Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Boron clusters with 46, 48, 50 atoms: competition among core-shell, bilayer and quasi-planar structures

Linwei Sai,[a,#] Xue Wu,[b,#] Nan Gao[b], Jijun Zhao*[,b] and R. Bruce King[c]

[a] *Department of Mathematics and Physics, Hohai University, Changzhou 213022, China.*

[b] *Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China.*

[c] *Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, GA 30602, USA.*

Table S1. Energy differences (ΔE), binding energy (E_b), HOMO-LUMO gap (E_{HL}), and coordination number (CN) of the low-lying isomers of B_{46} clusters with structures given in Figure S1 from PBE/DND and TPSSh/6-311G(d) calculations.

Isomer	ΔE (eV)		E_b (eV)		E_{HL} (eV)		CN
	PBE	TPSSh	PBE	TPSSh	PBE	TPSSh	
I	0	0	5.71	5.07	1.07	1.56	5.26
II	0.67	0.20	5.69	5.07	0.46	0.80	4.78
III	0.29	0.68	5.70	5.06	0.67	1.37	5.00
IV	0.15	0.88	5.70	5.05	0.63	1.09	4.78
V	0.84	0.50	5.69	5.06	0.21	0.57	4.70
VI	0.54	0.53	5.69	5.06	0.61	1.09	5.48
VII	0.94	0.53	5.68	5.06	0.42	0.88	4.70
VIII	0.43	0.63	5.70	5.06	0.84	1.28	5.65
IX	0.46	0.69	5.70	5.06	0.74	1.28	4.61
X	0.68	0.76	5.69	5.06	0.67	1.23	4.61
XI	0.54	0.76	5.69	5.06	0.61	1.08	4.87
XII	1.15	0.76	5.68	5.06	0.46	0.85	4.83
XIII	1.21	0.83	5.68	5.06	0.41	0.80	4.61
XIV	0.40	0.97	5.70	5.05	0.95	1.38	4.83

Table S2. Energy differences (ΔE), binding energy (E_b), HOMO-LUMO gap (E_{HL}) and coordination number (CN) of the low-lying isomers of B_{48} clusters with structures given in Figure S2 from PBE/DND and TPSSh/6-311G(d) calculations.

Isomer	ΔE (eV)		E_b (eV)		E_{HL} (eV)		CN
	PBE	TPSSh	PBE	TPSSh	PBE	TPSSh	
I	0	0	5.73	5.10	0.47	0.93	5.67
II	1.40	1.35	5.70	5.07	0.61	1.09	5.71
III	2.20	1.59	5.68	5.06	0.77	1.15	4.67
IV	1.32	1.77	5.70	5.06	0.51	0.96	4.71
V	1.08	0.54	5.78	5.09	0.52	0.41	4.69
VI	0.99	1.11	5.71	5.07	0.98	1.39	4.75
VII	1.02	1.49	5.71	5.07	0.88	1.34	5.29
VIII	2.02	1.62	5.69	5.06	0.33	0.71	4.71
IX	1.41	1.69	5.70	5.06	1.00	1.52	5.13
X	2.15	1.72	5.69	5.06	0.51	0.92	4.71
XI	1.40	1.84	5.70	5.06	0.48	0.92	4.79
XII	1.29	1.85	5.70	5.06	0.20	0.60	5.00
XIII	1.47	1.96	5.70	5.06	0.56	0.96	5.08
XIV	2.61	2.33	5.68	5.05	0.50	0.92	4.58

Table S3. Energy differences (ΔE), binding energy (E_b), HOMO-LUMO gap (E_{HL}), and coordination number (CN) of the low-lying isomers of B_{50} clusters with structures given in Figure S3 from PBE/DND and TPSSh/6-311G(d) calculations.

