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 IIIs, which originates from (a) Al₃⁻ and (b) FLi₂⁺ 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.
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 ($\eta$, in eV) of the most stable Al$_3$-X and Al$_3$-M compounds.

| species    | $\eta$ |
|------------|---------|
| 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   | 1fp     | 2.513  |
| Al$_3$-LiF$_2$ | IIfs  | 2.436  |
| Al$_3$-OLi$_3$ | III24-1 | 2.004  |
| Al$_3$-NLi$_4$ | IV24  | 1.959  |
Table S2. Relative energies $E_{\text{rel}}$ (kcal/mol), the lowest vibrational frequency $\nu_1$ (cm$^{-1}$), the characteristic vibrational frequency $\nu$ (cm$^{-1}$) and corresponding IR intensity (km/mol), NBO charge on the Al$_3$ subunit ($Q^{\text{Al3}}$, |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$_{\text{max}}$, ppm) of the 4ps and IV-24 compounds.

| Species   | solvent | orientation | $\nu_1$ | $\nu$ | intensity | $Q^{\text{Al3}}$ | gap | $E_a$ | $E_b$ | NICS$_{\text{max}}$ |
|-----------|---------|-------------|---------|-------|-----------|-------------------|-----|------|------|---------------------|
| 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               |
| species        | Location                                      |
|---------------|-----------------------------------------------|
| Al\textsubscript{3}-F | 1pp, geometric center of the Al\textsubscript{3} ring |
|               | 1sp, geometric center of the Al\textsubscript{3} ring |
| Al\textsubscript{3}-LiF\textsubscript{2} | 2ps-1, geometric center of the Al\textsubscript{3} ring |
|               | 2ss, geometric center of the Al\textsubscript{3} ring |
| Al\textsubscript{3}-BeF\textsubscript{3} | 3ps-1, geometric center of the Al\textsubscript{3} ring |
|               | 3ps-2, geometric center of the Al\textsubscript{3} ring |
|               | 3ss, geometric center of the Al\textsubscript{3} ring |
|               | 3ff, 0.6 Å below (toward BeF\textsubscript{3} subunit) the geometric center of the Al\textsubscript{3} ring |
| Al\textsubscript{3}-BF\textsubscript{4} | 4ps, geometric center of the Al\textsubscript{3} ring |
|               | 4ff, 0.3 Å below (toward BF\textsubscript{4} subunit) the geometric center of the Al\textsubscript{3} ring |
| 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 Al$_3$ Li$_2$ cage                      |
| Al$_3$-OLi$_3$ | III24-1: geometrical center of the Al$_3$ ring                           |
|            | III24-2: geometrical center of the Al$_3$ Li$_2$ 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

|       | x        | y        | z        |
|-------|----------|----------|----------|
| Al    | 0.0000000 | 0.0000000 | 0.0000000 |
| Al    | 0.0000000 | 0.0000000 | 2.5582160 |
| Al    | 2.1250040 | 0.0000000 | 1.4243700 |
| F     | -0.7844840 | 0.0000000 | -1.4702440 |

Al$_3$-F $1sp$ with $C_{2v}$ symmetry, 1-A1

|       | x        | y        | z        |
|-------|----------|----------|----------|
| Al    | 0.0000000 | 1.3741690 | -0.3461510 |
| Al    | 0.0000000 |-1.3741690 | -0.3461510 |
| Al    | 0.0000000 | 0.0000000 | 1.8291630 |
| F     | 0.0000000 | 0.0000000 | -1.6421340 |

Al$_3$-LiF$_2$ $2ps$-1 with $C_{2v}$ symmetry, 1-A1

|       | x        | y        | z        |
|-------|----------|----------|----------|
| Al    | 0.0000000 | 0.0000000 | 0.0000000 |
| Al    | 0.0000000 | 0.0000000 | 2.3929200 |
| Al    | 2.3088880 | 0.0000000 | 1.1964600 |
| Li    | 4.9379680 | 0.0000000 | 1.1964600 |
| F     | 3.6380440 | 0.0000000 | -0.0222420 |
| F     | 3.6380440 | 0.0000000 | 2.4151620 |

