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SUPPLEMENTARY INFORMATION

The Al≡Al triple bond in $Al_2X_5^+$ and $Al_2X_6^{2+}$(X=Li, Na) clusters with multiple alkali metals coordination

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Table of Contents

orbital energies are also given, unit: eV).

S17 Figure S14. a) AdNDP orbitals. b) LOL profile. c) ELF profile for $Al_2Li_5^+$ at the CCSD/6-311G(d) level. ON stands for the occupation number.

S18 Figure S15. a) AdNDP orbitals. b) LOL profile. c) ELF profile for $Al_2Li_6^{2+}$ at the CCSD/6-311G(d) level. ON stands for the occupation number.

S18 Figure S16. a) AdNDP orbitals. b) LOL profile. c) ELF profile for $Al_2Na_6^{2+}$ at the CCSD/6-311G(d) level. ON stands for the occupation number.

S19 Figure S17. Laplacian plot of the electron density $\nabla^2\rho(r)$, of $Al_2Li_5^+$(a), $Al_2Li_6^{2+}$(b), $Al_2Na_6^{2+}$(c) in different perspectives. Solid and dashed lines correspond to positive and negative regions of $\nabla^2\rho$, respectively.

S20 Scheme 1. Several potential reactions and thermodynamic values for the generation of C_1-Al_2Li_5, C_{4V}-$Al_2Li_5^+$, C_1-Al_2Li_6, D_{4h}-$Al_2Li_6^{2+}$, C_1-Al_2Na_5, D_{3h}-$Al_2Na_5^+$, C_1-Al_2Na_6 and D_{4h}-$Al_2Na_6^{2+}$.

S21 Table S3. Cartesian coordinates for optimized structures of $Al_2Li_5^+$, $Al_2Li_6^{2+}$, $Al_2Na_5^+$, and $Al_2Na_6^{2+}$ at the CCSD/6-311G(d) level.

S22 Table S4. Cartesian coordinates for optimized structures of Al_2Li_5, Al_2Li_6, Al_2Na_5, and Al_2Na_6 at the CCSD/6-311G(d) level.

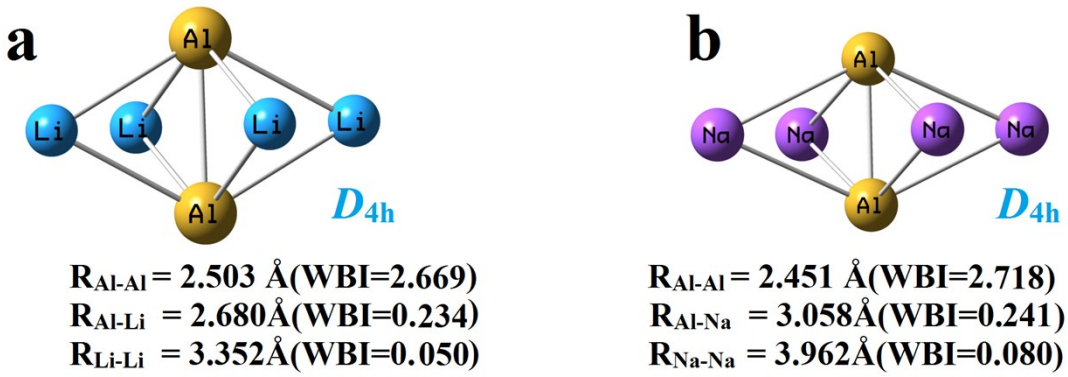


Figure S1. Optimized GEM structures together with important bond distances (in/Å) and WBIs of D_{4h}-Al_2Li_4 (a), and D_{4h}-Al_2Na_4(b) at the CCSD/6-311G(d) level.

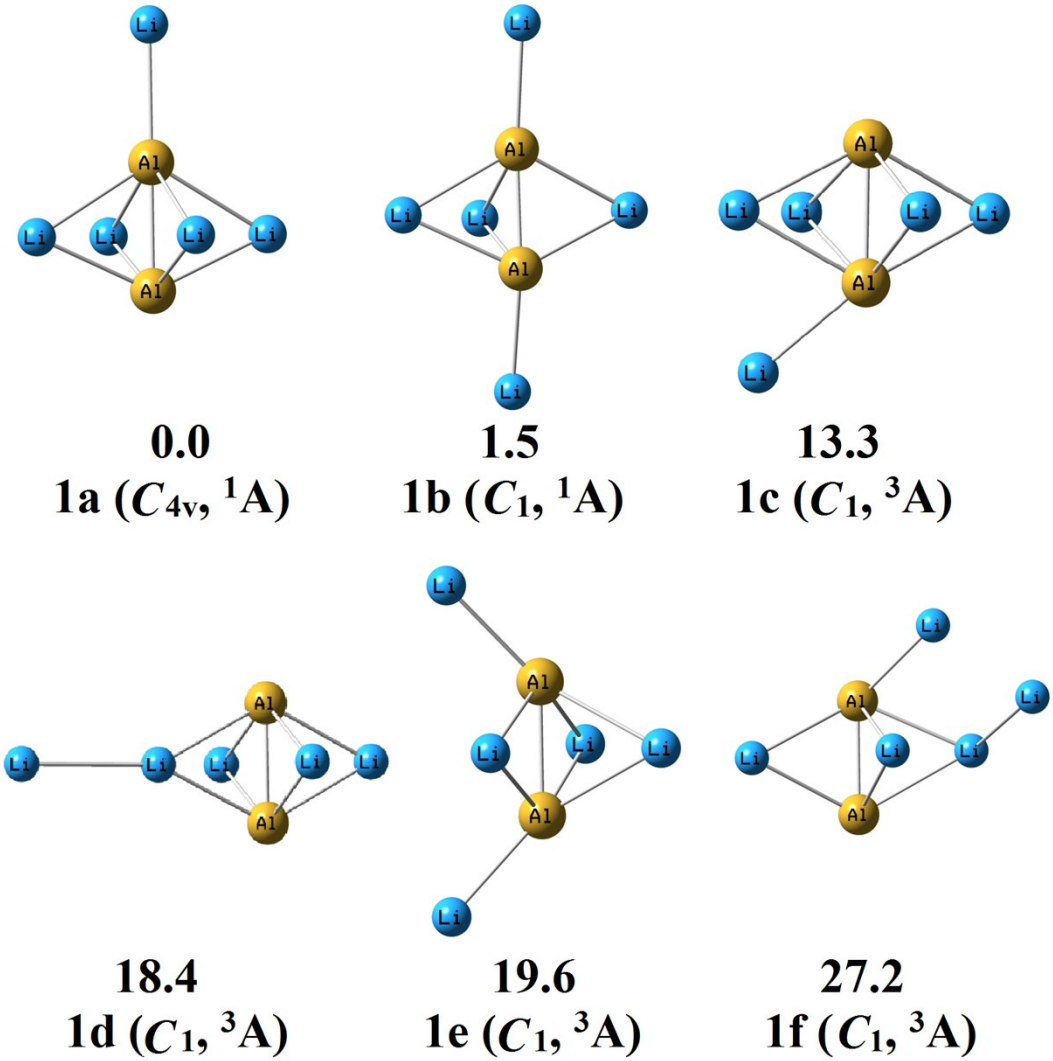


Figure S2. The lowest-lying isomers of $Al_2Li_5^+$. Optimized structures at the B3LYP/def2-TZVP level, relative single-point energies (kcal/mol) at the CCSD/6-311G(d) level.

