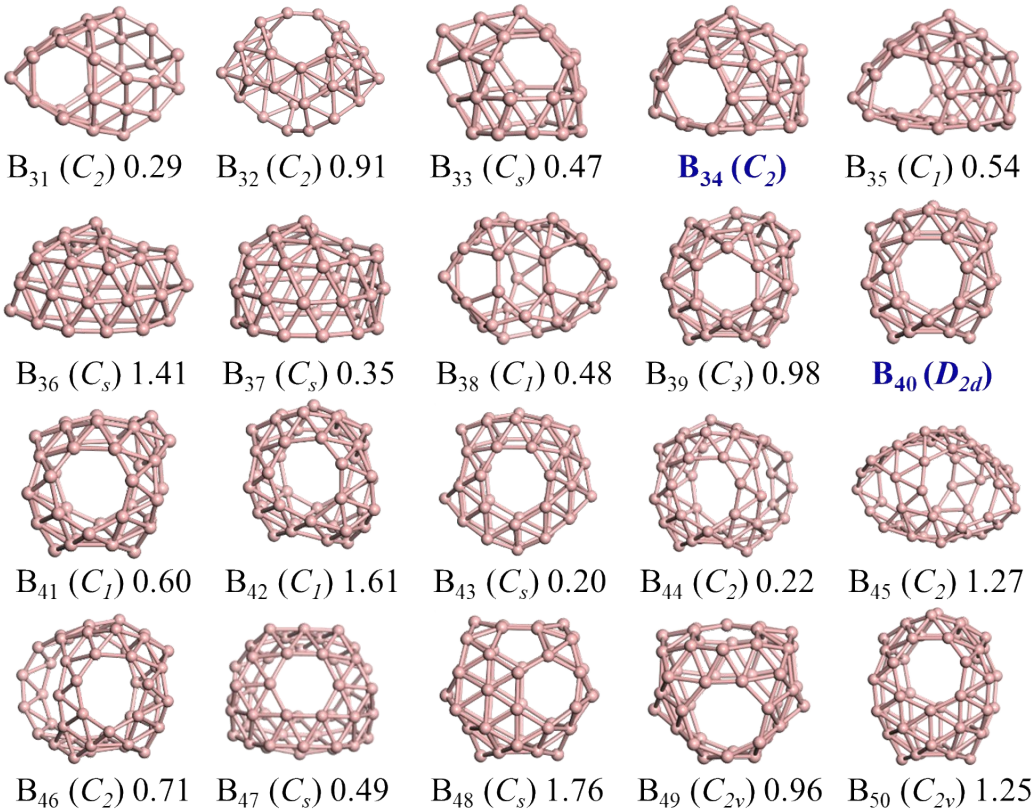

Fig. S2 The cage-like structures of neutral B_n (n = 31–50) clusters from TPSSh/6-311+G* calculations. The cluster symmetry and relative energy (in eV) are given at the below of each structure. The lowest energy structures are marked in blue.

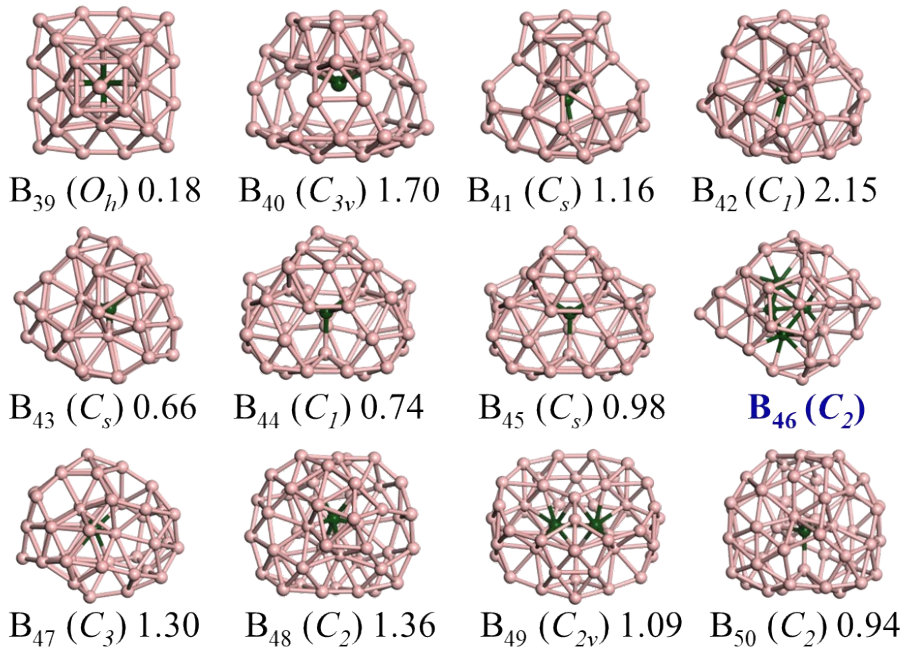

Fig. S3 The core-shell structures of neutral B_n (n = 39–50) clusters from TPSSh/6-311+G* calculations. The cluster symmetry and relative energy (in eV) are given at the below of each structure. The lowest energy structure is marked in blue. The inner atoms are marked in green.

