Supplementary Information

18-valence-electron rule lighted planar tetracoordinate carbon and nitrogen: the global energy minima of CAl_4Zn and NAl_4Zn^+

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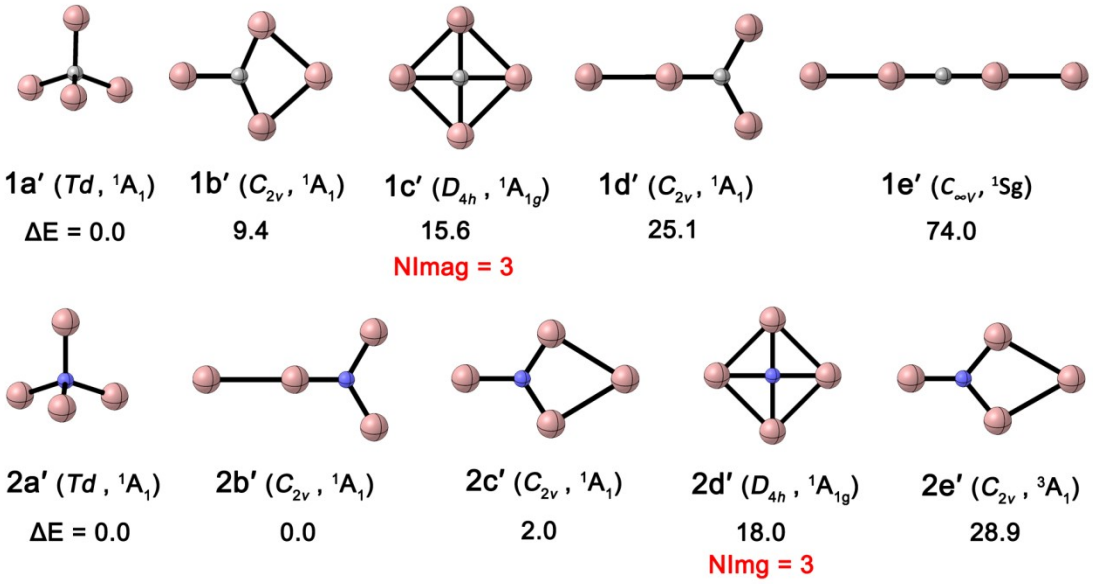

Fig.S1 Structures and relative energies (ΔE, in kcal mol^{-1} at CCSD(T) + ZPE$_{B2PLYP\text{-}D3(BJ)}$ level) of CAl_4 (**1a′**), NAl_4^+ (**2a′**) and their low-energy isomers.

