Electronic Supplementary Information

Electron-compensation: A valid strategy for chemically stabilizing boron-based clusters with hypercoordinate centre

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SI3: Cartesian coordinates of optimized structures shown in Fig. S1 and Fig. 2 at the PBE0/BS1 level.

Computational Methods

In the calculations for validating the strategy, geometry optimization and harmonic vibrational frequency analysis of all clusters were performed at the PBE0/BS1 level, where BS1 denotes a mixed basis set with cc-pVTZ for C, B, O, and S and cc-pVTZ-PP for Se, Te, and Po. Adaptive natural density partitioning (AdNDP)[1] analyses were performed at the PBE0/6-31G(d) levels. The thermodynamic stability was studied by the exploration of potential energy surfaces of **1a** using basin hopping algorithm.[2] The isomers were initially optimized at the PBE/DZVP level and then the 20 low-energy isomers were re-optimized at the PBE0/BS1 level. The single point energies of the five lowest isomers were calculated at the CCSD(T)/BS1 level considering the Gibbs free energy corrections obtained at the PBE0/BS1 level, which was reported in the text. The dynamic stability of **1a** was studied using 100 picoseconds Born-Oppenheimer molecular dynamic (BOMD) simulations at the PBE/DZVP level and concerned temperatures using the CP2K[3] package. Nucleus-independent chemical shift (NICS)[4] was calculated to assess the aromaticity of **1a**. The basin hopping algorithm was realized using the Tsinghua Global Minimum (TGmin) 2.0 program,[5] the CCSD(T) calculations were carried out using the MolPro 2012.1 package,[6] the CS-NICS and composition of each orbital in AdNDP were generated with the Multiwfn 3.7 code,[7] the EDA-NOCV[8,9] were performed at the PBE0/TZ2P[10] level using the ADF 2022 program package, [11] and all other calculations were performed using the Gaussian 16 package.[12]

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SI2: The structures of CB_4X_4 (X = O, S, Se, Te, Po), Wiberg bond orders of **1a**, NBO charges (in |e|) of **1a**, full AdNDP bonding patterns of **1a**, the shapes of deformation densities ($\Delta\rho$) for EDA-NOCV analysis of **1a**, concerned isomers of **1a**, and BOMD simulations of **1a.**
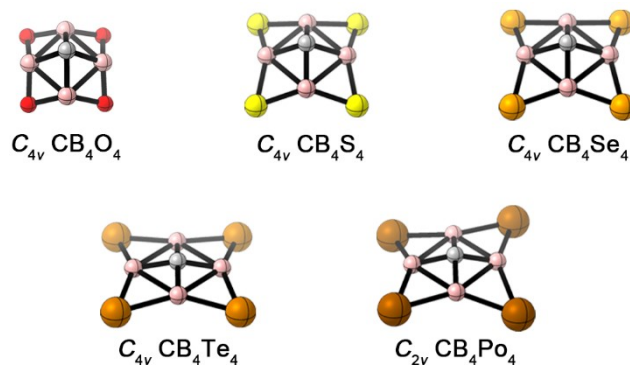
Fig. S1 PBE0/BS1-optimized structures of CB_4X_4 (X = O, S, Se, Te, Po), all of which are not planar.
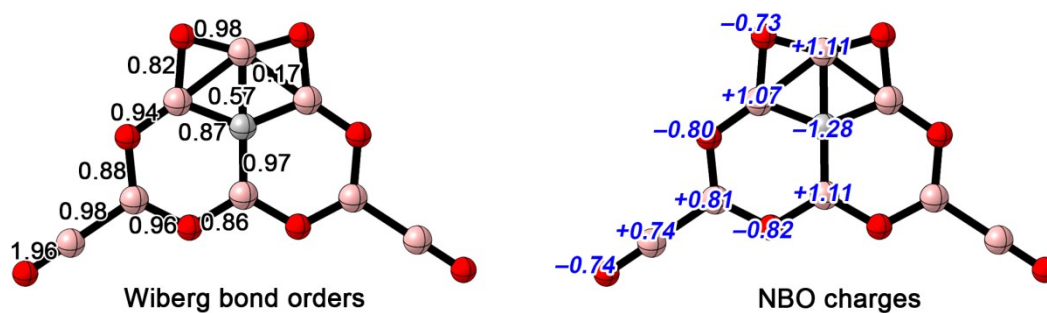
Fig. S2 The Wiberg bond orders and NBO charges (in |e|) of **1a**.