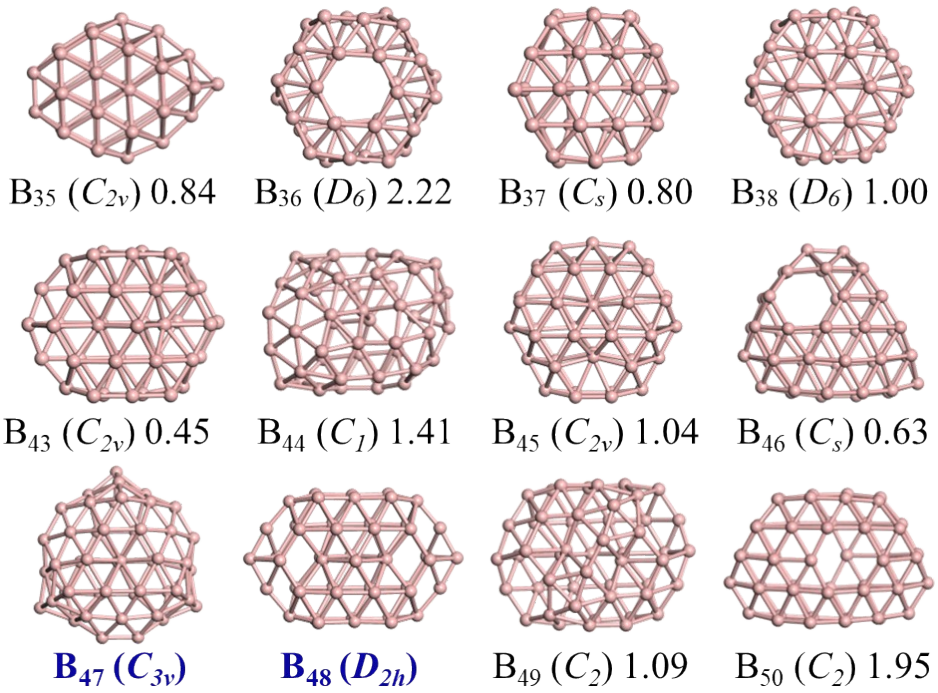

Fig. S4 The bilayer strcutures of neutral B_n (n = 35–50) clusters from TPSSh/6-311+G* calculations. The cluster symmetry and relative energy (in eV) are given at the below of each structure. The lowest energy structures are marked in blue.

Table S1. The energy differences of the representative isomers of B_n clusters (n = 46, 48, 50) in Fig. S1−S4 from TPSSh/6-311+G* and HSE06/6-311+G*.

Sizes	Isomers	ΔE(eV)	
		TPSSh/6-	HSE06/6-
B_{46}	I_Core-shell	0.00	0.00
	II_Quasi-planar	0.15	0.03
	IX_Bilayer	0.63	0.21
	XII_Cage	0.71	0.38
B_{48}	I_Bilayer	0.00	0.00
	IV_Core-shell	1.36	1.40
	VI_Quasi-planar	1.59	1.46
	VIII_Cage	1.69	1.15
B_{50}	I_Quasi-planar	0.00	0.00
	II_Core-shell	0.94	0.92
	IV_Cage	1.23	0.97
	XIV_Bilayer	1.95	1.94

Table S2(a) Structural motifs, point-group symmetries, relative energies ΔE, Binding energies (E_b) and HOMO-LUMO gap (E_{HL}) of the low-lying isomers of B_n (n = 31–34) clusters from TPSSh/6-311+G* calculations.

