Supporting Information

Canonical Zn-Zn pseudo-triple bond with double aromaticity in D_{5h}-$Zn_2Na_5^-$ cluster

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1. Supplementary figures

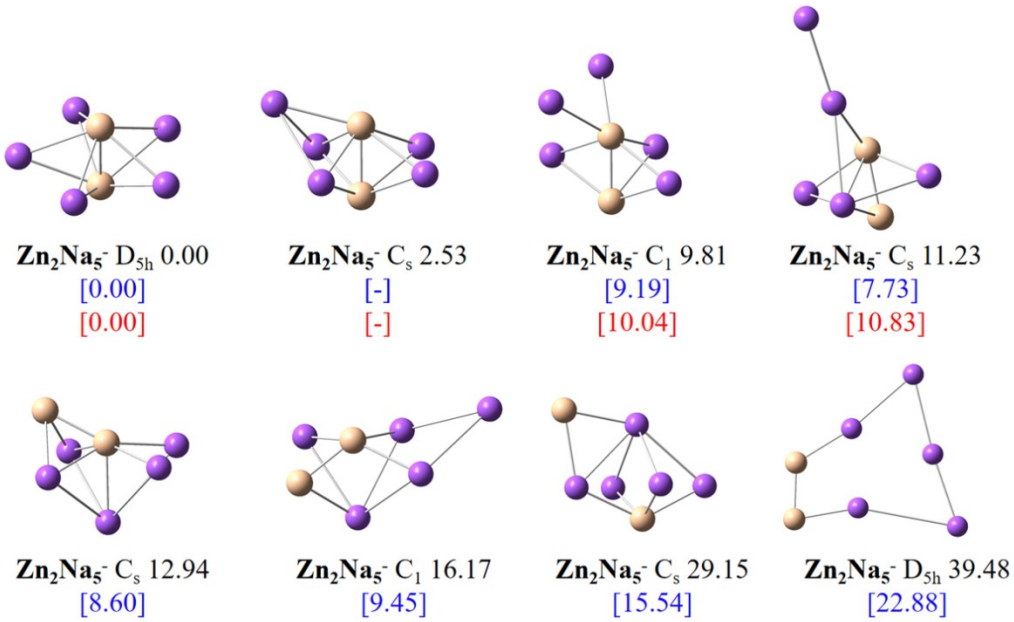


Figure S1. Optimized geometries of the isomers of $Zn_2Na_5^-$ cluster. Relative energies (kcal/mol) are computed at B3LYP/6-31G(d) level of theory. The energy values (kcal/mol) shown in blue were calculated at the CCSD/6-311G(d)/ LANL2DZ level (LANL2DZ for Zn, 6-311G(d) for Na) and the energy values (kcal/mol) shown in red were calculated at the TPSSh/6-311++G(d,p) level.

