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

Supporting Information

Endohedral Ca@B_{38}: stabilization of a B_{38}^{2-} borospherene dianion by metal-encapsulation

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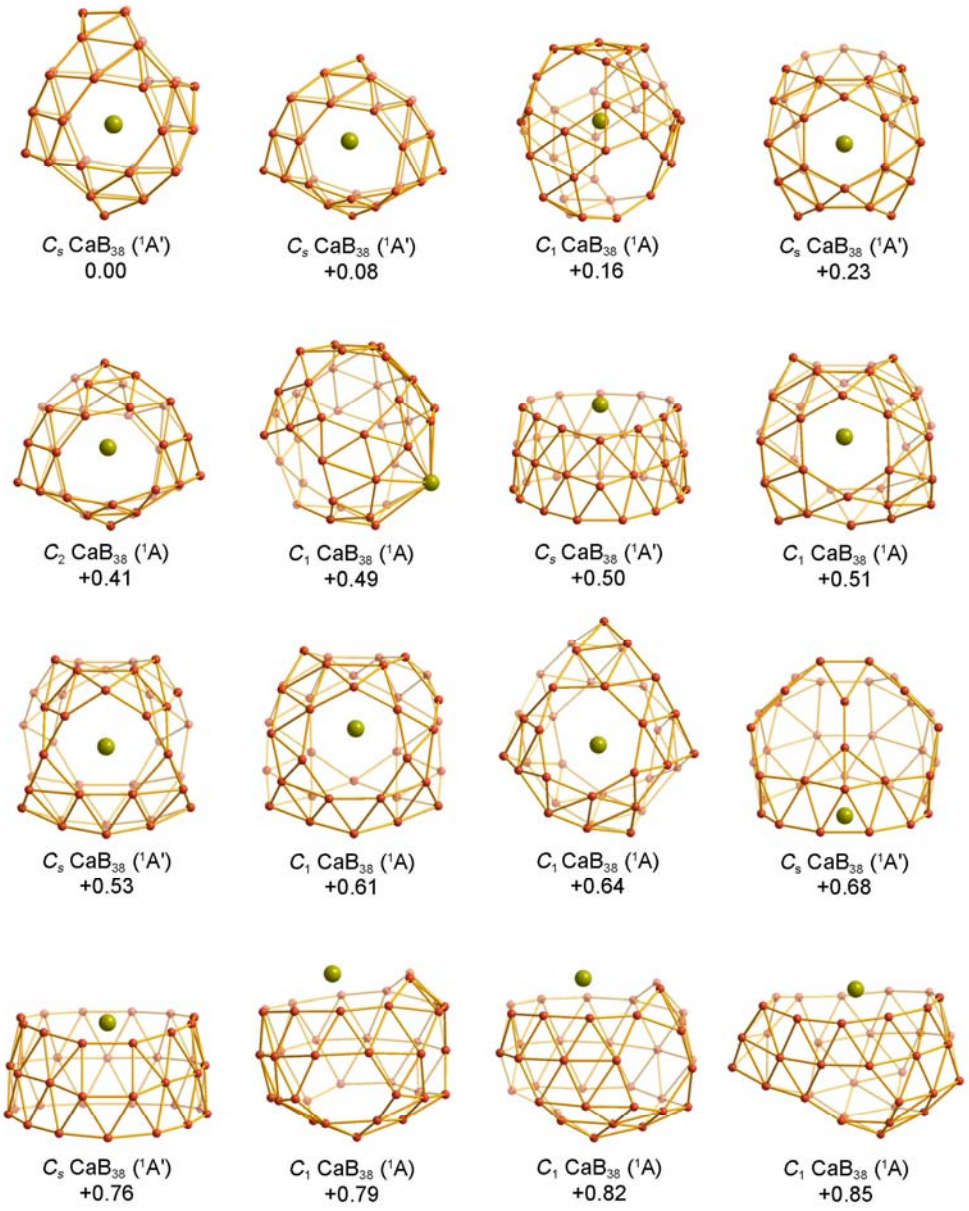
Fig. S1 Low-lying isomers of CaB_{38} with their relative energies indicated in eV at PBE0/6-311+G(d) levels.



