Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Planar B_{38}^- and B_{37}^- Clusters with A Double-Hexagonal Vacancy: Molecular Motifs for Borophenes

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Table S1. Experimental vertical detachment energies (VDEs) measured from photoelectron spectra of B_{38}^- and B_{37}^- compared with calculated VDEs at the TD-PBE0/6-311+G* level. All energies are in eV.

Feature	VDE_{exptl}[a]	Final states and their electronic configurations	VDE_{theo}
		C_s B_{38}^- (^{2}A")	
X	4.02(4)[b]	^{3}A" {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{1}}	4.125[c]
		^{1}A" {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{1}}	4.126
A	~4.3	^{3}A' {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{1} 25a"^{2} 26a"^{1} 32a'^{2}}	4.27
		^{1}A" {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{0} 32a'^{2}}	4.34
B	4.62(3)	^{3}A" {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{1} 25a"^{1} 26a"^{1} 32a'^{2}}	4.60
		^{1}A" {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{1} 26a"^{1} 32a'^{2}}	4.66
		^{1}A' {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{1} 25a"^{2} 26a"^{1} 32a'^{2}}	4.84
C	5.04(3)	^{1}A' {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{1} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	5.02
		^{3}A' {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{1} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	5.03
D	5.39(5)	^{3}A" {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{1} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	5.35
		^{1}A" {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{1} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	5.36
		^{3}A" {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{1} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	5.39
E	5.74(2)	^{1}A" {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{1} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	5.76
		^{3}A' {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{1} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	5.84
		^{1}A' {21a"^{2} 22a"^{2} 28a'^{2} 29a'^{1} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	5.93
F	5.9–6.3	^{1}A' {21a"^{2} 22a"^{2} 28a'^{1} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	6.32
		^{3}A' {21a"^{2} 22a"^{2} 28a'^{1} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	6.32
		^{1}A" {21a"^{2} 22a"^{1} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	6.34
		^{1}A" {21a"^{1} 22a"^{2} 28a'^{2} 29a'^{2} 23a"^{2} 24a"^{2} 30a'^{2} 31a'^{2} 25a"^{2} 26a"^{1} 32a'^{2}}	6.36
		C_1 B_{37}^- (^{1}A)	
X	3.88(4)[b]	^{2}A {…46a^2 47a^2 48a^2 49a^2 50a^2 51a^2 52a^2 53a^2 54a^2 55a^2 56a^1}	3.75[c]
A	4.30(5)	^{2}A {…46a^2 47a^2 48a^2 49a^2 50a^2 51a^2 52a^2 53a^2 54a^2 55a^1 56a^2}	4.28
B	~4.7	^{2}A {…46a^2 47a^2 48a^2 49a^2 50a^2 51a^2 52a^2 53a^2 54a^1 55a^2 56a^2}	4.74
C	4.87(5)	^{2}A {…46a^2 47a^2 48a^2 49a^2 50a^2 51a^2 52a^2 53a^1 54a^2 55a^2 56a^2}	4.89
D	5.17(3)	^{2}A {…46a^2 47a^2 48a^2 49a^2 50a^2 51a^2 52a^1 53a^2 54a^2 55a^2 56a^2}	5.14
E	5.41(3)	^{2}A {…46a^2 47a^2 48a^2 49a^2 50a^2 51a^1 52a^2 53a^2 54a^2 55a^2 56a^2}	5.49
F	5.67(5)	^{2}A {…46a^2 47a^2 48a^2 49a^2 50a^1 51a^2 52a^2 53a^2 54a^2 55a^2 56a^2}	5.75
G	6.10(5)	^{2}A {…46a^2 47a^2 48a^2 49a^1 50a^2 51a^2 52a^2 53a^2 54a^2 55a^2 56a^2}	6.03
H	6.22(2)	^{2}A {…46a^2 47a^2 48a^1 49a^2 50a^2 51a^2 52a^2 53a^2 54a^2 55a^2 56a^2}	6.24
		^{2}A {…46a^2 47a^1 48a^2 49a^2 50a^2 51a^2 52a^2 53a^2 54a^2 55a^2 56a^2}	6.31

[a] Numbers in parentheses represent the experimental uncertainty in the last digit.

