

Supporting Information

Endohedral charge-transfer complex Ca@B_{37}^- : stabilization of a B_{37}^{3-} borospherene trianion by metal-encapsulation

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Fig. S1 Low-lying isomers of CaB_{37}^- with their relative energies indicated in eV at CCSD(T)/6-311G(d)//PBE0/6-311+G(d) (in curly brackets) and PBE0/6-311+G(d) levels.

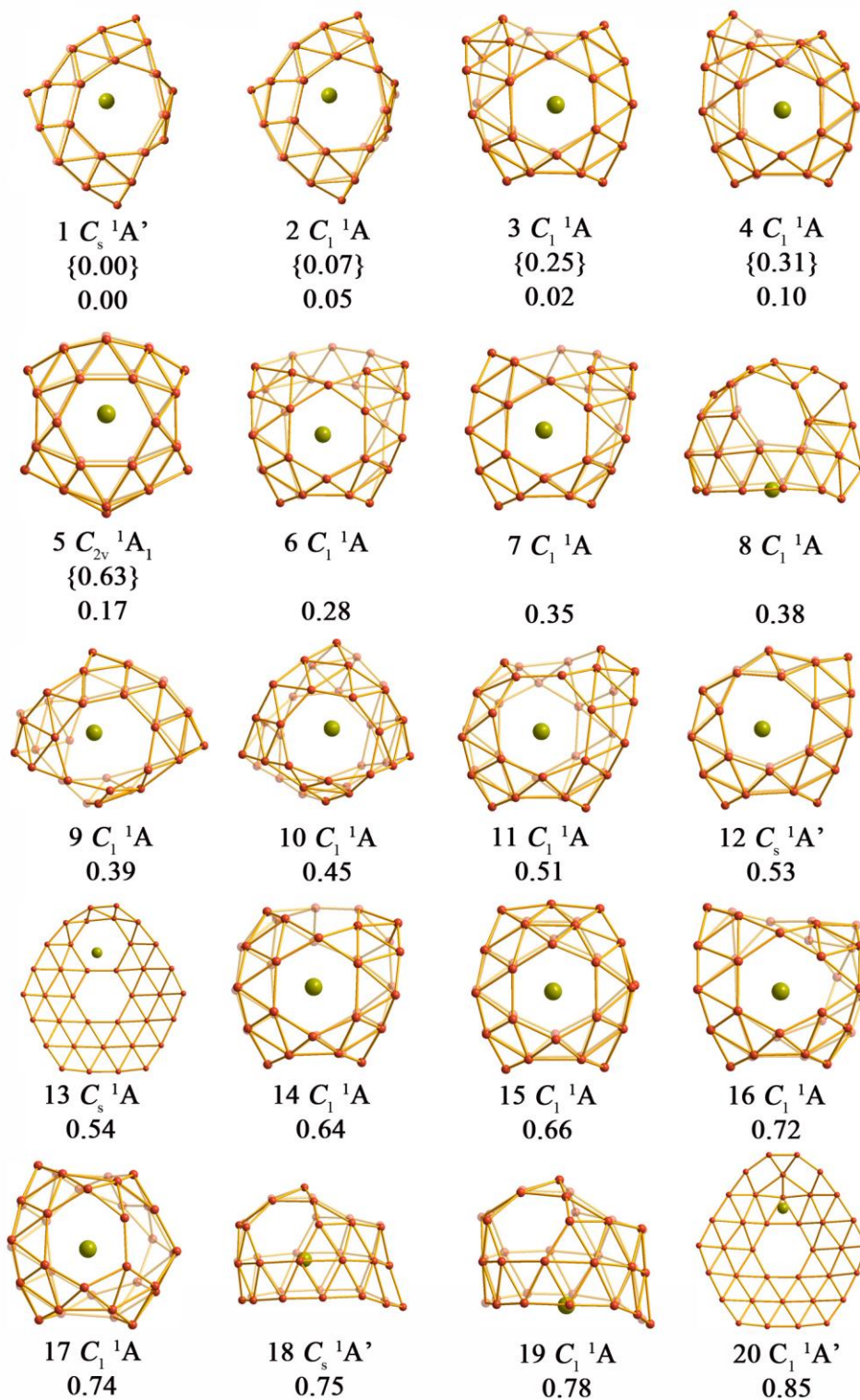


Fig.S2 Simulated PES spectra of (a) C_s Ca@B_{37}^- (**1**) and (b) C_1 Ca@B_{37}^- (**2**) at TD-PBE0.