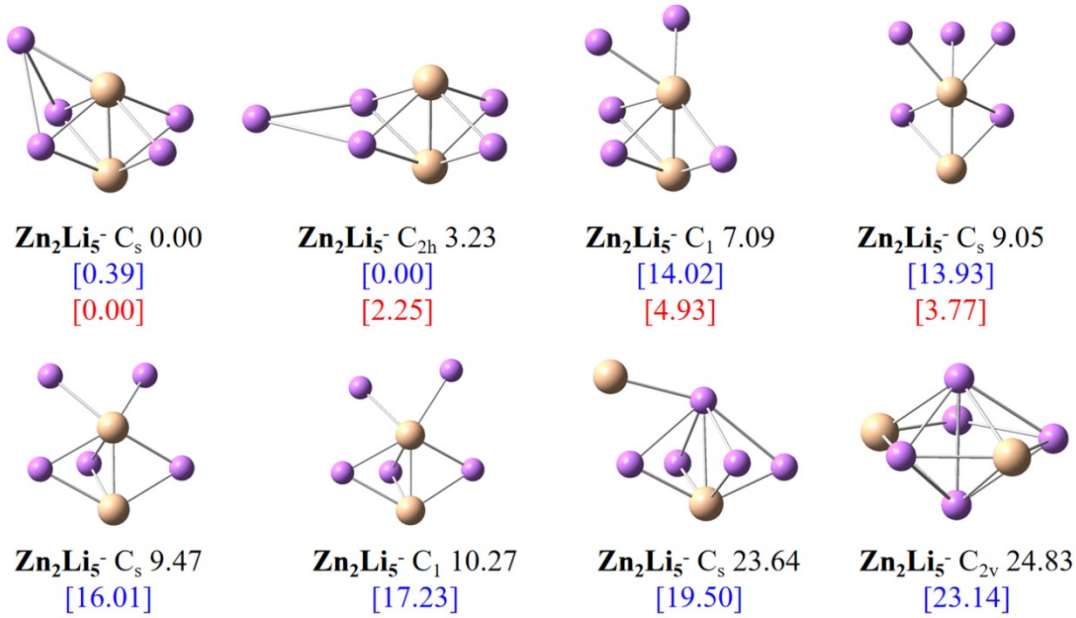


Figure S2. Optimized geometries of the isomers of $Zn_2Li_5^-$ cluster. Relative energies (kcal/mol) are computed at B3LYP/6-31G(d) level of theory. The energy values (kcal/mol) shown in blue were calculated at the CCSD/6-311G(d)/LANL2DZ level (LANL2DZ for Zn, 6-311G(d) for Li) and the energy values (kcal/mol) shown in red were calculated at the TPSSh/6-311++G(d,p) level.

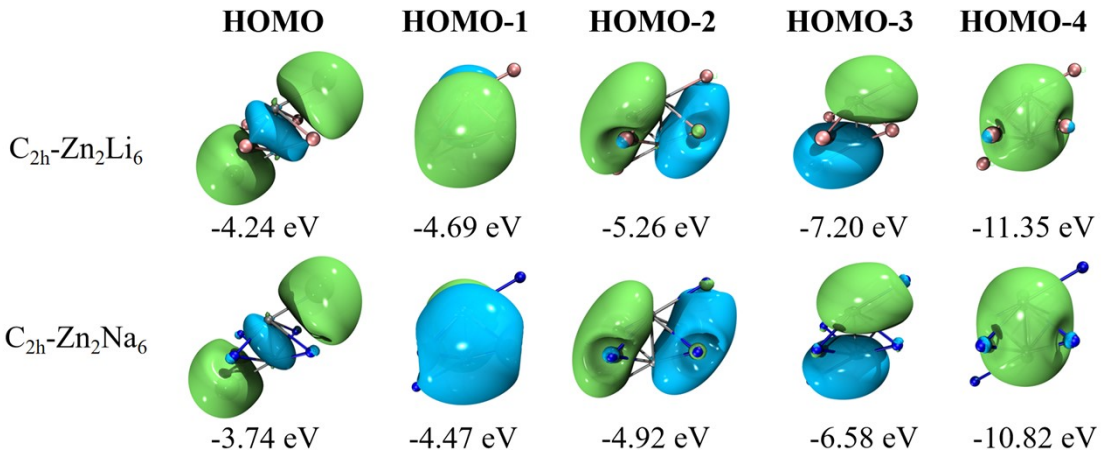


Figure S3. The important FMOs of C_{2h}-Zn_2Li_6 and C_{2h}-Zn_2Na_6 structures. Computed at the CCSD/6-311G(d)/LANL2DZ level (LANL2DZ for Zn, 6-311G(d) for Na, Li).