[b] Experimental ADEs of B_{38}^- and B_{37}^- are estimated to be 3.91 ± 0.05 and 3.76 ± 0.05 eV, respectively.

[c] Theoretical ADEs at the PBE0/6-311+G* level are 4.06 and 3.67 eV for C_s B_{38}^- (**1**, ^{2}A") and C_1 B_{37}^- (**2**, ^{1}A), respectively.

Figure S1. Selected low-lying isomers of B_{38}^- at the PBE0/6-311+G* level. Relative energies are indicated in eV, with corrections for zero-point energies at the same level. The point group symmetry and spectroscopic state of each isomer are also given.

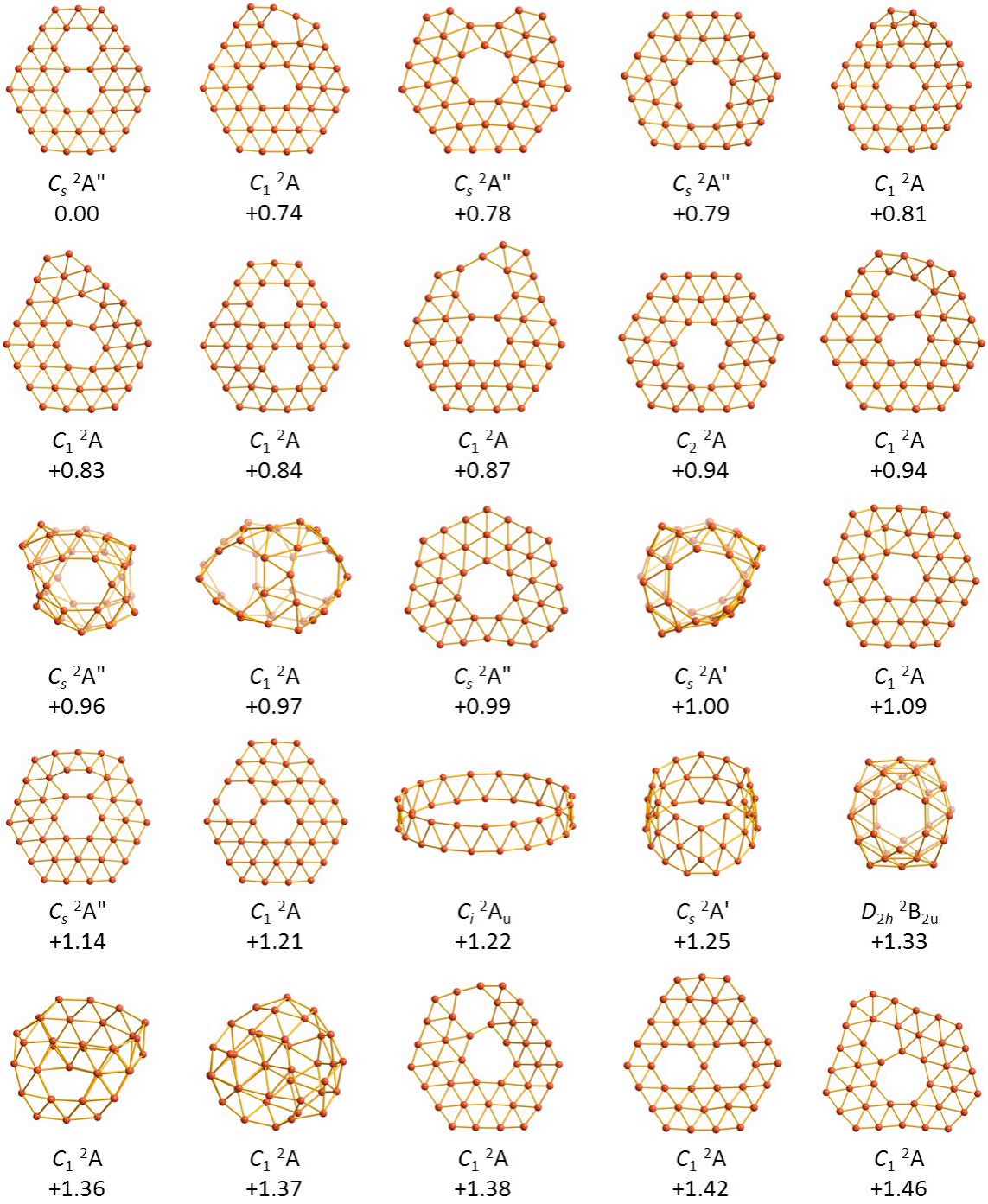
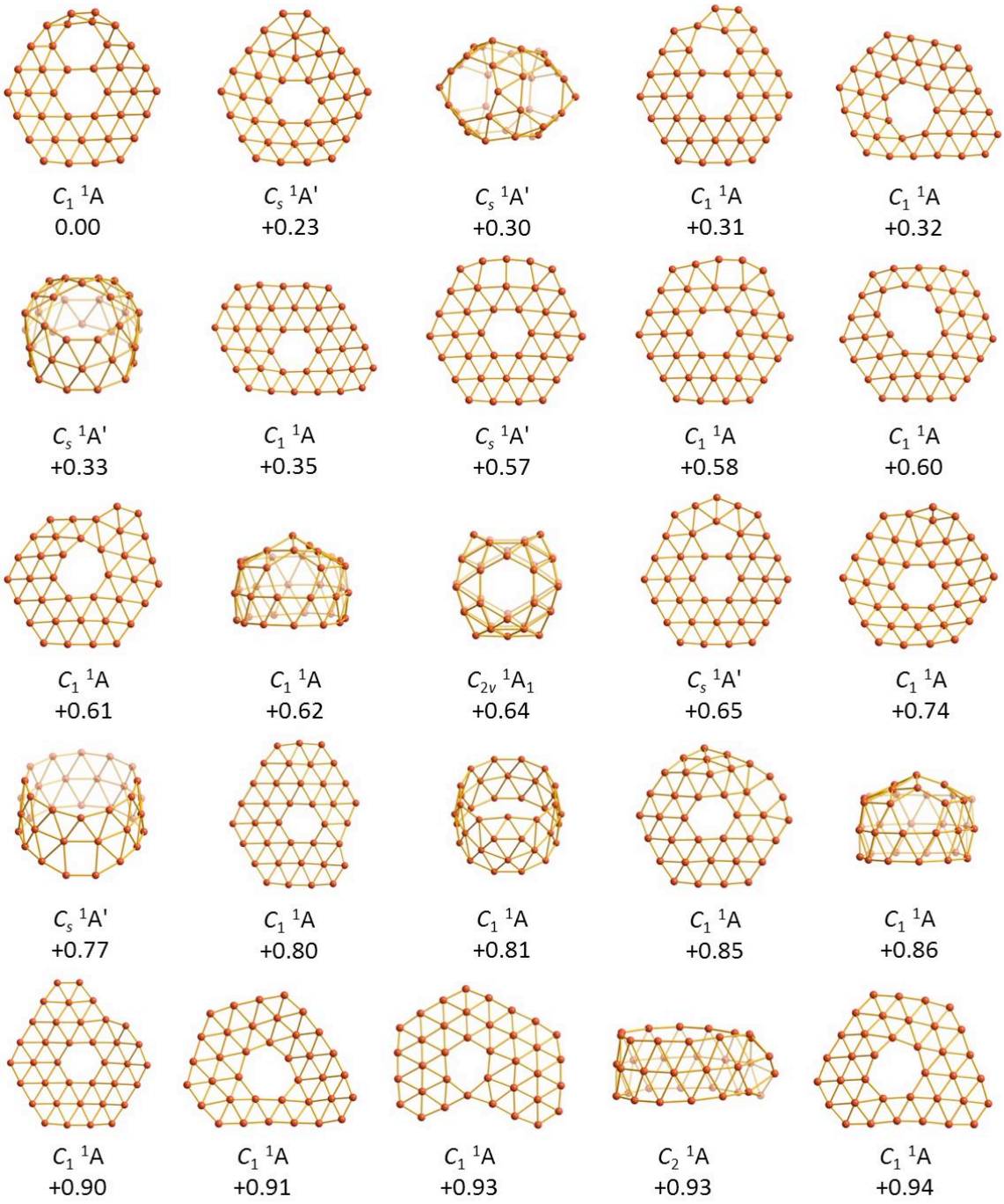