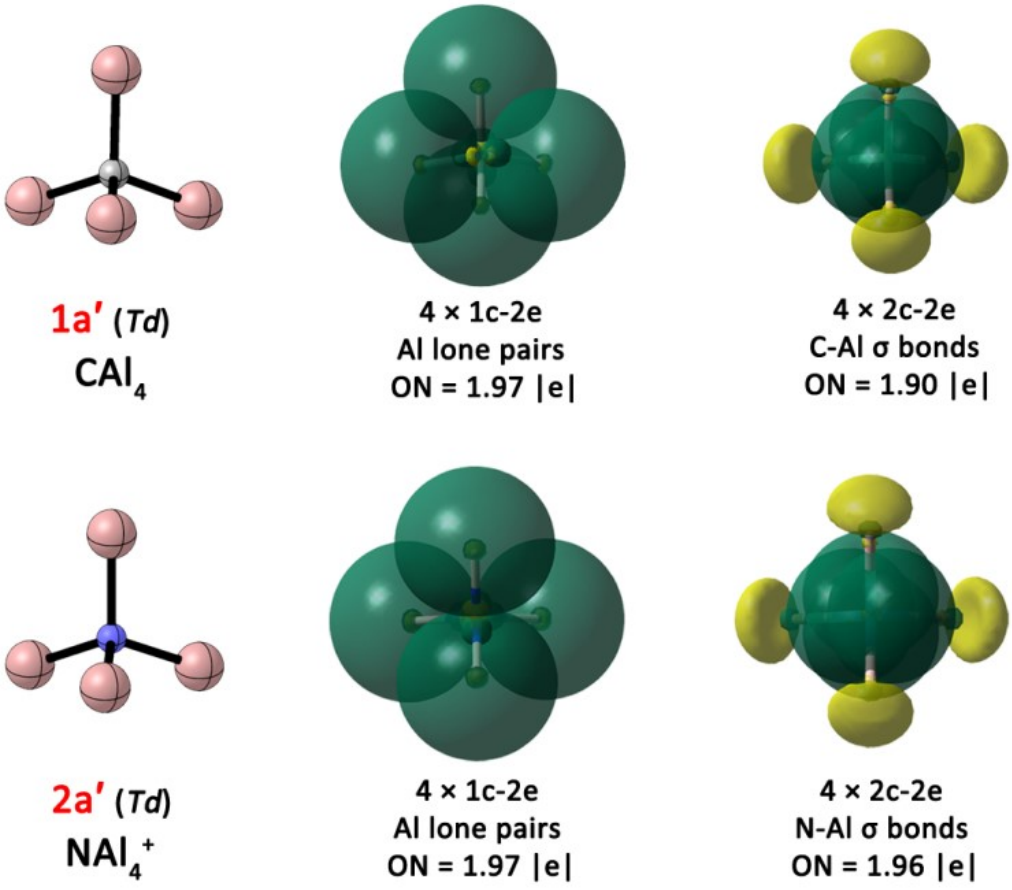

Fig.S2 AdNDP bonding patterns with occupation numbers (ONs) of CAl_4 and NAl_4^+ (**1a′** and **2a′**).

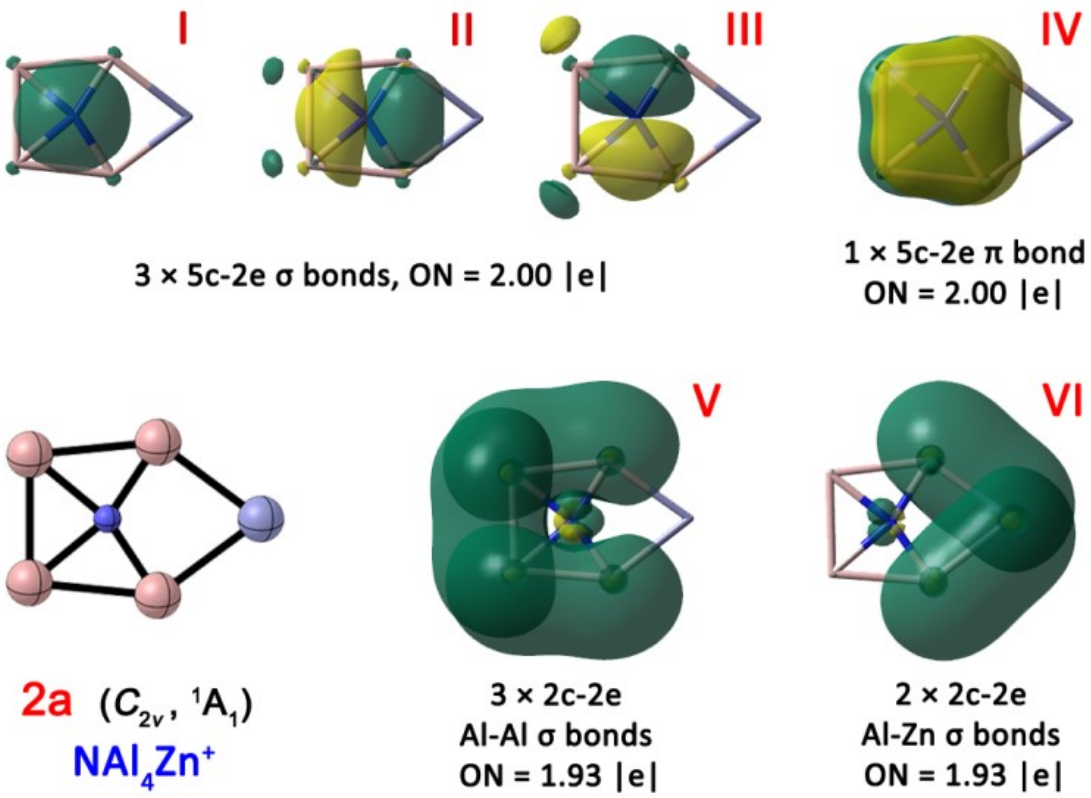

Fig.S3 AdNDP bonding patterns with occupation numbers (ONs) of NAl_4Zn^+ (**2a**).

