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Supporting Information available for:

The behavior of the Aluminum Trimer when Combining with Different Superatom Clusters

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1. Figures and Tables

Figure S1. The valence molecular orbitals of **IIfs**, which originates from (a) Al_3^- and (b) FLi_2^+ subunits, respectively.

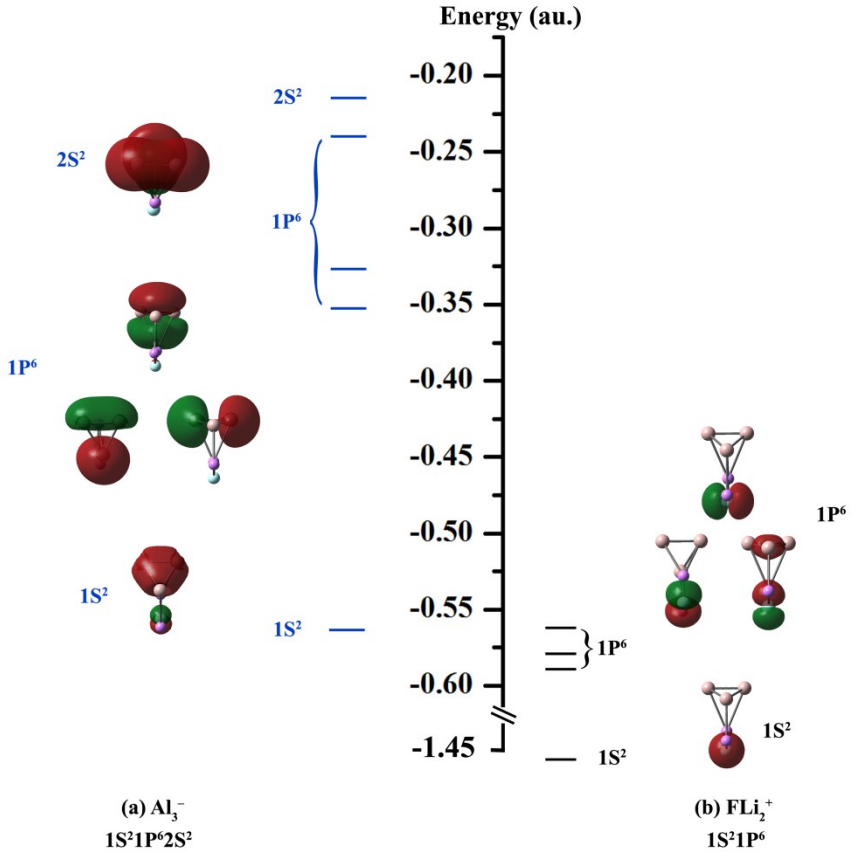
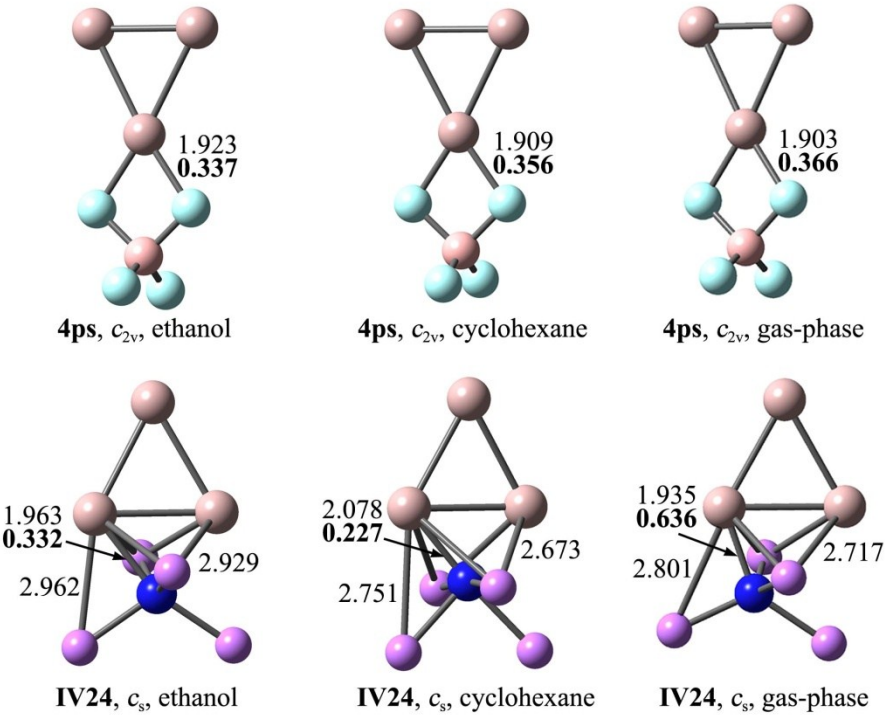


