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

Electronic Supporting Information

Probing the structural and electronic properties of Zirconium doped boron clusters: Zr distorted B_{12} ligand framework

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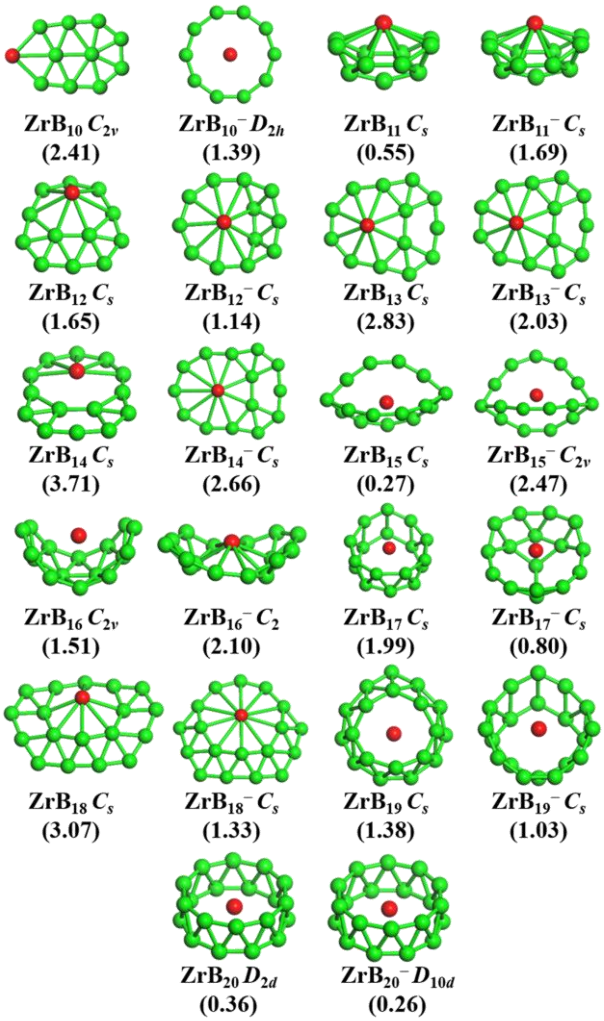

Figure S1. The metastable structures of ZrB_n^Q (n = 10-20, Q = 0, -1) clusters along with the point group symmetry and the relative energy difference compared with the lowest-energy structures.

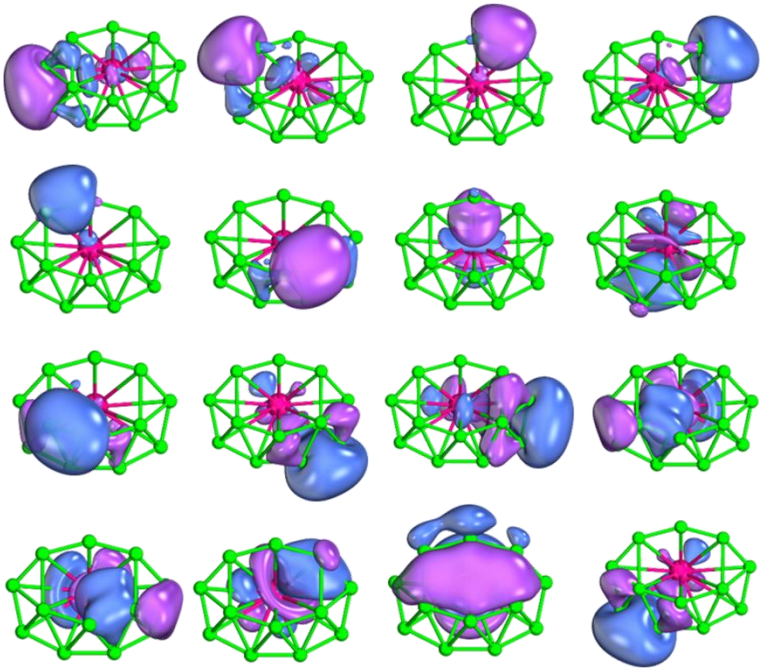

Figure S2. The intrinsic bond orbitals of anionic ZrB_{12}^- cluster visualized using the IBO localization method. The iso-surfaces enclose 80% of the orbital's electron density.