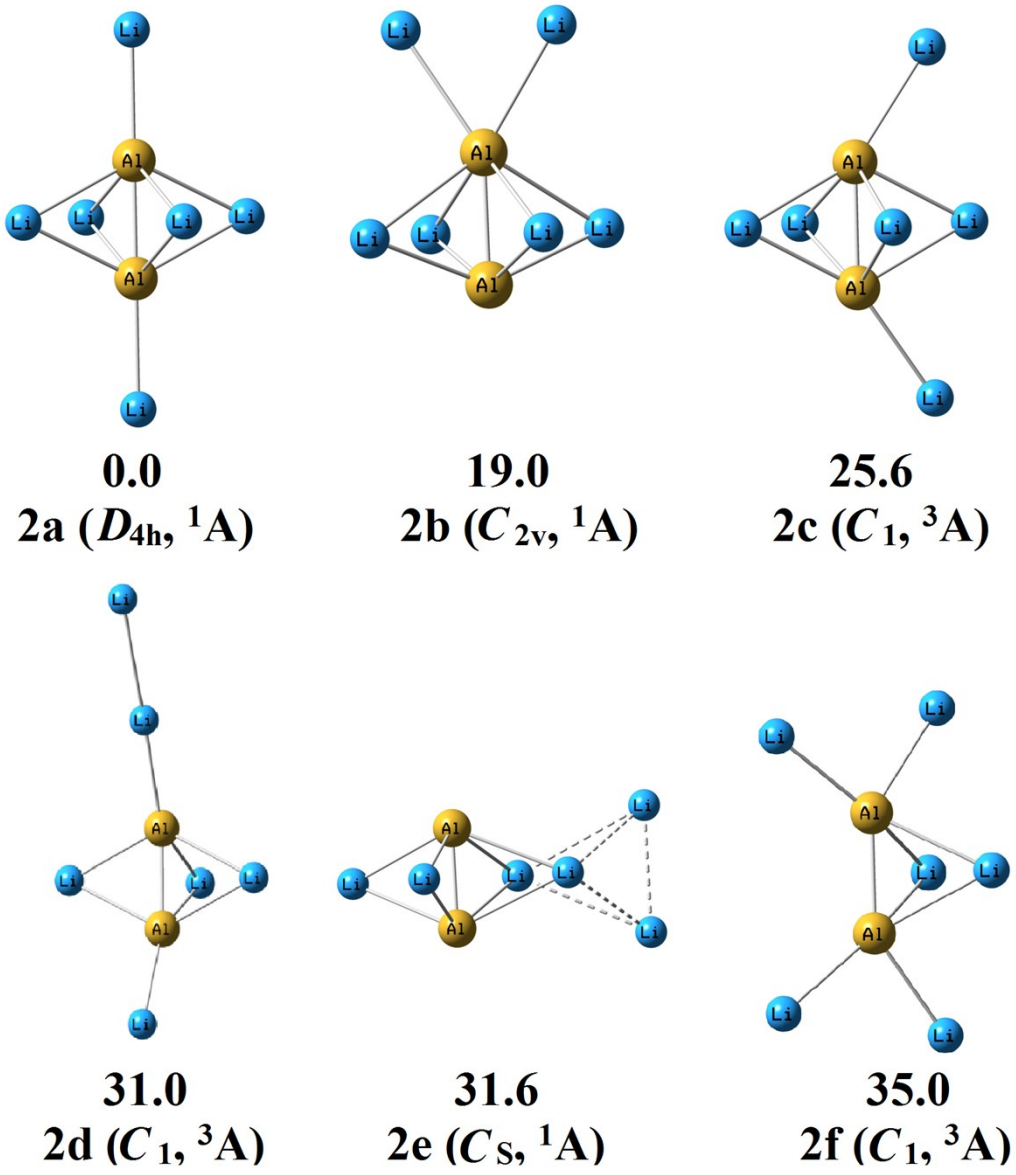


Figure S3. The lowest-lying isomers of $Al_2Li_6^{2+}$. Optimized structures at the B3LYP/def2-TZVP level, relative single-point energies (kcal/mol) at the CCSD/6-311G(d) level.

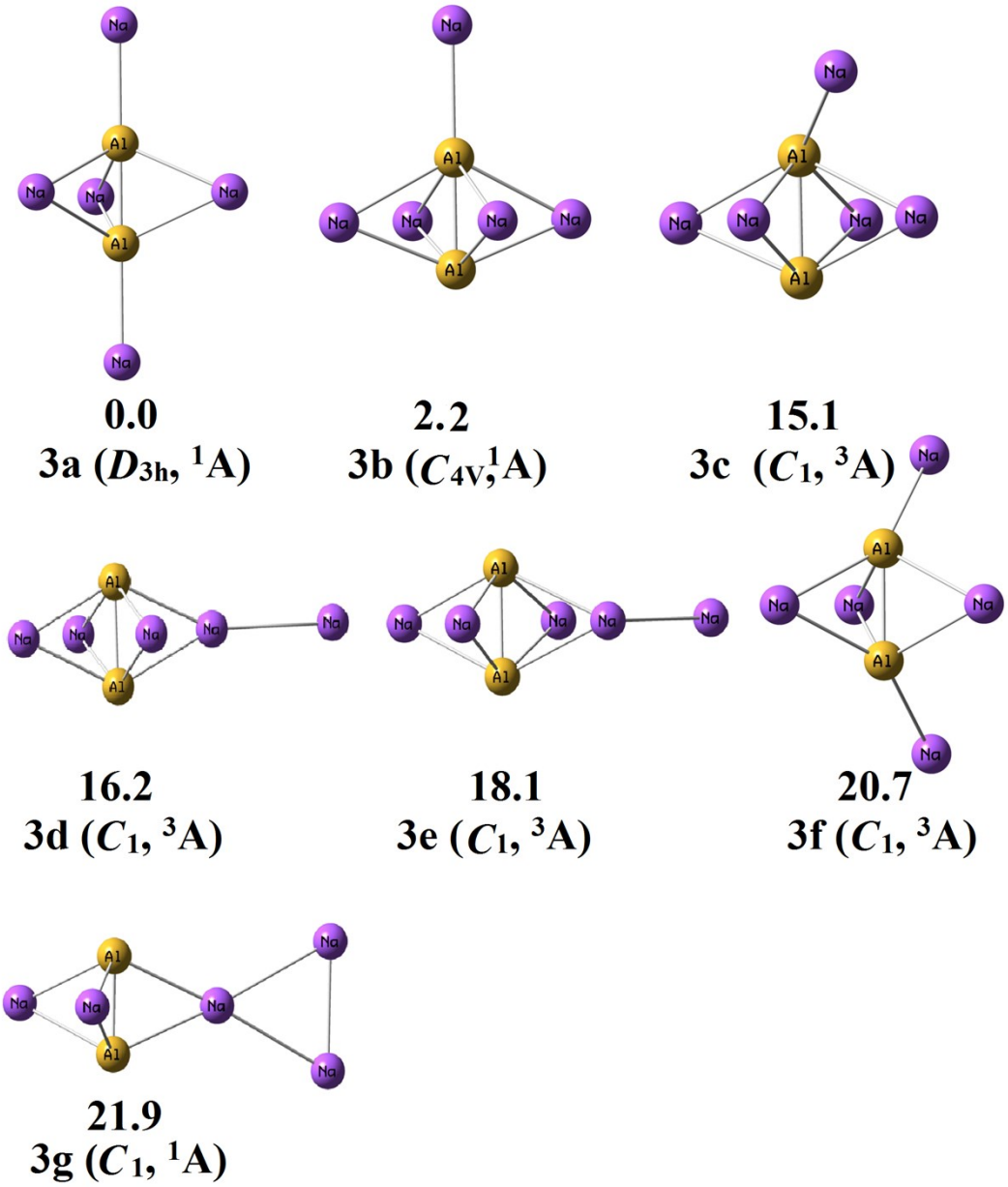


Figure S4. The lowest-lying isomers of $Al_2Na_5^+$. Optimized structures at the B3LYP/def2-TZVP level, relative single-point energies (kcal/mol) at the CCSD/6-311G(d)level.