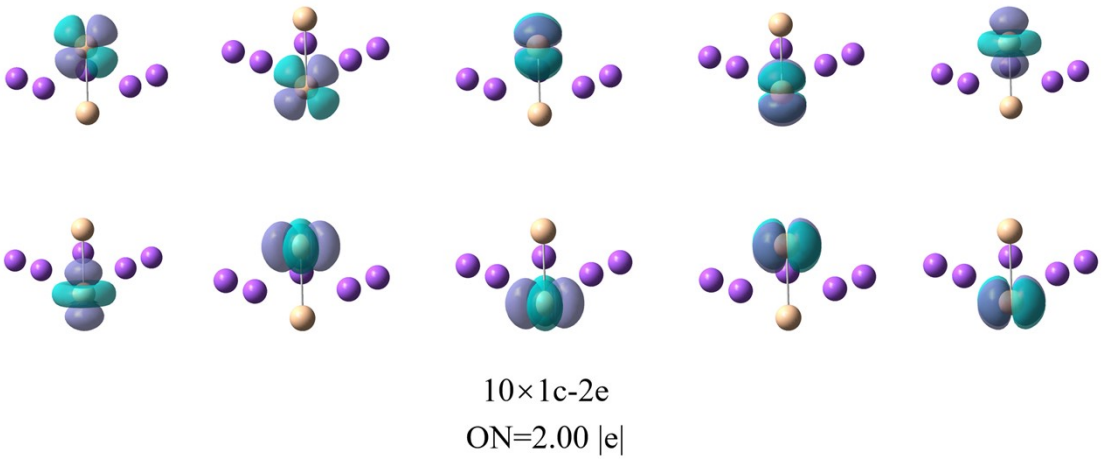


Figure S4. Ten lone pairs of electrons occupy the d orbital of Zn.