Figure S2. Selected low-lying isomers of B_{37}^- at the PBE0/6-311+G* level. Relative energies are indicated in eV, with corrections for zero-point energies at the same level. The point group symmetry and spectroscopic state of each isomer are also given.



(**Figure 2** continued …)

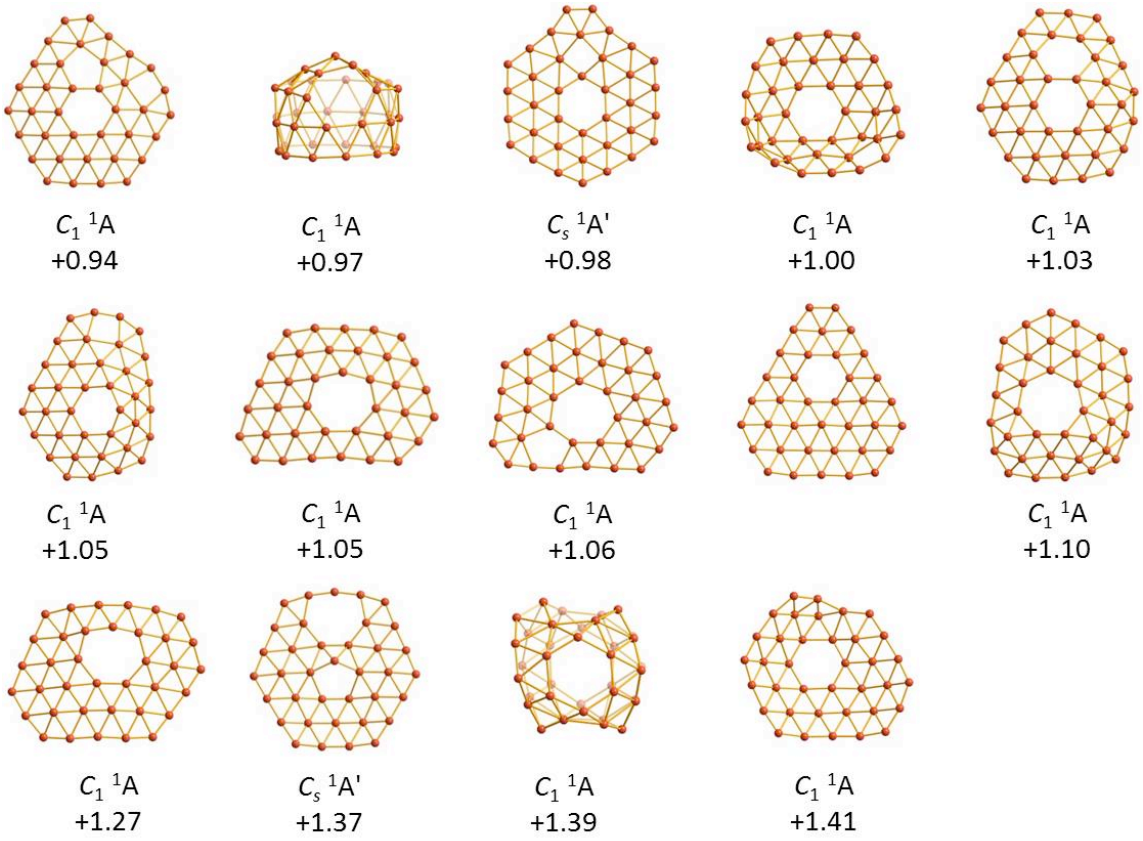


Figure S3. Spin-polarized orbital energy order of the global minimum of B_{38}^- (**1**, C_s, $^2A''$) at the