Al$_3$-LiF$_2$ $2ss$ with $C_{2v}$ symmetry, 1-A’

|       | x        | y        | z        |
|-------|----------|----------|----------|
| Al    | 0.0000000 | 0.0000000 | 0.0000000 |
| Al    | 0.0000000 | 0.0000000 | 2.5191230 |
| Al    | 2.1897600 | 0.0000000 | 1.2737760 |
| F     | 0.5481100 | 0.0000000 | -1.7077000 |
| F     | 3.4032120 | 0.0000000 | -0.0469120 |
| Li    | 2.3786360 | 0.0000000 | -1.5700880 |
**Al₃-LiF₂ 2ps-2 with Cᵥ 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 |

**Al₃-BeF₃ 3ps-1 with Cᵥ 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 |

**Al₃-BeF₃ 3ps-2 with Cᵥ symmetry, 1-A1**

|        |         |         |         |
|--------|---------|---------|---------|
| Al     | 0.00000000 | 0.00000000 | 0.19960600 |
| Al     | 0.00000000 | 1.20007000 | 2.45598600 |
| Al     | 0.00000000 | -1.2000700 | 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 |

**Al₃-BeF₃ 3ss with Cᵥ symmetry, 1-A1**

|        |         |         |         |
|--------|---------|---------|---------|
| Al     | 0.00000000 | 0.00000000 | 0.00000000 |
| Al     | 0.00000000 | 0.00000000 | 2.59820300 |
| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| Al      | 2.2179 | 0.0000 | 1.3533 |
| F       | 3.1445 | 0.0000 | 3.0165 |
| F       | 0.9370 | 0.0000 | 4.2554 |
| Be      | 2.4714 | 0.0000 | 4.4032 |
| F       | 3.1538 | 0.0000 | 5.6190 |

**Al₃-BeF₃** with $C_{3v}$ symmetry, 1-A1

| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| Al      | 0.0000 | 0.0000 | 0.0000 |
| Al      | 0.0000 | 0.0000 | 2.7704 |
| Al      | 2.3993 | 0.0000 | 1.3852 |
| F       | 2.3346 | 1.9715 | 1.3852 |
| F       | 0.0323 | 1.9715 | 2.7144 |
| F       | 0.0323 | 1.9715 | 0.0559 |
| Be      | 0.7998 | 1.8692 | 1.3852 |

**Al₃-BF₄** with $C_{2v}$ symmetry, 1-A1

| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| Al      | 0.0000 | 0.0000 | 0.0000 |
| Al      | 0.0000 | 0.0000 | 2.5589 |
| Al      | 2.1255 | 0.0000 | 1.1340 |
| F       | -1.5319 | 1.1483 | 5.4302 |
| B       | -1.2184 | 0.0000 | 4.8426 |
| F       | -1.5319 | -1.1483 | 5.4302 |
| F       | 0.2397 | 0.0000 | 4.4465 |
| F       | -1.7013 | 0.0000 | 3.4109 |

**Al₃-BF₄** with $C_{3v}$ symmetry, 1-A1

| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| Al      | 0.0000 | 0.0000 | 0.0000 |
| Al      | 0.0000 | 0.0000 | 2.7249 |
| Al      | 2.3598 | 0.0000 | 1.3625 |
| F       | 0.1233 | 2.1096 | 2.5113 |
(2) Al$_3$-M compounds

Al$_3$-Li Ifp with $C$_3v symmetry, 1-A1

| Atom | X    | Y    | Z    |
|------|------|------|------|
| Al   | 0.0000000 | 1.4505380 | -0.1755850 |
| Al   | 1.2562020 | -0.7252690 | -0.1755850 |
| Al   | -1.2562020 | -0.7252690 | -0.1755850 |
| Li   | 0.0000000 | 0.0000000 | 2.2826080 |
| Element | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------|---------------|---------------|---------------|
| Li      | -2.78773800   | 1.57294200    | 0.00000000    |
| F       | -1.44578800   | 2.61662000    | 0.00000000    |