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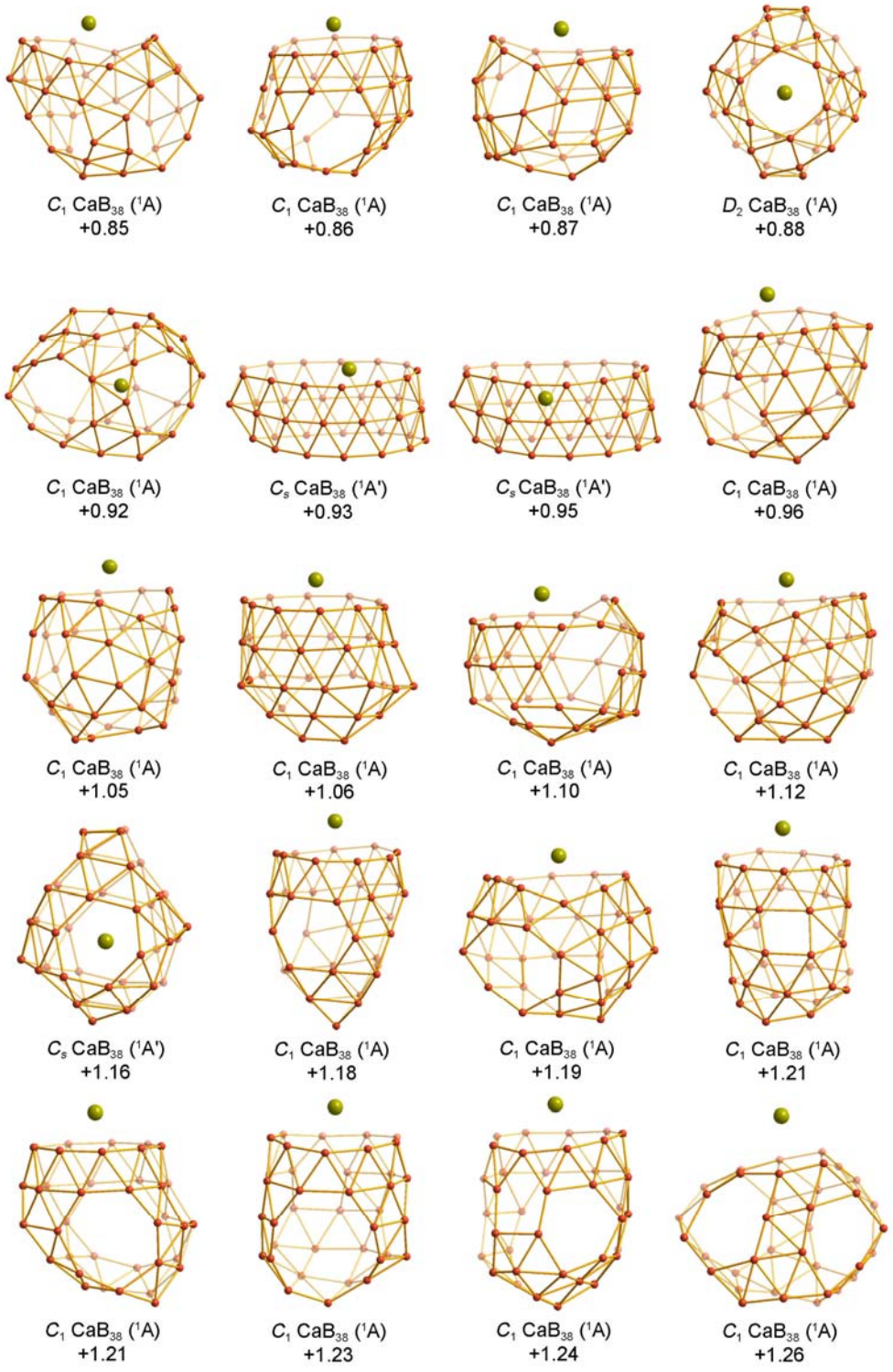
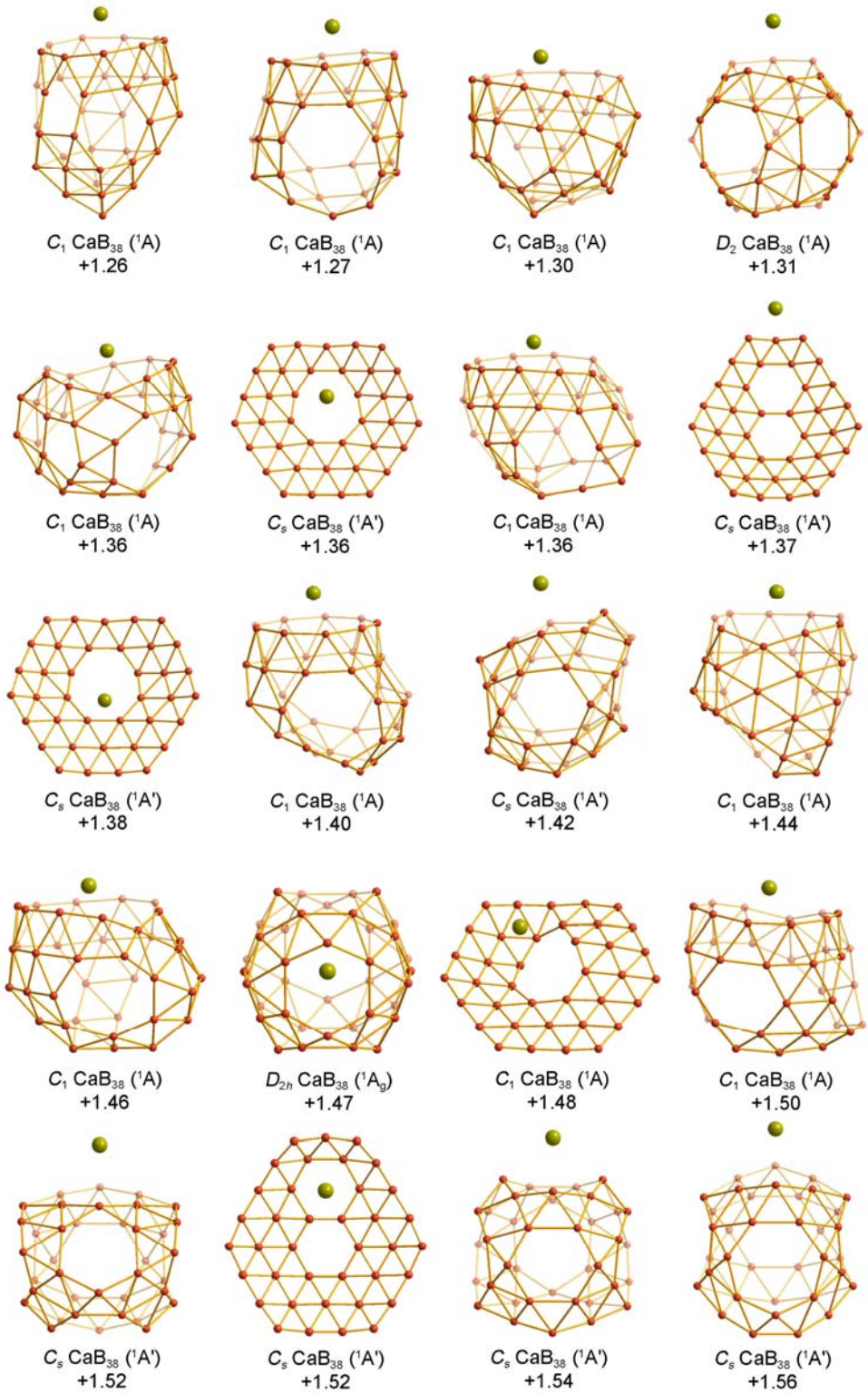