PBE0/6-311+G* level. The α/β pair of orbitals are connected by a blue line, and the unpaired orbital, α-26a″, is shaded in pink. The neutral final states, C_s B_{38} ($^3A''$) and C_s B_{38} ($^1A''$) are indicated in red, upon removing an electron from the anion C_s B_{38}^- ($^2A''$) ground state.

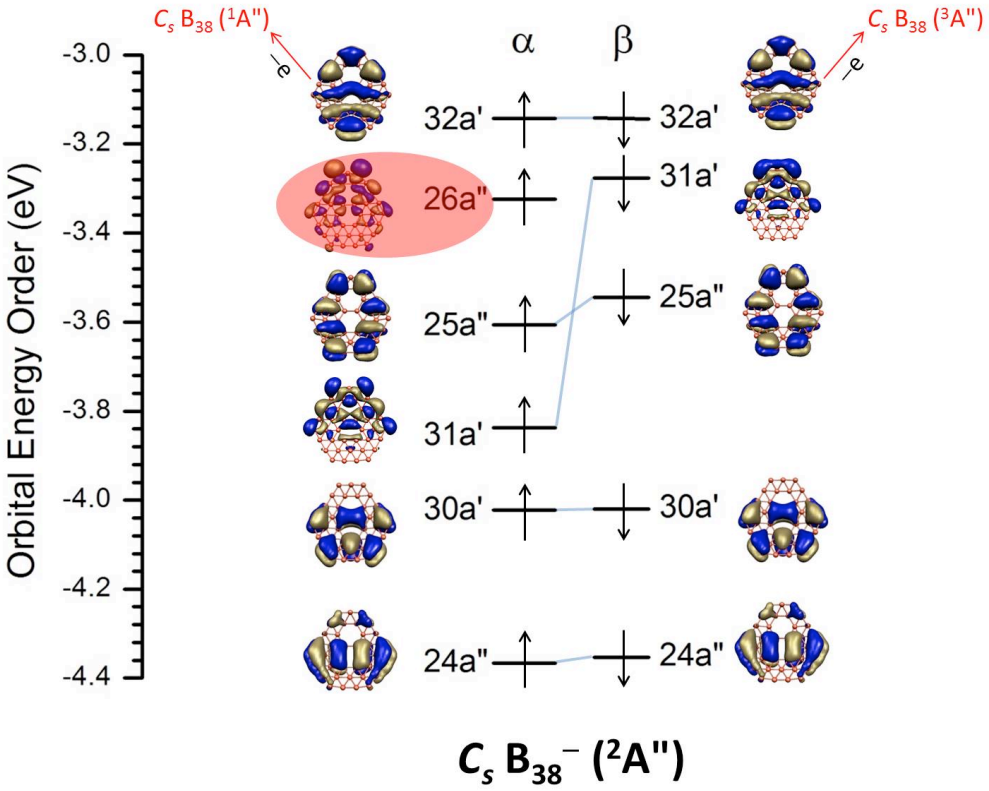


Figure S4. Comparison of the π-CMOs of (a) C_s B_{38}^-, (b) C_1 B_{37}^-, and (c) D_{6h} $C_{24}H_{12}$.