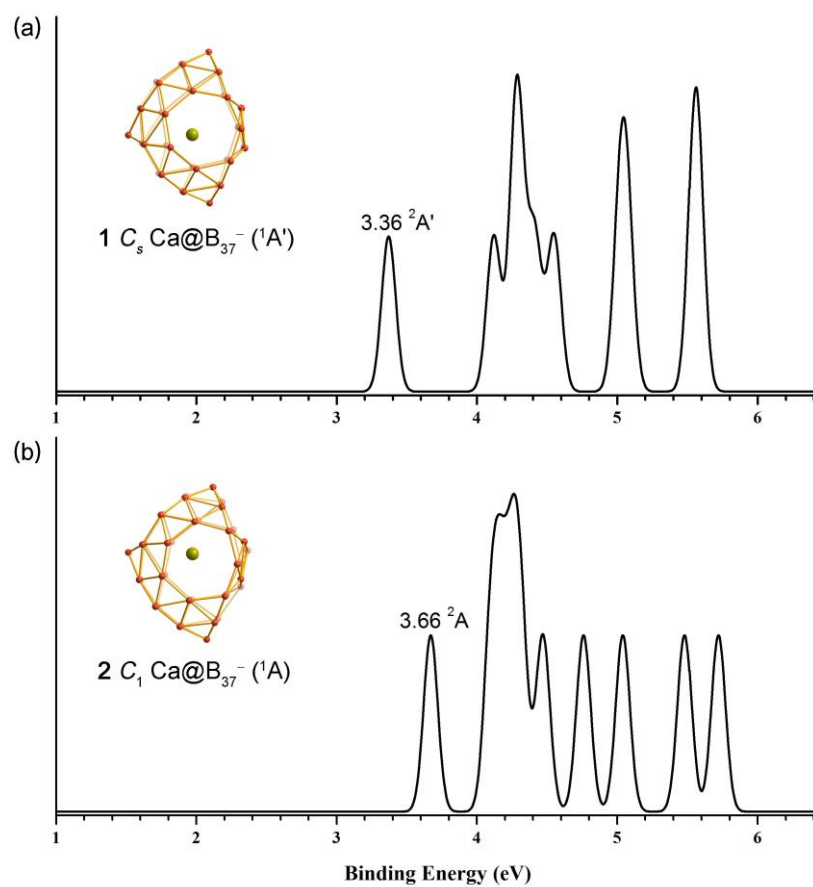


Table S1 Optimized coordinates (Å) of C_s $Ca@B_{37}^-$ (**I**), C_s B_{37}^{3-} (**II**), and the second-fifth isomers of CaB_{37}^- at PBE0/6-311+G(d) level.