C_1 CaB_{38} (^1A)
+0.85
C_1 CaB_{38} (^1A)
+0.86
C_1 CaB_{38} (^1A)
+0.87
D_2 CaB_{38} (^1A)
+0.88
C_1 CaB_{38} (^1A)
+0.92
C_s CaB_{38} ($^1A'$)
+0.93
C_s CaB_{38} ($^1A'$)
+0.95
C_1 CaB_{38} (^1A)
+0.96
C_1 CaB_{38} (^1A)
+1.05
C_1 CaB_{38} (^1A)
+1.06
C_1 CaB_{38} (^1A)
+1.10
C_1 CaB_{38} (^1A)
+1.12
C_s CaB_{38} ($^1A'$)
+1.16
C_1 CaB_{38} (^1A)
+1.18
C_1 CaB_{38} (^1A)
+1.19
C_1 CaB_{38} (^1A)
+1.21
C_1 CaB_{38} (^1A)
+1.21
C_1 CaB_{38} (^1A)
+1.23
C_1 CaB_{38} (^1A)
+1.24
C_1 CaB_{38} (^1A)
+1.26

(Continued)


C_1 CaB_{38} (^1A)
+1.26
C_1 CaB_{38} (^1A)
+1.27
C_1 CaB_{38} (^1A)
+1.30
D_2 CaB_{38} (^1A)
+1.31
C_1 CaB_{38} (^1A)
+1.36
C_s CaB_{38} ($^1A'$)
+1.36
C_1 CaB_{38} (^1A)
+1.36
C_s CaB_{38} ($^1A'$)
+1.37
C_s CaB_{38} ($^1A'$)
+1.38
C_1 CaB_{38} (^1A)
+1.40
C_s CaB_{38} ($^1A'$)
+1.42
C_1 CaB_{38} (^1A)
+1.44
C_1 CaB_{38} (^1A)
+1.46
D_{2h} CaB_{38} (^1A_g)
+1.47
C_1 CaB_{38} (^1A)
+1.48
C_1 CaB_{38} (^1A)
+1.50
C_s CaB_{38} ($^1A'$)
+1.52
C_s CaB_{38} ($^1A'$)
+1.52
C_s CaB_{38} ($^1A'$)
+1.54
C_s CaB_{38} ($^1A'$)
+1.56

(Continued)

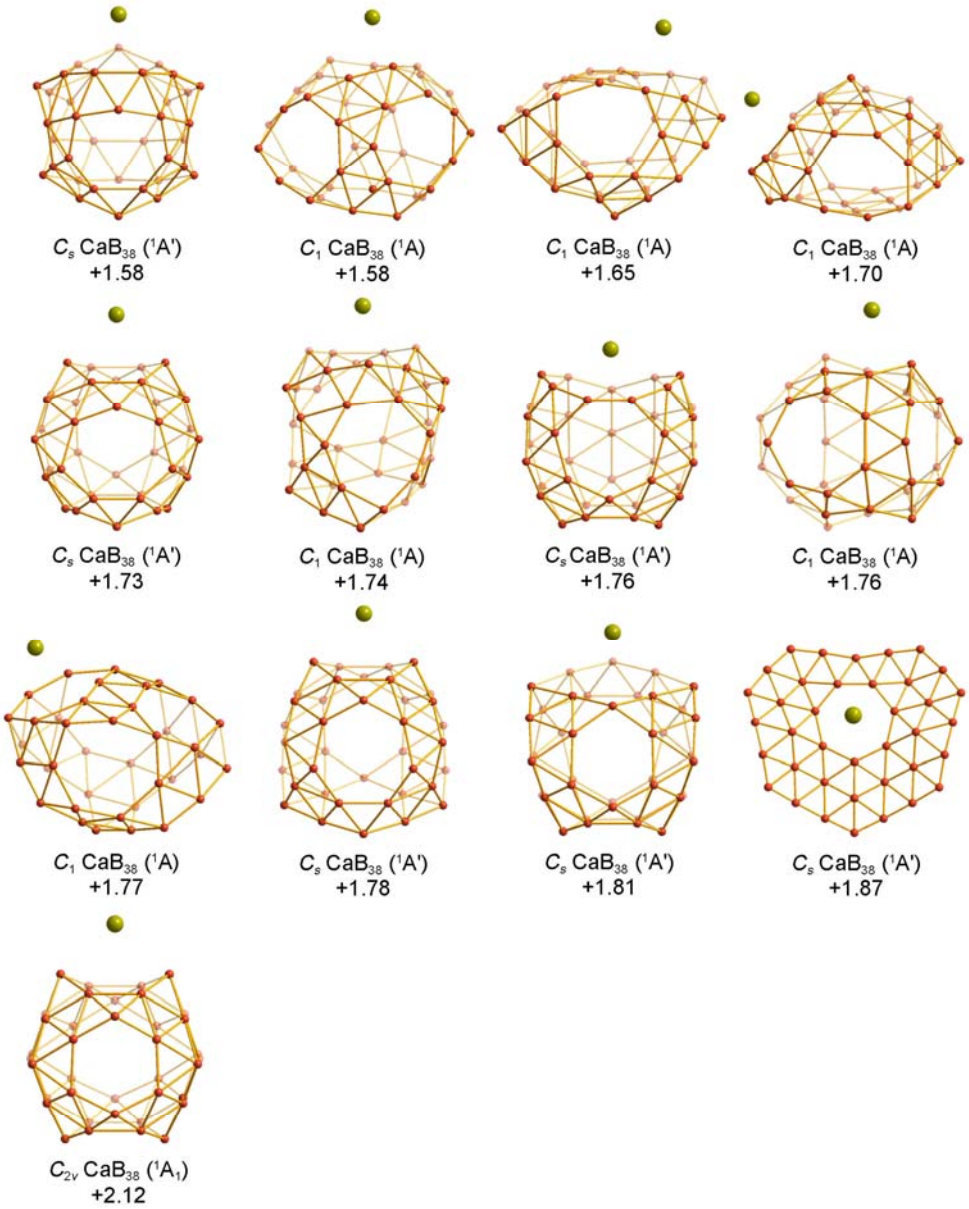

C_s CaB_{38} ($^1A'$)
+1.58
C_1 CaB_{38} (^1A)
+1.58
C_1 CaB_{38} (^1A)
+1.65
C_1 CaB_{38} (^1A)
+1.70
C_s CaB_{38} ($^1A'$)
+1.73
C_1 CaB_{38} (^1A)
+1.74
C_s CaB_{38} ($^1A'$)
+1.76
C_1 CaB_{38} (^1A)
+1.76
C_1 CaB_{38} (^1A)
+1.77
C_s CaB_{38} ($^1A'$)
+1.78
C_s CaB_{38} ($^1A'$)
+1.81
C_s CaB_{38} ($^1A'$)
+1.87
C_{2v} CaB_{38} ($^1A_1$)
+2.12