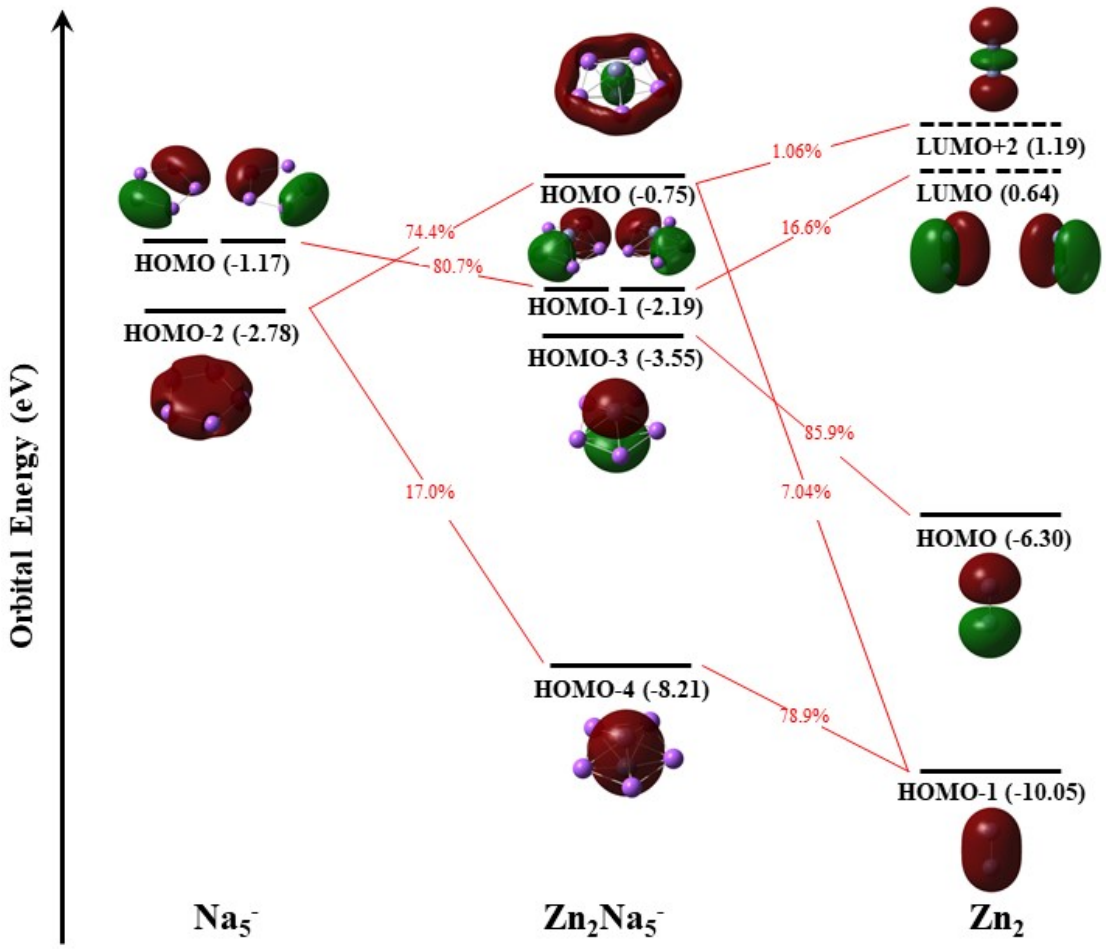


Figure S5. The dominant FMO correlation diagram of D_{5h}-$Zn_2Na_5^-$ between Na_5^- and Zn_2 fragments calculated at the CCSD/6-311G(d)/LANL2DZ level. The horizontal dashed and solid lines represent virtual and occupied molecular orbitals, respectively (the orbital energies are also given in brackets, unit: eV). It can be observed that the Na_5^- delocalized (HOMO-2) orbital lie in the equatorial plane contribute 74.4% to the σ orbital of Zn-Zn (HOMO) in D_{5h}-$Zn_2Na_5^-$.

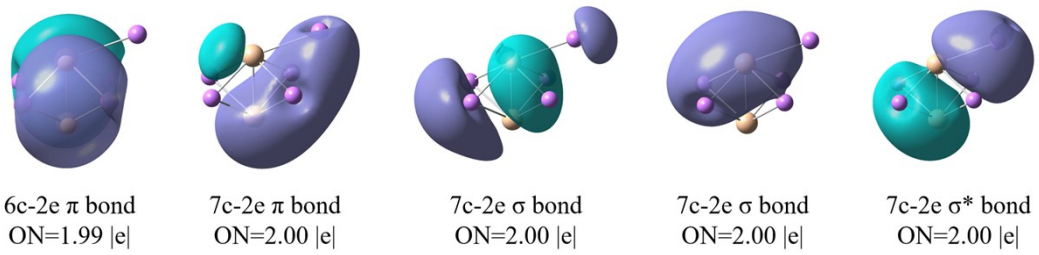


Figure S6. AdNDP orbitals of C_s-$Zn_2Li_5^-$ cluster. Occupation numbers (ON) are also shown, the unit is |e|. Computed at CCSD/6-311G(d)/LANL2DZ level of theory.

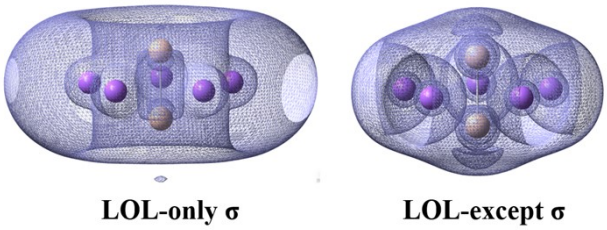


Figure S7. Only σ and except σ separated LOL of D_{5h}-$Zn_2Na_5^-$ calculated at CCSD/6-311G(d)/LANL2DZ level of theory.

