Electronic Supplementary Information

All-metal Baird aromaticity

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Table S1. Relative energies (kcal mol^{-1}) in the lowest-lying singlet and triplet states.

	Closed-shell singlet	Triplet	Open-shell singlet
CBD [B3LYP]	0.0	5.9	\
CBD [CCSD(T)]	0.0 (*0.012*)[a]	11.9 (*0.011*)	\
Al_4^{4-} [B3LYP]	0.0	1.6	\
Al_4^{4-} [CCSD(T)]	0.0 (*0.080*)	3.0 (*0.097*)	\
$Li_3Al_4^-$ [B3LYP]	0.0	-0.5	-1.0
$Li_3Al_4^-$ [CCSD(T)]	0.0 (*0.025*)	0.9 (*0.056*)	2.0 (*0.059*)
$Li_3Ga_4^-$ [B3LYP]	0.0	-1.7	-2.1
$Li_3Ga_4^-$ [CCSD(T)]	0.0 (*0.020*)	-1.8 (*0.035*)	-0.9 (*0.035*)
Be_2B_6 [B3LYP]	0.0	-8.2	-5.4
Be_2B_6 [CCSD(T)]	0.0 (*0.024*)	-2.7 (*0.020*)	1.6 (*0.045*)
$Be_2B_7^+$ [B3LYP]	0.0	-12.6	-9.2
$Be_2B_7^+$ [CCSD(T)]	0.0 (*0.021*)	-7.3 (*0.018*)	-2.7 (*0.029*)

[a] The T_1 diagnostic values are given in parentheses. Except for the triplet states of Al_4^{4-} and $Li_3Al_4^-$, the T_1 test is below the recommended threshold of 0.044 for open-shell species (see ref. J. C. Rienstra-Kiracofe, W. D. Allen, H. F. Schaefer III, J. *Phys. Chem. A* 2000, **104**, 9823–9840). For closed-shell species the T_1 recommended threshold is 0.02. Except for the closed-shell singlet states of Al_4^{4-}, the T_1 test of closed-shell singlets is below the recommended threshold.

