Supplementary Information

Non-monotonic Structure-Property Relationships in Small Iron-Doped Boron Clusters: A DFT Study of B_nFe (n = 3-6)

Supporting computational details, frequency verification, Cartesian coordinates, and supplementary numerical summaries.

S1. Frequency verification

Cluster	Imag.	Low positive modes (<200 cm^-1)	Count
B3Fe	0	59.23, 152.35	2
B4Fe	0		0
B5Fe	0	64.59, 86.44, 137.50, 155.96	4
B6Fe	0	89.65, 103.48, 154.14	3

All final reoptimized structures show zero imaginary frequencies.

S2. Coordinate summary

System	Charge	Mult.	Final energy (Eh)	Fe-B min (Å)	Fe-B max (Å)	H-H (Å)
B3Fe	0	2	-1337.529452	1.7087	1.7087	
B4Fe	0	1	-1362.264929	1.7581	1.7586	
B5Fe	0	4	-1387.224382	1.8354	2.3413	
B6Fe	0	3	-1411.760999	1.7758	1.8628	
B3Fe-H2	0	2	-1339.038990	1.9477	2.0947	2.0576
B4Fe-H2	0	1	-1363.737832	1.8891	3.5450	0.8801
B5Fe-H2	0	4	-1388.597470	1.9700	4.7282	0.7966
B6Fe-H2	0	3	-1413.355874	1.9784	3.7263	0.7981

S3. Cartesian coordinates of minima

B3Fe (charge = 0, multiplicity = 2, energy = -1337.529452 Eh)

```
4
B3Fe
Fe  0.00000000  0.00000000  0.00010432
B  -1.47999559  0.00000000  0.85414670
B   1.47999559  0.00000000  0.85414670
B   0.00000000  0.00000000 -1.70864545
```

B4Fe (charge = 0, multiplicity = 1, energy = -1362.264929 Eh)

```
5
B4Fe
Fe  0.00017067  0.00028139  0.00013499
B  -0.02685925 -1.32631320  1.15361041
B  -0.43764218 -0.60174182 -1.59259256
B   1.61517601  0.69382006 -0.05829747
B  -1.15156205  1.23277172  0.49657768
```

B5Fe (charge = 0, multiplicity = 4, energy = -1387.224382 Eh)

```
6
B5Fe
Fe  0.00000040  0.00000017 -1.10613980
B  -0.00000027 -0.00000016 -2.94149659
B   1.27334262  0.00000000  0.75667962
B  -0.00000006 -0.85321318  1.07417495
B  -0.00000005  0.85321316  1.07417515
B  -1.27334264  0.00000001  0.75667936
```

B6Fe (charge = 0, multiplicity = 3, energy = -1411.760999 Eh)

```
7
B6Fe
Fe  0.33784100  1.05241800 -0.74545568
B   2.19991388  1.05241800 -0.79732498
B   0.33784100  1.05241800  1.05260540
B  -1.52423189  1.05241800 -0.79732498
B   0.33784100  2.91449089 -0.79732499
B   0.33784100  1.05241800 -2.52127677
B   0.33784100 -0.80965488 -0.79732500
```

S4. Cartesian coordinates of H2-interaction structures

B3Fe-H2 (charge = 0, multiplicity = 2, energy = -1339.038990 Eh)

```
6
B3Fe-H2
Fe -0.94967093 -0.87789996  0.29715803
B  -0.34778641 -0.08669134  1.97202899
B   0.31231614  0.64368293  0.73748301
B   0.41874010  0.24215622 -0.82571871
H  -0.72936873 -0.04923524 -1.33845714
H   1.29815736  0.12798739 -1.64105969
```

B4Fe-H2 (charge = 0, multiplicity = 1, energy = -1363.737832 Eh)

```
7
B4Fe-H2
Fe  0.09695043  0.53468275  2.12976029
B   0.76973790 -0.21146154  0.34923619
B  -0.56237351 -0.10281870 -0.95853116
B   0.85651589 -0.62786081 -1.13196969
B  -0.82826098  0.38305346  0.48976016
H  -0.63751187  1.18389898  3.47039380
H  -1.19772979  1.19289079  2.79163726
```

B5Fe-H2 (charge = 0, multiplicity = 4, energy = -1388.597470 Eh)

```
8
B5Fe-H2
Fe  1.15729134 -0.01988965 -1.62662246
B  -0.67839073 -0.03394957 -0.91185473
B  -1.66848380  0.02536369  2.16403294
B  -0.11896875  0.04822148  1.86306959
B   0.43045867  0.02412636  0.39172861
B  -1.29597861 -0.00759098  0.57203754
H   2.72196394 -0.41069048 -2.48718588
H   2.65210873  0.37440915 -2.60234193
```

B6Fe-H2 (charge = 0, multiplicity = 3, energy = -1413.355874 Eh)

```
9
B6Fe-H2
Fe -1.16845048  1.62999546 -1.15312797
B   1.91180452  0.74485330 -0.12244880
B   1.87202705  1.80146166  0.99430545
B  -1.75831753  0.53554282 -2.69211388
B   0.54738510  1.71011026  0.06181181
B  -0.32884094  0.04842701 -2.31606083
B   0.68626672  0.53339899 -1.14414603
H  -1.91034926  3.03053694 -0.17986073
H  -2.45270769  2.88545839 -0.74717224
```