Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Unveiling the potential of superalkali cation Li_3^+ for capturing nitrogen

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Table S1 Second order stabilization energies (kcal/mol) of the orbital interactions in the low-lying $Li_3^+(N_2)_n$ (n = 1-4) complexes.

	LP (N1)→ s(Li1)	LP (N2)→ s(Li2)	LP (N2)→ s(Li1)	LP (N3)→ s(Li3)	LP (N3)→ s(Li2)	LP (N3)→ s(Li1)	LP (N4)→ s(Li3)	LP (N4)→ s(Li2)	LP (N4)→ s(Li1)
I	11.72								
II-1	12.04	12.04							
II-2	12.33		12.33						
III-1	12.30	12.30		12.30					
III-2	12.53		12.53	12.36					
III-3	13.49		13.49			13.40			
IV-1	12.59		12.59		12.68		12.68		
IV-2	13.55		13.57			13.57		12.57	
IV-3	12.77		12.77		12.77			12.77	
IV-4	13.63		13.63			13.63			13.63

Table S2 NMR shielding constants and ^{15}N chemical shifts (both in ppm) of the lowest-lying $Li_3^+(N_2)_n$ (n = 1–4) complexes at the MP2/6-311+G(d) computational level.

System	σ Li1	σ Li3	σ N1	σ N1’	σ N4	σ N4’	δ predicted (N1)	δ predicted (N1′)
$Li_3^+(N_2)$	91.95	94.61	-10.72	-42.55			-95.5	-64.0
$Li_3^+(N_2)_2$	92.05	95.15	-11.29	-41.66			-95.0	-64.8
$Li_3^+(N_2)_3$	92.24	92.24	-11.90	-40.62			-94.4	-65.9
$Li_3^+(N_2)_4$	92.47	91.42	-12.20	-39.67	-19.23	-42.35	-94.1	-66.8