Figure S2. Optimized structures of the Al_3-BF_4 (**4ps**) and Al_3-NLi_4 (**IV-24**) compounds at the MP2/6-311+G(3df) level in solvent and gas phase, respectively. Bond lengths (Å) and Laplacian of the electron density at a bond critical point $\nabla^2\rho(r)$ (in au., bold font) that connects Al_3 and BF_4/NLi_4 subunits.



4ps, c_{2v}, ethanol

4ps, c_{2v}, cyclohexane

4ps, c_{2v}, gas-phase

IV24, c_s, ethanol

IV24, c_s, cyclohexane

IV24, c_s, gas-phase

Figure S3. The characteristic vibration mode of the (a) Al_3-BF_4 (**4ps**) and (b) Al_3-NLi_4 (**IV-24**) compounds in solvents and gas phase, respectively.

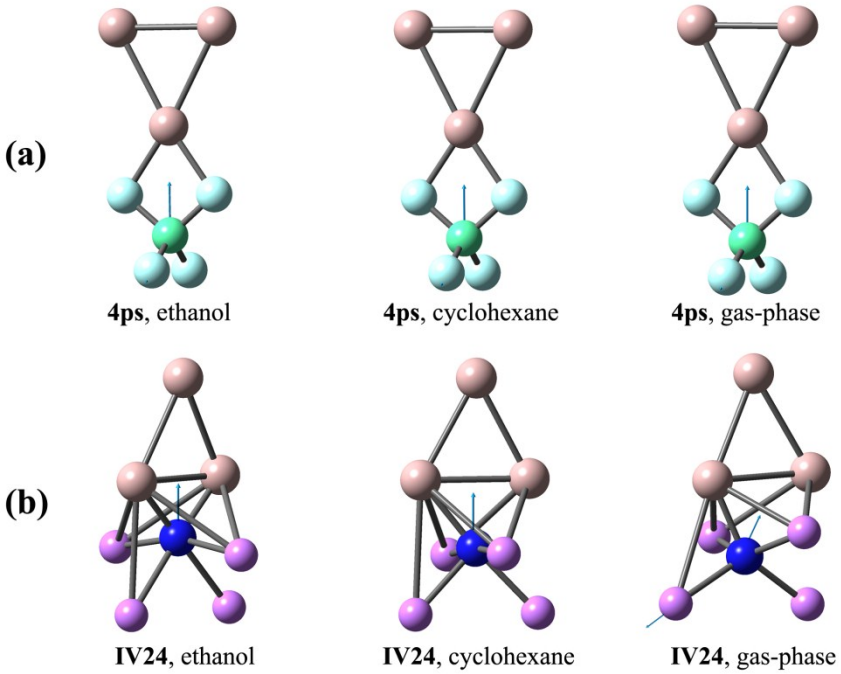


Figure S4. Valence molecular orbitals of Al_3^+ and Al_3^- ions.