Isomer	ΔE (eV)		E_b (eV)		E_{HL} (eV)		CN
	PBE	TPSSh	PBE	TPSSh	PBE	TPSSh	
I	0	0	5.72	5.10	0.89	1.28	4.76
II	0.04	0.94	5.72	5.08	0.47	0.88	5.52
III	0.57	1.25	5.71	5.07	0.39	0.89	4.88
IV	1.31	2.00	5.70	5.06	0.43	0.91	4.72
V	0.40	1.15	5.71	5.07	0.65	1.04	5.12
VI	1.25	1.34	5.70	5.07	0.60	0.91	4.76
VII	0.81	1.47	5.71	5.07	1.09	1.56	5.80
VIII	0.70	1.62	5.71	5.07	0.61	1.05	4.64
IX	0.80	1.66	5.71	5.06	0.65	1.17	4.92
X	1.59	1.69	5.69	5.06	0.77	1.11	4.76
XI	0.69	1.76	5.71	5.06	0.41	0.90	4.92
XII	0.68	1.77	5.71	5.06	0.46	0.87	5.12
XIII	0.72	1.81	5.71	5.06	0.55	1.14	4.84
XIV	1.98	1.97	5.68	5.06	0.70	1.14	4.88

Table S4. Relative energies (eV) of nine selected B_{20} isomers: *a*, *b*, and *c* from Kiran et al. [1], *d*, *e*, *f*, *g*, *h*, and *i* from Li et al. [2]. All isomers are fully relaxed with respective method, except that the CCSD(T) results are from single-point energy calculation based on MP2 geometries. All computations were combined with 6-311G(d) basis set.

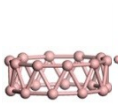
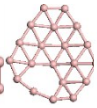
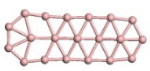
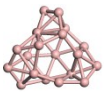
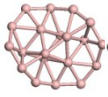
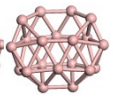
	 *a* (D_{2d})	 *b* (C_1)	 *c* (C_s)	 *d* (C_2)	 *e* (C_1)	 *f* (C_1)	 *g* (C_2)	 *h* (C_s)	 *i* (D_{2d})
CCSD(T)	0	0.48	0.71	1.47	1.87	1.97	2.32	2.80	3.45
TPSSh	0	0.62	0.79	1.58	1.99	2.12	2.36	3.09	3.28
HSE06	0	0.69	0.95	1.59	1.97	2.31	2.67	3.05	3.67
B2PLYP	0	1.04	1.30	3.59	4.39	3.92	3.89	5.81	5.25
MP2	0	0.69	1.13	1.07	0.94	1.89	2.63	1.15	3.32

Table S5. The energy differences of the representative isomers of B_n clusters (n=46, 48, 50) in Figure 1 of main text from TPSSh/6-311G(d) and HSE06/6-311G(d) functional. Zero-point energy correction is included at 0 K, and thermal correction energy at room temperature is further included at 298 K.

		TPSSh		HSE06	
Size	Isomer	ΔE/eV (0 K)	ΔE/eV (298 K)	ΔE/eV (0 K)	ΔE/eV (298 K)
B_{46}	bilayer	0.68	0.68	0.27	0.46
	cage	0.88	0.90	0.54	0.75
	core-shell	0.00	0.11	0.05	0.36
	quasi-planar	0.20	0.00	0.00	0.00
B_{48}	bilayer	0.00	0.00	0.00	0.00
	cage	1.77	1.70	1.25	1.17
	core-shell	1.35	1.39	1.43	1.48
	quasi-planar	1.59	1.31	1.44	1.16
B_{50}	bilayer	2.00	2.11	1.90	2.02
	cage	1.25	1.39	0.99	1.13
	core-shell	0.94	1.22	1.01	1.30
	quasi-planar	0.00	0.00	0.00	0.00

Table S6. Binding energy (E_b) and HOMO-LUMO gap (E_{HL}) of the representative isomers of B_n clusters (n=46, 48, 50) with structures given in Figure 1 from HSE06/6-311G(d) calculations.