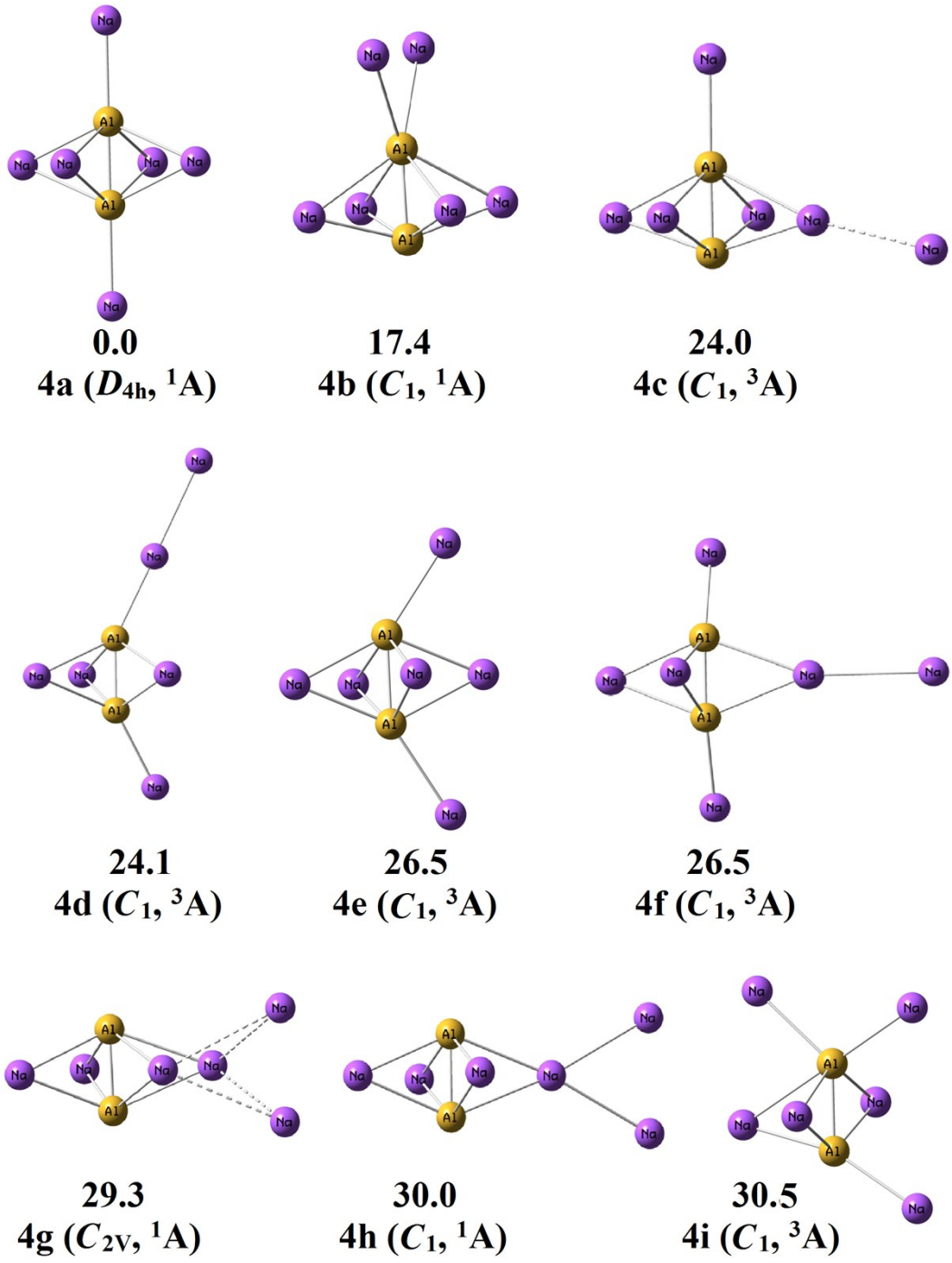


Figure S5. The lowest-lying isomers of $Al_2Na_6^{2+}$. Optimized structures at the B3LYP/def2-TZVP level, relative single-point energies (kcal/mol) at the CCSD/6-311G(d) level.

Table S1. Important results information of the structures of clusters, including the spin states, relative energies (kcal/mol), Al-Al bond length (R/Å), Wiberg Bond Indices (WBI_{Al-Al}) and NPA charge (NPA/|e|). They all calculated at the B3LYP/def2-TZVP level.

Molecule-$Al_2Li_5^+$	Spin States	Relative Energies(kcal/mol)	R_{Al-Al}(Å)	WBI_{Al-Al}	NPA_{Al-Al}(|e|)
Ⅰ	Singlet	0.0	2.52	2.50	-1.529
Ⅱ	Singlet	1.5	2.43	2.76	-0.795
Ⅲ	Triplet	13.3	2.54	1.61	-1.031
Ⅳ	Triplet	18.4	2.48	1.30	-1.199
Ⅴ	Triplet	19.6	2.54	1.60	-1.223
Ⅵ	Triplet	27.2	2.49	1.55	-0.558

Molecule-$Al_2Li_6^{2+}$	Spin States	Relative Energies(kcal/mol)	R_{Al-Al}(Å)	WBI_{Al-Al}	NPA_{Al-Al}(|e|)
Ⅰ	Singlet	0.0	2.45	2.73	-1.708
Ⅱ	Singlet	19.0	2.50	2.29	-1.364
Ⅲ	Triplet	25.6	2.52	1.70	-1.340
Ⅳ	Triplet	31.0	2.45	2.18	-1.111
Ⅴ	Singlet	31.6	2.36	2.47	-0.558
Ⅵ	Triplet	35.0	2.48	1.76	-1.045

Molecule-$Al_2Na_5^+$	Spin States	Relative Energies(kcal/mol)	R_{Al-Al}(Å)	WBI_{Al-Al}	NPA_{Al-Al}(|e|)
Ⅰ	Singlet	0.0	2.44	2.64	-1.547
Ⅱ	Singlet	2.2	2.51	2.29	-1.247
Ⅲ	Triplet	15.1	2.55	1.92	-1.034
Ⅳ	Triplet	16.2	2.51	2.01	-0.932
Ⅴ	Triplet	18.1	2.53	2.02	-0.901
Ⅵ	Triplet	20.7	2.54	1.79	-1.127
Ⅵ	Singlet	21.9	2.42	2.54	-0.650

Molecule-$Al_2Na_6^{2+}$	Spin States	Relative Energies(kcal/mol)	R_{Al-Al}(Å)	WBI_{Al-Al}	NPA_{Al-Al}(|e|)
Ⅰ	Singlet	0.0	2.47	2.55	-1.551
Ⅱ	Singlet	17.4	2.49	2.40	-1.318
Ⅲ	Triplet	24.0	2.45	2.35	-1.092
Ⅳ	Triplet	24.1	2.48	2.19	-1.101
Ⅴ	Triplet	26.5	2.56	1.82	-1.327
Ⅵ	Triplet	26.5	2.46	2.16	-1.087
Ⅶ	Singlet	29.3	2.40	2.68	-0.714
Ⅷ	Singlet	30.0	2.41	2.64	-0.716
Ⅸ	Triplet	30.5	2.55	1.80	-1.357

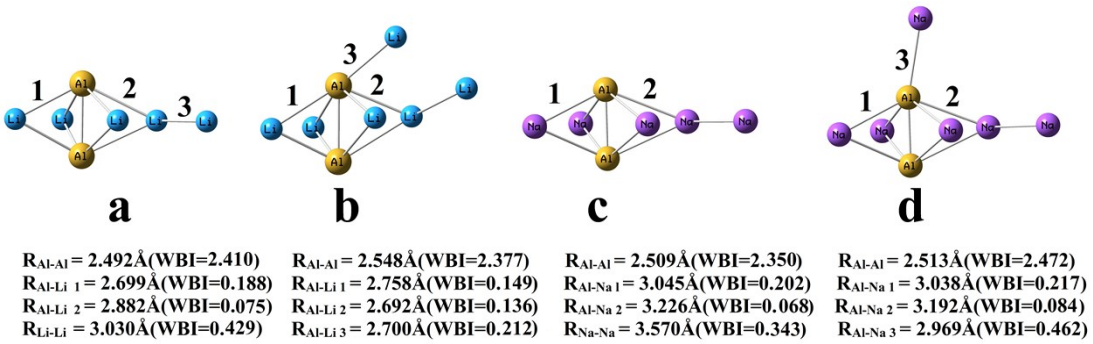


Figure S6. Optimized GEM structures at the CCSD/6-311G(d) level for C_1-Al_2Li_5 (a), C_1-Al_2Li_6 (b), C_1-Al_2Na_5 (c) and C_1-Al_2Na_6 (d). Together with important bond distances (in/Å) and Wiberg bond indices (WBIs) at the same level.