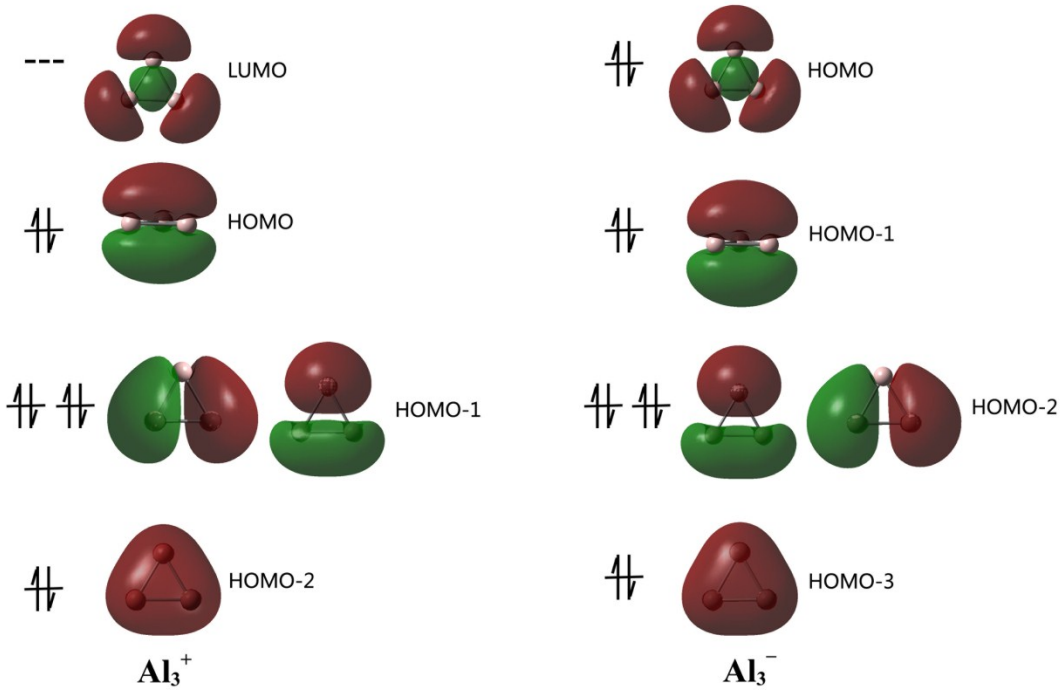


Table S1. The hardness (η, in eV) of the most stable Al_3-X and Al_3-M compounds.

species		η
Al_3-F	**1pp**	2.532
Al_3-LiF_2	**2ps-1**	2.472
Al_3-BeF_3	**3ps-1**	2.561
Al_3-BF_4	**4ps**	2.569
Al_3-Li	**Ifp**	2.513
Al_3-FLi_2	**IIfs**	2.436
Al_3-OLi_3	**III24-1**	2.004
Al_3-NLi_4	**IV24**	1.959

Table S2. Relative energies E_{rel} (kcal/mol), the lowest vibrational frequency υ_1 (cm^{-1}), the characteristic vibrational frequency υ (cm^{-1}) and corresponding IR intensity (km/mol), NBO charge on the Al_3 subunit (Q^{Al3}, |e|), HOMO-LUMO gaps (eV), binding energy per atom E_a (kcal/mol), bond energies E_b (kcal/mol), and the maximum negative NICS values ($NICS_{max}$, ppm) of the **4ps** and **IV-24** compounds.

Species		solvent	orientation	υ_1	υ	intensity	Q^{Al3}	gap	E_a	E_b	$NICS_{max}$
Al_3-BF_4	**4ps**	ethanol	point-to-side	20	1092.7	924.4	0.768	6.02	86.5	168.1	-30.0
		cyclohexane	point-to-side	27	1108.6	805.0	0.762	5.79	86.7	167.0	-30.4
		gap-phase	point-to-side	38	1121.4	711.2	0.757	5.68	86.9	166.4	-40.3
Al_3-NLi_4	**IV-24**	ethanol	side-to-face	101	636.5	1717.2	-0.559	4.65	60.9	176.0	-24.0
		cyclohexane	side-to-face	78	592.5	825.0	-0.737	4.35	55.0	116.0	-24.9
		gap-phase	side-to-face	24	646.9	208.0	-0.361	4.11	54.1	94.7	-28.5