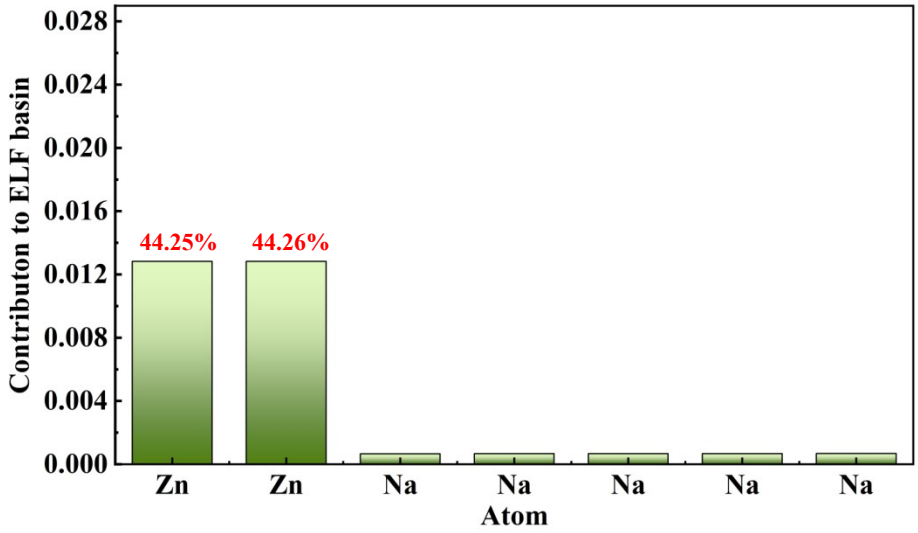


Figure S8. The diagram shows the contribution of each atom towards the Zn-Zn ELF basin in D_{5h}-$Zn_2Na_5^-$.

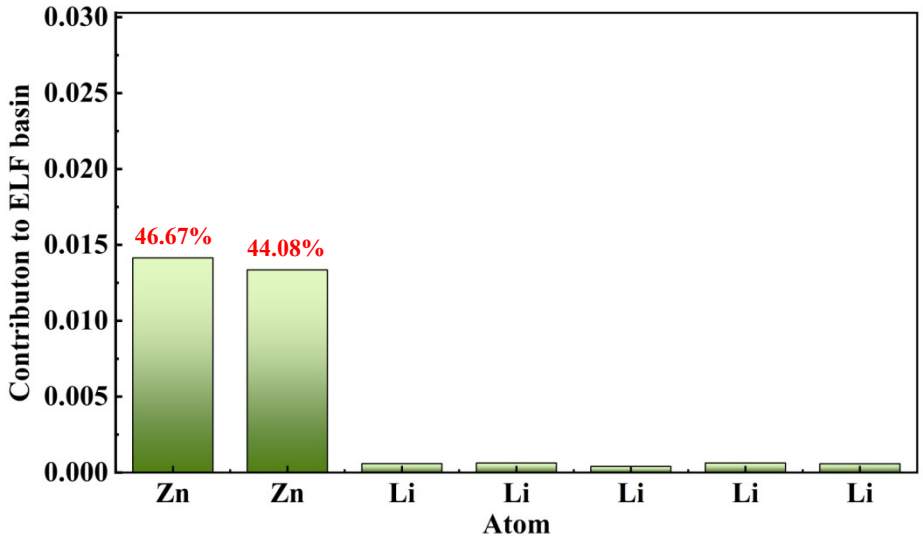


Figure S9. The diagram shows the contribution of each atom towards the Zn-Zn ELF basin in C_s-$Zn_2Li_5^-$.

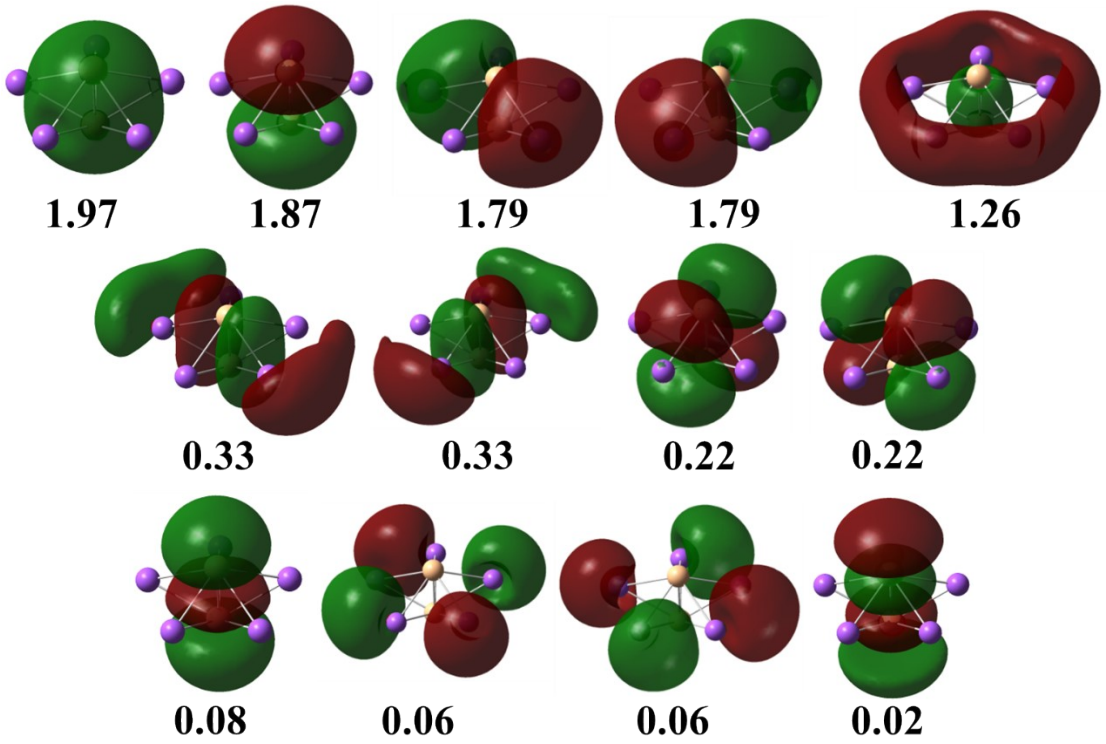
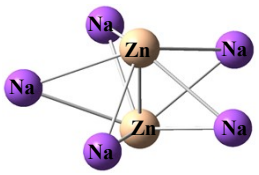
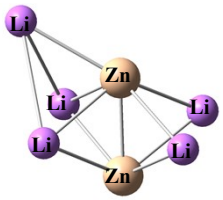