Sizes	Isomers	Symmetry	ΔE (eV)	E_b (eV)	E_{HL} (eV)
B_{31}	I_Tubular	C_s	0.00	5.09	1.43
	II_Quasi-Planar	C_s	0.05	5.08	1.51
	III_Cage	C_2	0.29	5.08	1.75
	IV_Quasi-Planar	C_1	0.30	5.08	0.97
	V_Tubular	C_2	0.40	5.07	0.83
	VI_Cage	C_1	0.41	5.07	1.55
	VII_Cage	C_2	0.42	5.07	1.17
	VIII_Tubular	C_s	0.47	5.07	1.11
	IX_Cage	C_1	0.49	5.07	1.40
	X_Cage	C_s	0.49	5.07	1.42
	XI_Cage	C_1	0.54	5.07	1.07
B_{32}	I_Tubular	D_{16d}	0.00	5.12	1.51
	II_Quasi-Planar	C_s	0.64	5.11	1.65
	III_Cage	C_2	0.91	5.10	2.23
	IV_Tubular	C_s	0.98	5.10	1.43
	V_Tubular	C_s	1.17	5.09	1.45
	VI_Cage	C_2	1.23	5.09	1.55
	VII_Cage	C_s	1.33	5.09	1.87
	VIII_Cage	C_2	1.44	5.08	1.57
	IX_Cage	C_s	1.46	5.08	1.81
	X_Cage	C_s	1.71	5.08	1.65
B_{33}	I_Quasi-Planar	C_s	0.00	5.11	0.79
	II_Tubular	D_{11h}	0.05	5.10	0.82
	III_Quasi-Planar	C_s	0.20	5.10	1.08
	IV_Quasi-Planar	C_1	0.23	5.10	1.13
	V_Tubular	C_s	0.26	5.10	1.61
	VI_Quasi-Planar	C_1	0.42	5.09	1.05
	VII_Cage	C_s	0.47	5.09	0.96
	VIII_Cage	C_s	0.47	5.09	0.96
	IX_Quasi-Planar	C_1	0.56	5.09	1.29
	X_Tubular	C_s	0.56	5.09	1.20
	XI_Cage	C_2	0.57	5.09	2.08
B_{34}	I_Cage	C_2	0.00	5.13	1.97
	II_Cage	C_s	0.09	5.12	2.02
	III_Tubular	D_{17d}	0.16	5.12	0.45
	IV_Cage	C_s	0.27	5.12	1.55
	V_Quasi-Planar	C_1	0.29	5.11	0.78
	VI_Cage	C_s	0.34	5.11	1.88
	VII_Cage	C_1	0.53	5.11	1.79
	VIII_Cage	C_1	0.63	5.11	1.80
	IX_Quasi-Planar	C_{2v}	0.69	5.10	1.13
	X_Tubular	C_s	0.77	5.10	1.10

Table S2(b) Structural motifs, point-group symmetries, relative energies ΔE, Binding energies (E_b) and HOMO-LUMO gap (E_{HL}) of the low-lying isomers of B_n (n = 35–38) clusters from TPSSh/6-311+G* calculations.

Sizes	Isomers	Symmetry	ΔE	E_b (eV)	E_{HL} (eV)
B_{35}	I_Quasi-Planar	C_s	0.00	5.13	1.10
	II_Cage	C_1	0.54	5.12	1.14
	III_Cage	C_2	0.67	5.11	1.16
	IV_Cage	C_1	0.76	5.11	1.07
	V_Cage	C_2	0.81	5.11	1.04
	VI_Cage	C_2	0.81	5.11	1.04
	VII_Bilayer	C_{2v}	0.84	5.11	0.82
	VIII_Bilayer	C_s	0.91	5.10	1.32
	IX_Tubular	C_s	1.22	5.10	1.27
	X_Cage	C_s	1.31	5.09	1.22
B_{36}	I_Quasi-Planar	C_{6v}	0.00	5.17	1.50
	II_Tubular	D_{12h}	0.87	5.14	0.51
	III_Cage	C_s	1.41	5.13	1.48
	IV_Bilayer	D_6	2.22	5.10	1.86
	V_Cage	C_2	2.25	5.10	1.54
	VI_Cage	C_2	2.31	5.10	1.32
	VII_Tubular	C_s	2.42	5.10	1.08
	VIII_Tubular	C_s	2.42	5.10	1.08
	IX_Tubular	C_s	2.79	5.09	0.74
	X_Bilayer	C_s	3.24	5.07	1.08
B_{37}	I_Quasi-Planar	C_1	0.00	5.14	1.18
	II_Quasi-Planar	C_1	0.22	5.13	1.23
	III_Quasi-Planar	C_1	0.22	5.13	1.04
	IV_Cage	C_s	0.35	5.13	1.33
	V_Quasi-Planar	C_s	0.37	5.13	1.18
	VI_Quasi-Planar	C_1	0.54	5.12	0.91
	VII_Tubular	C_1	0.57	5.12	1.41
	VIII_Tubular	C_1	0.57	5.12	1.44
	IX_Quasi-Planar	C_1	0.58	5.12	0.95
	X_Tubular	C_s	0.66	5.12	1.29
	XI_Bilayer	C_s	0.80	5.12	1.12
B_{38}	I_Quasi-Planar	C_s	0.00	5.15	0.72
	II_Cage	C_1	0.48	5.14	1.83
	III_Cage	D_{2h}	0.51	5.14	1.60
	IV_Tubular	C_s	0.82	5.12	1.44
	V_cage	C_s	0.89	5.12	0.95
	VI_Bilayer	D_6	1.00	5.12	0.86
	VII_cage	C_s	1.18	5.12	0.87
	VIII_Tubular	C_s	1.31	5.11	1.01
	IX_Tubular	C_s	1.33	5.11	0.98
	X_Tubular	C_s	1.55	5.10	0.90
	XI_Bilayer	D_{2h}	3.25	5.06	1.17

Table S2(c) Structural motifs, point-group symmetries, relative energies ΔE, Binding energies (E_b) and HOMO-LUMO gap (E_{HL}) of the low-lying isomers of B_n (n = 39–42) clusters from TPSSh/6-311+G* calculations.