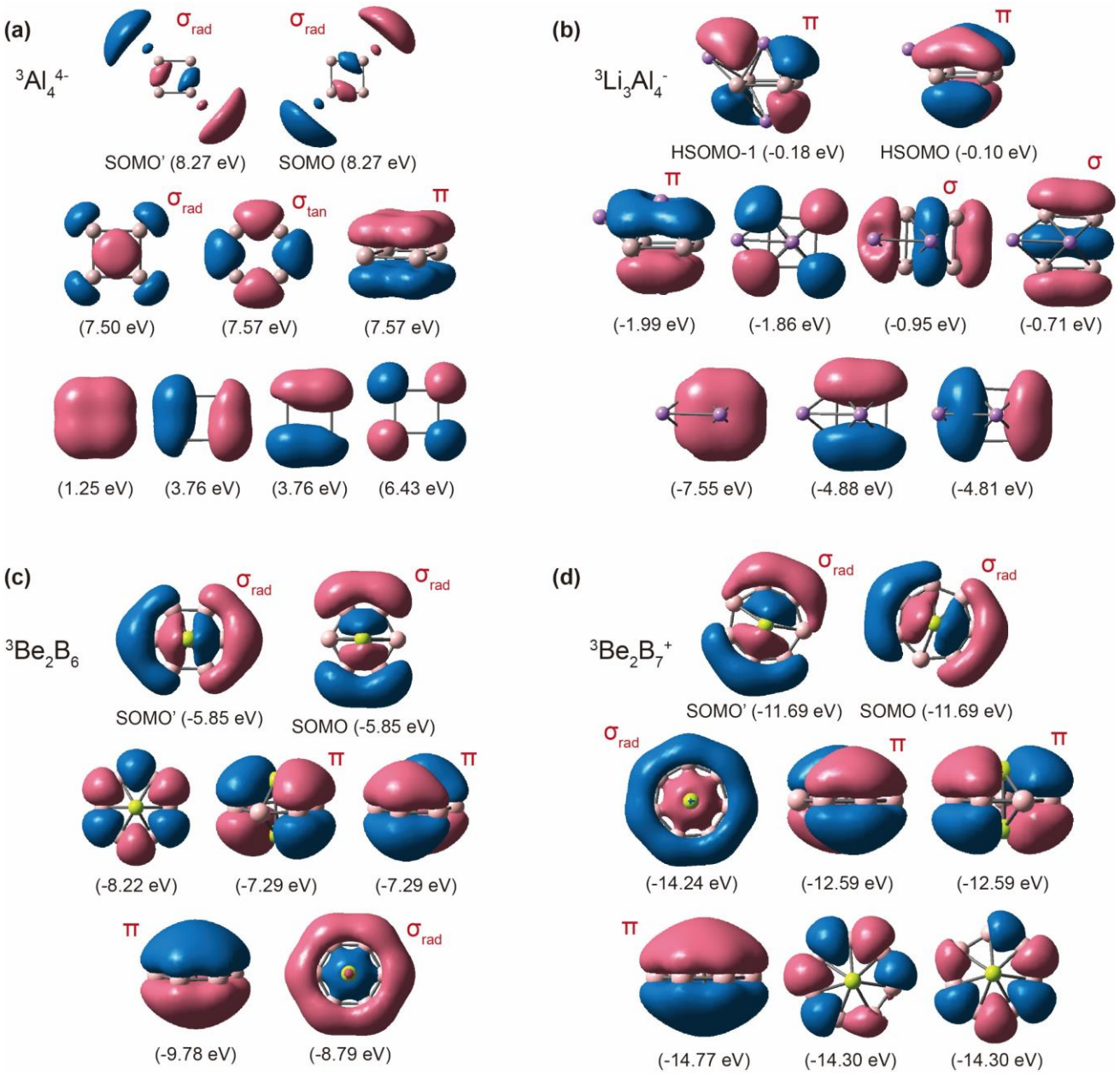

Fig. S1 Valence molecular orbitals of $^3Al_4^{4-}$ (a), $^3Li_3Al_4^-$ (b), $^3Be_2B_6$ (c), and $^3Be_2B_7^+$ (d) in the α subspaces at the UB3LYP level. The isovalue for MOs is 0.03 a.u., except for the SOMOs of $^3Al_4^{4-}$ (0.02 a.u.).

