Supporting Information: Zn_2-supported B_7 wheel structure for the global minimum of B_7Zn_2 cluster

Energy decomposition analysis, density deformation, charge profiles and density of states for B_7Zn_2 clusters.

Table S1 Energy Descomposition Analysis for the Zn_2-B_7 interaction in both neutral and anionic counterparts. For neutral B_7Zn_2, unrestricted calculations were performed. Values in eV.

	Zn_2B_7		$Zn_2B_7^-$	
ΔE_{Pauli}	12.49		13.85	
ΔE_{Elstat}	-6.69	43.8%[a]	-8.68	51.8%[a]
ΔE_{Orb}	-8.39	55.0%[a]	-7.88	47.1%[a]
ΔE_{Disp}	-0.18	1.2%[a]	-0.18	1.1%[a]
ΔE_{Int}	-2.78		-2.88	
$\Delta\rho 1$	-6.37	75.9%[b]	-5.57	70.6%[b]
$\Delta\rho 2$	-0.55	6.5%[b]	-0.89	11.3%[b]
$\Delta\rho 3$	-0.50	6.0%[b]	-0.26	3.4%[b]

[a]Percentage contribution to stabilization terms.
[b]Percentage contribution to ΔE_{Orb}, see Figure S1.

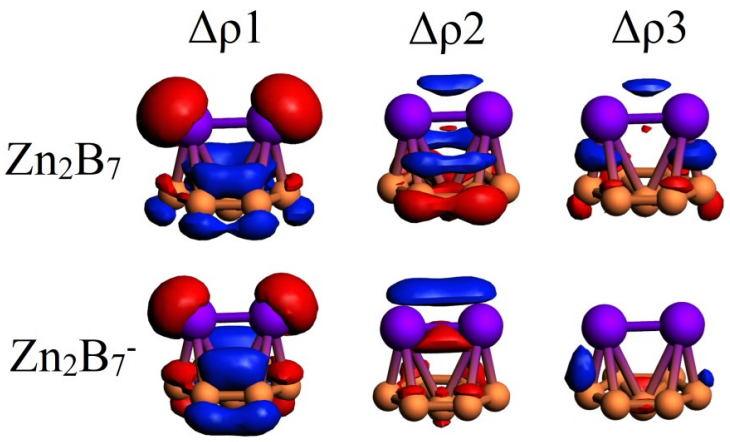


Figure S1 Density deformation related to the contributions to the overall orbital interactions (ΔE_{Orb}), provided by $\Delta\rho 1$, $\Delta\rho 2$, and, $\Delta\rho 3$, in the Zn_2-B_7 interaction.

Table S2 Zn-Zn Mayer bond order (Zn-Zn BO), Hirshfeld charge analysis of both Zn_2 and B_7 fragments (qZn_2/qB_7), and population of Zn_2 based orbitals, for the free Zn_2 dimer and related B_7 structures.

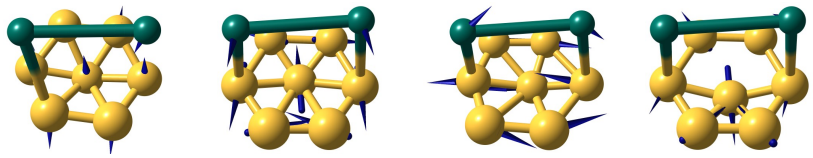
	Zn_2	Zn_2B_7	$Zn_2B_7^-$
Zn-Zn BO	0.02	0.50	0.44
qZn_2	0.00	0.60	0.33
qB_7		-0.60	-1.33
σ-Zn_2	2.00	1.94	1.92
σ^*-Zn_2	2.00	0.81	0.92

Table S3 The vertical ionization energy, vertical electron affinity and HOMO–LUMO gap (Δ_{H-L}) for open-shell structures via the representations of α- (spin up) and β-orbital (spin down) of **7M2.y** (y=1-4) clusters. The energy is given in eV.