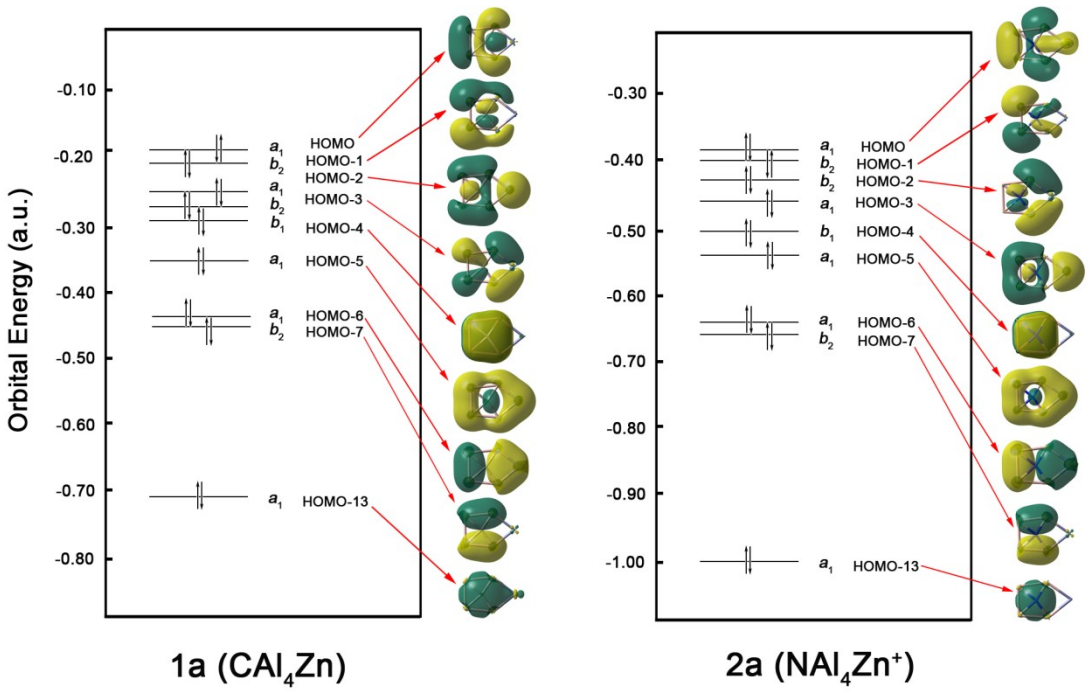

Fig.S4 The orbital energy spectrums and the valence canonical molecular orbitals of **1a** and **2a**.

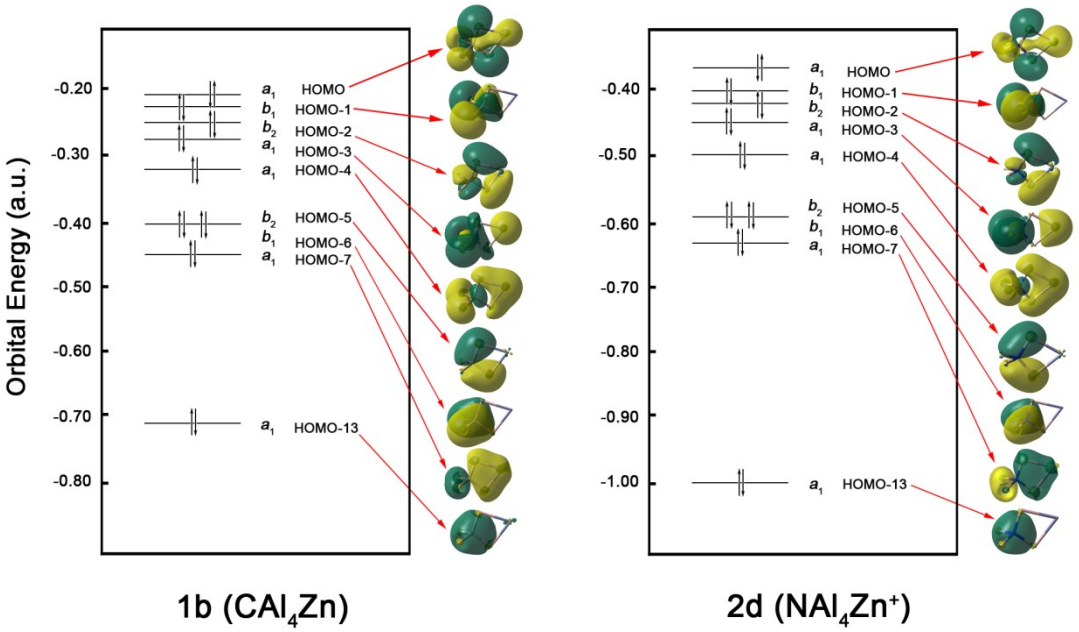

Fig.S5 The orbital energy spectrums and the valence canonical molecular orbitals of **1b** and **2d**.