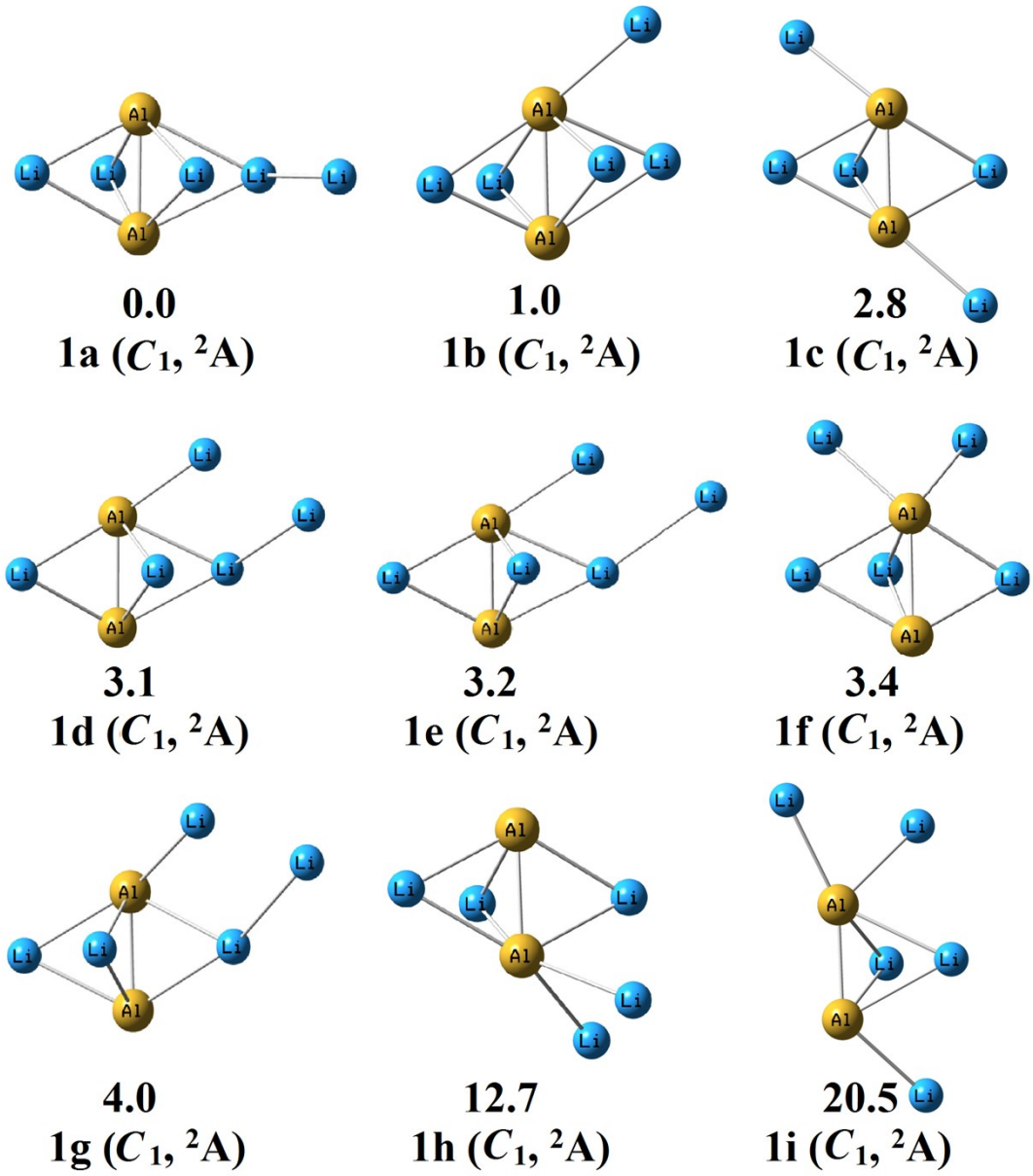


Figure S7. The lowest-lying isomers of Al_2Li_5. Optimized structures at the B3LYP/def2-TZVP level, relative energies (kcal/mol) at the CCSD/6-311G(d) level.

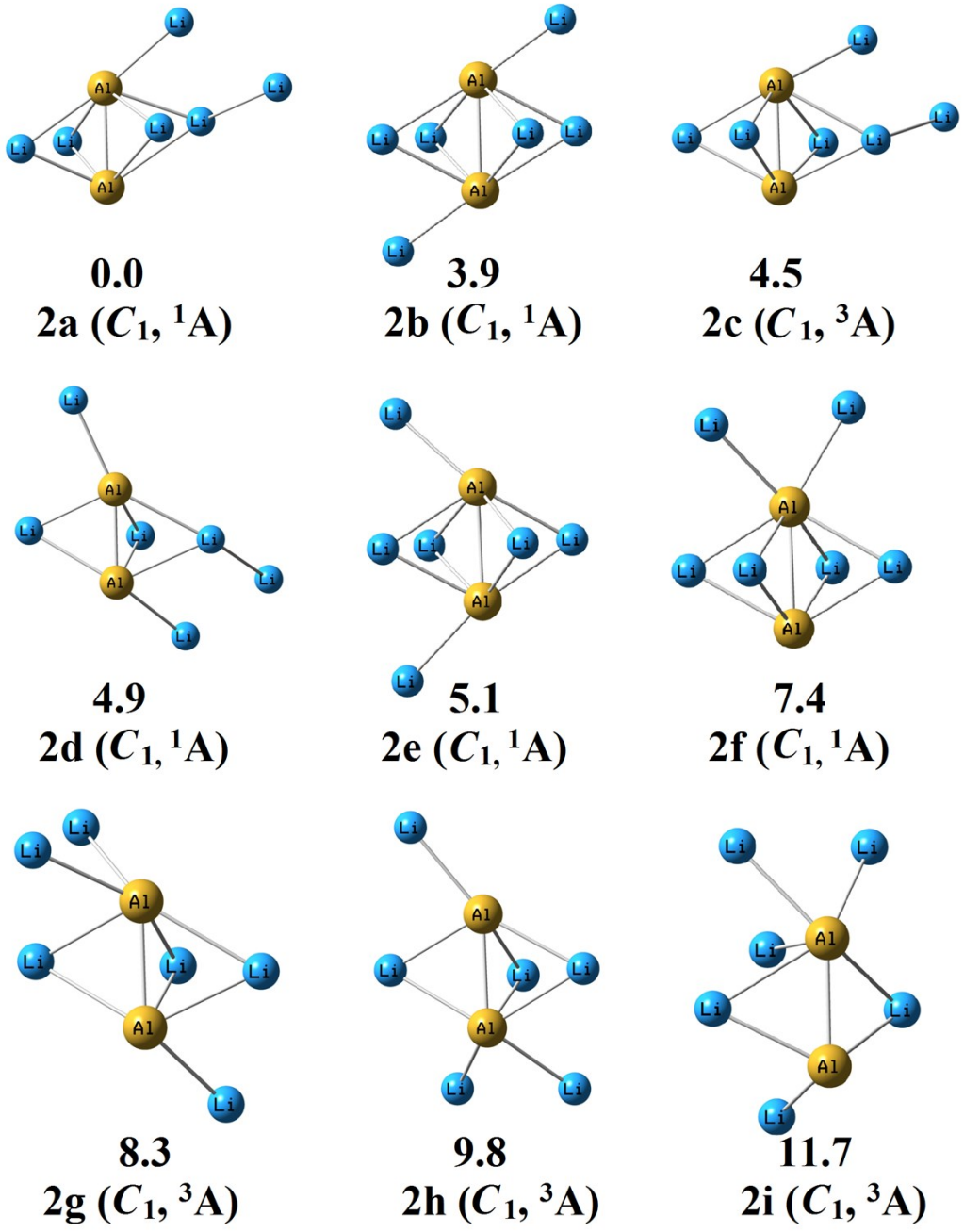


Figure S8. The lowest-lying isomers of Al_2Li_6. Optimized structures at the B3LYP/def2-TZVP level, relative single-point energies (kcal/mol) at the CCSD/6-311G(d) level.