Table S3. Location of the maximum negative NICS value of the Al_3-X compounds.

species		Location
Al_3-F	**1pp**	geometrical center of the Al_3 ring
	1sp	geometrical center of the Al_3 ring
Al_3-LiF_2	**2ps-1**	geometrical center of the Al_3 ring
	2ss	geometrical center of the Al_3 ring
Al_3-BeF_3	**3ps-1**	geometrical center of the Al_3 ring
	3ps-2	geometrical center of the Al_3 ring
	3ss	geometrical center of the Al_3 ring
	3ff	0.6 Å below (toward BeF_3 subunit) the geometrical center of the Al_3 ring
Al_3-BF_4	**4ps**	geometrical center of the Al_3 ring
	4ff	0.3 Å below (toward BF_4 subunit) the geometrical center of the Al_3 ring

Table S4. Location of the maximum negative NICS value of the Al_3-M compounds.

species		Location
Al_3-Li	**Ifp**	geometrical center of the Al_3 ring
	Ipp	geometrical center of the Al_3 ring
Al_3-FLi_2	**IIfs**	0.3 Å up (away from FLi_2 subunit) the geometrical center of the Al_3 ring
	IIss	geometrical center of the Al3Li2 cage
Al_3-OLi_3	**III24-1**	geometrical center of the Al_3 ring
	III24-2	geometrical center of the Al3Li2 cage
	IIIfs	0.3 Å up (away from OLi_3 subunit) the geometrical center of the Al_3 ring
Al_3-NLi_4	**IV24**	geometrical center of the Al_3 ring
	IVfs	geometrical center of the Al_3 ring

2. Cartesian coordinates and electronic states for the Al_3-X and Al_3-M compounds at the MP2/6-311+G(3df) level

(1) Al_3-X compounds

Al_3-F **1pp** with C_{2v} symmetry, 1-A1

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.55821600
Al	2.12500400	0.00000000	1.42437000
F	-0.78448400	0.00000000	-1.47024400

Al_3-F **1sp** with C_{2v} symmetry, 1-A1

Al	0.00000000	1.37416900	-0.34615100
Al	0.00000000	-1.37416900	-0.34615100
Al	0.00000000	0.00000000	1.82916300
F	0.00000000	0.00000000	-1.64213400

Al_3-LiF_2 **2ps-1** with C_{2v} symmetry, 1-A1

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.39292000
Al	2.30888800	0.00000000	1.19646000
Li	4.93796800	0.00000000	1.19646000
F	3.63804400	0.00000000	-0.02224200
F	3.63804400	0.00000000	2.41516200

Al_3-LiF_2 **2ss** with C_{2v} symmetry, 1-A'

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.51912300
Al	2.18976000	0.00000000	1.27377600
F	0.54811000	0.00000000	-1.70770000
F	3.40321200	0.00000000	-0.04691200
Li	2.37863600	0.00000000	-1.57008800

Al_3-LiF_2 **2ps-2** with C_s symmetry, 1-A'

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	3.19113300
Al	2.12356700	0.00000000	1.80171000
Li	-2.13782600	0.00000000	4.68895500
F	-1.06499400	-1.23265400	3.94468400
F	-1.06499400	1.23265400	3.94468400

Al_3-BeF_3 **3ps-1** with C_{2v} symmetry, 1-A1

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.56747500
Al	2.12578200	0.00000000	1.12769100
F	-1.84718500	0.00000000	6.04955800
Be	-1.19474100	0.00000000	4.81965100
F	-1.70956200	0.00000000	3.35620800
F	0.30564100	0.00000000	4.42523900

Al_3-BeF_3 **3ps-2** with C_{2v} symmetry, 1-A1

Al	0.00000000	0.00000000	0.19960600
Al	0.00000000	1.20007000	2.45598600
Al	0.00000000	-1.20007000	2.45598600
F	0.00000000	0.00000000	-3.74389600
F	-1.13689300	0.00000000	-1.29700600
Be	0.00000000	0.00000000	-2.35233600
F	1.13689300	0.00000000	-1.29700600