Eight O 1c-2e lone pairs, ON = 1.92–1.99 |e|

Fourteen B-O
2c-2e σ bonds
ON = 1.94–1.99 |e|

Two B-B 2c-2e σ bonds, ON = 1.98 |e|

Four B-O 2c-2e π bonds, ON = 2.00 |e|

Six B-O-B 3c-2e π bonds, ON = 1.99 |e|

1a

Three 5c-2e σ bonds, ON = 1.96 |e|

One 5c-2e π bond, ON = 1.96 |e|
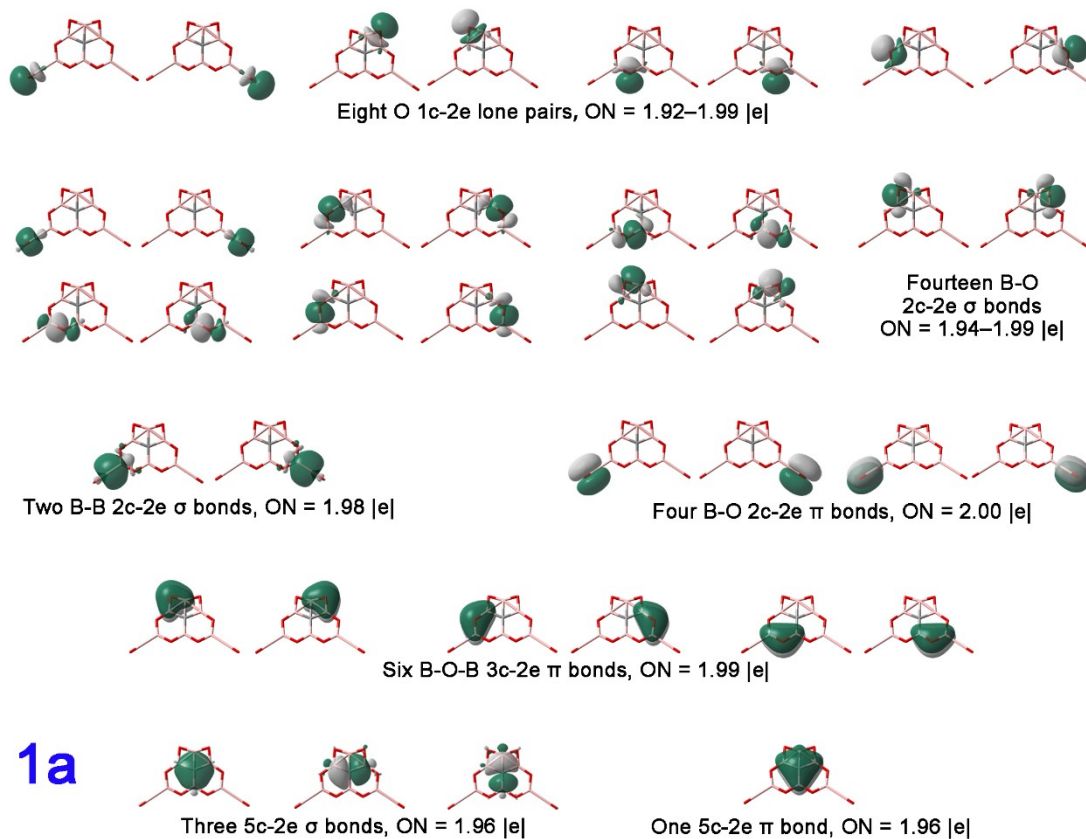
Fig. S3 Full sets of AdNDP bonding patterns for clusters **1a**.