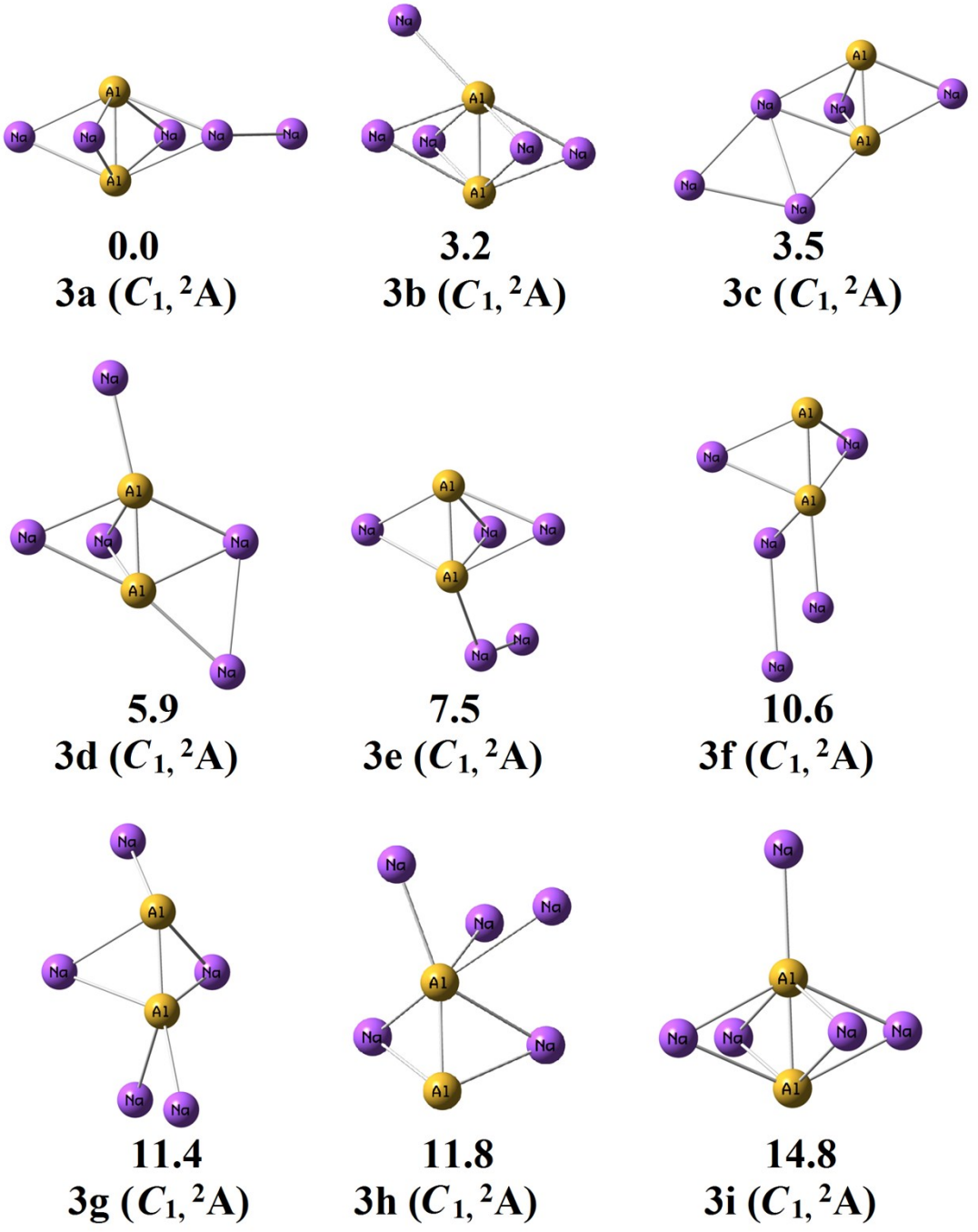


Figure S9. The lowest-lying isomers of Al_2Na_5. Optimized structures at the B3LYP/def2-TZVP level, relative single-point energies (kcal/mol) at the CCSD/6-311G(d) level.

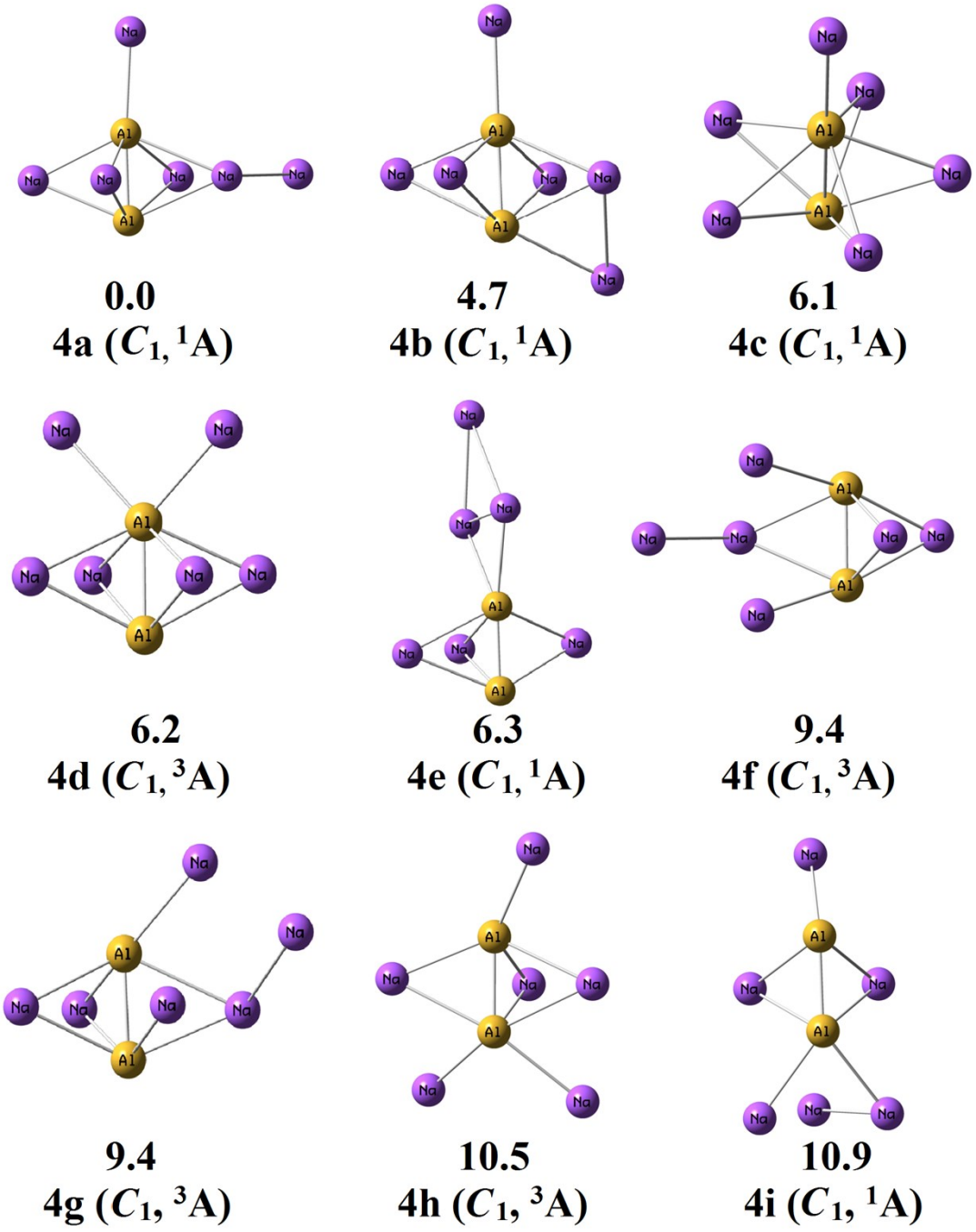


Figure S10. The lowest-lying isomers of Al_2Na_6. Optimized structures at the B3LYP/def2-TZVP level, relative single-point energies (kcal/mol) at the CCSD/6-311G(d) level.

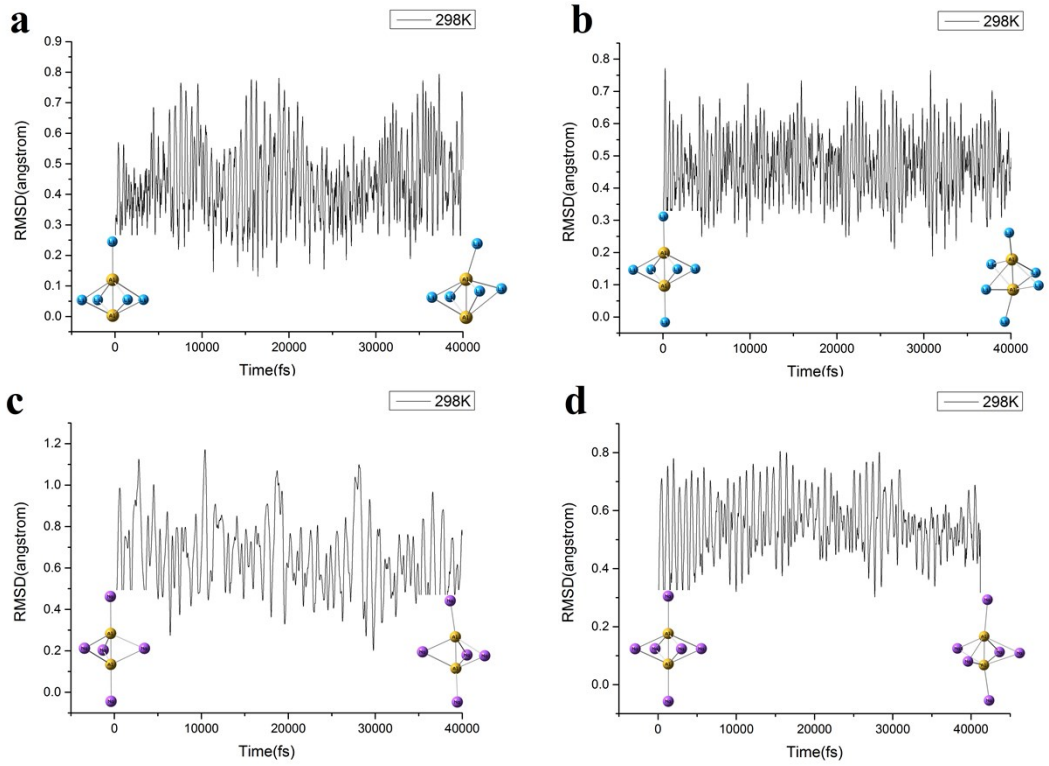
Table S2. Important results information of the structures of clusters, including the spin states, relative energies (kcal/mol), Al-Al bond length (R/Å), Wiberg Bond Indices (WBI_{Al-Al}) and NPA charge (NPA/|e|). They all calculated at the B3LYP/def2-TZVP level.