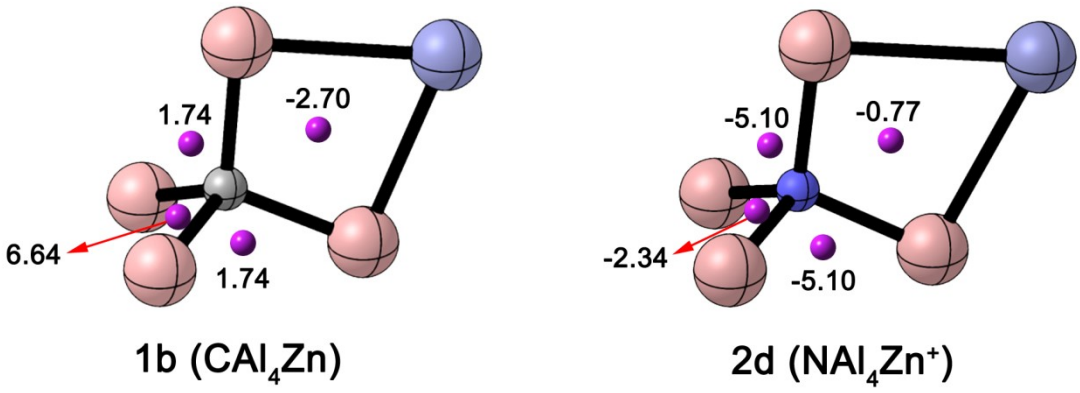

Fig.S6 The NICS results for **1b** and **2d** at the B3LYP/aug-cc-pVTZ level. The unit of NICS values is in ppm.

B2PLYP-D3(BJ)/aug-cc-pVTZ-optimized structures for structures shown in **Fig. 2**.

1a

C	0.00000000	0.00000000	-0.91643600
Al	0.00000000	1.33574000	-2.49650500
Al	0.00000000	-1.33574000	-2.49650500
Al	0.00000000	1.59862500	0.16667700
Al	0.00000000	-1.59862500	0.16667700
Zn	0.00000000	0.00000000	2.20247100

1b

C	0.00000000	0.00000000	-1.18064600
Al	0.00000000	1.64667300	-0.00159500
Al	1.64184800	0.00000000	-2.35164300
Al	0.00000000	-1.64667300	-0.00159500
Al	-1.64184800	0.00000000	-2.35164300
Zn	0.00000000	0.00000000	2.27560200

1c

C	-1.36927300	0.83856400	0.49849000
Al	-0.08500500	2.09604900	-0.26196500
Al	-2.53630300	-0.11738400	-0.69812400
Al	-0.39748000	-0.31123100	1.66965200
Al	-0.27068200	-1.91770500	-0.39720100
Zn	1.69929200	-0.05926200	-0.23505500

1d

C	-0.60267300	1.45886900	0.00000000
Al	0.10614600	0.93380900	1.69438700
Al	1.98015300	-0.06659100	0.00000000
Al	0.10614600	0.93380900	-1.69438700
Al	-2.15924200	2.63561900	0.00000000

Zn	0.10614600	-2.21432100	0.00000000

1e

C	1.71760000	0.54220100	0.00000000
Al	0.00000000	1.27163100	0.00000000
Al	1.43853600	-1.33917800	0.00000000
Al	3.36846300	1.57181300	0.00000000
Al	-2.78113100	1.15816500	0.00000000
Zn	-1.22139600	-1.26216000	0.00000000

2a

N	0.00000000	0.00000000	-0.89893200
Al	0.00000000	1.57159900	0.13727200
Al	0.00000000	-1.31541000	-2.49360900
Al	0.00000000	-1.57159900	0.13727200
Al	0.00000000	1.31541000	-2.49360900
Zn	0.00000000	0.00000000	2.25190900

2b

N	1.66838900	0.63774200	0.00000000
Al	-2.92779100	1.08248100	0.00000000
Al	3.24516100	1.69378100	0.00000000
Al	1.64017500	-1.21955900	0.00000000
Al	0.00000000	1.31014000	0.00000000
Zn	-1.23756100	-1.39110500	0.00000000

2c

N	0.96617800	-0.61848800	0.00000000
Al	2.35175500	2.67556300	0.00000000
Al	-0.12033100	-2.14352800	0.00000000

Al	0.00000000	0.95915200	0.00000000
Al	2.75227900	-0.31200500	0.00000000
Zn	-2.38504600	-0.36666400	0.00000000

2d

Al	0.00000000	1.64146000	-0.08343100
Al	1.64174800	0.00000000	-2.40311400
Al	0.00000000	-1.64146000	-0.08343100
Al	-1.64174800	0.00000000	-2.40311400
Zn	0.00000000	0.00000000	2.44629000
N	0.00000000	0.00000000	-1.24836200

2e

N	0.00000000	0.00000000	-0.54463700
Al	0.00000000	0.00000000	-5.33575900
Al	0.00000000	0.00000000	-2.30442200
Al	0.00000000	1.60341600	0.46930800
Al	0.00000000	-1.60341600	0.46930800
Zn	0.00000000	0.00000000	3.03109400