Fig. S2 Born-Oppenheimer molecular dynamics simulations of (a) C_s $Ca@B_{38}$ (**1**) and (b) C_s $Ca@B_{38}$ (the second lowest-lying isomer of CaB_{38} in Fig. 2) at 200K, 300K, and 500K for 30 ps, with the average root-mean-square-deviation (RMSD) values and maximum bond length deviation (MAXD) values indicated in Å. The approximate symmetries of typical structures picked up during the simulations are shown. The concerted transition mechanism of the second lowest-lying isomer C_s $Ca@B_{38}$ at 500K had been depicted in (c).

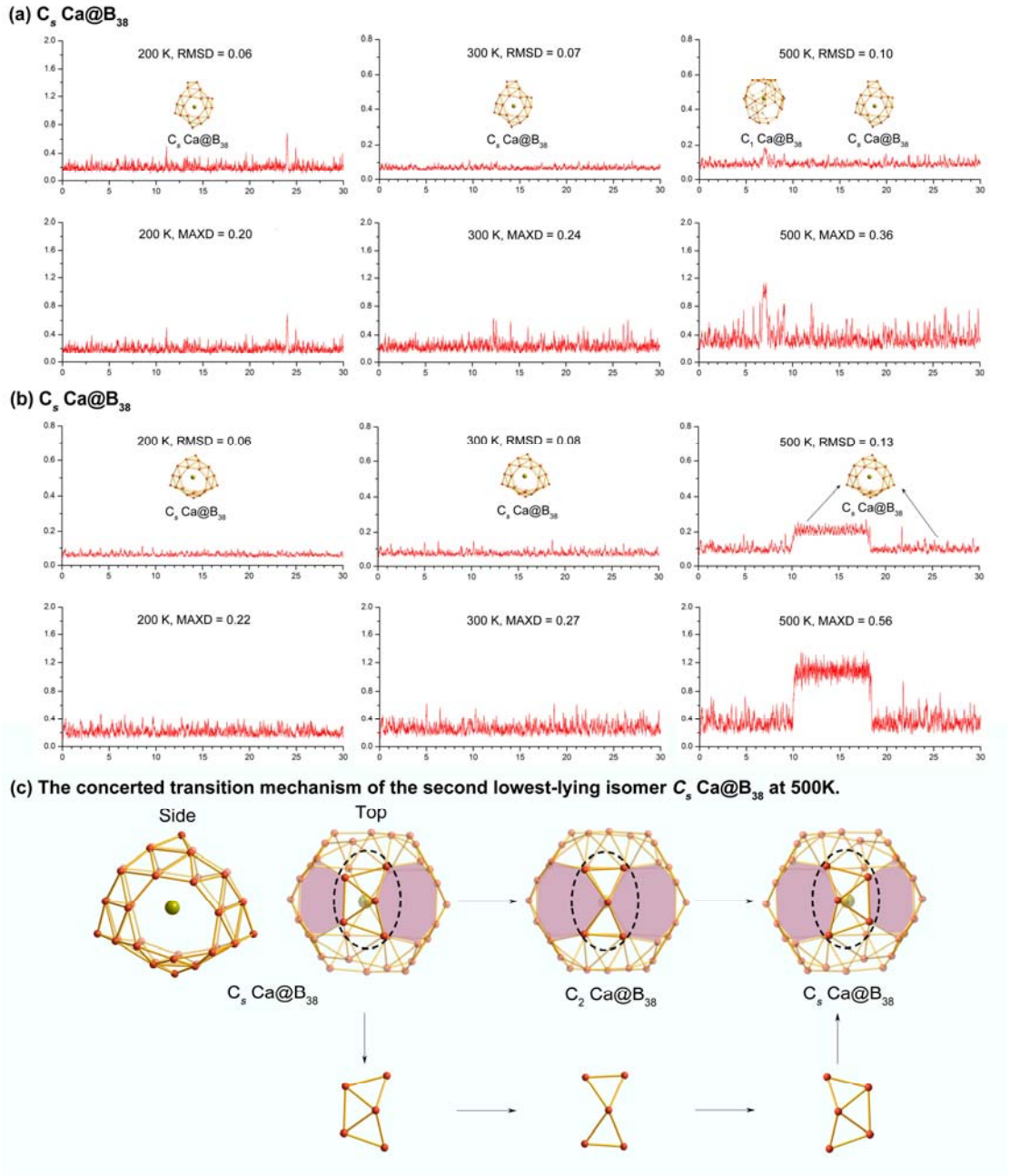


Fig. S3 Molecular orbital energy levels of C_s Ca@B_{38} (**1**) and C_s Ca@B_{38} (the second lowest-lying isomer of CaB_{38} in Fig. 2) compared with the D_{2d} B_{40} at the DFT-PBE0/6-311+G(d) level. The HOMO and LUMO pictures are described.