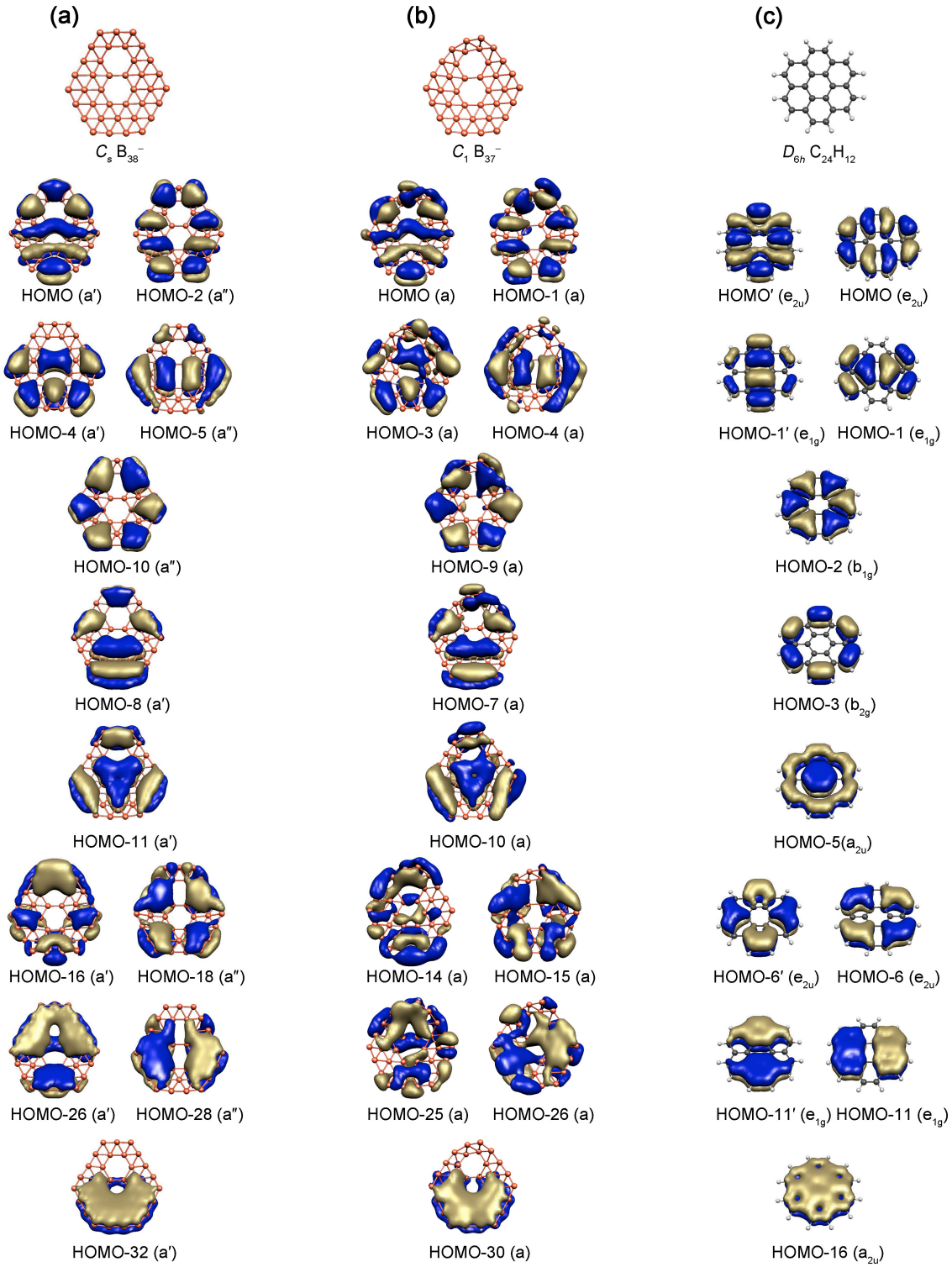


Table S2. Optimized coordinates of C_s B_{38}^- (**1**, $^2A''$) and C_1 B_{37}^- (**2**, ^1A) at the PBE0/6-311+G* level.

