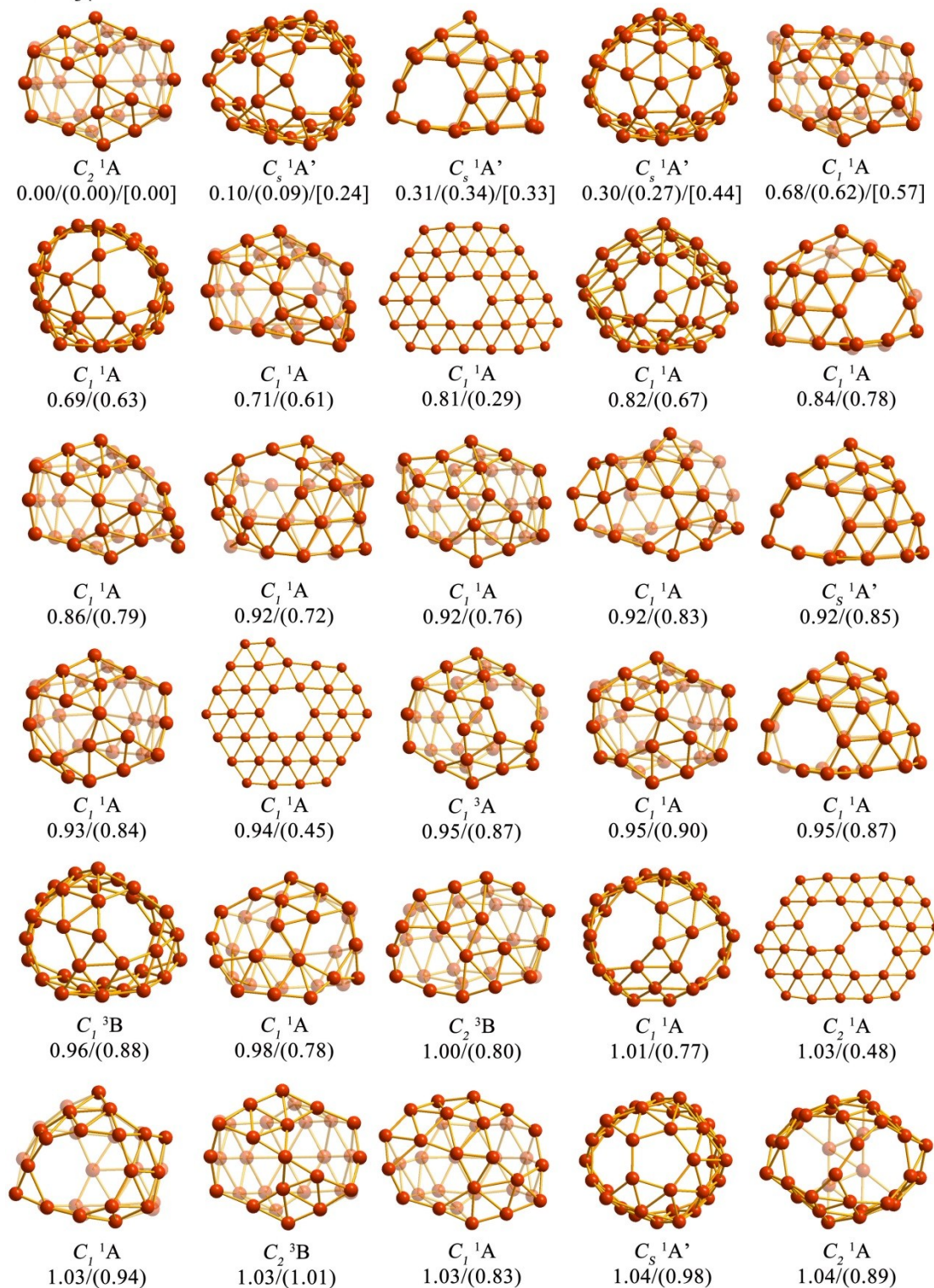


## Supporting Information

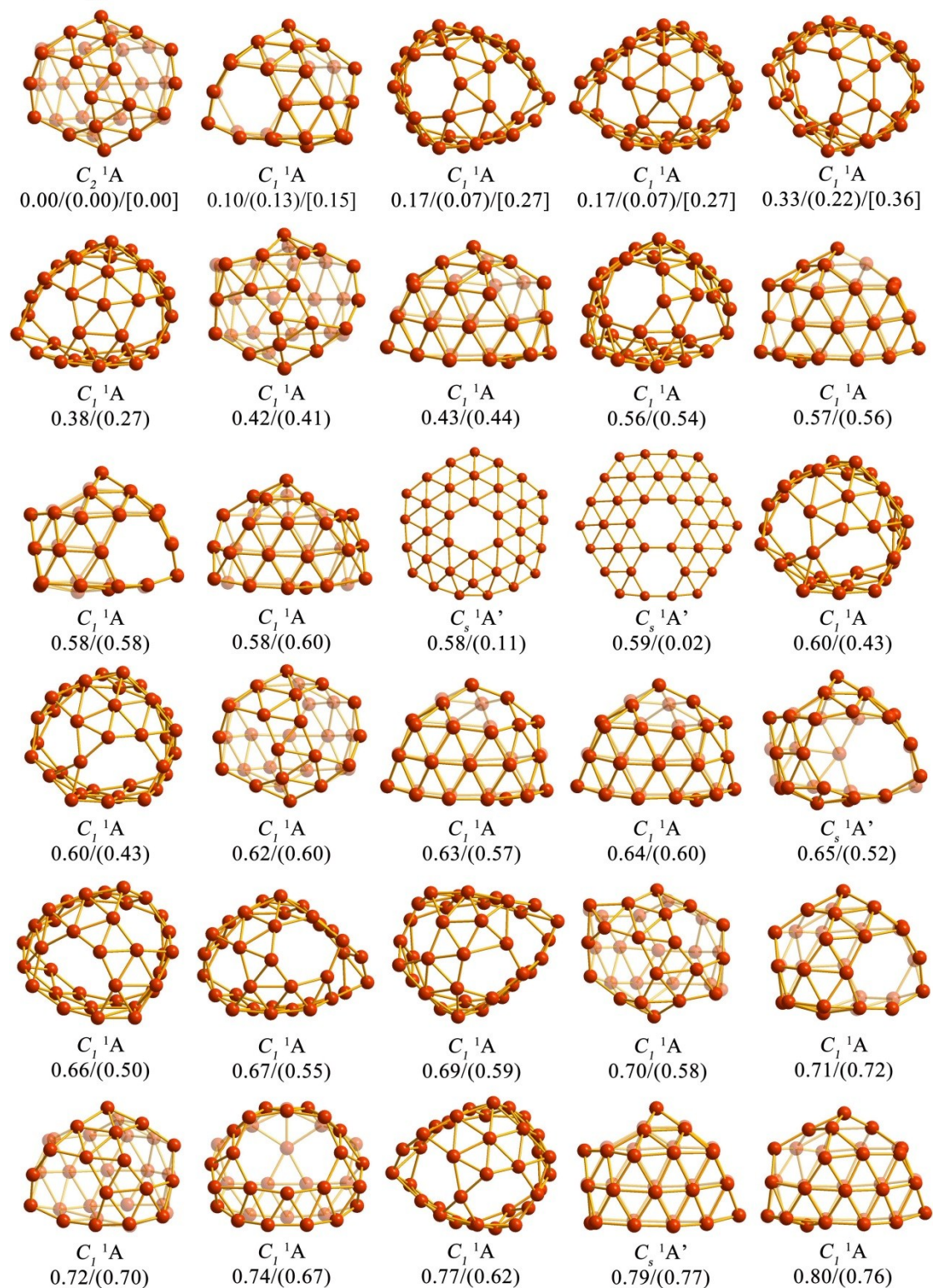
**Fig. S1** Thirty low-lying isomers of  $B_{34}$  with their relative energies (with zero-point corrections included) indicated in eV at PBE0/6-311+G(d), TPSSh/6-311+G(d) (in parenthesis) and CCSD(T)/6-31G(d) (in square brackets) levels.