Figure S10. Natural orbitals of the global minimum isomer of $Zn_2Na_5^-$ from CASSCF(10,13) and their occupation numbers.

2. Supplementary tables

2.1. Table S1. The lowest vibrational frequencies of D_{5h}-$Zn_2Na_5^-$, C_s-$Zn_2Li_5^-$ and C_s-$Zn_2Na_5^-$ are calculated at the CCSD/6-311G(d)/LANL2DZ level (LANL2DZ for Zn, 6-311G(d) for Na, Li).

Molecules	Structure	Lowest vibrational frequency (cm^{-1})
D_{5h}-$Zn_2Na_5^-$		37.41
C_s-$Zn_2Li_5^-$		70.75

Note: C_s-$Zn_2Na_5^-$ exhibits an imaginary frequency, further optimization will yield a D_{5h} structure.

2.2. Table S2. The bond length ($R_{Zn–Zn}$), $WBI_{Zn–Zn}$, $FC_{Zn–Zn}$, Natural electronic configuration of Zn of Zn–Zn bonding systems. Structures calculated and analyzed at the TPSSh/6-311++G(d,p) level.

Molecule	R (Å)	WBI	FC (mDyn Å^{-1})	Natural electronic configuration of Zn	NPA
D_{5h}-$Zn_2Na_5^-$	2.492	1.588	0.575	[core]4s$^{1.49}$3d$^{10.00}$4p$^{1.46}$	-0.97
C_{2h}-Zn_2Na_6	2.476	1.832	0.548	[core]4s$^{1.38}$3d$^{10.0}$4p$^{1.86}$	-1.25
D_{4h}-Zn_2Na_4	2.606	1.639	0.365	[core]4s$^{1.47}$3d$^{10.0}$4p$^{1.57}$	-1.05
C_s-$Zn_2Li_5^-$	2.470	1.669	0.580	[core]4s$^{1.26}$3d$^{9.99}$4p$^{1.45/2.02}$	-1.40
C_{2h}-Zn_2Li_6	2.480	1.613	0.538	[core]4s$^{1.26}$3d$^{9.99}$4p$^{1.96}$	-1.24
D_{4h}-Zn_2Li_4	2.519	1.588	0.497	[core]4s$^{1.38}$3d$^{9.99}$4p$^{1.56}$	-0.95
$Zn_2(CO)_4^*$	2.273	1.064	1.529	[core]4s$^{0.82}$3d$^{9.94}$4p$^{1.29}$	-0.06

Note: With an asterisk, the results were calculated to a single point on the same level for comparison.