**Al	extsubscript{3}FLi	extsubscript{2}I	extsubscript{I}ss** with C	extsubscript{s} symmetry, 1-A'

| Element | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------|---------------|---------------|---------------|
| 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	extsubscript{3}OLi	extsubscript{3}III	extsubscript{2}4-1** with C	extsubscript{1} symmetry, 1-A

| Element | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------|---------------|---------------|---------------|
| 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	extsubscript{3}OLi	extsubscript{3}III	extsubscript{2}4-2** with C	extsubscript{s} symmetry, 1-A'

| Element | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------|---------------|---------------|---------------|
| 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	extsubscript{3}OLi	extsubscript{3}III	extsubscript{fs}** with C	extsubscript{s} symmetry, 1-A'

| Element | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------|---------------|---------------|---------------|
| Al      | -2.78773800   | 1.57294200    | 0.00000000    |
| F       | -1.44578800   | 2.61662000    | 0.00000000    |
| Element | X | Y | Z |
|---------|---|---|---|
| Al      | 0.0000000 | 0.0000000 | 0.0000000 |
| Al      | 0.0000000 | 0.0000000 | 2.4282060 |
| Al      | 2.2480860 | 0.0000000 | 1.2141030 |
| Li      | 0.9122600 | 2.7183610 | 1.2141030 |
| Li      | 3.4989040 | 2.5804290 | 1.2141030 |
| O       | 2.2833240 | 3.8149030 | 1.2141030 |
| Li      | 2.2964560 | 5.4855960 | 1.2141030 |

**Al₃-NLi₄ IV²⁴ with C₃ symmetry, 1-A'**

| Element | X | Y | Z |
|---------|---|---|---|
| Al      | 0.0000000 | 0.0000000 | 0.0000000 |
| Al      | 0.0000000 | 0.0000000 | 2.6158690 |
| Al      | 2.2225200 | 0.0000000 | 1.3491620 |
| Li      | 4.4130800 | 0.0000000 | 3.0943590 |
| N       | 2.5614960 | 0.0000000 | 3.2545520 |
| Li      | 1.7070680 | 0.0000000 | 4.9790670 |
| Li      | 1.8839690 | -1.9160900 | 3.0169820 |
| Li      | 1.8839690 | 1.9160900 | 3.0169820 |

**Al₃-NLi₄ IV⁰ with C₃ symmetry, 1-A'**

| Element | X | Y | Z |
|---------|---|---|---|
| N       | -0.1717350 | 2.8284930 | 0.0000000 |
| Li      | -0.9426080 | 1.1380640 | 0.0000000 |
| Li      | -0.5918320 | 3.7024040 | 1.5140040 |
| Li      | 1.5551730 | 2.1971350 | 0.0000000 |
| Li      | -0.5918320 | 3.7024040 | -1.5140040 |
| Al      | -0.5918320 | -1.6799740 | -1.2151310 |
| Al      | -0.5918320 | -1.6799740 | 1.2151310 |
| Al      | 1.4079280 | -0.6415500 | 0.0000000 |

(3) Al₃-BF₄ (⁴ps) and Al₃-NLi₄ (IV²⁴) compounds in solvents

Al₃-BF₄ ⁴ps with C₂ᵥ symmetry in ethanol solvent, 1-A1
| Atoms  | X      | Y      | Z       |
|--------|--------|--------|---------|
| 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\textsubscript{3}-BF\textsubscript{4} 4ps with C\textsubscript{2v} symmetry in cyclohexane solvent, 1-A1**

| Atoms  | X      | Y      | Z       |
|--------|--------|--------|---------|
| 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\textsubscript{3}-NLi\textsubscript{4} IV24 with C\textsubscript{s} symmetry in ethanol solvent, 1-A’**

| Atoms  | X      | Y      | Z       |
|--------|--------|--------|---------|
| 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\textsubscript{3}-NLi\textsubscript{4} IV24 with C\textsubscript{s} symmetry in cyclohexane solvent, 1-A’**
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| Al      | -0.2150 | 2.3403  | 0.0000  |
| Al      | 0.0537  | 0.0862  | 1.2596  |
| Al      | 0.0537  | 0.0862  | -1.2596 |
| Li      | 0.0537  | -2.6453 | -1.5891 |
| N       | 0.1096  | -1.5651 | 0.0000  |
| Li      | 0.0537  | -2.6453 | 1.5891  |
| Li      | -2.0373 | -0.9357 | 0.0000  |
| Li      | 2.1403  | -1.0104 | 0.0000  |