Isomer	Structure	E_b (eV)	E_{HL} (eV)
B_{46} (I)	core-shell	5.30	1.53
B_{46} (II)	quasi-planar	5.30	0.72
B_{46} (III)	bilayer	5.29	1.34
B_{46} (IV)	cage	5.29	1.02
B_{48} (I)	bilayer	5.32	0.85
B_{48} (II)	core-shell	5.29	1.06
B_{48} (III)	quasi-planar	5.29	1.07
B_{48} (IV)	cage	5.30	0.84
B_{50} (I)	quasi-planar	5.33	1.21
B_{50} (II)	core-shell	5.31	0.82
B_{50} (III)	cage	5.31	0.86
B_{50} (IV)	bilayer	5.29	0.84

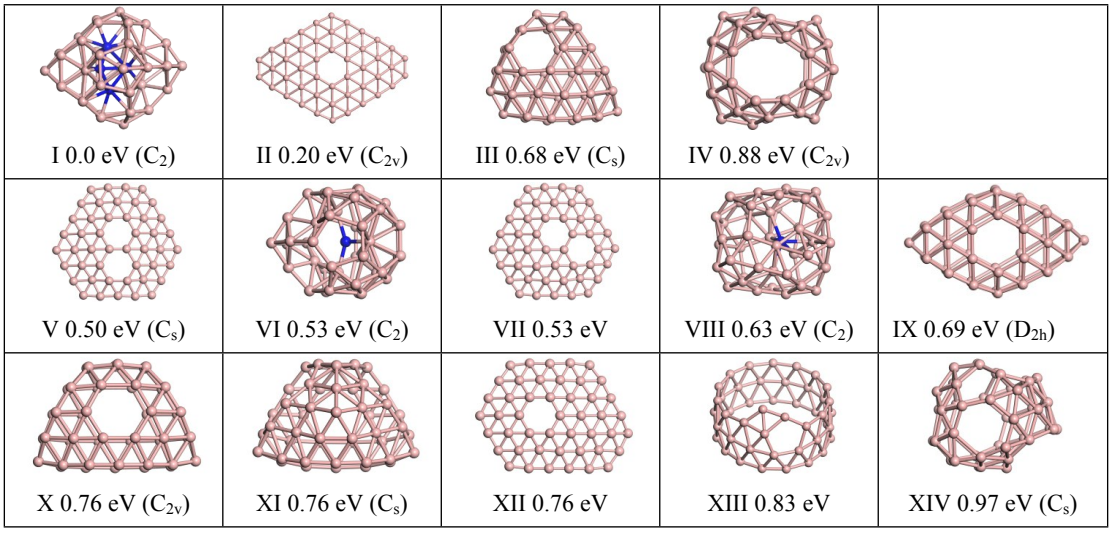


Figure S1 Structures and relative energy of the low-lying isomers of B_{46} clusters from TPSSh/6-311G(d) calculations. The point-group symmetry for each isomer is given in parenthesis. The interior atoms of the core-shell structures are highlighted in blue.