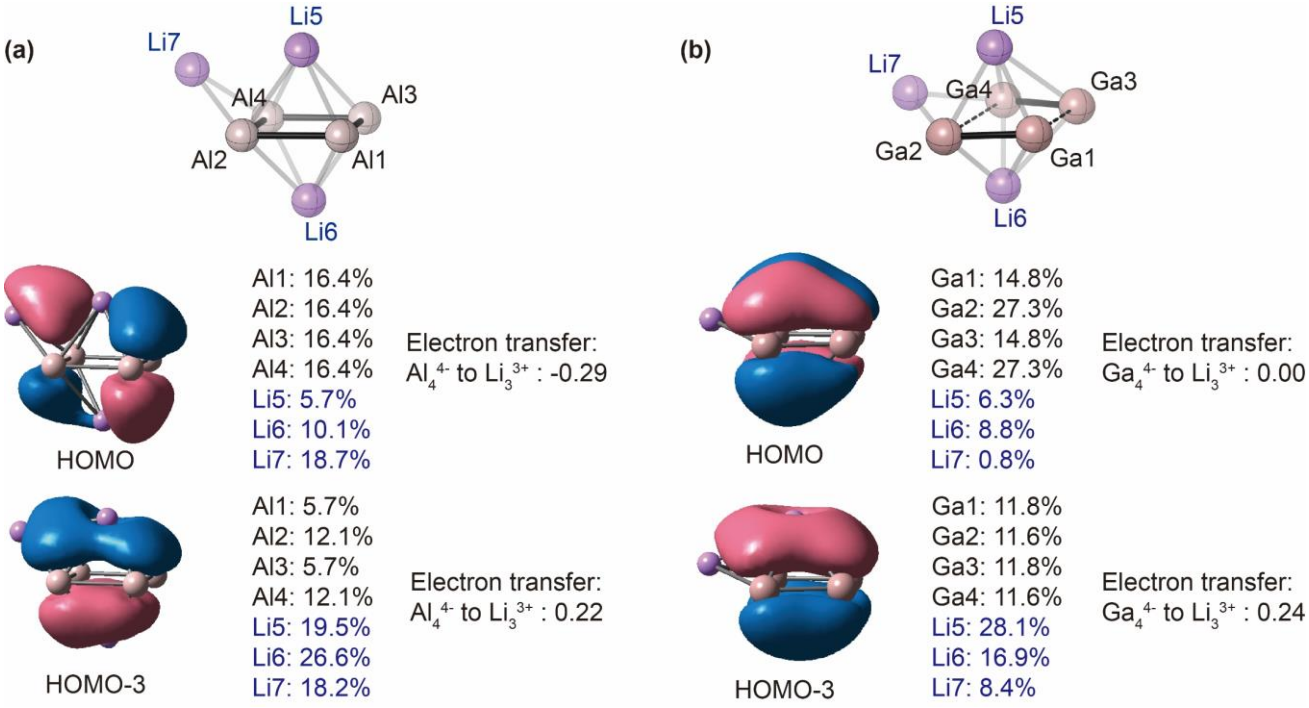

Fig. S2 Orbital and charge decomposition analyses for closed-shell $^1Li_3Al_4^-$ (a) and $^1Li_3Ga_4^-$ (b). The atomic contributions of π MOs (HOMO and HOMO-3) were calculated using the Ros-Schuit partition implemented in the Multiwfn program. In the formation of the HOMO of $^1Li_3Al_4^-$, 0.29 electrons are transferred from Li_3^{3+} to Al_4^{4-}, whereas almost no electron transfer occurs in the formation of the HOMO of $^1Li_3Ga_4^-$. Isovalue for MO contours: 0.03 a.u.

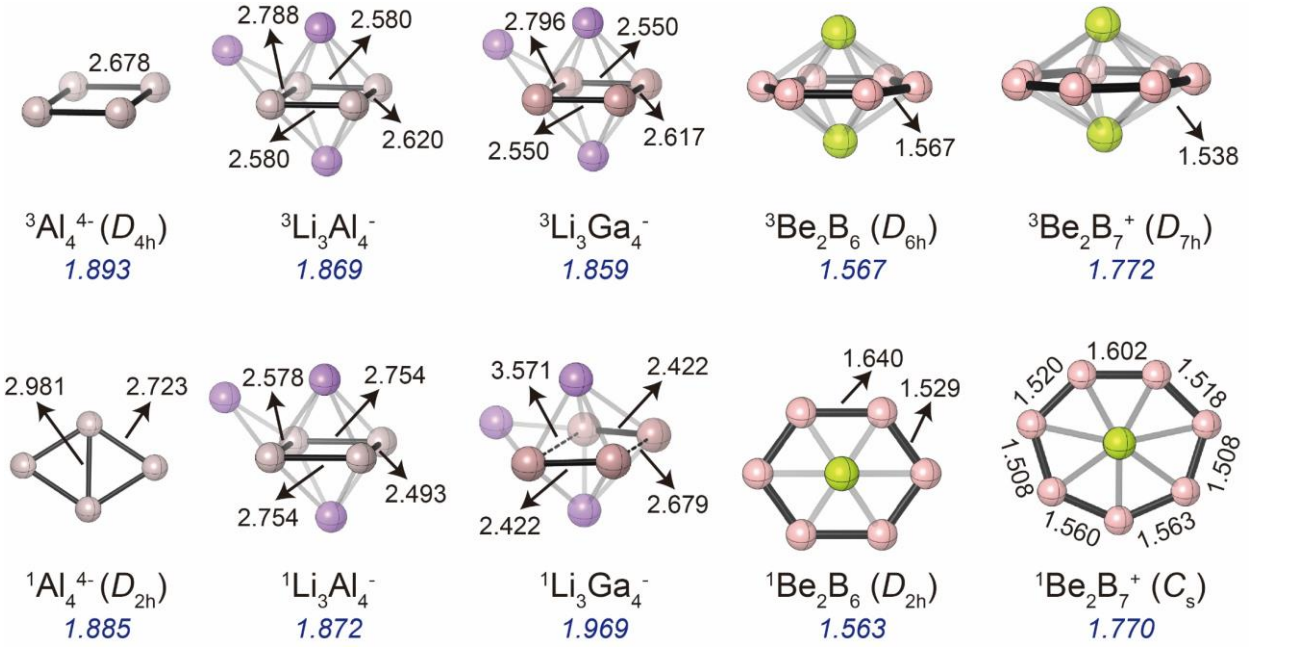

Fig. S3 Optimized geometries of Al_4^{4-} (a), $Li_3Al_4^-$ (b), $Li_3Ga_4^-$ (c), Be_2B_6 (d), and $Be_2B_7^+$ (e) in the spinless singlet state and the triplet state. Bond lengths are given in Å. Averaged distances (Å) from geometry centers to ring atoms are given in italic. Although the 4MR of $^1Li_3Ga_4^-$ is nearly broken, the HOMO-3 (Fig. S2) shows a complete conjugated pathway formed by four 4*p* orbitals without phase inversion.