Sizes	Isomers	Symmetry	ΔE	E_b (eV)	E_{HL} (eV)
B_{39}	I_Tubular	D_{13h}	0.00	5.17	0.78
	II_Core-Shell	O_h	0.18	5.17	0.64
	III_Quasi-Planar	C_s	0.29	5.16	1.19
	IV_Cage	C_3	0.98	5.14	2.23
	V_Cage	C_s	1.05	5.14	1.15
	VI_Cage	C_s	1.08	5.14	1.57
	VII_Cage	C_2	1.09	5.14	2.09
	VIII_Cage	C_2	1.09	5.14	2.09
	IX_Cage	C_2	1.09	5.14	2.09
	X_Core-Shell	C_{3v}	1.09	5.14	1.78
B_{40}	I_Cage	D_{2h}	0.00	5.19	2.40
	II_Cage	C_s	0.46	5.17	2.25
	III_Quasi-Planar	C_s	0.49	5.17	1.24
	IV_Quasi-Planar	C_s	0.70	5.16	1.31
	V_Cage	C_{2h}	0.93	5.16	1.96
	VI_Cage	C_1	1.22	5.15	2.13
	VII_Tubular	C_s	1.44	5.14	0.90
	VIII_Tubular	C_1	1.59	5.14	0.96
	IX_Tubular	C_s	1.65	5.14	1.16
	X_Core-Shell	C_{3v}	1.70	5.14	1.32
B_{41}	I_Quasi-Planar	C_s	0.00	5.17	0.55
	II_Cage	C_1	0.60	5.16	0.81
	III_Cage	C_s	0.60	5.16	0.98
	IV_Cage	C_s	0.66	5.16	1.56
	V_Cage	C_{2v}	0.94	5.15	0.90
	VI_Core-Shell	C_s	1.16	5.14	1.83
	VII_Core-Shell	C_s	1.27	5.14	1.11
	VIII_Cage	C_{2v}	1.38	5.14	0.81
	IX_Cage	C_{2v}	1.38	5.14	0.81
	X_Core-Shell	C_s	1.40	5.14	1.46
	XI_Core-Shell	C_s	1.41	5.14	1.22
	XII_Tubular	C_s	1.48	5.13	1.07
B_{42}	I_Tubular	D_{14h}	0.00	5.20	1.64
	II_Quasi-Planar	D_{7h}	0.59	5.18	1.39
	III_Cage	C_1	1.61	5.16	1.38
	IV_Cage	C_2	1.69	5.16	1.16
	V_Cage	C_{2v}	1.66	5.16	1.10
	VI_Cage	C_s	1.74	5.16	1.57
	VII_Cage	C_s	1.77	5.16	0.98
	VIII_Cage	C_3	1.87	5.16	2.02
	IX_Quasi-Planar	C_{2v}	1.95	5.15	0.91
	X_Cage	C_s	1.97	5.15	1.18
	XI_Core-Shell	C_1	2.15	5.15	1.23
	XII_Cage	C_2	2.46	5.14	0.73

Table S2(d) Structural motifs, point-group symmetries, relative energies ΔE, Binding energies (E_b) and HOMO-LUMO gap (E_{HL}) of the low-lying isomers of B_n (n = 43–46) clusters from TPSSh/6-311+G* calculations.