Molecule-Al_2Li_5	Spin States	Relative Energies(Kcal/mol)	R_{Al-Al}(Å)	WBI	NPA_{Al-Al}(|e|)
Ⅰ	Doublet	0.0	2.47	2.41	-1.172
Ⅱ	Doublet	1.0	2.57	1.69	-1.063
Ⅲ	Doublet	2.8	2.56	1.58	-1.085
Ⅳ	Doublet	3.1	2.45	1.81	-0.679
Ⅴ	Doublet	3.2	2.46	1.80	-0.698
Ⅵ	Doublet	3.4	2.67	1.14	-0.993
Ⅶ	Doublet	4.0	2.55	1.60	-1.010
Ⅷ	Doublet	12.7	2.49	1.58	-0.982
Ⅸ	Doublet	20.5	2.51	1.50	-0.719

Molecule-Al_2Li_6	Spin States	Relative Energies(Kcal/mol)	R_{Al-Al}(Å)	WBI	NPA_{Al-Al}(|e|)
Ⅰ	Singlet	0.0	2.54	2.38	-1.548
Ⅱ	Singlet	3.9	2.71	1.52	-1.237
Ⅲ	Triplet	4.5	2.57	1.41	-0.891
Ⅳ	Singlet	4.9	2.45	2.00	-0.998
Ⅴ	Singlet	5.1	2.66	1.44	-1.326
Ⅵ	Singlet	7.4	2.70	1.26	-1.388
Ⅶ	Triplet	8.3	2.56	1.39	-1.069
Ⅷ	Triplet	9.8	2.59	1.37	-1.189
Ⅸ	Triplet	11.7	2.63	1.10	-0.9569

Molecule-Al_2Na_5	Spin States	Relative Energies(Kcal/mol)	R_{Al-Al}(Å)	WBI	NPA_{Al-Al}(|e|)
Ⅰ	Doublet	0.0	2.52	2.35	-1.133
Ⅱ	Doublet	3.2	2.54	1.98	-1.066
Ⅲ	Doublet	3.5	2.50	1.89	-0.805
Ⅳ	Doublet	5.9	2.50	1.92	-1.034
Ⅴ	Doublet	7.5	2.51	1.86	-0.793
Ⅵ	Doublet	10.6	2.52	1.62	-0.694
Ⅶ	Doublet	11.4	2.51	1.70	-0.896
Ⅷ	Doublet	11.8	2.57	1.42	-0.866
Ⅸ	Doublet	14.8	2.53	2.13	-1.116

Molecule-Al_2Na_6	Spin States	Relative Energies(Kcal/mol)	R_{Al-Al}(Å)	WBI	NPA_{Al-Al}(|e|)
Ⅰ	Singlet	0.0	2.53	2.47	-1.4329
Ⅱ	Singlet	4.7	2.57	1.94	-1.1685
Ⅲ	Singlet	6.1	2.56	1.92	-1.0862
Ⅳ	Triplet	6.2	2.60	1.69	-1.2637
Ⅴ	Singlet	6.3	2.54	1.84	-0.9441
Ⅵ	Triplet	9.4	2.56	1.67	-0.9472
Ⅶ	Triplet	9.4	2.52	1.86	-0.9623
Ⅷ	Triplet	10.5	2.55	1.71	-1.1620
Ⅸ	Singlet	10.9	2.56	1.48	-0.7725



Figuer S11. Root-mean-square deviations (RMSD) of $Al_2Li_5^+$ (a), $Al_2Li_6^{2+}$ (b), $Al_2Na_5^+$ (c) and $Al_2Na_6^{2+}$ (d) during Born-Oppenheimer molecular dynamics (BOMD) simulations at 298K. The initial and final structural snapshots are also shown here.

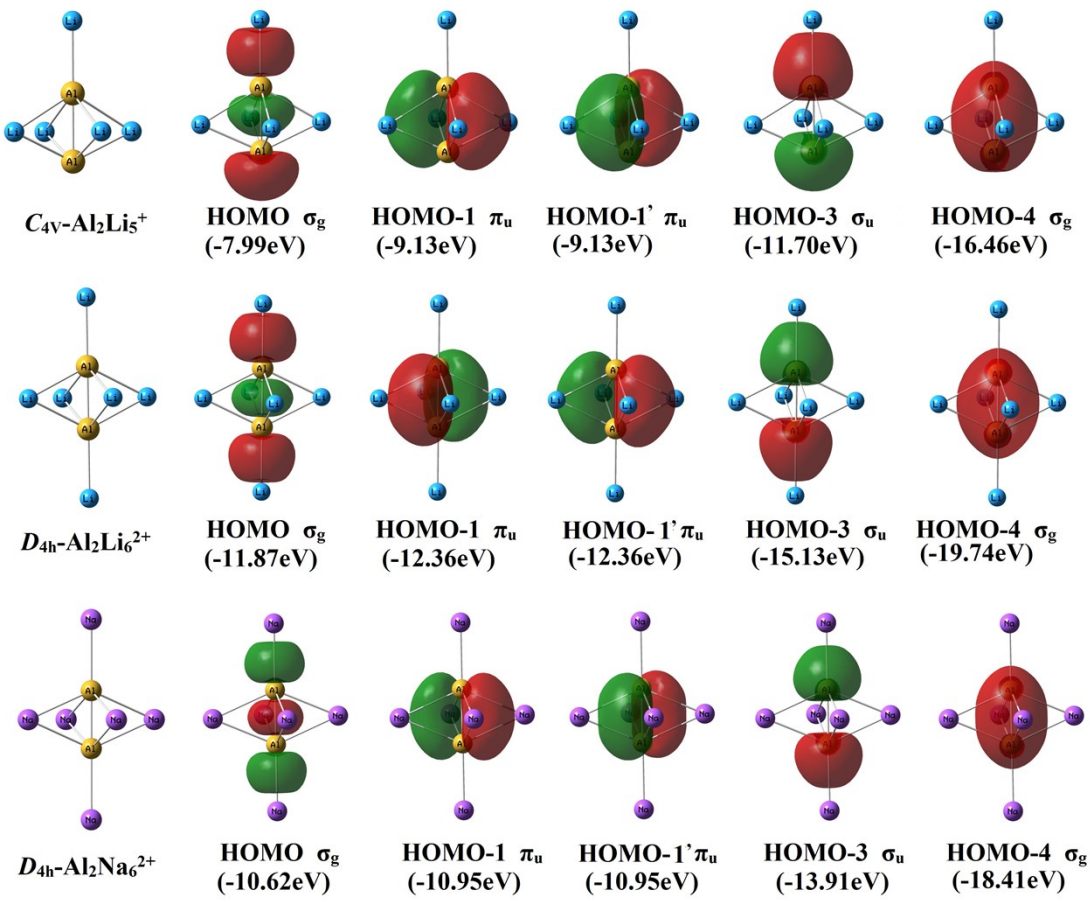


Figure S12. The global minimum of C_{4v}-$Al_2Li_5^+$ (a), D_{4h}-$Al_2Li_6^{2+}$ (b) and D_{4h}-$Al_2Na_6^{2+}$ (c) and their important FMOs at the CCSD/6-311G(d) level.

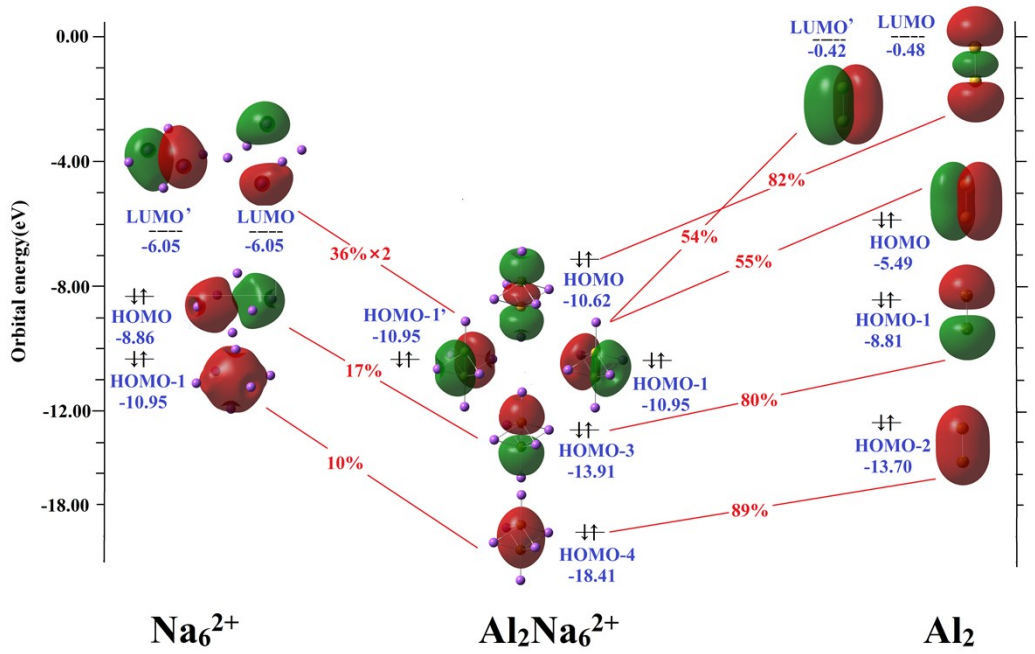


Figure S13. The dominant FMO correlation diagram in $Al_2Na_6^{2+}$ between Al_2 and Na_6^{2+} fragments calculated at the CCSD/6-311G(d) level. The horizontal dashed and solid lines represent virtual and occupied molecular orbitals, respectively. (the orbital energies are also given, unit: eV).