Table S2. Cartesian coordinates of optimized structures

Singlet CBD

E(B3LYP/aug-cc-pVTZ) = -154.736858397 a.u.

C 0.000116 0.664539 0.787163
C -0.000116 -0.664539 0.787163
C -0.000116 0.664522 -0.787211
C 0.000116 -0.664522 -0.787211
H 0.000270 -1.428964 -1.548318
H -0.000270 1.428964 -1.548318
H 0.000228 1.428653 1.548609
H -0.000228 -1.428653 1.548609

Triplet CBD

E(UB3LYP/aug-cc-pVTZ) = -154.727446531 a.u.

C 0.000000 1.015421 0.000000
C 1.015421 0.000000 0.000000
C 0.000000 -1.015421 0.000000
C -1.015421 0.000000 0.000000
H 0.000000 2.092814 0.000000
H 2.092814 0.000000 0.000000
H 0.000000 -2.092814 0.000000
H -2.092814 0.000000 0.000000

$^{3}Al_4^{4-}$

E(UB3LYP/6-311+G(d)) = -969.259216348 a.u.

Al -1.639308 0.947217 -0.000026
Al -0.947317 -1.639150 0.000026
Al 0.947310 1.639166 0.000026
Al 1.639315 -0.947233 -0.000026

$^{1}Al_4^{4-}$ (spinless)

E(B3LYP/6-311+G(d)) = -969.261690653 a.u.

Al 0.000000 1.491077 0.000000
Al 0.000000 0.000000 2.278657
Al 0.000000 0.000000 -2.278657
Al 0.000000 -1.491077 0.000000

$^{1}Al_4^{4-}$ (open-shell)

E(UB3LYP/6-311+G(d)) = -969.261862931 a.u.

Al 0.000000 1.502263 0.000000
Al 0.000000 0.000000 2.265225
Al 0.000000 0.000000 -2.265225
Al 0.000000 -1.502263 0.000000

$^{3}Li_3Al_4^{-}$

E(UB3LYP/aug-cc-pVTZ) = -992.453906665 a.u.

Al 1.440986 -1.309773 0.136356
Al -1.111256 -1.394117 -0.233350
Al 1.441029 1.309915 0.136434
Al -1.111102 1.394250 -0.233161
Li -0.203236 -0.001335 2.027265
Li 0.415275 -0.000356 -2.061178
Li -3.070552 0.000501 0.873373

$^{1}Li_3Al_4^{-}$ (spinless)

E(B3LYP/aug-cc-pVTZ) = -992.453111550 a.u.

Al 1.521326 -1.246665 0.140725
Al -1.203200 -1.288856 -0.256416
Al 1.521274 1.246705 0.140708
Al -1.203193 1.288866 -0.256401
Li -0.118604 -0.000095 2.036980
Li 0.491504 -0.000100 -2.077885
Li -3.129796 -0.000023 1.043570

$^1Li_3Al_4^-$ (open-shell)

E(UB3LYP/aug-cc-pVTZ) = -992.454683584 a.u.

Al 1.471862 -1.284970 0.137363

Al -1.150714 -1.340970 -0.242942

Al 1.471865 1.284966 0.137356

Al -1.150713 1.340970 -0.242941

Li -0.146361 0.000017 2.034069

Li 0.456315 -0.000001 -2.067493

Li -3.093257 0.000001 0.948471

$^3Li_4Al_4$

E(UB3LYP/aug-cc-pVTZ) = -999.949164991 a.u.

Al 1.229189 -1.359107 0.286656

Al -1.228413 -1.360077 -0.284824

Al 1.229055 1.359013 0.287394

Al -1.228203 1.360068 -0.285580

Li -0.457464 0.000048 2.057419

Li 0.455550 -0.000065 -2.056942

Li -3.339510 0.000224 0.623487

Li 3.334369 0.000240 -0.639760

$^3Li_3Ga_4^-$

E(UB3LYP/aug-cc-pVTZ(-PP)) = -1060.88192531 a.u.

Ga 1.341547 -1.311107 0.048475

Ga -1.202315 -1.395353 -0.108212

Ga 1.347119 1.305395 0.048582

Ga -1.196331 1.400449 -0.108301

Li -0.116285 0.000143 2.063586

Li 0.109205 -0.000213 -2.023477

Li -2.989787 0.006431 1.194256

$^1Li_3Ga_4^-$ (spinless)

E(B3LYP/aug-cc-pVTZ(-PP)) = -1060.87926169 a.u.