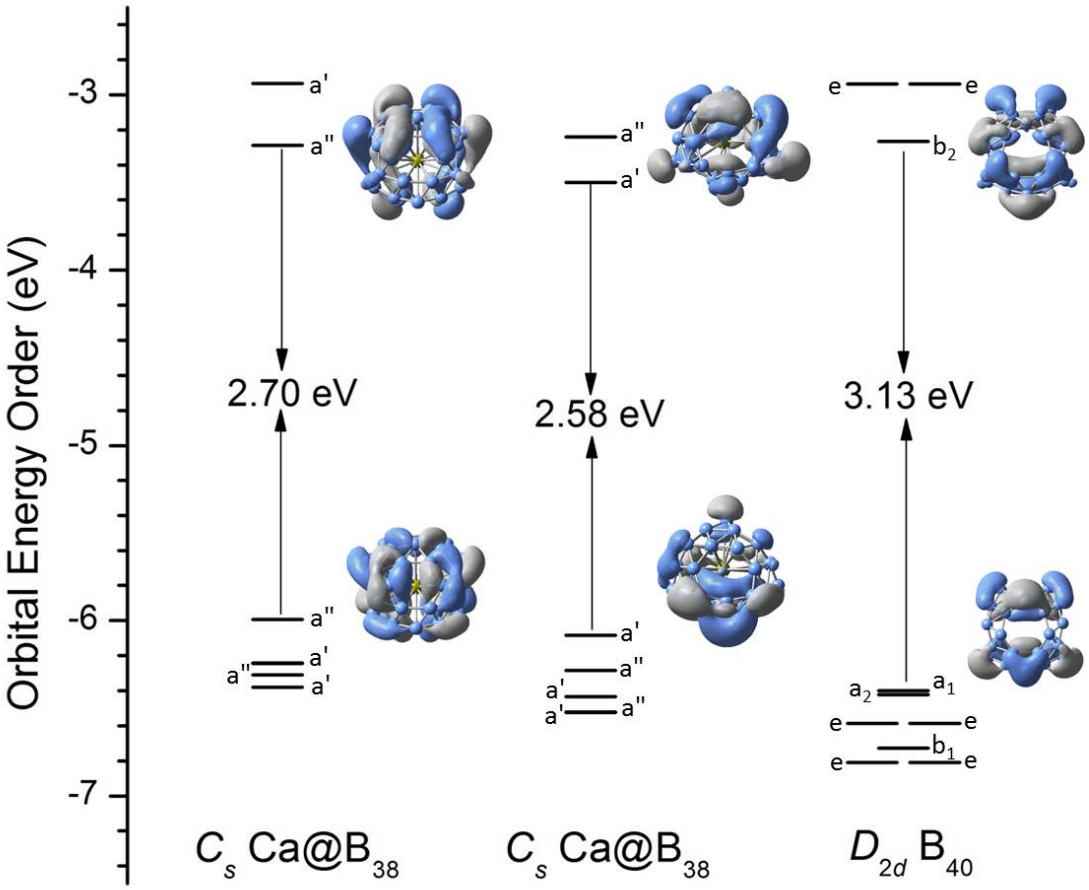


Fig. S4 Simulated IR (a) and Raman (b) spectra of C_s Ca@B_{38} (**1**) compared with the cage-like C_s B_{38}^{2-} (**2**).

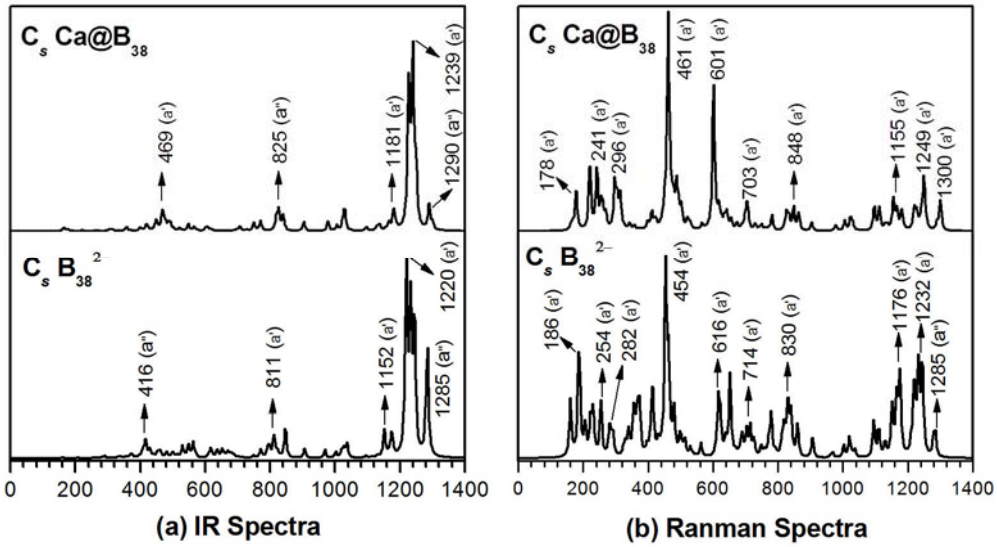


Table S1. Optimized coordinates (Å) of the typical isomers of $M@B_{38}$ (M = Ca, Sc, Y, Ti) and C_s B_{38}^{2-} at PBE0 level with the 6-311+G(d) basis set for B, Ca, Sc and Ti, with the stuttgart relativistic small-core pseudopotential and valence basis set for Y.

1. C_s $Ca@B_{38}$ (**1**)

B	−0.96646800	−2.32357600	1.93280700
B	0.50511400	−1.33987600	2.46835300
B	−2.59047000	0.52018500	0.88908400
B	−2.05272600	−1.02403000	1.48545000
B	−1.10191300	−1.00646100	−2.84861100
B	0.50511400	−1.33987600	−2.46835300
B	−0.52060500	−3.39329300	−0.83084100
B	−2.68111200	−0.87390800	0.00000000
B	0.88699500	−2.63582900	−1.43077400
B	0.88699500	−2.63582900	1.43077400
B	2.12420200	1.39358400	−1.40489700
B	0.79494000	2.56652900	−1.41406600
B	0.86808700	−3.38623500	0.00000000
B	−0.88770700	2.76264000	0.88474000
B	−1.65855600	0.45126800	−2.41353900
B	2.12420200	1.39358400	1.40489700
B	−0.52060500	−3.39329300	0.83084100
B	−1.65855600	0.45126800	2.41353900
B	−0.51659500	1.81463700	2.32325300
B	1.59387300	0.01484000	2.34587800
B	2.60290100	−0.26157900	0.87959200
B	1.97111000	−1.48026800	−1.75244800
B	0.79494000	2.56652900	1.41406600
B	−2.00227200	1.85569800	1.63122500
B	−2.59047000	0.52018500	−0.88908400
B	2.60290100	−0.26157900	−0.87959200
B	−0.51659500	1.81463700	−2.32325300
B	−2.00227200	1.85569800	−1.63122500
B	1.04459400	1.50465400	−2.64147000
B	2.90981200	1.10251400	0.00000000
B	−0.96646800	−2.32357600	−1.93280700
B	1.04459400	1.50465400	2.64147000
B	1.59387300	0.01484000	−2.34587800
B	−0.88770700	2.76264000	−0.88474000
B	−1.10191300	−1.00646100	2.84861100
B	−2.05272600	−1.02403000	−1.48545000
B	0.42084500	3.25964500	0.00000000
B	1.97111000	−1.48026800	1.75244800
Ca	0.00738300	0.26493500	0.00000000