2.3. Table S3. The bond length ($R_{Zn–Zn}$), $WBI_{Zn–Zn}$, $FC_{Zn–Zn}$, Natural electronic configuration of Zn of Zn–Zn bonding systems. Structures calculated and analyzed at the M06-2X/def2-TZVP level.

Molecule	R (Å)	WBI	FC (mDyn Å^{-1})	Natural electronic configuration of Zn	NPA
D_{5h}-$Zn_2Na_5^-$	2.659	1.520	0.453	[core]4s$^{1.44}$3d$^{10.00}$4p$^{1.41}$	-0.89
C_{2h}-Zn_2Na_6	2.683	1.546	0.370	[core]4s$^{1.35}$3d$^{10.0}$4p$^{1.73}$	-1.09
D_{4h}-Zn_2Na_4	2.832	1.377	0.264	[core]4s$^{1.46}$3d$^{10.0}$4p$^{1.40}$	-0.89
C_s-$Zn_2Li_5^-$	2.630	1.426	0.456	[core]4s$^{1.21/1.25}$3d$^{10.0}$4p$^{1.38/1.81}$	-1.09
C_{2h}-Zn_2Li_6	2.643	1.326	0.419	[core]4s$^{1.18}$3d$^{10.0}$4p$^{1.82}$	-1.01
D_{4h}-Zn_2Li_4	2.678	1.371	0.390	[core]4s$^{1.33}$3d$^{10.0}$4p$^{1.42}$	-0.76
$Zn_2(CO)_4^*$	2.273	1.192	--	[core]4s$^{0.77}$3d$^{9.96}$4p$^{1.39}$	-0.12

Note: With an asterisk, the results were calculated to a single point on the same level for comparison.

2.4. Table S4a. Orbital and component analysis of D_{5h}-$Zn_2Na_5^-$ structures. Computed at the CCSD/6-311G(d)/LANL2DZ level (LANL2DZ for Zn, 6-311G(d) for Na).

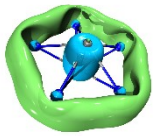
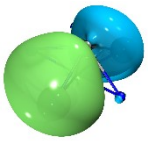
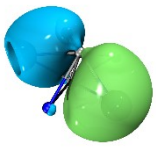
Orbital	HOMO	HOMO-1	HOMO-2
D_{5h}-$Zn_2Na_5^-$			
E/eV	-0.751	-2.191	-2.191
Component	Zn_1©4s~5.52% Zn_1©4p~0.61% Zn_2©4s~5.52% Zn_2©4p~0.61% Na©3s~78.65%	Zn_1©4p~27.89% Zn_2©4p~27.89% Na©3s~33.80%	Zn_1©4p~27.89% Zn_2©4p~27.89% Na©3s~31.15%

Table S4b. Orbital and component analysis of Cs-$Zn_2Li_5^-$ structures. Computed at the CCSD/6-311G(d)/LANL2DZ level (LANL2DZ for Zn, 6-311G(d) for Li).

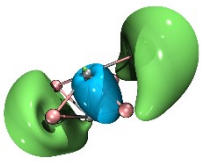
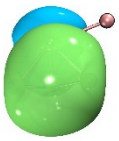
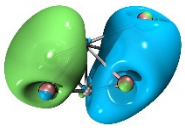
Orbital	HOMO	HOMO-1	HOMO-2
C_s-$Zn_2Li_5^-$			
E/eV	-0.618	-1.986	-2.502
Component	Zn_1©4p~10.99% Zn_2©4s~4.05% Zn_2©4p~2.89% Li©2s~66.81% Li©2p~13.60%	Zn_1©4p~29.36% Zn_2©4p~36.05% Li©2s~21.88% Li©2p~10.87%	Zn_1©4s~2.49% Zn_1©4p~17.73% Zn_2©4s~5.16% Zn_2©4p~34.46% Li©2p~10.87%

Table S4c. Orbital and component analysis of C_{2h}-Zn_2Li_6 structures. Computed at the CCSD/6-311G(d)/LANL2DZ level (LANL2DZ for Zn, 6-311G(d) for Li).