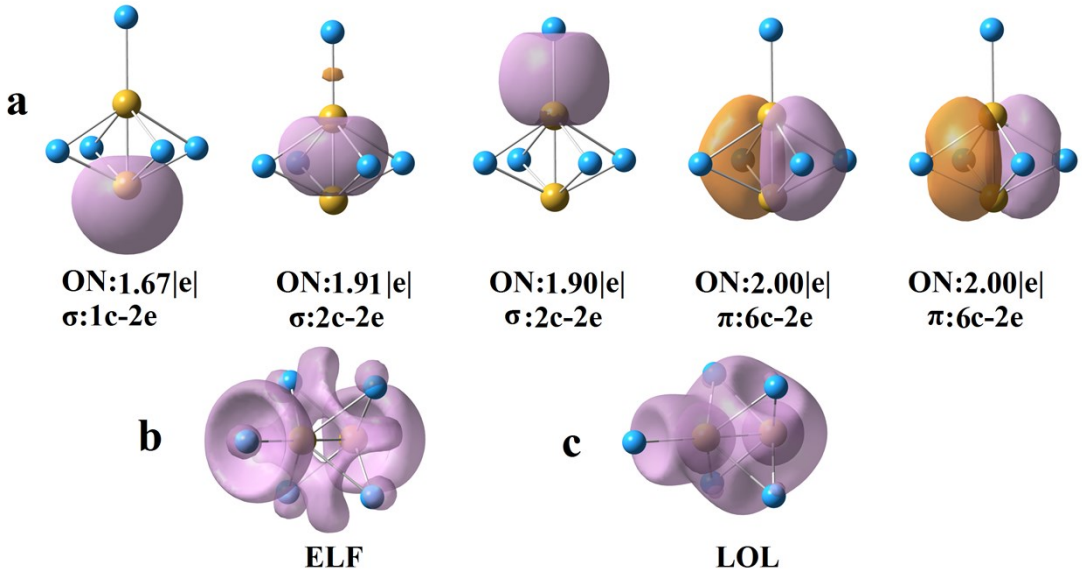


Figure S14. a) AdNDP orbitals. b) LOL profile. c) ELF profile for $Al_2Li_5^+$ at the CCSD/6-311G(d) level. ON stands for the occupation number.

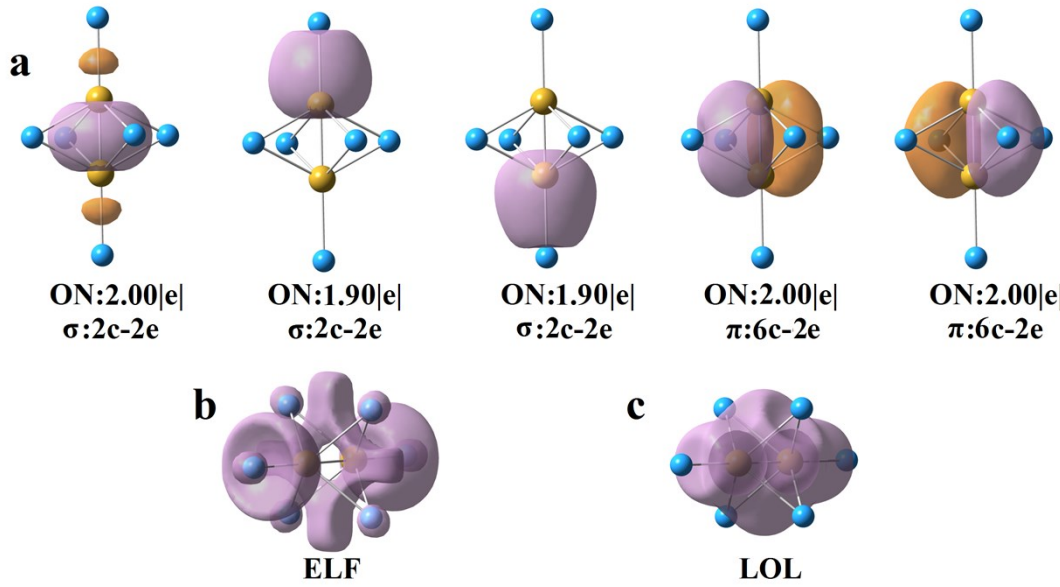


Figure S15. a) AdNDP orbitals. b) LOL profile. c) ELF profile for $Al_2Li_6^{2+}$ at the CCSD/6-311G(d) level. ON stands for the occupation number.

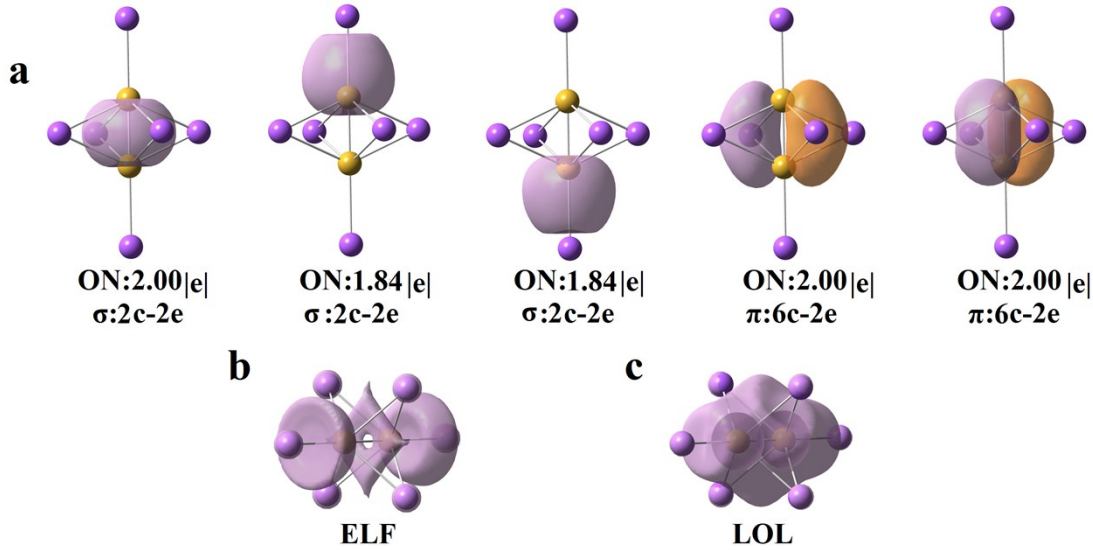


Figure S16. a) AdNDP orbitals. b) LOL profile. c) ELF profile for $Al_2Na_6^{2+}$ at the CCSD/6-311G(d) level. ON stands for the occupation number.