	IP	EA	$\Delta_{H-L}(\alpha)$	$\Delta_{H-L}(\beta)$
7M2.1	7.83	2.36	3.43	2.37
7M2.2	8.27	2.95	3.75	2.15
7M2.3	7.40	1.89	2.01	2.27
7M2.4	7.72	2.31	2.07	1.82

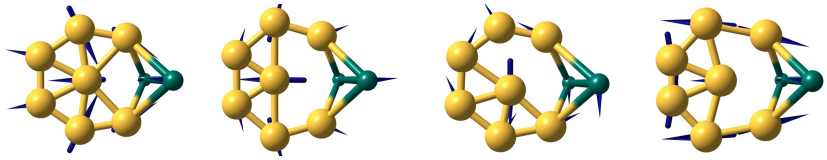
Table S4 Representative vibrational modes (in cm^{-1}) for **7M2.1** and **7M2.2** clusters. The displacement vectors are represented by blue arrows.

7M2.1



412.1 747.9 786.1 1127.6

7M2.2



521.4 702.8 828.4 1180.3

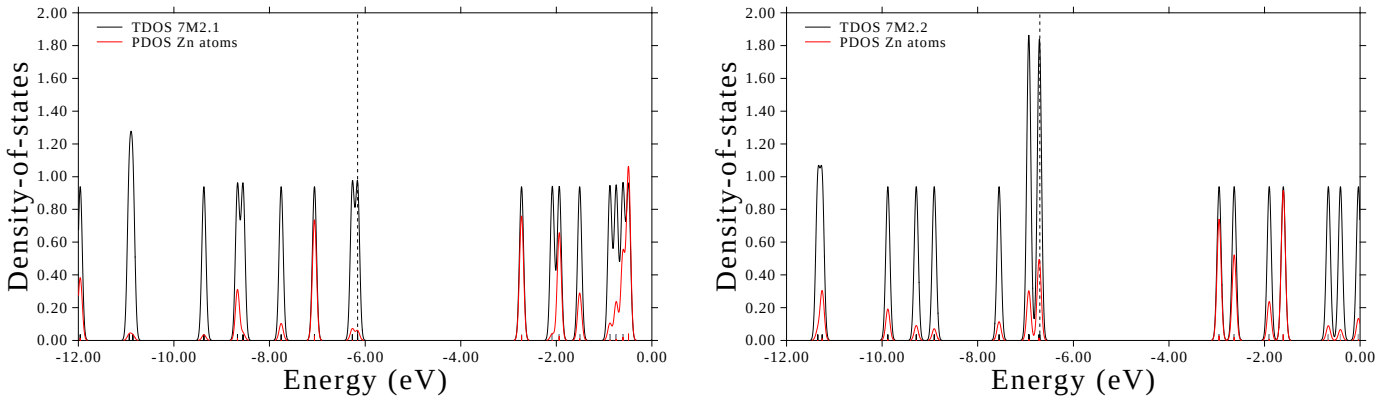
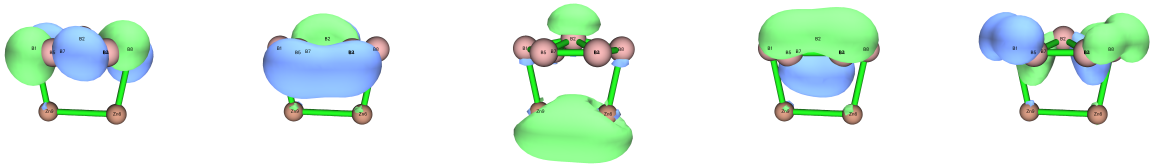


Figure S2 The total and partial density of states (TDOS, PDOS) **7M2.1** and **7M2.2** clusters. Vertical dashed line corresponds to the HOMO energy level.

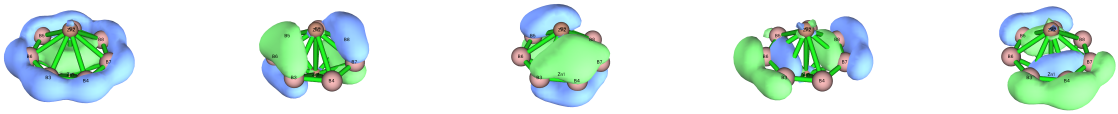
Table S5 Frontier molecular orbitals for **7M2.1** and **7M2.4** clusters.