2. C_s B_{38}^{2-} (**2**)

B	0.95071200	2.33214300	1.98674400
B	-0.49437800	1.30119200	2.48443200
B	2.44588500	-0.52566900	0.87381800
B	1.93867100	1.01557600	1.46565500
B	1.11199000	1.01670300	-2.91350400
B	-0.49437800	1.30119200	-2.48443200
B	0.51268400	3.36696600	-0.83773700
B	2.58444600	0.86516500	0.00000000
B	-0.88970000	2.58308400	-1.43520500
B	-0.88970000	2.58308400	1.43520500
B	-2.07054500	-1.42816900	-1.35994700
B	-0.74361600	-2.60781900	-1.39846700
B	-0.87687200	3.32168100	0.00000000
B	0.93911800	-2.75103300	0.88949000
B	1.64721400	-0.46046200	-2.46590700
B	-2.07054500	-1.42816900	1.35994700
B	0.51268400	3.36696600	0.83773700
B	1.64721400	-0.46046200	2.46590700
B	0.50180600	-1.81582400	2.31759900
B	-1.53060300	-0.08104900	2.31356900
B	-2.53991600	0.21609100	0.87574900
B	-1.96722300	1.43342400	-1.78530000
B	-0.74361600	-2.60781900	1.39846700
B	2.02489600	-1.86699500	1.70923300
B	2.44588500	-0.52566900	-0.87381800
B	-2.53991600	0.21609100	-0.87574900
B	0.50180600	-1.81582400	-2.31759900
B	2.02489600	-1.86699500	-1.70923300
B	-1.06130200	-1.59449000	-2.65296600
B	-2.92359900	-1.13254500	0.00000000
B	0.95071200	2.33214300	-1.98674400
B	-1.06130200	-1.59449000	2.65296600
B	-1.53060300	-0.08104900	-2.31356900
B	0.93911800	-2.75103300	-0.88949000
B	1.11199000	1.01670300	2.91350400
B	1.93867100	1.01557600	-1.46565500
B	-0.33535900	-3.32163900	0.00000000
B	-1.96722300	1.43342400	1.78530000

3. C_s Sc@B_{38} (**3**)

B	-0.85403200	-2.42523200	1.95878500
B	0.52876100	-1.34639500	2.52962000
B	-2.57312700	0.34287300	0.89816500
B	-1.93679400	-1.15123800	1.48680100
B	-1.06591400	-1.12031700	-2.91283800
B	0.52876100	-1.34639500	-2.52962000
B	-0.39388900	-3.47661400	-0.84615800
B	-2.57811800	-1.03369600	0.00000000
B	0.93126000	-2.67117500	-1.48216800
B	0.93126000	-2.67117500	1.48216800
B	2.04915600	1.45744000	-1.41083000
B	0.69317900	2.59124300	-1.42441300
B	0.97572100	-3.29796800	0.00000000
B	-1.00413800	2.70398700	0.88511300
B	-1.59899900	0.31831000	-2.38029800
B	2.04915600	1.45744000	1.41083000
B	-0.39388900	-3.47661400	0.84615800
B	-1.59899900	0.31831000	2.38029800
B	-0.59406800	1.77574600	2.32722400
B	1.54183100	0.03430200	2.35269900
B	2.50558800	-0.18119300	0.87505900
B	1.95742100	-1.43798900	-1.73824300
B	0.69317900	2.59124300	1.42441300
B	-2.06362200	1.71566900	1.60017200
B	-2.57312700	0.34287300	-0.89816500
B	2.50558800	-0.18119300	-0.87505900
B	-0.59406800	1.77574600	-2.32722400
B	-2.06362200	1.71566900	-1.60017200
B	0.97109700	1.52671200	-2.65509600
B	2.80137600	1.20000800	0.00000000
B	-0.85403200	-2.42523200	-1.95878500
B	0.97109700	1.52671200	2.65509600
B	1.54183100	0.03430200	-2.35269900
B	-1.00413800	2.70398700	-0.88511300
B	-1.06591400	-1.12031700	2.91283800
B	-1.93679400	-1.15123800	-1.48680100
B	0.29952700	3.25149600	0.00000000
B	1.95742100	-1.43798900	1.73824300
Sc	0.07478000	0.61140600	0.00000000