1. C_s $Ca@B_{37}^-$ (**I**)

B	1.35132000	0.82735600	2.31380100
B	-1.59472700	-1.58769500	-2.27265900
B	1.68217200	-2.02255700	-1.75526500
B	3.07425600	-0.09513300	0.00000000
B	-1.08331800	-2.71722200	1.30958400
B	-1.59472700	-1.58769500	2.27265900
B	0.04988800	-1.84594300	-2.24919100
B	1.21242100	-0.74818700	2.62342600
B	1.21242100	-0.74818700	-2.62342600
B	-1.08331800	-2.71722200	-1.30958400
B	2.41691400	1.12130200	0.89234200
B	2.41691400	1.12130200	-0.89234200
B	1.35132000	0.82735600	-2.31380100
B	2.40065800	-0.54970700	-1.41222100
B	-0.55362900	-3.53576300	0.00000000
B	0.04988800	-1.84594300	2.24919100
B	2.40065800	-0.54970700	1.41222100
B	0.66631100	-2.91271000	-0.89052500
B	1.68217200	-2.02255700	1.75526500
B	0.66631100	-2.91271000	0.89052500
B	-1.62761000	1.43435800	-2.26863700
B	-2.35389400	-1.03629100	0.81753000
B	0.32578300	3.07874800	0.86874700
B	-0.01960400	1.83269100	-2.08668900
B	-2.19380200	-0.08724900	2.18077000
B	-2.19380200	-0.08724900	-2.18077000
B	1.52816500	2.29140600	-1.63065200
B	-1.62761000	1.43435800	2.26863700
B	-2.35389400	-1.03629100	-0.81753000
B	-2.32339400	0.85272900	-0.81893300
B	0.32578300	3.07874800	-0.86874700
B	1.52816500	2.29140600	1.63065200
B	-0.01960400	1.83269100	2.08668900
B	-1.33667200	2.62250700	-1.26001100
B	-1.33667200	2.62250700	1.26001100
B	-0.96100300	3.58138600	0.00000000
B	-2.32339400	0.85272900	0.81893300
Ca	0.05978900	-0.26439000	0.00000000

2. $C_s B_{37}^{3-}$ (II)

B	1.31076100	-0.83540300	2.35830100
B	-1.59824900	1.73172900	-2.36393800
B	1.68934900	2.00537200	-1.77308800
B	3.03550600	0.00585700	0.00000000
B	-1.05201800	2.77414900	1.31352200
B	-1.59824900	1.73172900	2.36393800
B	0.05972400	1.83202100	-2.23735000
B	1.23264300	0.75182200	2.67210900
B	1.23264300	0.75182200	-2.67210900
B	-1.05201800	2.77414900	-1.31352200
B	2.30740300	-1.16389900	0.89335300
B	2.30740300	-1.16389900	-0.89335300
B	1.31076100	-0.83540300	-2.35830100
B	2.28240300	0.50780200	-1.34342100
B	-0.48637000	3.60388100	0.00000000
B	0.05972400	1.83202100	2.23735000
B	2.28240300	0.50780200	1.34342100
B	0.69621200	2.91210100	-0.88893700
B	1.68934900	2.00537200	1.77308800
B	0.69621200	2.91210100	0.88893700
B	-1.67682000	-1.39047100	-2.34433500
B	-2.02899300	1.10087700	0.81237800
B	0.23818200	-3.05416100	0.88573200
B	-0.08061300	-1.81278400	-2.12180100
B	-2.08057400	0.18504100	2.23324700
B	-2.08057400	0.18504100	-2.23324700
B	1.45970500	-2.31983900	-1.68260300
B	-1.67682000	-1.39047100	2.34433500
B	-2.02899300	1.10087700	-0.81237800
B	-2.09186300	-0.72670500	-0.81295600
B	0.23818200	-3.05416100	-0.88573200
B	1.45970500	-2.31983900	1.68260300
B	-0.08061300	-1.81278400	2.12180100
B	-1.40971600	-2.54605200	-1.28292900
B	-1.40971600	-2.54605200	1.28292900
B	-1.06420900	-3.51293600	0.00000000
B	-2.09186300	-0.72670500	0.81295600