Ga -1.339688 -1.279423 0.017859

Ga -1.785573 1.100364 -0.046473

Ga 1.339701 -1.279416 0.017875

Ga 1.785561 1.100376 -0.046485

Li 0.000002 0.337407 1.912968

Li -0.000001 0.406838 -1.879320

Li -0.000009 2.956117 0.557667

$^1Li_3Ga_4^-$ (open-shell)

E(UB3LYP/aug-cc-pVTZ(-PP)) = -1060.88254479 a.u.

Ga 1.397919 -1.266520 0.049526

Ga -1.259661 -1.312115 -0.113898

Ga 1.398030 1.266464 0.049532

Ga -1.259691 1.312131 -0.113918

Li -0.025192 0.000249 2.060406

Li 0.194724 0.000149 -2.033988

Li -3.027699 0.000019 1.304093

$^3Li_4Ga_4$

E(UB3LYP/aug-cc-pVTZ(-PP)) = -1068.37664250 a.u.

Ga 1.235171 1.357035 -0.140827

Ga -1.234993 1.357245 0.140638

Ga 1.235079 -1.357042 -0.141450

Ga -1.234926 -1.357232 0.141259

Li -0.169661 0.000226 -2.077834

Li 0.167994 0.000221 2.078178

Li -3.149972 -0.000245 -1.029999

Li 3.148226 -0.000274 1.033578

$^3Be_2B_6$

E(UB3LYP/aug-cc-pVTZ) = -178.452779837 a.u.

B -1.567523 0.006047 0.000001

B -0.788957 -1.354391 0.000000

B 0.778481 -1.360439 0.000000

B 1.567522 -0.006050 0.000000

B 0.788958 1.354391 0.000000

B -0.778481 1.360439 0.000000

Be -0.000001 0.000002 1.101389

Be 0.000000 0.000002 -1.101390

$^1Be_2B_6$ (spinless)

E(B3LYP/aug-cc-pVTZ) = -178.439716326 a.u.

B -0.820200 1.242967 -0.000006

B -1.711415 0.000014 0.000000

B -0.820224 -1.242946 0.000008

B 0.820208 -1.242966 -0.000003

B 1.711402 -0.000003 -0.000005

B 0.820219 1.242967 0.000004

Be 0.000008 -0.000021 1.135658

Be 0.000007 -0.000019 -1.135656

$^1Be_2B_6$ (open-shell)

E(UB3LYP/aug-cc-pVTZ) = -178.448293217 a.u.

B 1.334617 0.844378 0.000123

B -0.065792 1.539970 -0.000101

B -1.405865 0.729724 -0.000015

B -1.335205 -0.844841 0.000094

B 0.065615 -1.539587 -0.000032

B 1.406435 -0.730021 -0.000162

Be 0.000129 0.000263 1.103299

Be 0.000115 0.000209 -1.103182

$^3Be_2B_7^+$

E(UB3LYP/aug-cc-pVTZ) = -203.045898508 a.u.

B -0.129027 1.767318 0.000001

B -0.650578 -1.648338 0.000000

B -1.694337 -0.519073 0.000000

B 1.751761 -0.267487 0.000000

B 1.301346 1.202814 0.000000

B -1.462243 1.001055 0.000000

B 0.883083 -1.536373 0.000000

Be -0.000003 0.000052 1.075573

Be -0.000003 0.000051 -1.075573

$^1Be_2B_7^+$ (spinless)

E(B3LYP/aug-cc-pVTZ) = -203.025889953 a.u.

B 1.888525 0.380320 -0.000003

B -1.874170 0.422080 0.000002

B -0.781233 1.478103 0.000001

B -0.023098 -1.658298 0.000002

B 1.417995 -1.052817 0.000001

B 0.820253 1.459340 -0.000003

B -1.448826 -1.025044 0.000003

Be 0.000343 -0.002306 1.100837

Be 0.000350 -0.002300 -1.100840

$^1Be_2B_7^+$ (open-shell)

E(UB3LYP/aug-cc-pVTZ) = -203.040619985 a.u.

B 0.528334 -1.675909 -0.000096

B 0.249523 1.739874 -0.000005

B 1.533196 0.897425 0.000045

B -1.745207 -0.142449 0.000036

B -0.999473 -1.486778 0.000033

B 1.659484 -0.637421 0.000012

B -1.227230 1.304919 -0.000010

Be 0.000864 0.000215 1.075825

Be 0.000852 0.000208 -1.075845