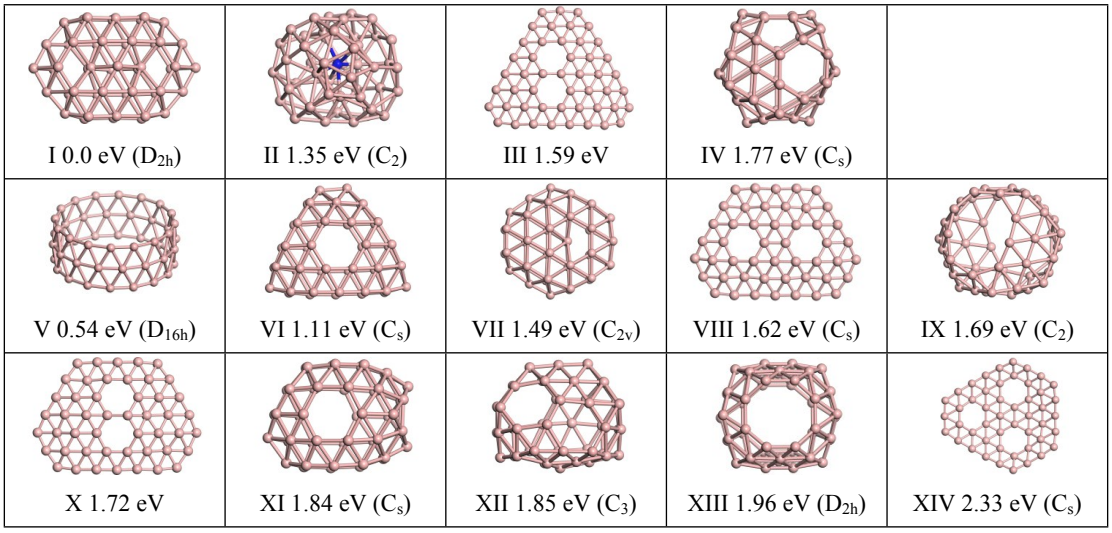


Figure S2 Structures and relative energy of the low-lying isomers of B_{48} clusters from TPSSh/6-311G(d) calculations. The point-group symmetry for each isomer is given in parenthesis. The interior atoms of the core-shell structures are highlighted in blue.

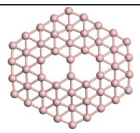
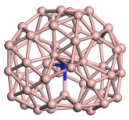
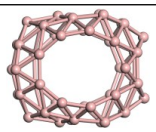
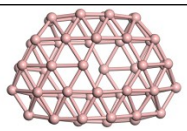
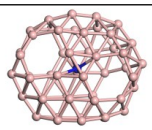
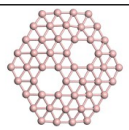
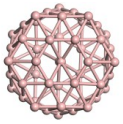
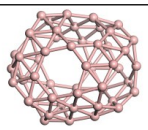
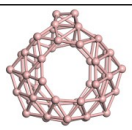
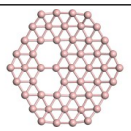
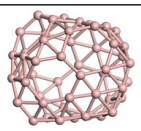
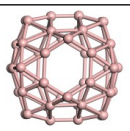
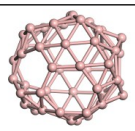
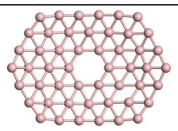
 I 0.0 eV (C_{2v})	 II 0.94 eV (C_2)	 III 1.25 eV C_{2v})	 IV 2.00 eV (C_2)	
 V 1.15 eV (C_2)	 VI 1.34 eV (C_2)	 VII 1.47 eV (C_{6v})	 VIII 1.62 eV (D_2)	 IX 1.66 eV (C_2)
 X 1.69 eV	 XI 1.76 eV (C_2)	 XII 1.77 eV (C_{2h})	 XIII 1.81 eV (C_2)	 XIV 1.97 eV (C_s)

Figure S3 Structures and relative energy of the low-lying isomers of B_{50} clusters from TPSSh/6-311G(d) calculations. The point-group symmetry for each isomer is given in parenthesis. The interior atoms of the core-shell structures are highlighted in blue.