A

$\Delta E_{orb(1)} = -314.9$

B

$\Delta E_{orb(2)} = -311.4$

C

$\Delta E_{orb(3)} = -25.0$
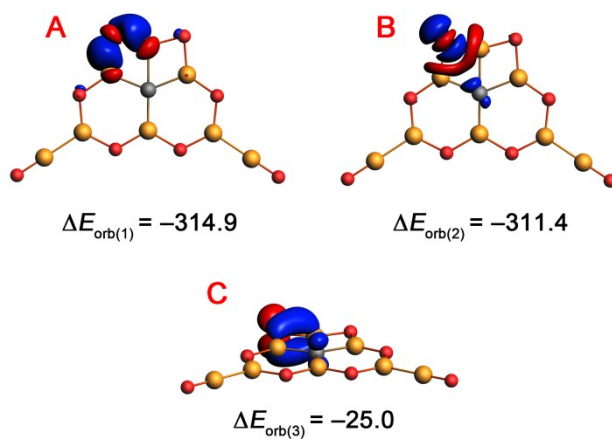
Fig. S4 The shapes of deformation densities ($\Delta\rho$) for EDA-NOCV analysis of **CB$_8$O$_8$**. The corresponding orbital value is given in kcal mol^{-1}. The isovalues of the surfaces are 0.01 for $\Delta\rho_{orb(1)-(2)}$, 0.003 for $\Delta\rho_{orb(3)}$. The direction of charge flow is from red to blue.
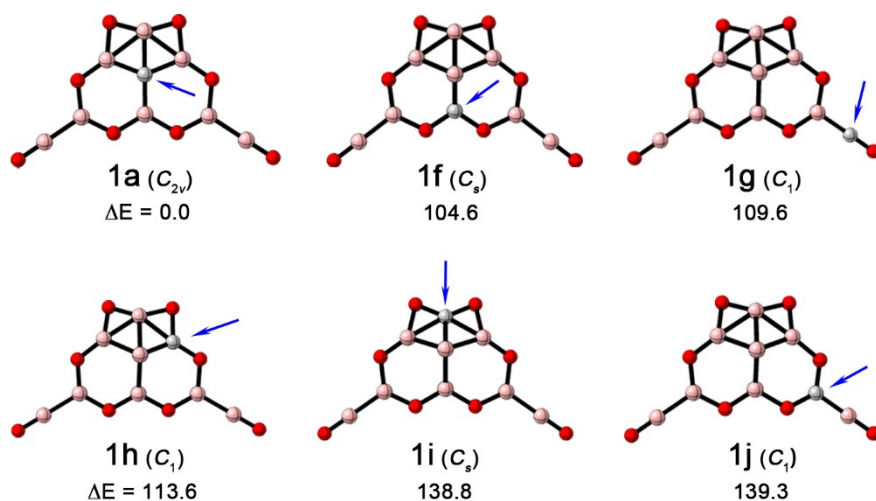
Fig. S5 Structures and relative energies (ΔE, in kcal mol^{-1} at the CCSD(T)//PBE0 level) of **1a** and its isomers constructed by exchanging the positions of carbon and boron in **1a**.
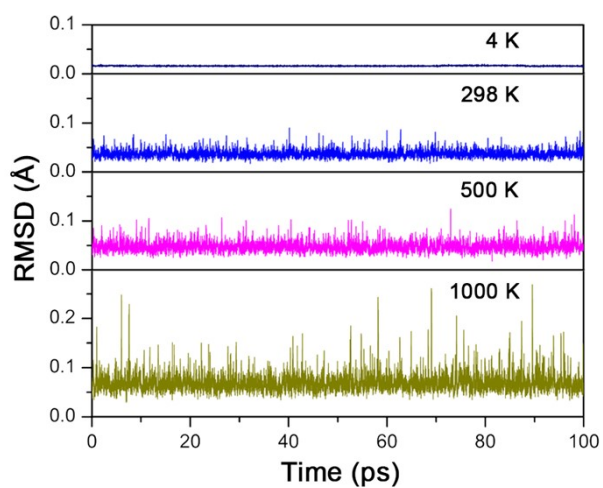
Fig. S6 Root-mean-square deviation (RMSD, in Å) for **1a** in BOMD simulations at 4, 298, 500, and 1000 K. The simulations were performed at the PBE/DZVP level.

SI3: Cartesian coordinates of optimized structures shown in Fig. S1 and Fig. 2 at the PBE0/BS1 level.

