Supporting Information

Structure Evolution of Chromium-Doped Boron Clusters: Toward the Formation of Endohedral Boron Cages

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Fig. S1. Structures of low-lying isomers of CrB₈. Bottom labels are point-group symmetries, spin multiplicities and relative energies to the ground state at PBE0/Cr/Stuttgart/B/6-311G* level of theory. Zero-point energy corrections were included for all isomers at the same level of theory.
Fig. S2. Structures of low-lying isomers of CrB$_{10}$. Bottom labels are point-group symmetries, spin multiplicities and relative energies to the ground state at PBE0/Cr/Stuttgart/B/6-311G* level of theory. Zero-point energy corrections were included for all isomers at the same level of theory.
Fig. S3. Structures of low-lying isomers of CrB$_{12}$. Bottom labels are point-group symmetries, spin multiplicities and relative energies to the ground state at PBE0/Cr/Stuttgart/B/6-311G* level of theory. Zero-point energy corrections were included for all isomers at the same level of theory.
**Fig. S4.** Structures of low-lying isomers of CrB$_{14}$. Bottom labels are point-group symmetries, spin multiplicities and relative energies to the ground state at PBE0/Cr/Stuttgart/B/6-311G* level of theory. Zero-point energy corrections were included for all isomers at the same level of theory.
Fig. S5. Structures of low-lying isomers of CrB₁₆. Bottom labels are point-group symmetries, spin multiplicities and relative energies to the ground state at PBE0/Cr/Stuttgart/B/6-311G* level of theory. Zero-point energy corrections were included for all isomers at the same level of theory.
Fig. S6. Structures of low-lying isomers of CrB$_{18}$. Bottom labels are point-group symmetries, spin multiplicities and relative energies to the ground state at PBE0/Cr/Stuttgart/B/6-311G* level of theory. Zero-point energy corrections were included for all isomers at the same level of theory.
Fig. S7. Structures of low-lying isomers of CrB$_{20}$. Bottom labels are point-group symmetries, spin multiplicities and relative energies to the ground state at PBE0/Cr/Stuttgart/B/6-311G* level of theory. Zero-point energy corrections were included for all isomers at the same level of theory.
**Fig. S8.** Structures of low-lying isomers of CrB$_{22}$. Bottom labels are point-group symmetries, spin multiplicities and relative energies to the ground state at PBE0/Cr/Stuttgart/B/6-311G* level of theory. Zero-point energy corrections were included for all isomers at the same level of theory.
Fig. S9. Electron spin density of CrB$_{12}$, CrB$_{14}$ and CrB$_{16}$ shows that with the addition of boron atoms, the magnetism of Chromium is vanished. The mul represent the charge spin multiplicity.
**Fig. S10.** The chemical bonding picture of CrB$_{16}$ obtained from AdNDP analyses. ON stands for occupation number. Residual valence electrons of all atoms in the search list: 5.17.
Fig. S11. Total and projected density of states for the double-ring tubular CrB_{16} cluster. The dashed line highlights the position of HOMO.
Fig. S12. Total and projected density of states for the endohedral cage-like CrB$_{20}$ cluster. The dashed line highlights the position of HOMO.
Table S1. Cartesian coordinates of the lowest-energy structure of CrB$_8$

|   | Cr   | B    | B    | B    | B    | B    | B    | B    | B    |
|---|------|------|------|------|------|------|------|------|------|
|   | 7.455200 | 7.685000 | 8.303500 |      |      |      |      |      |      |
|   | 6.400700  | 6.288800  | 6.501800  |      |      |      |      |      |      |
|   | 9.099400  | 8.465000  | 6.572800  |      |      |      |      |      |      |
|   | 9.107500  | 6.921800  | 6.573000  |      |      |      |      |      |      |
|   | 6.386100  | 9.069500  | 6.501500  |      |      |      |      |      |      |
|   | 7.512100  | 7.685000  | 6.136500  |      |      |      |      |      |      |
|   | 7.888300  | 9.420800  | 6.541000  |      |      |      |      |      |      |
|   | 7.906500  | 5.953300  | 6.541400  |      |      |      |      |      |      |
|   | 5.724000  | 7.675600  | 6.484000  |      |      |      |      |      |      |
**Table S2.** Cartesian coordinates of the lowest-energy structure of CrB$_{10}$