3. C_1 Ca@B₃₇⁻ (2)

B	-0.73269300	-2.83724900	0.51359500
B	1.46872500	2.51915600	-1.10413800
B	2.23579100	1.20168000	1.89416800
B	-0.13912900	-0.74873300	2.97834900
B	2.62858000	-0.85470300	-1.57390000
B	1.49192700	-1.87529100	-2.09806500
B	1.80563900	2.01226800	0.48549800
B	0.83799300	-2.55887400	0.76394700
B	0.77582700	1.91047500	1.85598000
B	2.76225900	1.64677900	-0.90430800
B	-0.55533800	-1.97185200	1.97560500
B	-0.60174400	0.78230100	2.66797100
B	-0.80258700	2.23177700	1.79944600
B	1.07086800	0.28139900	2.57500400
B	3.60973100	0.25839800	-0.88410800
B	1.87336700	-1.99847500	-0.49407400
B	1.10519600	-1.44602000	2.15317400
B	3.09630800	0.80972300	0.57052400
B	2.29340200	-1.92632900	1.12084400
B	3.08944500	-0.88390300	0.15056800
B	-1.59608300	2.68331700	-0.97841700
B	1.03105900	-0.28916000	-2.41925800
B	-2.94863400	-1.08655800	0.36087500
B	-1.89057700	2.15929300	0.56819800
B	-0.01873100	-1.58947200	-2.61164800
B	-0.07594600	2.69615300	-1.51174400
B	-2.06354500	1.25220000	2.00376000
B	-1.54866000	-1.66080200	-2.12952400
B	0.64353300	1.27059900	-2.05419900
B	-1.11835200	1.44721200	-2.03294400
B	-2.93894700	0.66207800	0.80253200
B	-2.00568100	-2.10490500	1.18455400
B	-1.83030000	-2.21240000	-0.54261600
B	-2.64979000	1.49416500	-0.81855600
B	-2.82187300	-1.15973400	-1.38203900
B	-3.51149800	0.11546000	-0.61202400
B	-0.67366400	-0.02947900	-2.54434300
Ca	-0.32397000	-0.05012400	0.06782800

4. C_1 Ca@B₃₇⁻ (3)

B	0.95911000	2.04232000	-1.76212200
B	0.31597400	0.64022600	-2.56030800
B	-1.31781300	0.24367100	-2.41908800
B	-2.23737600	1.10727200	-1.40704300
B	-1.54052800	2.61051100	-0.51287600
B	-0.05232000	3.07200900	-0.96612500
B	1.97656700	-1.86490100	-1.22412900
B	1.44835500	-0.67785500	-2.49948000
B	1.97652600	0.85063400	-2.32662200
B	2.38134000	1.46601100	-0.88126700
B	2.92085300	0.32438600	0.32576100
B	2.95732400	-1.26297300	-0.06148300
B	-0.41346800	2.11566000	2.14001700
B	0.53745600	0.89723900	2.62011000
B	2.12135000	0.76771200	1.84440600
B	2.49474700	1.87572200	0.71275800
B	1.29524900	2.63665200	-0.11471200
B	-0.24184500	2.74788500	0.64376300
B	-0.75815000	-2.06858600	1.72748300
B	0.35591500	-2.94584700	0.90348300
B	1.76867900	-2.27414700	0.46590100
B	2.35945500	-0.94607300	1.44743200
B	1.46116300	-0.46120400	2.73148600
B	-0.14812600	-0.71859100	2.70939400
B	0.69860500	-2.15223700	-2.23495100
B	0.56620600	-2.73817000	-0.72244800
B	-1.03228500	-2.77996300	0.07111100
B	-2.35144500	-2.20059400	-0.63584100
B	-2.36456600	-0.60226200	-1.41223100
B	-0.23166800	-0.93190600	-2.72177300
B	-2.24376500	-1.68683400	0.97201300
B	-1.73238200	-0.85304700	2.25476300
B	-1.21885200	0.69613900	2.30718700
B	-1.72514400	1.96161600	1.14988800
B	-2.88912300	1.86829300	-0.04264300
B	-3.41842900	0.41343600	-0.41595400
B	-3.40030900	-1.14524900	-0.13255400
Ca	0.18068000	-0.00673900	0.00667300