Sizes	Isomers	Symmetry	ΔE	E_b (eV)	E_{HL} (eV)
B_{43}	I_Quasi-Planar	C_s	0.00	5.17	0.64
	II_Tubular	C_s	0.18	5.16	0.90
	III_Tubular	C_s	0.19	5.16	0.75
	IV_Cage	C_s	0.20	5.16	0.92
	V_Tubular	C_s	0.20	5.16	0.84
	VI_Cage	C_{2v}	0.34	5.16	1.11
	VII_Cage	C_s	0.36	5.16	1.07
	VIII_Quasi-Planar	C_s	0.36	5.16	0.72
	IX_Bilayer	C_{2v}	0.45	5.15	1.01
	X_Quasi-Planar	C_1	0.57	5.15	0.93
	XI_Core-Shell	C_s	0.66	5.15	1.09
B_{44}	I_Quasi-Planar	C_s	0.00	5.17	1.15
	II_Quasi-Planar	C_1	0.13	5.16	1.01
	III_Quasi-Planar	C_s	0.21	5.16	0.74
	IV_Cage	C_2	0.22	5.17	1.42
	V_Cage	C_2	0.25	5.16	1.31
	VI_Quasi-Planar	C_s	0.37	5.16	1.23
	VII_Tubular	C_s	0.45	5.16	1.00
	VIII_Cage	C_2	0.65	5.15	1.03
	IX_ Core-Shell	C_1	0.74	5.15	1.18
	X_Cage	D_{2d}	0.77	5.15	1.15
	XI_Tubular	C_2	1.02	5.14	0.93
	XII_Bilayer	C_1	1.41	5.14	1.37
B_{45}	I_Tubular	D_{15h}	0.00	5.19	0.77
	II_Core-Shell	C_s	0.98	5.17	0.70
	III_Bilayer	C_{2v}	1.04	5.17	0.75
	IV_Quasi-Planar	C_1	1.19	5.17	0.87
	V_Quasi-Planar	C_s	1.19	5.17	0.87
	VI_Cage	C_2	1.27	5.17	1.37
	VII_Core-Shell	C_s	1.37	5.16	1.07
	VIII_Core-Shell	C_s	1.37	5.16	1.07
	IX_Cage	C_{3v}	1.53	5.16	0.76
B_{46}	I_Core-Shell	C_2	0.00	5.18	1.56
	II_Quasi-Planar	C_{2v}	0.15	5.18	0.79
	III_Tubular	C_1	0.45	5.17	0.79
	IV_Quasi-Planar	C_s	0.48	5.17	0.57
	V_Quasi-Planar	C_1	0.50	5.17	0.88
	VI_Core-Shell	C_2	0.53	5.17	1.09
	VII_Tubular	C_s	0.59	5.17	0.90
	VIII_Core-Shell	C_2	0.61	5.17	1.28
	IX_Bilayer	D_{2h}	0.63	5.17	1.27
	X_Bilayer	C_s	0.65	5.17	1.37
	XI_Bilayer	C_s	0.65	5.17	1.37
	XII_Cage	C_2	0.71	5.17	1.48

Table S2(e) Structural motifs, point-group symmetries, relative energies ΔE, Binding energies (E_b) and HOMO-LUMO gap (E_{HL}) of the low-lying isomers of B_n (n = 47–50) clusters from TPSSh/6-311+G* calculations.

Sizes	Isomers	Symmetry	ΔE	E_b (eV)	E_{HL} (eV)
B_{47}	I_Bilayer	C_{3v}	0.00	5.18	1.50
	II_Quasi-Planar	C_s	0.17	5.17	1.09
	III_Core-Shell	C_3	0.30	5.17	1.27
	IV_Cage	C_s	0.49	5.17	1.04
	V_Cage	C_{2v}	0.51	5.17	0.79
	VI_Cage	C_{2v}	0.66	5.17	1.27
	VII_Tubular	C_s	0.69	5.16	0.58
	VIII_Cage	C_s	0.73	5.16	0.88
	IX_Cage	C_s	0.73	5.16	0.88
B_{48}	I_Bilayer	D_{2h}	0.00	5.21	0.92
	II_Tubular	D_{16h}	0.50	5.19	0.46
	III_Bilayer	C_{2v}	1.09	5.18	1.39
	IV_Core-Shell	C_2	1.36	5.18	1.09
	V_Bilayer	C_{2v}	1.45	5.17	1.34
	VI_Quasi-Planar	C_1	1.59	5.17	1.15
	VII_Quasi-Planar	C_s	1.63	5.17	0.71
	VIII_Cage	C_2	1.69	5.17	1.52
	IX_Quasi-Planar	C_1	1.73	5.17	0.91
	X_Cage	C_2	1.76	5.17	1.32
	XI_Cage	C_s	1.76	5.17	0.96
B_{49}	I_Quasi-Planar	C_{2v}	0.00	5.20	0.91
	II_Cage	C_{2v}	0.96	5.19	0.57
	III_Core-Shell	C_{2v}	1.09	5.18	1.62
	IV_Bilayer	C_2	1.09	5.18	1.08
	V_Bilayer	C_s	1.21	5.18	1.03
	VI_Cage	C_{2v}	1.32	5.18	1.39
	VII_Tubular	C_s	1.36	5.17	0.78
	VIII_Tubular	C_1	1.41	5.17	0.56
B_{50}	I_Quasi-Planar	C_{2v}	0.00	5.21	1.28
	II_Core-Shell	C_2	0.94	5.19	0.88
	III_Core-Shell	C_2	1.13	5.18	1.04
	IV_Cage	C_{2v}	1.23	5.18	0.88
	V_Quasi-Planar	C_2	1.34	5.18	0.90
	VI_Cage	D_{6d}	1.47	5.18	1.55
	VII_Cage	D_2	1.59	5.17	1.05
	VIII_Cage	C_2	1.65	5.17	1.17
	IX_Tubular	C_s	1.67	5.17	0.56
	X_Quasi-Planar	C_s	1.70	5.17	1.11
	XI_Cage	C_2	1.74	5.17	1.05
	XII_Cage	C_2	1.76	5.17	0.90
	XIII_Cage	C_{2h}	1.77	5.17	0.86
	XIV_Bilayer	C_2	1.95	5.16	0.90