|   |          |          |          |
|---|----------|----------|----------|
| Cr| 8.645702 | 7.211105 | 9.087777 |
| B | 6.864284 | 5.502427 | 8.372888 |
| B | 9.020988 | 6.792001 | 6.580219 |
| B | 6.223682 | 8.009082 | 9.405405 |
| B | 7.034672 | 8.899758 | 8.364290 |
| B | 6.140807 | 6.438990 | 9.408009 |
| B | 8.380391 | 9.298630 | 7.612701 |
| B | 6.573325 | 7.140929 | 7.972259 |
| B | 9.297176 | 8.326311 | 6.784362 |
| B | 7.732423 | 7.833989 | 7.008769 |
| B | 7.780659 | 5.980770 | 7.161953 |
Table S3. Cartesian coordinates of the lowest-energy structure of CrB\textsubscript{12}

|   |   |   |   |
|---|---|---|---|
| Cr | 7.408980 | 12.00170 | 8.925550 |
| B  | 9.988865 | 11.74960 | 8.455016 |
| B  | 6.096917 | 13.38786 | 7.367074 |
| B  | 6.357480 | 10.60534 | 6.954414 |
| B  | 5.577452 | 11.92594 | 7.033333 |
| B  | 8.845510 | 11.98716 | 7.179896 |
| B  | 7.263334 | 12.05038 | 6.669873 |
| B  | 9.479504 | 13.25263 | 8.456912 |
| B  | 8.000589 | 13.41764 | 7.265269 |
| B  | 7.903353 | 10.32969 | 7.184238 |
| B  | 8.413115 | 14.41734 | 8.614398 |
| B  | 6.952396 | 14.47569 | 8.143725 |
| B  | 9.308192 | 10.48736 | 7.905393 |
Table S4. Cartesian coordinates of the lowest-energy structure of CrB$_{14}$

|   |   |   |   |
|---|---|---|---|
| Cr | 8.128003 | 9.281546 | 9.685618 |
| B  | 7.890778  | 10.49034  | 7.634534  |
| B  | 7.618474  | 11.34589  | 8.887793  |
| B  | 9.237603  | 7.786292  | 8.152818  |
| B  | 10.11191 | 9.055685  | 8.813913  |
| B  | 9.305986  | 10.67073  | 8.418975  |
| B  | 7.896232  | 10.49345  | 11.73542  |
| B  | 7.620565  | 11.34703  | 10.48153  |
| B  | 9.241713  | 7.788647  | 11.21756  |
| B  | 10.11438 | 9.056974  | 10.55232  |
| B  | 9.309338  | 10.67265  | 10.94699  |
| B  | 8.751063  | 9.127525  | 7.529478  |
| B  | 8.756863  | 9.130798  | 11.84024  |
| B  | 9.560383  | 7.535482  | 9.684950  |
| B  | 10.28896 | 10.43102  | 9.681860  |
Table S5. Cartesian coordinates of the lowest-energy structure of CrB$_{16}$

|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| Cr | 9.624430  | 9.754655  | 9.617720  |
| B  | 8.821323  | 8.619560  | 11.23690  |
| B  | 10.45231  | 8.033580  | 10.94501  |
| B  | 10.00375  | 9.545160  | 11.77099  |
| B  | 8.919185  | 9.365770  | 7.598717  |
| B  | 10.41296  | 11.815044 | 10.07717  |
| B  | 7.805689  | 8.478948  | 9.995451  |
| B  | 11.42911  | 9.306202  | 10.74312  |
| B  | 9.307754  | 11.74265  | 8.908493  |
| B  | 9.316485  | 7.518392  | 9.953526  |
| B  | 10.80018  | 10.86572  | 11.30281  |
| B  | 9.742898  | 10.75500  | 7.521438  |
| B  | 7.520514  | 9.350567  | 8.686934  |
| B  | 11.60741  | 10.54971  | 9.771393  |
| B  | 8.164130  | 10.78749  | 8.342902  |
| B  | 8.759641  | 8.108065  | 8.555354  |
| B  | 10.934278 | 11.22797  | 8.467739  |
Table S6. Cartesian coordinates of the lowest-energy structure of CrB$_{18}$