5. C_1 Ca@B₃₇⁻ (4)

B	2.01457500	-1.33534000	1.60728200
B	0.53029500	-1.16132300	2.54355600
B	-0.67997900	-2.11287900	2.07699200
B	-0.82110800	-2.75860900	0.57605900
B	0.67938100	-2.84736000	-0.37165800
B	2.06218500	-2.42338100	0.38716200
B	-0.10692900	2.07456700	1.86389400
B	0.21772600	0.57913600	2.73569400
B	1.73086300	-0.04602900	2.62055800
B	2.61516500	0.29556400	1.29232700
B	2.27773900	1.81823700	0.43658300
B	1.11128900	2.76669000	1.02904700
B	1.46373100	-1.08289800	-2.55302000
B	1.30732100	0.53215700	-2.53877400
B	2.23095800	1.45402500	-1.28945000
B	3.12630100	0.57782600	-0.26405900
B	2.77972800	-0.97710500	0.06272300
B	1.87166100	-1.85831900	-1.15729100
B	-1.81198700	1.48439100	-1.51803800
B	-1.81330500	2.70872800	-0.37293600
B	-0.37726800	2.95518900	0.34139900
B	1.12235400	2.63285200	-0.60836800
B	0.96417700	2.08943200	-2.12541900
B	-0.35250400	1.18124000	-2.44455600
B	-1.31802400	1.05696100	2.36087300
B	-1.66892100	2.03837500	1.13326300
B	-2.89070000	1.52918800	-0.03817300
B	-3.65425100	0.16695100	0.23931500
B	-1.95443900	-1.55208100	1.13638000
B	-1.15223800	-0.55998700	2.33365000
B	-2.65228100	0.01013800	-1.12328600
B	-1.55913700	0.06391300	-2.30231300
B	-0.09825500	-0.56711100	-2.63628600
B	0.29800500	-2.10259700	-1.91331400
B	-0.81546900	-2.98781600	-1.06654300
B	-2.15930900	-2.41583000	-0.37741400
B	-3.22805200	-1.27082900	-0.10953900
Ca	0.17767600	0.01098500	0.00842000

6. C_{2v} Ca@B₃₇⁻ (5)

B	0.00000000	1.65347900	-2.74043000
B	0.00000000	-1.67450500	2.72818600
B	2.56573800	0.00000000	1.66925100
B	1.62215300	2.63029400	0.04495800
B	0.85074600	-2.25071600	-1.37901700
B	0.00000000	-1.65347900	-2.74043000
B	1.39084500	-0.89655500	2.40159000
B	1.39142700	0.84221200	-2.22300200
B	1.39084500	0.89655500	2.40159000
B	0.87567100	-2.34325300	1.46726700
B	0.85074600	2.25071600	-1.37901700
B	0.87567100	2.34325300	1.46726700
B	0.00000000	1.67450500	2.72818600
B	2.26694200	1.43316100	0.96660600
B	1.62215300	-2.63029400	0.04495800
B	1.39142700	-0.84221200	-2.22300200
B	2.29559700	1.40070400	-0.79716200
B	2.26694200	-1.43316100	0.96660600
B	2.66608600	0.00000000	-1.59346500
B	2.29559700	-1.40070400	-0.79716200
B	-2.56573800	0.00000000	1.66925100
B	-1.62215300	-2.63029400	0.04495800
B	-0.85074600	2.25071600	-1.37901700
B	-1.39084500	0.89655500	2.40159000
B	-1.39142700	-0.84221200	-2.22300200
B	-1.39084500	-0.89655500	2.40159000
B	-0.87567100	2.34325300	1.46726700
B	-0.85074600	-2.25071600	-1.37901700
B	-0.87567100	-2.34325300	1.46726700
B	-2.26694200	-1.43316100	0.96660600
B	-1.62215300	2.63029400	0.04495800
B	-1.39142700	0.84221200	-2.22300200
B	-2.29559700	-1.40070400	-0.79716200
B	-2.26694200	1.43316100	0.96660600
B	-2.66608600	0.00000000	-1.59346500
B	-2.29559700	1.40070400	-0.79716200
B	0.00000000	0.00000000	-3.01004700
Ca	0.00000000	0.00000000	0.23950100