4. C_{2v} Sc@B_{38} (4)

B	-2.31832900	0.83696200	1.31153300
B	0.00000000	2.68271800	-1.76145400
B	1.42233600	-2.24369300	-0.93533200
B	-0.89606100	-1.40255700	-2.37374300
B	2.31311800	0.84731900	-1.45358900
B	1.40328100	-2.21330400	0.78263500
B	2.31832900	0.83696200	1.31153300
B	-1.40328100	-2.21330400	0.78263500
B	0.00000000	2.67481900	1.61587200
B	2.31311800	-0.84731900	-1.45358900
B	-1.40328100	2.21330400	0.78263500
B	0.00000000	-2.67481900	1.61587200
B	2.72873400	-1.63589600	-0.07219500
B	0.00000000	2.68070200	-0.05922900
B	0.89606100	-1.40255700	-2.37374300
B	-2.31832900	-0.83696200	1.31153300
B	-1.42233600	-2.24369300	-0.93533200
B	-0.90059300	-1.41082800	2.29346900
B	-1.64973000	0.00000000	-2.71220800
B	2.72873400	1.63589600	-0.07219500
B	1.42233600	2.24369300	-0.93533200
B	0.90059300	1.41082800	2.29346900
B	1.65051500	0.00000000	2.60701000
B	-2.72873400	-1.63589600	-0.07219500
B	0.00000000	-2.68271800	-1.76145400
B	-0.90059300	1.41082800	2.29346900
B	-1.65051500	0.00000000	2.60701000
B	0.00000000	-2.68070200	-0.05922900
B	-0.89606100	1.40255700	-2.37374300
B	1.40328100	2.21330400	0.78263500
B	-1.42233600	2.24369300	-0.93533200
B	2.31832900	-0.83696200	1.31153300
B	1.64973000	0.00000000	-2.71220800
B	-2.31311800	-0.84731900	-1.45358900
B	0.90059300	-1.41082800	2.29346900
B	0.89606100	1.40255700	-2.37374300
B	-2.31311800	0.84731900	-1.45358900
B	-2.72873400	1.63589600	-0.07219500
Sc	0.00000000	0.00000000	0.57354800

5. C_s Y@B_{38} (**5**)

B	-0.90341500	-2.37470600	1.90589800
B	0.52264200	-1.36029300	2.52755300
B	-2.62216300	0.42900700	0.91064500
B	-2.01731000	-1.09192800	1.48834800
B	-1.07225100	-1.06888700	-2.87175700
B	0.52264200	-1.36029300	-2.52755300
B	-0.46259400	-3.48062400	-0.84830600
B	-2.67423700	-0.94586600	0.00000000
B	0.87761800	-2.68853000	-1.47107900
B	0.87761800	-2.68853000	1.47107900
B	2.12207600	1.38530200	-1.42052100
B	0.76789200	2.53672600	-1.42121000
B	0.90774000	-3.34934100	0.00000000
B	-0.92504000	2.71060900	0.88811600
B	-1.62326100	0.37027200	-2.38234800
B	2.12207600	1.38530200	1.42052100
B	-0.46259400	-3.48062400	0.84830600
B	-1.62326100	0.37027200	2.38234800
B	-0.54335900	1.77447900	2.33291900
B	1.59210600	-0.01142100	2.36124600
B	2.57414600	-0.26016900	0.88438800
B	1.95481600	-1.49489300	-1.74293000
B	0.76789200	2.53672600	1.42121000
B	-2.03014900	1.77718600	1.61217200
B	-2.62216300	0.42900700	-0.91064500
B	2.57414600	-0.26016900	-0.88438800
B	-0.54335900	1.77447900	-2.33291900
B	-2.03014900	1.77718600	-1.61217200
B	1.02650200	1.48086200	-2.65285500
B	2.87744200	1.11089100	0.00000000
B	-0.90341500	-2.37470600	-1.90589800
B	1.02650200	1.48086200	2.65285500
B	1.59210600	-0.01142100	-2.36124600
B	-0.92504000	2.71060900	-0.88811600
B	-1.07225100	-1.06888700	2.87175700
B	-2.01731000	-1.09192800	-1.48834800
B	0.39099400	3.20950200	0.00000000
B	1.95481600	-1.49489300	1.74293000
Y	0.00276300	0.34728600	0.00000000

6. C_{2v} Y@B_{38} (**6**)

B	-2.28846400	1.35010600	-0.90118000
B	0.00000000	-1.70012000	-2.84039300
B	1.40615800	-0.85424900	2.26951800
B	-0.88949500	-2.25749200	1.40724500
B	2.28846400	-1.35010600	-0.90118000
B	1.40615800	0.85424900	2.26951800
B	2.28846400	1.35010600	-0.90118000
B	-1.40615800	0.85424900	2.26951800
B	0.00000000	1.70012000	-2.84039300
B	2.31532800	-1.36649400	0.85645900
B	-1.39731500	0.85026900	-2.34226500
B	0.00000000	1.71506700	2.77721500
B	2.74535300	0.00000000	1.64458700
B	0.00000000	0.00000000	-2.88675300
B	0.88949500	-2.25749200	1.40724500
B	-2.31532800	1.36649400	0.85645900
B	-1.40615800	-0.85424900	2.26951800
B	-0.88949500	2.25749200	1.40724500
B	-1.61548500	-2.57417700	-0.02616800
B	2.72109500	0.00000000	-1.73585500
B	1.39731500	-0.85026900	-2.34226500
B	0.86660900	2.23485600	-1.44220100
B	1.61548500	2.57417700	-0.02616800
B	-2.74535300	0.00000000	1.64458700
B	0.00000000	-1.71506700	2.77721500
B	-0.86660900	2.23485600	-1.44220100
B	-1.61548500	2.57417700	-0.02616800
B	0.00000000	0.00000000	2.79593100
B	-0.86660900	-2.23485600	-1.44220100
B	1.39731500	0.85026900	-2.34226500
B	-1.39731500	-0.85026900	-2.34226500
B	2.31532800	1.36649400	0.85645900
B	1.61548500	-2.57417700	-0.02616800
B	-2.31532800	-1.36649400	0.85645900
B	0.88949500	2.25749200	1.40724500
B	0.86660900	-2.23485600	-1.44220100
B	-2.28846400	-1.35010600	-0.90118000
B	-2.72109500	0.00000000	-1.73585500
Y	0.00000000	0.00000000	0.14283100