(a)  $B_{34}$



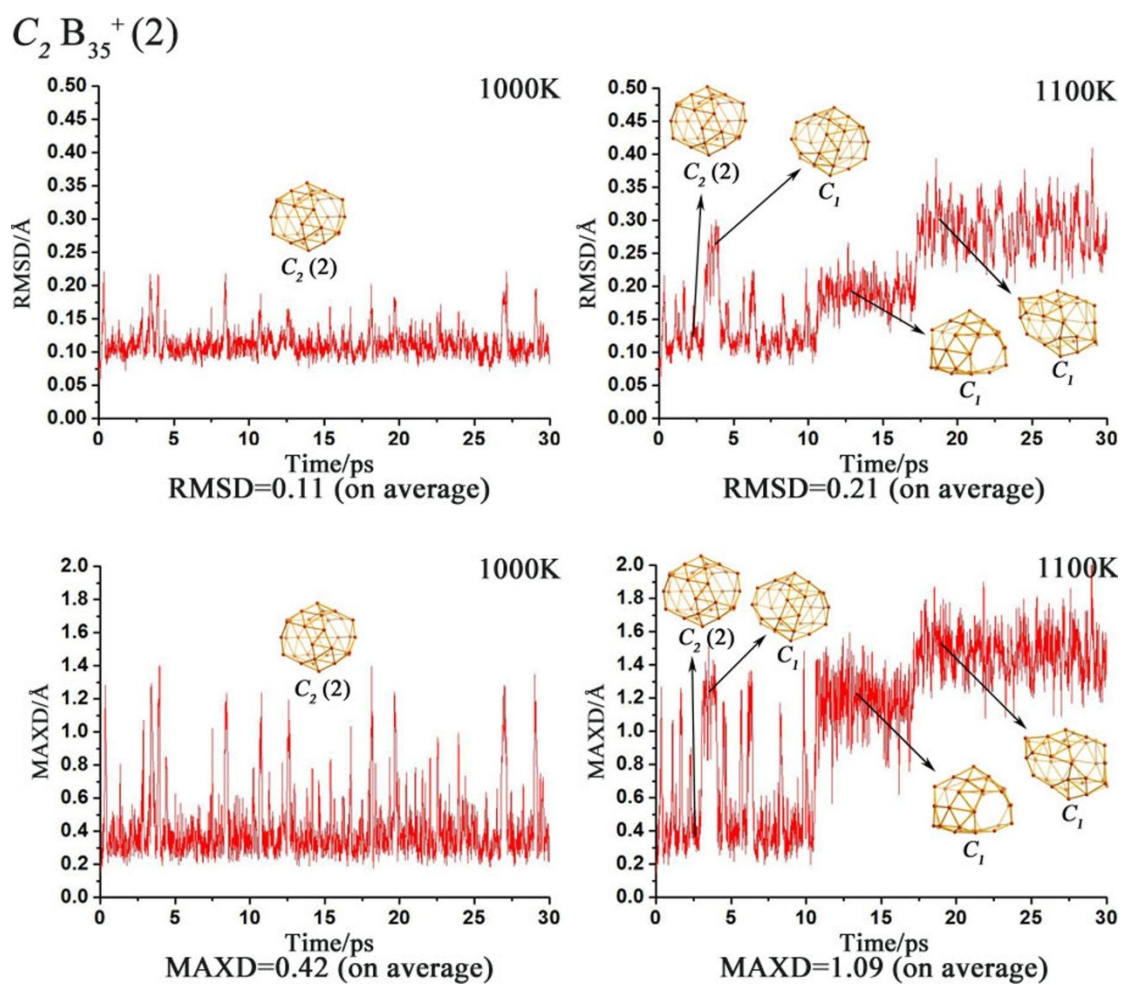
**Fig. S2** Thirty low-lying isomers of  $B_{35}^+$  with their relative energies (with zero-point corrections included) indicated in eV at PBE0/6-311+G(d), TPSSH/6-311+G(d) (in parenthesis) and CCSD(T)/6-31G(d) (in square brackets) levels.