CB_4O_4

C	0.00032300	0.00059600	-1.16034600
B	0.96142900	-0.79119200	-0.20042600
B	0.79085800	0.96126400	-0.20180000
B	-0.79104000	-0.96097100	-0.20159300
B	-0.96090900	0.79081800	-0.20132900
O	-0.17758800	1.82550300	0.34374100
O	1.82623400	0.17732000	0.34336900
O	0.17724700	-1.82576700	0.34308300
O	-1.82634700	-0.17745300	0.34328400

CB_4S_4

C	0.00030800	-0.00011400	1.04213600
B	0.80623600	1.11493700	0.32630900
B	-1.11472600	0.80594700	0.32614100
B	1.11501400	-0.80637300	0.32620600
B	-0.80644500	-1.11456200	0.32620600
S	0.38557700	-2.40223300	-0.19954300
S	-2.40239000	-0.38551000	-0.19971700
S	-0.38559500	2.40220200	-0.19951300
S	2.40226800	0.38559900	-0.19979700

CB_4Se_4

C	0.00080100	-0.00037900	1.00610000
B	-1.28852100	0.58008100	0.38653700
B	-0.58092600	-1.28896200	0.38683400
B	0.58029500	1.28916400	0.38654100
B	1.29001100	-0.58090700	0.38641500
Se	2.45227500	0.92933900	-0.10089200
Se	0.92941600	-2.45187800	-0.10164200
Se	-2.45244600	-0.92924300	-0.10085400
Se	-0.92951200	2.45194000	-0.10156100

CB$_4$Te$_4$

B	-1.06367400	1.06367400	0.22285200
B	1.06367400	1.06367400	0.22285200
B	-1.06367400	-1.06367400	0.22285200
B	1.06367400	-1.06367400	0.22285200
C	0.00000000	0.00000000	0.51486500
Te	0.00000000	2.96924700	-0.03628000
Te	2.96924700	0.00000000	-0.03628000
Te	0.00000000	-2.96924700	-0.03628000
Te	-2.96924700	0.00000000	-0.03628000

CB$_4$Po$_4$

B	-1.03099300	1.06940600	0.29248600
B	1.03099300	1.06940600	0.29248600
B	-1.03099300	-1.06940600	0.29248600
B	1.03099300	-1.06940600	0.29248600
C	0.00000000	0.00000000	0.66372900
Po	0.00000000	3.08980700	0.20216900
Po	2.96393300	0.00000000	-0.26069300
Po	0.00000000	-3.08980700	0.20216900
Po	-2.96393300	0.00000000	-0.26069300

CB$_6$O$_6$

B	0.34938200	-1.21248300	0.32377100
B	-1.64946500	0.00043800	0.00262800
O	1.39194800	-2.04246700	-0.18734800
B	2.07673500	0.86957900	0.04181500
B	0.34984000	1.21185300	0.32240400
O	-0.98795700	1.21112800	0.03266200
O	1.39328800	2.04206300	-0.18607800
O	-0.98874200	-1.21068200	0.03527100
O	3.00082400	-0.00014700	-0.53724100
B	2.07521400	-0.86988400	0.03847800
C	1.06974000	-0.00022100	0.90604700
B	-3.33213600	0.00050300	-0.12721300
O	-4.53014700	0.00026700	-0.21297900

1a

B	0.00000000	0.00000000	0.66267063
B	0.00000000	-2.40568994	0.74391573
O	0.00000000	1.19351709	1.36363858
O	0.00000000	2.53725400	-0.63443349
B	-0.00000000	2.40568994	0.74391573
B	0.00000000	0.00000000	-2.46754938
B	0.00000000	-1.42570104	-1.40645531
O	0.00000000	-2.53725400	-0.63443349
O	0.00000000	-1.30614409	-2.82386330
O	0.00000000	-1.19351709	1.36363858
O	-0.00000000	1.30614409	-2.82386330
B	-0.00000000	1.42570104	-1.40645531
C	0.00000000	0.00000000	-0.83719537
B	0.00000000	3.81290211	1.67712947
B	0.00000000	-3.81290211	1.67712947
O	0.00000000	4.81554213	2.33851240
O	0.00000000	-4.81554213	2.33851240