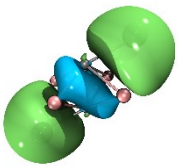
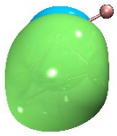
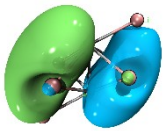
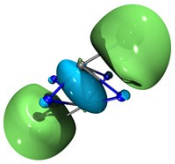
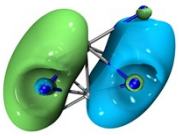
Orbital	HOMO	HOMO-1	HOMO-2
C_{2h}-Zn_2Li_6			
E/eV	-4.240	-4.687	-5.262
Component	Zn_1©4p~14.49% Zn_2©4p~14.49% Li©2s~48.89% Li©2p~17.69%	Zn_1©4p~32.60% Zn_2©4p~32.60% Li©2s~21.57% Li©2p~10.32%	Zn_1©4s~8.03% Zn_1©4p~23.61% Zn_2©4s~8.03% Zn_2©4p~23.61% Li©2s~20.17% Li©2p~13.43%

Table S4d. Orbital and component analysis of C_{2h}-Zn_2Na_6 structures. Computed at the CCSD/6-311G(d)/LANL2DZ level (LANL2DZ for Zn, 6-311G(d) for Na).

Orbital	HOMO	HOMO-1	HOMO-2
C_{2h}-Zn_2Na_6			
E/eV	-3.739	-4.472	-4.921
Component	Zn_1©4s~2.39% Zn_1©4p~8.81% Zn_2©4s~2.39% Zn_2©4p~8.81% Na©3s~65.63% Na©3p~6.31%	Zn_1©4p~36.05% Zn_2©4p~36.05% Na©3s~19.75% Na©3p~2.94%	Zn_1©4s~4.61% Zn_1©4p~27.21% Zn_2©4s~4.61% Zn_2©4p~27.21% Na©3s~25.66% Na©3p~7.90%

Note: "Zn_1" denotes the Zn atom located above and "Zn_2" denotes the Zn atom located below.

2.5. Table S5. Topological parameters of electron density, ρ, laplacian of electron density, $\nabla^2\rho$, local electronic energy density, H(r), ratio of potential energy density to kinetic energy density, |V(r)|/G(r). Every value is in Au. Computed at TPSSh/6-311++G(d,p).

Molecule	ρ	$\nabla^2\rho$	H(r)	|V(r)|/G(r)
D_{5h}-$Zn_2Na_5^-$	0.042	0.058	-0.013	1.47
C_s-$Zn_2Li_5^-$	0.045	0.062	-0.014	1.48
C_{2h}-Zn_2Li_6	0.045	0.060	-0.014	1.50
C_{2h}-Zn_2Na_6	0.044	0.056	-0.014	1.50
D_{4h}-Zn_2Li_4	0.038	0.070	-0.010	1.37
D_{4h}-Zn_2Na_4	0.032	0.059	-0.007	1.32
$Zn_2(CO)_4^*$	0.069	0.052	-0.030	1.70

Note: With an asterisk, the results were calculated to a single point on the same level for comparison.

Scheme S1. Cartesian coordinates of the optimized geometries

D_{5h}- $Zn_2Na_5^-$

Na	-2.92789900	0.11523100	0.00056200
Na	2.30090200	-1.81415300	-0.00025300
Na	-0.79508000	2.81998700	-0.00010400
Na	-1.01430900	-2.74877000	-0.00021500
Na	2.43642800	1.62762100	-0.00007800
Zn	0.00009400	-0.00002500	1.32335900
Zn	-0.00010900	0.00005600	-1.32332700

C_s-$Zn_2Li_5^-$

Li	-0.60627300	1.78626300	1.57275300
Li	0.35854600	-1.47778200	-1.65674500
Li	2.83554900	-2.02341700	-0.00010900
Li	0.35905100	-1.47744500	1.65702400
Li	-0.60655400	1.78525300	-1.57363400
Zn	-1.38086800	-0.29077400	0.00009600
Zn	1.14683600	0.43148700	-0.00002500