|  |  |  |  |
|---|---|---|---|
| Cr | 9.484292 | 9.598221 | 9.596623 |
| B | 8.976945 | 10.45209 | 7.577232 |
| B | 8.521071 | 9.643048 | 11.75060 |
| B | 9.730086 | 11.54307 | 8.491449 |
| B | 7.573799 | 10.27316 | 8.942234 |
| B | 8.074629 | 9.163772 | 7.808622 |
| B | 8.921591 | 7.755554 | 8.350101 |
| B | 9.767626 | 8.876038 | 7.511701 |
| B | 10.74662 | 10.07216 | 7.990947 |
| B | 9.447378 | 8.251537 | 11.23415 |
| B | 10.24903 | 9.594576 | 11.67276 |
| B | 10.99756 | 10.76240 | 10.86963 |
| B | 9.232151 | 11.02627 | 11.29130 |
| B | 8.329586 | 11.36782 | 9.859221 |
| B | 7.770250 | 8.555643 | 10.83934 |
| B | 11.20853 | 10.96310 | 9.260464 |
| B | 9.916308 | 11.83123 | 10.04379 |
| B | 7.537472 | 8.571655 | 9.234528 |
| B | 8.814145 | 7.516334 | 9.931367 |
Table S7. Cartesian coordinates of the lowest-energy structure of CrB$_{20}$

| Element | x    | y    | z    |
|---------|------|------|------|
| Cr      | 9.584947 | 9.635535 | 9.630617 |
| B       | 9.753406 | 9.785738 | 11.81456 |
| B       | 8.983707 | 9.789686 | 7.524600 |
| B       | 7.520008 | 9.070878 | 10.15126 |
| B       | 8.580328 | 7.691453 | 9.809075 |
| B       | 9.959386 | 7.519548 | 8.889377 |
| B       | 11.82478 | 9.913027 | 9.901116 |
| B       | 11.02234 | 11.27526 | 9.374230 |
| B       | 9.342607 | 11.82279 | 9.525436 |
| B       | 10.36000 | 8.703804 | 7.790768 |
| B       | 11.32468 | 9.941580 | 8.313984 |
| B       | 10.03502 | 11.13862 | 8.094803 |
| B       | 8.391316 | 11.10006 | 8.366722 |
| B       | 7.637407 | 9.634861 | 8.600584 |
| B       | 8.708270 | 8.306085 | 8.119140 |
| B       | 10.89440 | 10.66063 | 11.06416 |
| B       | 9.225208 | 11.25880 | 11.07611 |
| B       | 8.164302 | 10.00949 | 11.36525 |
| B       | 8.702090 | 8.436803 | 11.24436 |
| B       | 10.15248 | 7.706890 | 10.53178 |
| B       | 11.11716 | 8.944666 | 11.05500 |
**Table S8.** Cartesian coordinates of the lowest-energy structure of CrB$_{22}$

|  |  |  |  |
|---|---|---|---|
| Cr | 9.633957 | 9.811267 | 9.887219 |
| B  | 11.00359 | 10.00034 | 7.899784 |
| B  | 8.709324 | 10.84326 | 11.91010 |
| B  | 8.834966 | 7.548270 | 9.876499 |
| B  | 10.54646 | 7.571715 | 9.570152 |
| B  | 9.913372 | 11.95653 | 9.268650 |
| B  | 8.414387 | 11.40262 | 8.865994 |
| B  | 11.54533 | 8.549652 | 10.60443 |
| B  | 9.504776 | 9.446677 | 7.497333 |
| B  | 7.961305 | 11.31284 | 10.53267 |
| B  | 10.01762 | 7.896601 | 11.09237 |
| B  | 11.75764 | 9.477294 | 9.263734 |
| B  | 7.393579 | 10.16376 | 9.518860 |
| B  | 10.60263 | 8.418262 | 8.196409 |
| B  | 9.524230 | 11.89029 | 10.95246 |
| B  | 10.79828 | 9.224353 | 11.84426 |
| B  | 11.04902 | 11.51433 | 10.50062 |
| B  | 8.360643 | 8.323800 | 11.18953 |
| B  | 11.37080 | 11.16110 | 8.982868 |
| B  | 8.073254 | 9.942856 | 8.097206 |
| B  | 8.724533 | 8.356861 | 8.449228 |
| B  | 10.36217 | 10.76718 | 11.93347 |
| B  | 7.663247 | 9.770044 | 11.20857 |