1b

B	0.89989010	-1.23847142	0.04876399
O	2.26056832	1.20569006	-0.00602244
O	0.00000000	2.30316493	0.00680591
O	-2.26056832	1.20569006	-0.00602244
B	0.89989010	1.23847142	0.04876399
B	2.92326675	-0.00000000	-0.01639385
O	2.26056832	-1.20569006	-0.00602244
O	0.00000000	-2.30316493	0.00680591
B	-0.89989010	1.23847142	0.04876399
B	-2.92326675	-0.00000000	-0.01639385
B	-0.89989010	-1.23847142	0.04876399
C	0.00000000	0.00000000	0.14454002
O	-2.26056832	-1.20569006	-0.00602244
B	-4.61068697	0.00000000	-0.04808888
B	4.61068697	0.00000000	-0.04808888
O	-5.81120509	0.00000000	-0.06961681
O	5.81120509	0.00000000	-0.06961681

1c

B	0.04804800	-0.28904800	-0.09418000
B	2.37216000	-0.89665900	0.00746500
O	-1.28237700	-0.61809300	-0.01606000
O	-3.57234200	-0.02157700	0.04039700
B	-2.25552600	0.35280100	0.02687700
B	0.72710800	2.73538000	0.04621900
B	1.95182600	1.44070200	-0.07275600
O	2.83405500	0.41293500	0.01442800
O	2.10743800	2.82565700	0.05848900
O	1.04686400	-1.23981800	-0.00674300
O	-2.00235800	1.70434500	0.07600600
B	-0.70397300	2.11044900	-0.00693600
C	0.43961700	1.16418900	-0.21953500
B	-4.15680700	-1.20530700	0.01202800
B	3.52678100	-2.12971000	0.02978300
O	-4.75410400	-2.25626100	-0.01310000
O	4.34960100	-3.00446000	0.04342300

1d

B	0.34405300	-0.73990600	0.00049800
B	-1.96470700	-1.39153900	-0.00015400
O	1.67675400	-1.18725800	0.00036100
O	2.53135900	1.02601700	0.00004000
B	2.75095300	-0.37520200	0.00016600
B	-1.49474200	3.36347000	-0.00039900
B	-1.55727200	0.97920300	0.00030500
O	-2.40832000	-0.09956800	0.00005100
O	-2.16161400	2.22514800	-0.00032400
O	-0.63263500	-1.70328700	0.00000000
O	-0.86562500	4.39857400	-0.00036500
B	1.23905500	1.23318300	0.00048300
C	-0.06279800	0.75304500	0.00117100
B	4.33004600	-0.94775100	0.00004400
B	-3.09450600	-2.64756300	-0.00024000
O	5.45882000	-1.35420300	-0.00078800
O	-3.89719100	-3.54139200	-0.00029300

1e

B	0.06021800	-0.55468700	0.18051400
B	2.43535800	-0.83743500	-0.00738100
O	-1.24951900	-1.02604000	0.10589300
O	-3.46732400	-0.16481500	-0.01790200
B	-2.12271500	0.03987300	0.07274300
B	0.24098700	2.48988200	-0.04038600
B	1.66428600	1.39256000	0.08303300
O	2.70061600	0.52301900	-0.04279000
O	1.56485200	2.78898600	-0.17751900
O	1.17040300	-1.36129900	0.05260100
O	-1.05510500	2.87969000	-0.12894000
B	-1.18030700	1.48149000	0.14457400
C	0.24166600	0.93000000	0.36473600
B	-4.20214000	-1.26543600	-0.08299200
B	3.75037100	-1.89559400	-0.06258000
O	-4.93662200	-2.22282700	-0.14572500
O	4.68766400	-2.64587100	-0.09887200

1f

B	-2.35497900	-0.69626800	0.00712400
O	1.10826500	-1.28920100	0.08413300
O	2.53893500	0.66169900	-0.01615900
B	2.35495400	-0.69628400	0.00695100
B	0.00001200	2.47300700	-0.04217800
B	-1.46714600	1.48264400	0.18345300
O	-2.53892800	0.66171300	-0.01610900
O	-1.29690300	2.83124700	-0.22788000
O	-1.10828400	-1.28919400	0.08418900
O	1.29695000	2.83126700	-0.22770300
B	1.46716500	1.48262400	0.18350200
B	3.68329700	-1.72412400	-0.09773300
B	-3.68332600	-1.72408600	-0.09769900
O	4.63566900	-2.45215400	-0.17011800
O	-4.63568500	-2.45212500	-0.17017300
B	-0.00000100	0.85713000	0.60042800
C	-0.00000400	-0.54987300	0.25988600