Al_3-BeF_3 **3ss** with C_{2v} symmetry, 1-A1

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.59820300

Al	2.21790400	0.00000000	1.35335100
F	3.14448700	0.00000000	3.01645500
F	0.93703700	0.00000000	4.25543900
Be	2.47135700	0.00000000	4.40312300
F	3.15380000	0.00000000	5.61900400

Al_3-BeF_3 **3ff** with C_{3v} symmetry, 1-A1

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.77043300
Al	2.39926600	0.00000000	1.38521500
F	2.33460700	1.97150600	1.38521600
F	0.03233000	1.97150600	2.71443700
F	0.03233000	1.97150600	0.05599600
Be	0.79975500	1.86919000	1.38521600

Al_3-BF_4 **4ps** with C_{2v} symmetry, 1-A1

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.55893400
Al	2.12551200	0.00000000	1.13403300
F	-1.53193700	1.14827600	5.43023500
B	-1.21844500	0.00000000	4.84266000
F	-1.53193700	-1.14827600	5.43023500
F	0.23969700	0.00000000	4.44650400
F	-1.70133200	0.00000000	3.41089900

Al_3-BF_4 **4ff** with C_{3v} symmetry, 1-A1

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.72492500
Al	2.35985400	0.00000000	1.36246200
F	0.12332900	2.10959700	2.51131200

F	2.11319600	2.10959700	1.36246200
F	0.12332900	2.10959700	0.21361200
B	0.78661800	2.66069900	1.36246200
F	0.78661800	3.98882600	1.36246200

(2) Al_3-M compounds

Al_3-Li **Ifp** with C_{3v} symmetry, 1-A1

Al	0.00000000	1.45053800	-0.17558500
Al	1.25620200	-0.72526900	-0.17558500
Al	-1.25620200	-0.72526900	-0.17558500
Li	0.00000000	0.00000000	2.28260800

Al_3-Li **Ipp** with C_{2v} symmetry, 1-A

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.55990900
Al	2.11427900	0.00000000	1.11666000
Li	-1.23896300	0.00000000	4.90567100

Al_3-FLi_2 **IIfs** with C_s symmetry, 1-A'

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.56930200
Al	2.12958300	0.00000000	1.13187700
Li	0.63742500	2.70837000	1.37001200
Li	-0.65864600	2.45539900	3.80851900
F	-0.05977200	3.57859600	2.68176000

Al_3-FLi_2 **II23** with C_s symmetry, 1-A'

Al	0.72620800	-1.62626800	0.00000000
Al	2.71799700	0.11200100	0.00000000
Al	-1.79995000	-1.04826500	0.00000000
Li	0.00000000	1.68150100	0.00000000

Li	-2.78773800	1.57294200	0.00000000
F	-1.44578800	2.61662000	0.00000000

Al_3-FLi_2 **IIss** with C_s symmetry, 1-A'

Al	0.72620800	-1.62626800	0.00000000
Al	2.71799700	0.11200100	0.00000000
Al	-1.79995000	-1.04826500	0.00000000
Li	0.00000000	1.68150100	0.00000000
Li	-2.78773800	1.57294200	0.00000000
F	-1.44578800	2.61662000	0.00000000

Al_3-OLi_3 **III24-1** with C_1 symmetry, 1-A

Al	-0.48540100	-0.55831800	-0.63292500
Al	1.13278300	1.36171400	-0.08674900
Al	1.83172900	-1.02077800	0.19311500
Li	-0.73431700	0.18079300	1.77249500
Li	-1.72533200	1.85807200	-0.23136900
Li	-3.07418300	-1.28452300	0.07959800
O	-1.95336800	0.07036700	0.24788700

Al_3-OLi_3 **III24-2** with C_s symmetry, 1-A'