7. C_s Ti@B_{38} (7)

B	0.72824800	2.51089400	1.96950800
B	-0.54849600	1.30875500	2.48344600
B	2.62525300	-0.13358800	0.88747900
B	1.90527000	1.32802800	1.48374800
B	1.05053700	1.23725600	-2.91579700
B	-0.54849600	1.30875500	-2.48344600
B	0.16354800	3.50093800	-0.83678300
B	2.54647500	1.24848200	0.00000000
B	-1.10025500	2.62607600	-1.50631300
B	-1.10025500	2.62607600	1.50631300
B	-1.91894900	-1.60300300	-1.39927500
B	-0.48450800	-2.62189600	-1.43055200
B	-1.19109400	3.17080300	0.00000000
B	1.21676000	-2.53626600	0.87697500
B	1.70040100	-0.16083700	-2.40231700
B	-1.91894900	-1.60300300	1.39927500
B	0.16354800	3.50093800	0.83678300
B	1.70040100	-0.16083700	2.40231700
B	0.73021700	-1.64024400	2.30302100
B	-1.44218000	-0.14352200	2.31922800
B	-2.51376000	-0.01673400	0.88199400
B	-1.99289000	1.29054200	-1.67582500
B	-0.48450800	-2.62189600	1.43055200
B	2.22772800	-1.52189800	1.62582200
B	2.62525300	-0.13358800	-0.88747900
B	-2.51376000	-0.01673400	-0.88199400
B	0.73021700	-1.64024400	-2.30302100
B	2.22772800	-1.52189800	-1.62582200
B	-0.83509800	-1.59447500	-2.68701200
B	-2.73779300	-1.41190000	0.00000000
B	0.72824800	2.51089400	-1.96950800
B	-0.83509800	-1.59447500	2.68701200
B	-1.44218000	-0.14352200	-2.31922800
B	1.21676000	-2.53626600	-0.87697500
B	1.05053700	1.23725600	2.91579700
B	1.90527000	1.32802800	-1.48374800
B	-0.03568000	-3.22704300	0.00000000
B	-1.99289000	1.29054200	1.67582500
Ti	-0.36490000	-0.78190800	0.00000000

8. C_{2v} Ti@B_{38} **(8)**

B	-1.38668900	0.85504500	2.36362100
B	1.68656100	2.62358300	-0.11430200
B	0.84890500	-2.18026800	-1.51553700
B	2.21956400	-1.22459700	0.71468400
B	1.43509500	0.85159000	-2.45714700
B	-0.84890500	-2.18026800	-1.51553700
B	-1.43509500	0.85159000	-2.45714700
B	-0.85212400	-2.18876200	1.31938500
B	-1.68656100	2.62358300	-0.11430200
B	1.43509500	-0.85159000	-2.45714700
B	-0.85212400	2.18876200	1.31938500
B	-1.68656100	-2.62358300	-0.11430200
B	0.00000000	-1.57091000	-2.81255300
B	0.00000000	2.62119800	-0.10770800
B	2.36420500	-1.42682800	-1.03521300
B	-1.38668900	-0.85504500	2.36362100
B	0.85212400	-2.18876200	1.31938500
B	-2.21956400	-1.22459700	0.71468400
B	2.65803200	0.00000000	1.65147400
B	0.00000000	1.57091000	-2.81255300
B	0.84890500	2.18026800	-1.51553700
B	-2.36420500	1.42682800	-1.03521300
B	-2.67112900	0.00000000	-1.76670600
B	0.00000000	-1.65479900	2.70271300
B	1.68656100	-2.62358300	-0.11430200
B	-2.21956400	1.22459700	0.71468400
B	-2.65803200	0.00000000	1.65147400
B	0.00000000	-2.62119800	-0.10770800
B	2.21956400	1.22459700	0.71468400
B	-0.84890500	2.18026800	-1.51553700
B	0.85212400	2.18876200	1.31938500
B	-1.43509500	-0.85159000	-2.45714700
B	2.67112900	0.00000000	-1.76670600
B	1.38668900	-0.85504500	2.36362100
B	-2.36420500	-1.42682800	-1.03521300
B	2.36420500	1.42682800	-1.03521300
B	1.38668900	0.85504500	2.36362100
B	0.00000000	1.65479900	2.70271300
Ti	0.00000000	0.00000000	0.80990900

9. C_s Ca@B_{38} (the second isomer of CaB_{38} in Fig. 2)

B	1.92827600	-1.18886000	2.75194900
B	0.53715200	1.44934400	2.69829700
B	-0.33017000	-2.26913100	1.37991800
B	1.33599000	-1.95234700	1.36086400
B	1.92827600	-1.18886000	-2.75194900
B	1.80487300	0.42589500	-2.38046000
B	3.32952800	-0.20514400	0.00000000
B	0.56990600	-2.49315500	0.00000000
B	2.61710900	0.99756900	-0.85170800
B	1.80487300	0.42589500	2.38046000
B	-1.53795700	2.28097500	-0.92345400
B	-2.47585400	1.16741700	-1.64886700
B	2.61710900	0.99756900	0.85170800
B	-2.86028800	-1.62979700	0.00000000
B	0.46225200	-1.80460100	-2.82870100
B	-1.53795700	2.28097500	0.92345400
B	2.70143800	-0.71230400	1.43401100
B	0.46225200	-1.80460100	2.82870100
B	-1.83102200	-0.22053900	2.30066200
B	-1.03939500	1.33601300	2.39427800
B	0.12032500	2.49912800	1.42785700
B	1.66890500	1.97419500	-1.70073100
B	-2.82918600	-0.21839000	0.84981000
B	-2.04642600	-1.70236200	1.40835300
B	-0.33017000	-2.26913100	-1.37991800
B	0.12032500	2.49912800	-1.42785700
B	-1.83102200	-0.22053900	-2.30066200
B	-1.12298900	-1.64301900	-2.74820900
B	-1.03939500	1.33601300	-2.39427800
B	-0.42955900	3.05823300	0.00000000
B	2.70143800	-0.71230400	-1.43401100
B	-2.47585400	1.16741700	1.64886700
B	0.53715200	1.44934400	-2.69829700
B	-2.04642600	-1.70236200	-1.40835300
B	-1.12298900	-1.64301900	2.74820900
B	1.33599000	-1.95234700	-1.36086400
B	-2.82918600	-0.21839000	-0.84981000
B	1.66890500	1.97419500	1.70073100
Ca	-0.13405700	0.10797500	0.00000000