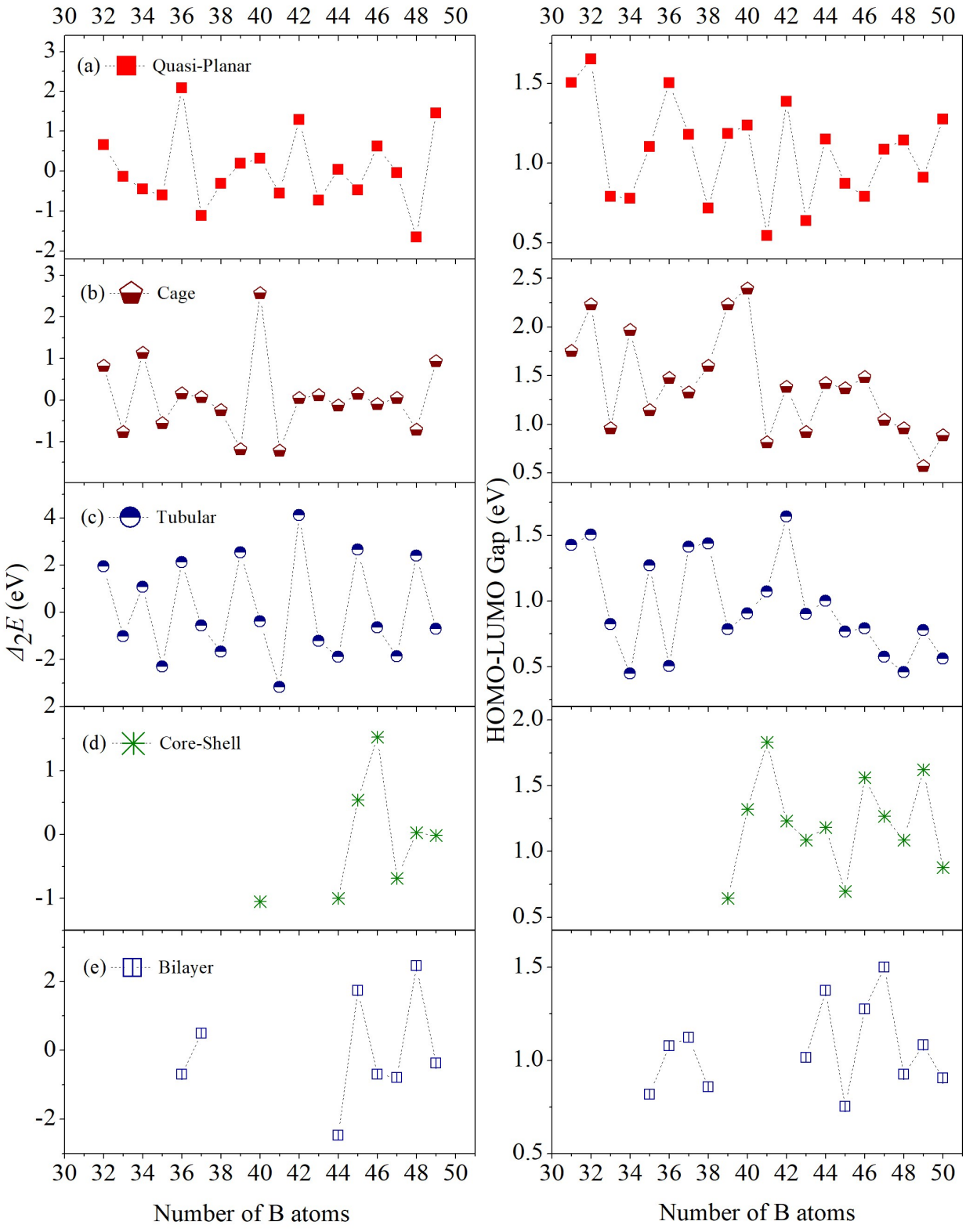

Fig. S5 Second order energy difference of different structural patterns (Δ_2E) and HOMO-LUMO gap (E_{HL}) of B_n (n = 31–50) cluster: (a) quasi-planar, (b) cage, (c) tubular, (d) core-shell and (e) bilayer structures.