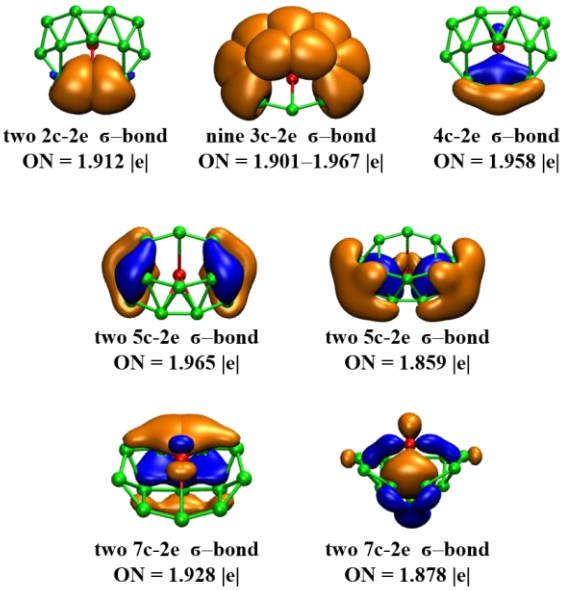

Figure S3. Chemical bonding pattern of anionic ZrB_{12}^- cluster shown by the AdNDP analysis. ON stands for occupation numbers.

Table S1. The calculated bond lengths R (Å) and lowest vibrational frequencies (cm^{-1}) of B_2, Zr_2 and ZrB_2 at different levels together with their corresponding experimental values.

Method	Cluster					
	B_2		Zr_2		ZrB_2	
	R/Å	ω	R/Å	ω	R/Å(Zr-B)	ω
HF	1.639	942.41	2.242	433.09	2.071	635.82
B3LYP	1.617	1002.11	2.252	425.86	2.078	597.02
PW91	1.616	1015.12	2.239	434.88	2.063	617.79
B3PW91	1.617	1012.13	2.243	431.45	2.067	611.03
PBE	1.617	1012.13	2.257	417.14	2.064	619.33
CCSD	1.639	940.69	2.288	394.53	2.204	586.53
PBE0	**1.607**	**1085.64**	**2.239**	**404.32**	**2.083**	**589.40**
Exp.	**1.590**[1]	**1051.30**[1]	**2.240**[2]	**305.70**[2]		
Theor.[3]	**1.653**				**2.102**	

Table S2. Detailed results of the calculated electronic states, symmetries, averaged binding energies (E_b), and HOMO-LUMO energy gaps (E_{gap}) for the ground state ZrB_n^Q (n = 10-20, Q = 0, -1) clusters.

ZrB_n					ZrB_n^-				
n	State	Sym.	E_b	E_{gap}	n	State	Sym.	E_b	E_{gap}
10	1-A_1	C_{2v}	7.92	2.20	10	2-A_2	C_{2v}	8.05	0.97
11	2-A"	C_s	8.05	1.78	11	3-A"	C_s	8.21	2.06
12	3-A"	C_s	8.10	2.83	12	2-A"	C_s	8.29	2.78
13	2-A'	C_s	7.99	1.72	13	1-A'	C_{4v}	8.23	2.17
14	1-A'	C_s	8.24	2.64	14	2-A'	C_s	8.38	1.21
15	2-A_1	C_{2v}	8.19	1.87	15	1-A_1	C_{2v}	8.46	1.89
16	1-A'	C_s	8.28	1.91	16	2-A	C_s	8.44	1.66
17	2-A"	C_s	8.32	1.88	17	1-A'	C_s	8.45	2.39
18	1-A_1	C_{2v}	8.41	1.53	18	2-B_1	C_{2v}	8.52	1.67
19	2-A"	C_s	8.34	1.71	19	1-A'	C_s	8.55	1.64
20	1-A'	C_s	8.47	1.98	20	2-A'	C_s	8.54	1.10

Table S3. The calculated VDE, ADE for the ground state ZrB_n^Q (n = 10-20, Q = 0, -1) clusters

Size	VDE	ADE
10	1.937	1.659
11	2.418	2.246
12	2.920	2.796
13	2.560	2.673
14	2.619	2.319
15	3.592	3.310
16	3.219	2.991
17	2.602	2.488
18	2.729	2.438
19	3.565	4.528
20	2.621	1.799

References

1. K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 4. Constants of Diatomic Molecules (*Van Nostrand Reinhold*, New York, 1979).
2. J. R. Lombardi and B. Davis. *Chem. Rev.* 2002, **102**, 2431.
3. J. G. Yao, X. W. Wang and Y. X. Wang, *Chem. Phys.* 2008, **351**, 1-6.