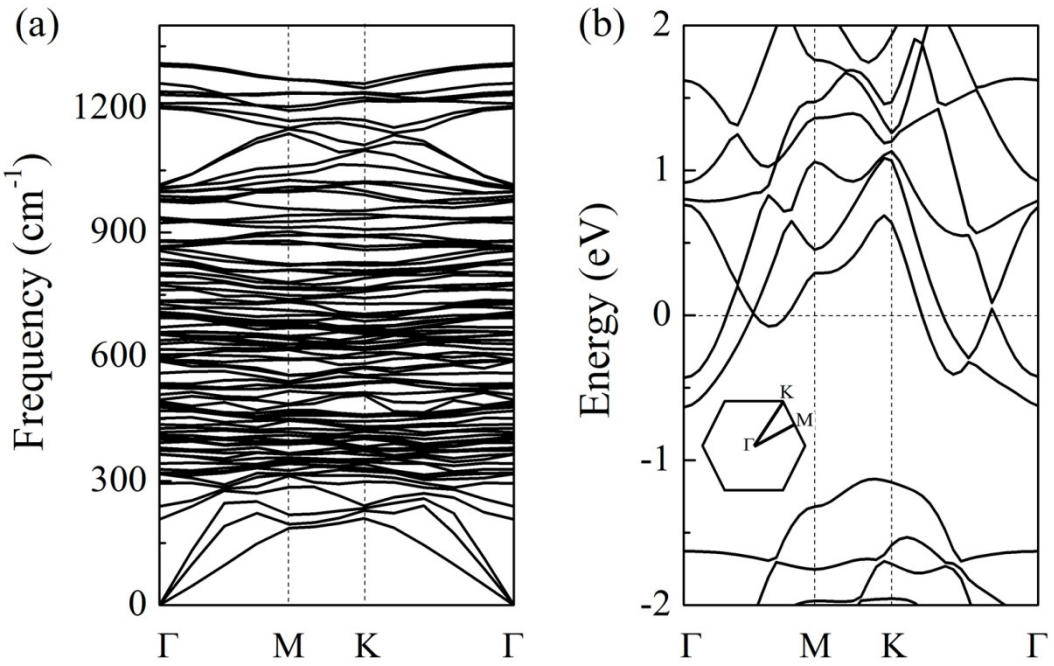


Figure S4 (a) Phonon dispersion and (b) band structure of the bilayer boron sheet in Figure 2 of main text. The 1st Brillouin zone of the reciprocal space is presented as inset in (b).

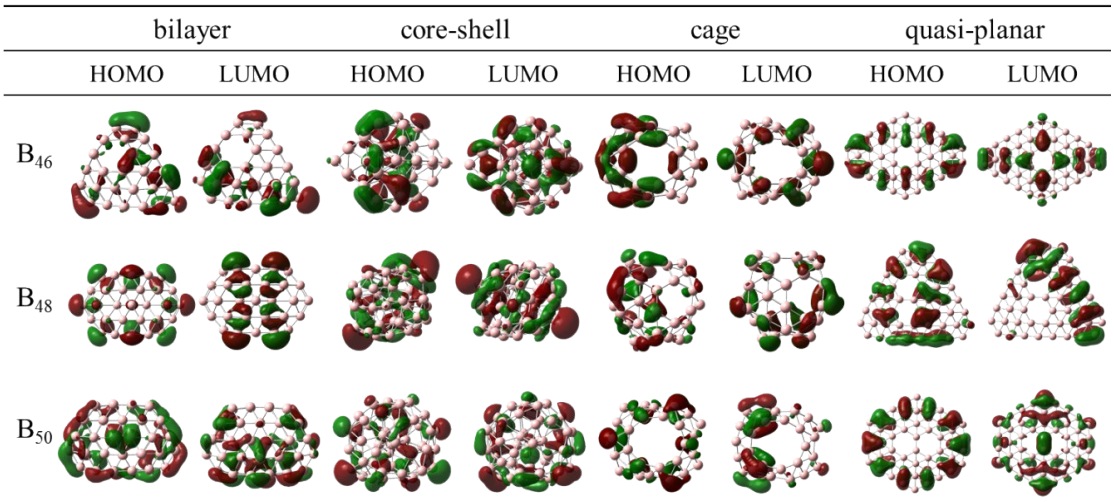


Figure S5 The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the representative isomers of B_n clusters (n=46, 48, 50) in Figure 1 of main text.

References

1. B. Kiran, S. Bulusu, H.-J. Zhai, S. Yoo, X. C. Zeng and L.-S. Wang, *PNAS*, 2005, 102, 961-964.
2. F. Y. Li, P. Jin, D. E. Jiang, L. Wang, S. B. Zhang, J. Zhao and Z. Chen, *J. Chem. Phys.*, 2012, 136, 074302.