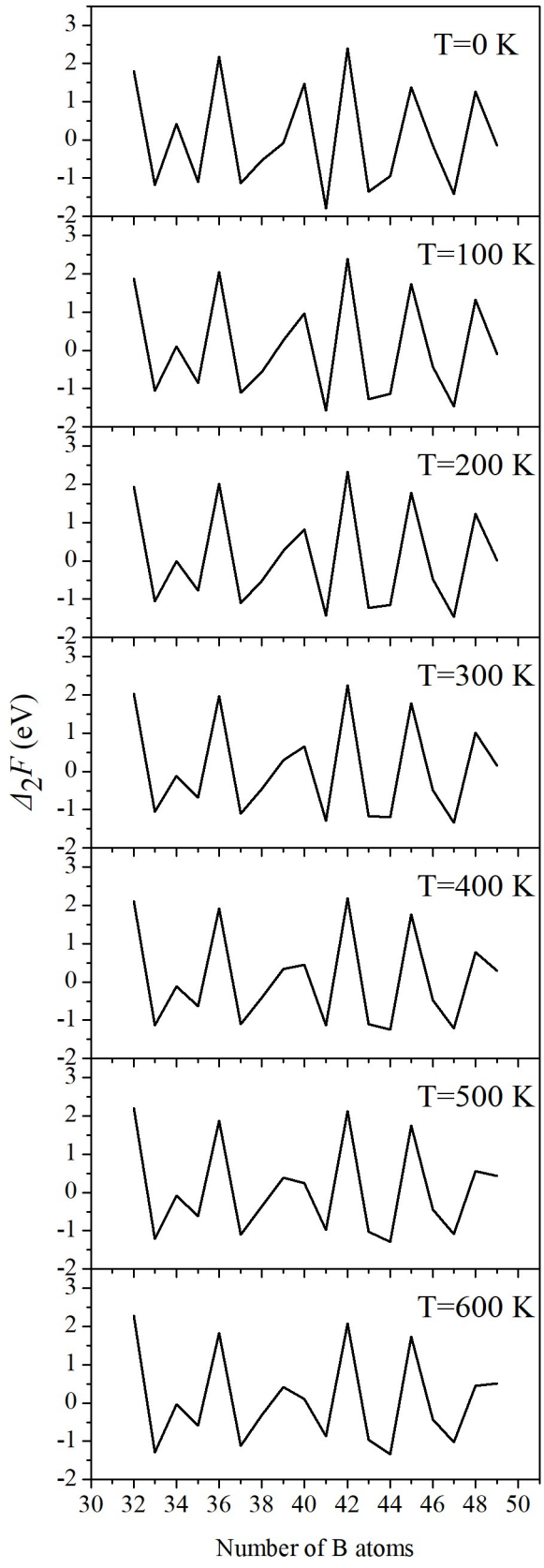

Fig. S6 Second order difference of Helmholtz free-energy ($\Delta_2 F$) of B_n (n = 31–50) cluster at different temperatures.

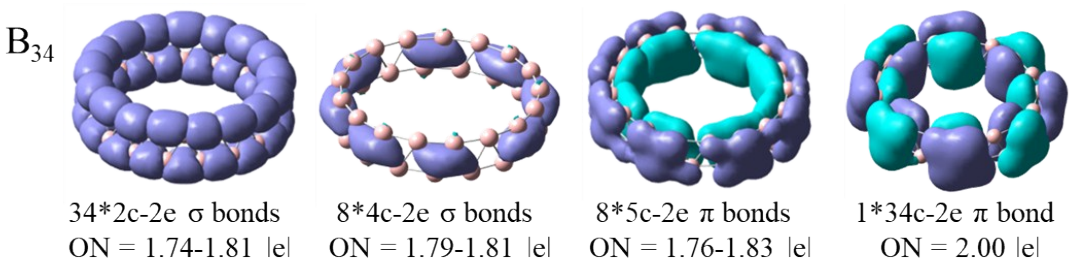

Fig. S7. AdNDP chemical bonding analyses of the double-ring tubular B_{34}. ON denotes occupation number.