7M2.1



HOMO-3 HOMO-2 HOMO-1 HOMO LUMO

7M2.4



HOMO-3 HOMO-2 HOMO-1 HOMO LUMO

Cartesian coordinates of representative B_7Zn_2 clusters, obtained by using the Orca program and the PBE0/Def2-TZVP approach. For each cluster, the charge state and spin multiplicity are given.

7M2.1 0, 2

B	-1.48468968805429	-0.16861862643522	0.50844481070897
B	0.12922516635192	0.04980226976932	0.83914360214435
B	0.78284013331416	1.44920353159999	0.23503314286272
B	1.09477206163736	-1.26303100763559	0.53322503850541
B	-0.51773186229070	-1.44689772316720	0.52519278815405
Zn	1.33582593170948	-0.20542911260106	-1.66967110401735
B	-0.82976651665877	1.27301494699143	0.25951132743633
B	1.74973799294483	0.19809481843228	0.49534409369620
Zn	-1.02786416592875	-0.20963898141036	-1.68290875174398

7M2.2 0, 2

B	-0.32424105361400	-0.26165786802271	1.50495891897197
B	0.06295163516645	-0.33631635411647	-0.32889392240490
B	0.27917454177419	1.49815098962180	-0.65483898761716
B	-0.00097877499225	-2.01873813928066	-0.70781285487724
B	-0.27826439129777	-1.65215128900866	0.78270510701150
B	0.31137617252334	-1.07004690548393	-1.87062368036379
Zn	1.11513608200286	1.33972482112829	1.34049067709060
B	0.43373404545555	0.48485778312230	-1.84157420292416
Zn	-1.33738330189425	1.51051371612366	0.78029416557408

7M2.3 0, 2

B	-1.38776818148408	0.07198103457209	1.10877039480688
B	0.22681267049961	0.09050994770027	0.60305071506714
B	0.53681725181056	1.60966102294020	-0.12034867823808
B	0.38448651540182	-1.17304756372920	-0.54036338061338
B	-0.84320253889526	-1.23417900134264	0.44291224299003
Zn	2.52477681230466	-1.25045752014244	-0.46366533597879
B	-0.70201067691040	1.48704953449675	0.82744652296894
B	1.11686577433162	0.33280843842215	-0.83618063928179
Zn	-1.19432963807156	0.39611494124743	-1.33973491542759

7M2.4 0, 2

Zn	-1.30869156167890	-0.00974399650075	0.00151743214576
Zn	1.30911152161145	0.00606163473148	-0.00095089038530
B	0.00396027850074	-0.89137142970320	-1.58137247709333
B	-0.00610687196401	0.66962436512400	-1.76345133320105
B	0.00959154527309	-1.32550418134370	1.29397502413000
B	0.01048545130787	-1.78333670648231	-0.23610720961102
B	-0.01099564048608	1.71283247790773	-0.58416186067158
B	-0.00763544039173	1.48698957380748	1.01546355199584
B	0.00028071782757	0.13444726245926	1.85508876269066

7M2.5 0, 2

B	0.24894775083226	-0.54456412382267	1.87577525591645
B	0.33620411097868	-0.56490676479674	0.15758599061660
B	1.49831768855164	0.83442900416186	-0.22067694345280
B	-1.10042956463607	-1.56150104416079	-0.36447787099025
B	-0.78986033234304	-1.43448353152373	1.15496664858026
B	-0.73771093492061	-0.68841878519686	-1.60647114152290
B	1.28373392556640	0.41388100626373	1.24941464085124
Zn	0.57945972433149	0.83297900303255	-2.02224836670149

Zn	-2.03144344747423	0.57356991907946	-0.45185813650607

7M2.6 0, 2

B	-1.60925643228336	-0.11858675857859	0.79736847389450
B	0.05649442618271	0.05612674242472	0.91064997208880
B	0.56364151527496	1.42762762508225	0.08321492555722
B	0.85302754518955	-1.30635536345825	0.33152372623851
B	-0.71229260095248	-1.41762303280191	0.68715261890973
Zn	2.05249139099900	-0.22002110913870	-1.93511106547808
B	-0.99139595292148	1.29225871081903	0.46589586549999
B	1.55145940911987	0.14416873061751	0.10015563435639
Zn	-0.53182024758352	-0.18109542942246	-1.39753520332036