(b)  $B_{35}^+$





**Fig. S3** Born–Oppenheimer molecular dynamics simulations of  $C_2 B_{35}^+$  (1) at 1000K and 1100K. The root-mean-square-deviation (RMSD) and maximum bond length deviation (MAXD) values (on average) are indicated in Å.



**Table S1** Optimized coordinates of  $C_2 B_{34}$  (1) and  $C_2 B_{35}^+$  (2) at PBE0/6-311+G(d).1.  $C_2 B_{34}$  (1)

B	1.17399900	2.31146900	1.29408300
B	-2.31668600	0.99825700	-1.00204400
B	0.81271100	-1.49765900	-1.94346800
B	2.41915600	-0.22524900	0.59223300
B	2.31668600	-0.99825700	-1.00204400
B	-0.05370200	-1.56473400	2.39752100
B	-1.67405200	0.06098700	-2.27184800
B	2.05774700	0.70304100	-0.80613200
B	-0.81271100	1.49765900	-1.94346800
B	0.00000000	0.00000000	-2.37487500
B	0.05370200	1.56473400	2.39752100
B	-1.52104400	2.78936900	1.01795800
B	0.08758900	2.74342800	-1.42784900
B	0.00000000	3.10276000	0.17624600
B	0.94902900	1.38698800	-1.90318600
B	1.52104400	-2.78936900	1.01795800
B	2.32302800	1.39672000	0.64998800
B	2.66141500	-1.88676100	0.31901300
B	0.00000000	-3.10276000	0.17624600
B	-0.16086400	3.06143800	1.81194200
B	-1.32541300	2.36262800	-0.62562200
B	-1.17399900	-2.31146900	1.29408300
B	-2.41915600	0.22524900	0.59223300
B	1.20938600	0.53633200	1.58546000
B	-2.05774700	-0.70304100	-0.80613200
B	-2.66141500	1.88676100	0.31901300
B	-0.08758900	-2.74342800	-1.42784900
B	1.67405200	-0.06098700	-2.27184800
B	-1.20938600	-0.53633200	1.58546000
B	0.00000000	0.00000000	2.64628400
B	1.32541300	-2.36262800	-0.62562200
B	-2.32302800	-1.39672000	0.64998800
B	0.16086400	-3.06143800	1.81194200
B	-0.94902900	-1.38698800	-1.90318600

2.  $C_2 B_{35}^+$  (2)

B	-1.22120000	2.27548200	-1.19993100
B	2.34144500	0.96541900	1.11212400
B	-0.82015100	-1.47892000	2.03227700
B	-2.60252500	-0.16734900	-0.43359700
B	-2.34144500	-0.96541900	1.11212400
B	0.22967600	-1.42679800	-2.33264200
B	1.67455300	0.04025900	2.37290000
B	-2.12375700	0.74870400	0.94165100
B	0.82015100	1.47892000	2.03227700
B	0.00000000	0.00000000	2.45346200
B	-0.22967600	1.42679800	-2.33264200
B	1.52095500	2.70121400	-0.93185900
B	-0.07558900	2.71517600	1.49646000
B	0.00000000	2.99071400	-0.12124700
B	-0.94049600	1.39727500	2.02889300
B	-2.44716000	1.45459700	-0.48560700
B	-2.69383700	-1.83654900	-0.21947800
B	0.00000000	-2.99071400	-0.12124700
B	0.16176300	2.91101000	-1.76264700
B	1.36492300	2.33230400	0.70855800
B	1.22120000	-2.27548200	-1.19993100
B	2.60252500	0.16734900	-0.43359700
B	-1.74293100	0.64296900	-1.71709000
B	2.12375700	-0.74870400	0.94165100
B	2.69383700	1.83654900	-0.21947800
B	0.07558900	-2.71517600	1.49646000
B	-1.67455300	-0.04025900	2.37290000
B	1.74293100	-0.64296900	-1.71709000
B	0.77639100	0.13628200	-2.71549500
B	-1.36492300	-2.33230400	0.70855800
B	2.44716000	-1.45459700	-0.48560700
B	-0.16176300	-2.91101000	-1.76264700
B	0.94049600	-1.39727500	2.02889300
B	-0.77639100	-0.13628200	-2.71549500
B	-1.52095500	-2.70121400	-0.93185900