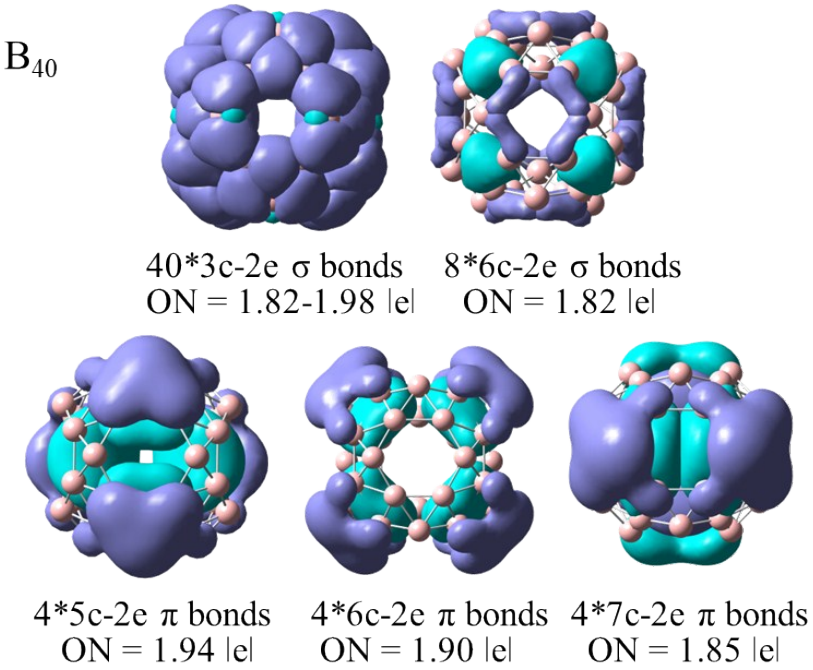

Fig. S8. AdNDP chemical bonding analyses of the B_{40} cage. ON denotes occupation number. The AdNDP analysis identifies 40 3c-2e σ bonds on the B_3 triangles and eight 6c-2e σ bonds, three different π systems: four 5c-2e bonds, four 6c-2e bonds and four 7c-2e bonds distributed evenly over the cage surface along the interwoven BDCs.

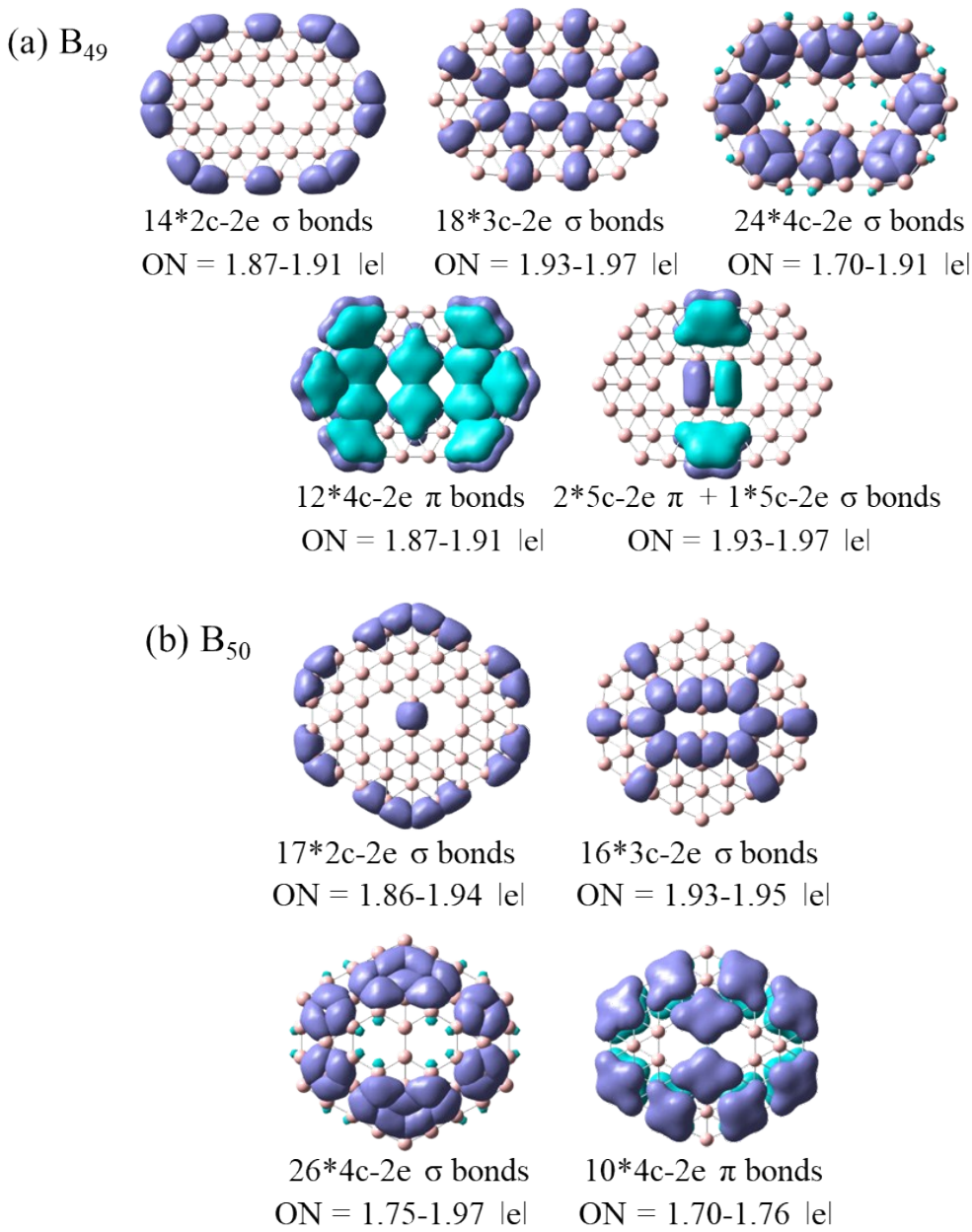

Fig. S9. AdNDP chemical bonding analyses of the quasi-planar for their closed-shell (a) B_{49}^- and (b) B_{50} clusters. ON denotes occupation number.