Al	1.49055400	-0.91016900	0.00000000
Al	0.63650500	1.45484900	0.00000000
Al	-0.49670400	-2.34871300	0.00000000
Li	-1.17898900	0.13187000	1.26390400
Li	-1.17898900	0.13187000	-1.26390400
Li	-1.56292300	3.28946700	0.00000000
O	-1.17898900	1.59910000	0.00000000

Al_3-OLi_3 **IIIfs** with C_s symmetry, 1-A'

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.42820600
Al	2.24808600	0.00000000	1.21410300
Li	0.91226000	2.71836100	1.21410300
Li	3.49890400	2.58042900	1.21410300
O	2.28332400	3.81490300	1.21410300
Li	2.29645600	5.48559600	1.21410300

Al_3-NLi_4 **IV24** with C_s symmetry, 1-A'

Al	0.00000000	0.00000000	0.00000000
Al	0.00000000	0.00000000	2.61586900
Al	2.22252000	0.00000000	1.34916200
Li	4.41300800	0.00000000	3.09435900
N	2.56149600	0.00000000	3.25455200
Li	1.70706800	0.00000000	4.97906700
Li	1.88396900	-1.91609000	3.01698200
Li	1.88396900	1.91609000	3.01698200

Al_3-NLi_4 **IVfs** with C_s symmetry, 1-A'

N	-0.17173500	2.82849300	0.00000000
Li	-0.94260800	1.13806400	0.00000000
Li	-0.59183200	3.70240400	1.51400400
Li	1.55517300	2.19713500	0.00000000
Li	-0.59183200	3.70240400	-1.51400400
Al	-0.59183200	-1.67997400	-1.21513100
Al	-0.59183200	-1.67997400	1.21513100
Al	1.40792800	-0.64155000	0.00000000

(3) Al_3-BF_4 (**4ps**) and Al_3-NLi_4 (**IV24**) compounds in solvents

Al_3-BF_4 **4ps** with C_{2v} symmetry in ethanol solvent, 1-A1

Al	0.00000000	1.21188100	2.77884600
Al	0.00000000	0.00000000	0.52215500
Al	0.00000000	-1.21188100	2.77884600
F	-1.14520700	0.00000000	-2.75877500
B	0.00000000	0.00000000	-2.07192100
F	1.14520700	0.00000000	-2.75877500
F	0.00000000	-1.09783600	-1.05669200
F	0.00000000	1.09783600	-1.05669200

Al_3-BF_4 **4ps** with C_{2v} symmetry in cyclohexane solvent, 1-A1

Al	0.00000000	1.20776800	2.77085300
Al	0.00000000	0.00000000	0.51420700
Al	0.00000000	-1.20776800	2.77085300
F	-1.14674100	0.00000000	-2.75048100
B	0.00000000	0.00000000	-2.07561000
F	1.14674100	0.00000000	-2.75048100
F	0.00000000	-1.09908500	-1.04667600
F	0.00000000	1.09908500	-1.04667600

Al_3-NLi_4 **IV24** with C_s symmetry in ethanol solvent, 1-A'

Al	-0.16960200	2.38817100	0.00000000
Al	0.03636800	0.15948800	1.25057800
Al	0.03636800	0.15948800	-1.25057800
Li	0.03636800	-2.79792700	-1.40915300
N	0.09216700	-1.35276200	0.00000000
Li	0.03636800	-2.79792700	1.40915300
Li	-2.04909900	-1.47314700	0.00000000
Li	2.18105700	-1.50552200	0.00000000

Al_3-NLi_4 **IV24** with C_s symmetry in cyclohexane solvent, 1-A'

Al	-0.21504700	2.34030900	0.00000000
Al	0.05373100	0.08622100	1.25962600
Al	0.05373100	0.08622100	-1.25962600
Li	0.05373100	-2.64529800	-1.58908500
N	0.10961600	-1.56509600	0.00000000
Li	0.05373100	-2.64529800	1.58908500
Li	-2.03728200	-0.93574700	0.00000000
Li	2.14024600	-1.01035500	0.00000000