(1) C_s B_{38}^- (^{2}A")

B	−0.39689900	2.50776300	1.69526400
B	0.09795500	2.47284600	3.29977500
B	0.24919900	1.07693600	4.16092200
B	−0.23575300	−0.37532000	3.30256700
B	−0.78772000	1.04947600	0.81489300
B	−0.67919100	−1.85194400	0.82332800
B	0.34081500	−1.77174900	4.09025800
B	−0.08384800	3.90786500	0.82802600
B	−0.32203500	−1.79946300	2.45961200
B	0.29240100	3.87994500	2.49676500
B	0.49852100	−0.34663300	4.77687100
B	0.39072500	−3.21808600	3.27293700
B	−0.14062100	−3.25093900	1.65412700
B	0.44120900	−4.65659800	0.82274400
B	−0.67919100	−1.85194400	−0.82332800
B	−0.32203500	−1.79946300	−2.45961200
B	−0.14062100	−3.25093900	−1.65412700
B	0.44120900	−4.65659800	−0.82274400
B	0.65485700	−4.49326000	−2.38133300
B	0.39072500	−3.21808600	−3.27293700
B	0.34081500	−1.77174900	−4.09025800
B	−0.23575300	−0.37532000	−3.30256700
B	0.49852100	−0.34663300	−4.77687100
B	0.09795500	2.47284600	−3.29977500
B	0.24919900	1.07693600	−4.16092200
B	−0.39689900	2.50776300	−1.69526400
B	0.29240100	3.87994500	−2.49676500
B	−0.08384800	3.90786500	−0.82802600
B	−0.42048600	1.09536600	−2.44670000
B	−0.42048600	1.09536600	2.44670000
B	−0.25184600	−3.26429100	0.00000000
B	−0.78772000	1.04947600	−0.81489300
B	0.65485700	−4.49326000	2.38133300
B	0.66669400	5.15956400	1.61027300
B	0.56771900	5.24696000	0.00000000
B	0.66669400	5.15956400	−1.61027300
B	−0.72376200	−0.37710400	1.64538100
B	−0.72376200	−0.37710400	−1.64538100

(**2**) C_1 B_{37}^- (^{1}A)

B	−0.31792600	−3.27773800	0.15001600
B	1.12247200	−3.92873300	−0.62320800
B	2.55323200	−3.17936300	−0.34061000
B	2.58963000	−1.85983900	0.73435000
B	1.15072000	−0.91449700	1.06656100
B	−0.29941400	−1.70375000	0.89068700
B	1.27580300	0.71589300	0.89932800
B	3.94571500	−0.98080600	0.76572300
B	−1.72040100	−3.90870100	−0.59382600
B	4.17470800	0.53891100	0.29124700
B	−0.30734200	−4.51172500	−0.94417100
B	−1.72935300	−2.39904000	0.29373700
B	3.86079400	−2.23284600	−0.27713300
B	4.79232100	0.72193200	−1.24703600
B	2.78144000	1.50116800	0.45504200
B	2.77826300	2.98138600	−0.32407800
B	−0.11247800	1.61036500	0.76137900
B	−1.62722900	0.85851400	0.72527500
B	−1.49213300	2.47770400	0.31574500
B	−0.02263300	3.23770200	0.17929600
B	1.44595900	3.92729800	−0.47992600
B	0.06412800	4.63849800	−0.68496500
B	−1.38908200	4.06899000	−0.41726400
B	−2.88316300	3.34873600	−0.36289800
B	−2.99493800	1.75421300	0.21173500
B	−4.22403900	2.53887500	−0.54241200
B	−4.55013400	−0.63555700	−0.29787400
B	−4.47040400	0.99938600	−0.27739700
B	−3.14415300	−1.53039200	0.16847000
B	−4.44023900	−2.18203700	−0.60119500
B	−3.17302200	−3.10718500	−0.44843400
B	−3.13511300	0.11205900	0.45132500
B	1.14297900	−2.44494900	0.34025800
B	1.41085700	2.33324000	0.44495100
B	−1.71314800	−0.78124000	0.72093200
B	4.00994400	1.97260300	−0.69250700
B	4.64738000	−0.75907200	−0.71112200