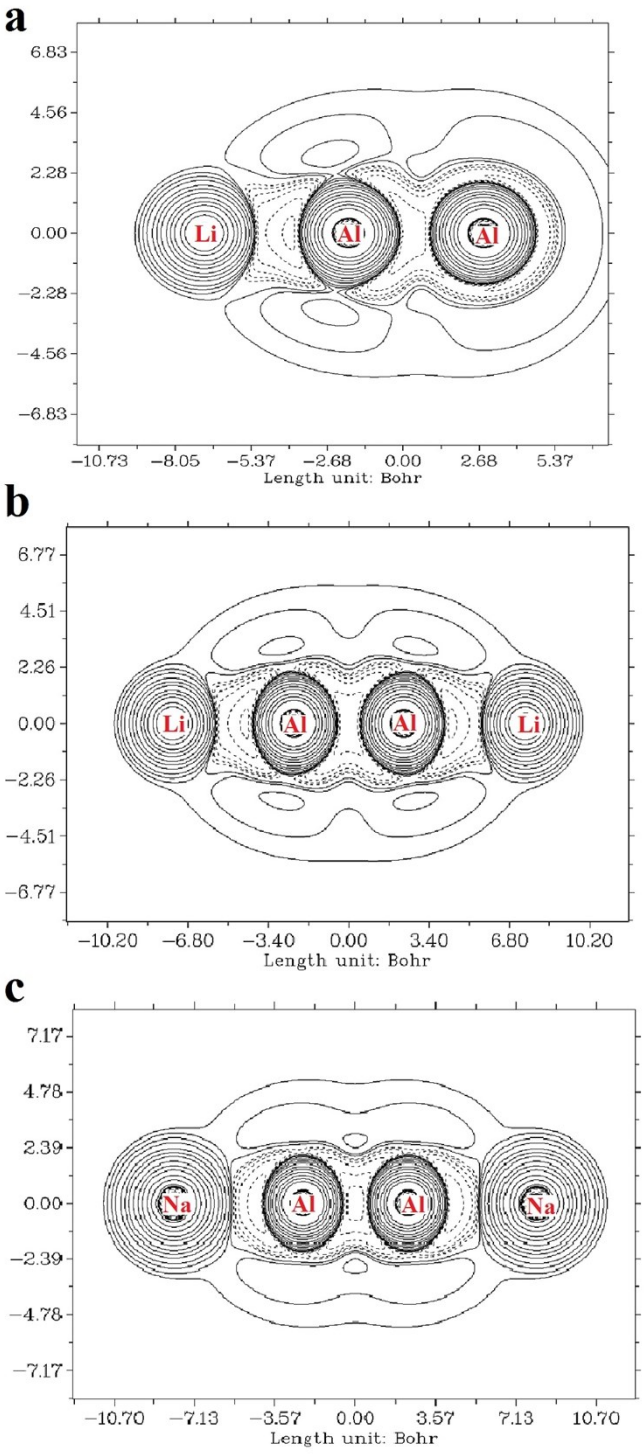


Figure S17. Laplacian plot of the electron density $\nabla^2\rho(r)$, of $Al_2Li_5^+$(a), $Al_2Li_6^{2+}$(b), $Al_2Na_6^{2+}$(c) in different perspectives. Solid and dashed lines correspond to positive and negative regions of $\nabla^2\rho$, respectively.

Scheme 1. Several potential reactions and thermodynamic values for the generation of C_1-Al_2Li_5, C_{4V}-$Al_2Li_5^+$, C_1-Al_2Li_6, D_{4h}-$Al_2Li_6^{2+}$, C_1-Al_2Na_5, D_{3h}-$Al_2Na_5^+$, C_1-Al_2Na_6 and D_{4h}-$Al_2Na_6^{2+}$.

$$\boldsymbol{D_{4h}\text{-}Al_2Li_4 + Li = C_1\text{-}Al_2Li_5} \qquad \boldsymbol{\Delta G = -22.05\ kcal/mol}$$

$$\boldsymbol{D_{4h}\text{-}Al_2Li_4 + Li^+ = C_{4V}\text{-}Al_2Li_5^+} \qquad \boldsymbol{\Delta G = -63.03 kcal/mol}$$

$$\boldsymbol{C_1\text{-}Al_2Li_5 + Li = C_1\text{-}Al_2Li_6} \qquad \boldsymbol{\Delta G = -29.17 kcal/mol}$$

$$\boldsymbol{D_{4h}\text{-}Al_2Li_4 + 2Li^+ = D_{4h}\text{-}Al_2Li_6^{2+}} \qquad \boldsymbol{\Delta G = -60.83 kacl/mol}$$

$$\boldsymbol{C_{4V}\text{-}Al_2Li_5^+ + Li^+ = D_{4h}\text{-}Al_2Li_6^{2+}} \qquad \boldsymbol{\Delta G = 2.19 kcal/mol}$$

$$\boldsymbol{D_{4h}\text{-}Al_2Na_4 + Na = C_1\text{-}Al_2Na_5} \qquad \boldsymbol{\Delta G = -15.67 kcal/mol}$$

$$\boldsymbol{D_{4h}\text{-}Al_2Na_4 + Na^+ = D_{3h}\text{-}Al_2Na_5^+} \qquad \boldsymbol{\Delta G = -56.18 kacl/mol}$$

$$\boldsymbol{C_1\text{-}Al_2Na_5 + Na = C_1\text{-}Al_2Na_6} \qquad \boldsymbol{\Delta G = -16.71 kcal/mol}$$

$$\boldsymbol{D_{4h}\text{-}Al_2Na_4 + 2Na^+ = D_{3h}\text{-}Al_2Na_6^{2+}} \qquad \boldsymbol{\Delta G = -51.66 kcal/mol}$$

$$\boldsymbol{D_{3h}\text{-}Al_2Na_5^+ + Na^+ = D_{4h}\text{-}Al_2Na_6^{2+}} \qquad \boldsymbol{\Delta G = 4.53 kacl/mol}$$

Table S3. Cartesian coordinates for optimized structures of $Al_2Li_5^+$, $Al_2Li_6^{2+}$, $Al_2Na_5^+$, and $Al_2Na_6^{2+}$ at the CCSD/6-311G(d) level.

$Al_2Li_5^+$ (C_{4v}, ^1A)

Li	0.00000000	2.42444450	0.39986648
Li	0.00000000	-2.42444450	0.39986648
Li	0.00000000	-0.00000000	-3.71594610
Li	-2.42444450	-0.00000000	0.39986648
Li	2.42444450	0.00000000	0.39986648
Al	0.00000000	-0.00000000	-1.02113346
Al	0.00000000	0.00000000	1.51055521

$Al_2Li_6^{2+}$ (D_{4h}, ^1A)

Li	-0.00000000	2.53027834	0.00000000
Li	-2.53027834	-0.00000000	0.00000000
Li	-0.00000000	-0.00000000	-3.95040198
Li	0.00000000	-0.00000000	3.95040198
Li	2.53027834	0.00000000	0.00000000
Li	0.00000000	-2.53027834	0.00000000
Al	0.00000000	0.00000000	1.23073334
Al	-0.00000000	0.00000000	-1.23073334

$Al_2Na_5^+$ (D_{3h}, ^1A)

Na	-0.00000000	2.79534858	0.00000000
Na	0.00000000	-0.00000000	-4.13069466
Na	-2.42084289	-1.39767429	0.00000000
Na	2.42084289	-1.39767429	0.00000000
Na	0.00000000	-0.00000000	4.13069466
Al	0.00000000	0.00000000	1.21780642
Al	-0.00000000	0.00000000	-1.21780642

$Al_2Na_6^{2+}$ (D_{4h}, ^1A)

Na	0.00000000	0.00000000	4.25676351
Na	-2.88787913	0.00000000	-0.00000000
Na	0.00000000	2.88787913	-0.00000000
Na	0.00000000	-2.88787913	-0.00000000
Na	2.88787913	0.00000000	-0.00000000
Na	-0.00000000	0.00000000	-4.25676351
Al	0.00000000	-0.00000000	-1.23073033
Al	0.00000000	-0.00000000	1.23073033

Table S4. Cartesian coordinates for optimized structures of Al_2Li_5, Al_2Li_6, Al_2Na_5, and Al_2Na_6 at the CCSD/6-311G(d) level.

Al_2Li_5 (C_1, ^2A)

Li	-1.740339	0.001070	-1.362101
Li	2.123506	-0.001946	1.663363
Li	-4.469773	0.000267	0.000118
Li	-1.740226	-0.001222	1.361546
Al	0.426721	-1.237231	-0.000855
Al	0.427333	1.237518	0.000513
Li	2.125933	0.000588	-1.661446

Al_2Li_6 (C_1,^1A)

Li	-1.318905	-0.782612	-1.412557
Li	2.175948	0.669665	1.609724
Li	2.176645	0.670054	-1.609066
Li	-2.686713	1.536697	-0.000032
Li	-4.189791	-1.230047	-0.000014
Li	-1.318715	-0.782506	1.412696
Al	1.211967	-1.124332	-0.000104
Al	-0.020845	1.105582	-0.000069

Al_2Na_5 (C_1, ^2A)

Na	-1.560299	-1.675054	0.001077
Na	2.857283	1.960853	0.000726
Na	-4.713753	0.000281	-0.000359
Na	-1.559958	1.673405	-0.000185
Al	0.894843	-0.000946	1.254129
Al	0.894688	-0.000418	-1.254557
Na	2.861826	-1.957872	-0.000752

Al_2Na_6 (C_1, ^1A)

Na	1.585168	-0.448075	1.674544
Na	1.586491	-0.463263	-1.673604
Na	4.769903	-0.352065	0.001093
Na	-0.290169	3.637125	-0.010148
Na	-2.823095	-0.565076	-1.935132
Na	-2.815274	-0.549277	1.943168
Al	-0.863198	0.723637	-0.004620
Al	-0.840131	-1.789257	0.004687