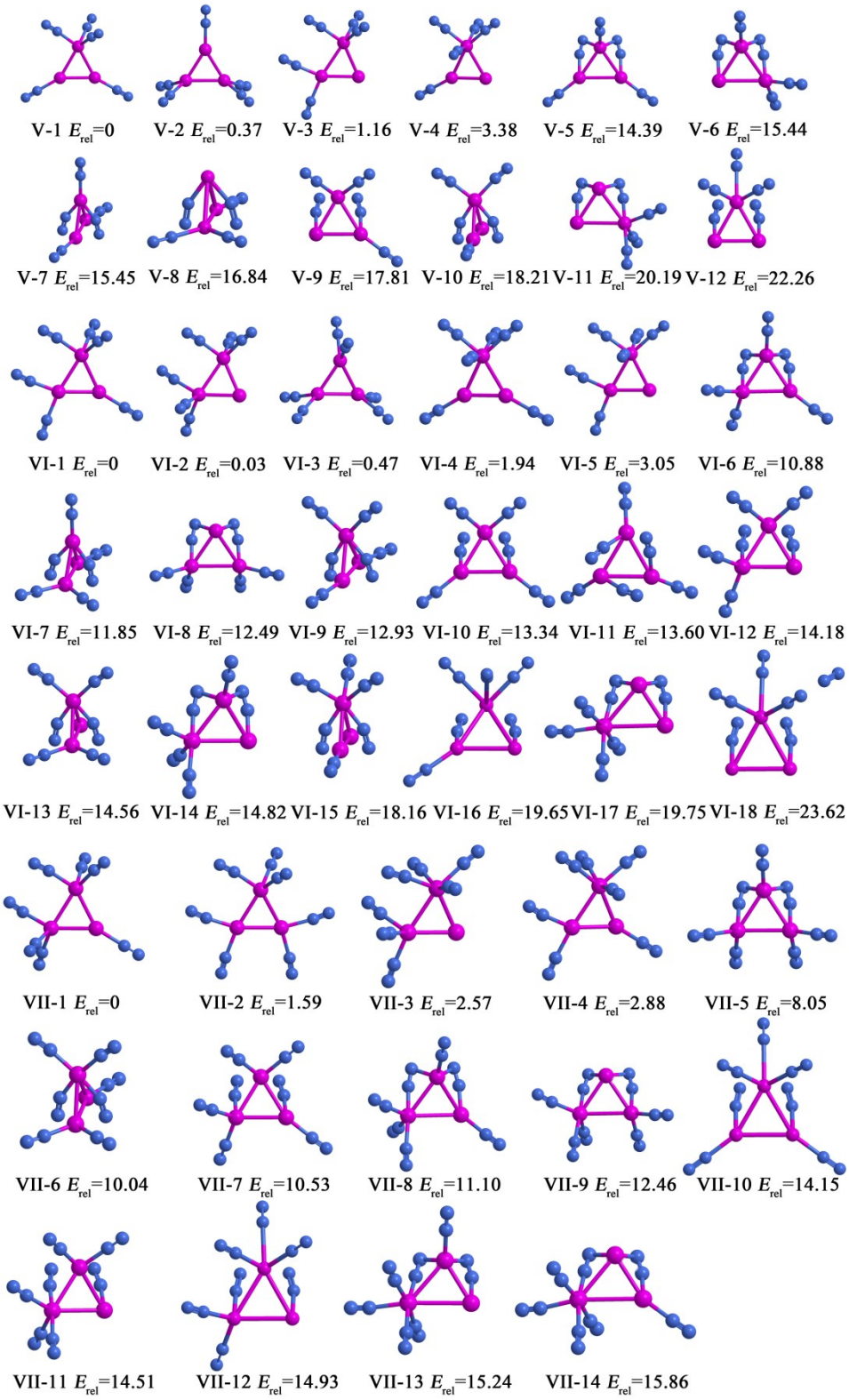

Fig. S1 Optimized structures of the $Li_3^+(N_2)_n$ (n = 5–7) complexes and their relative energies (E_{rel}, in kcal/mol) at the MP2/6-311+G(d) level.

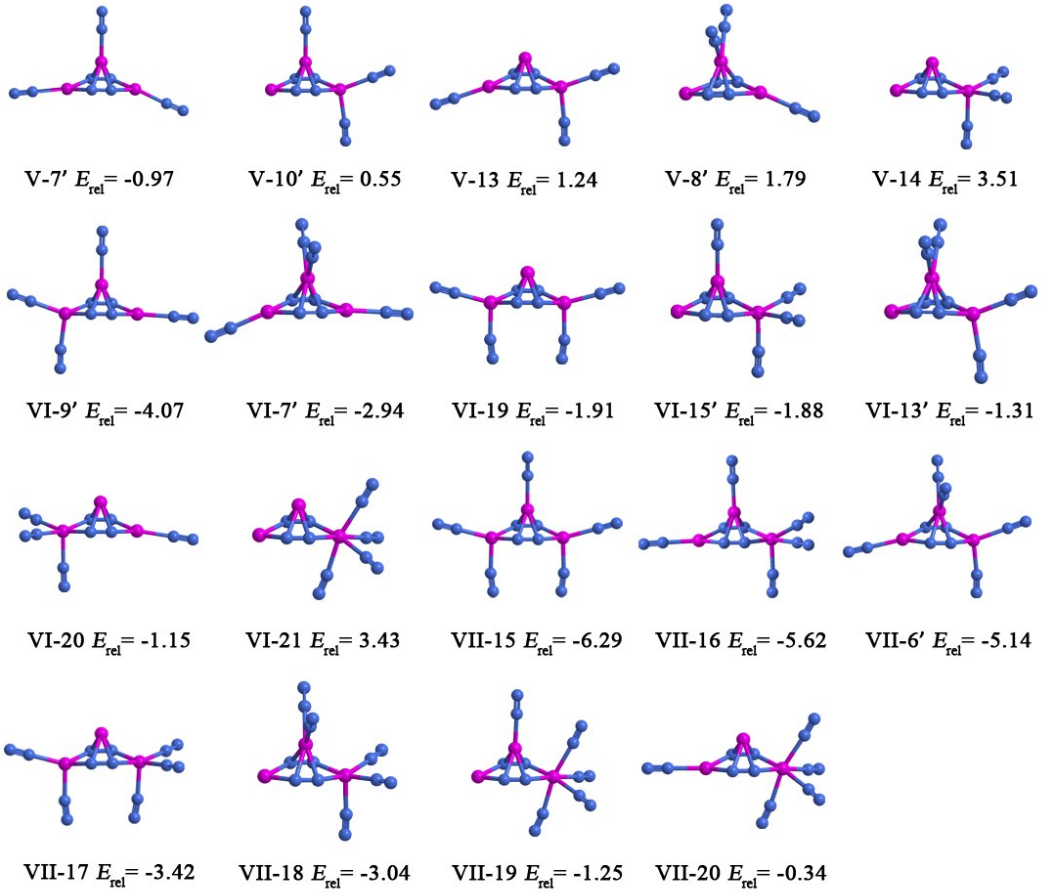

Fig. S2 Optimized structures of the $[Li_3(N_2)_n]^+$ (n = 5–7) isomers (with complete Li_3 ring cleavage) and their relative energies (E_{rel}, in kcal/mol) at the MP2/6-311+G(d) level.

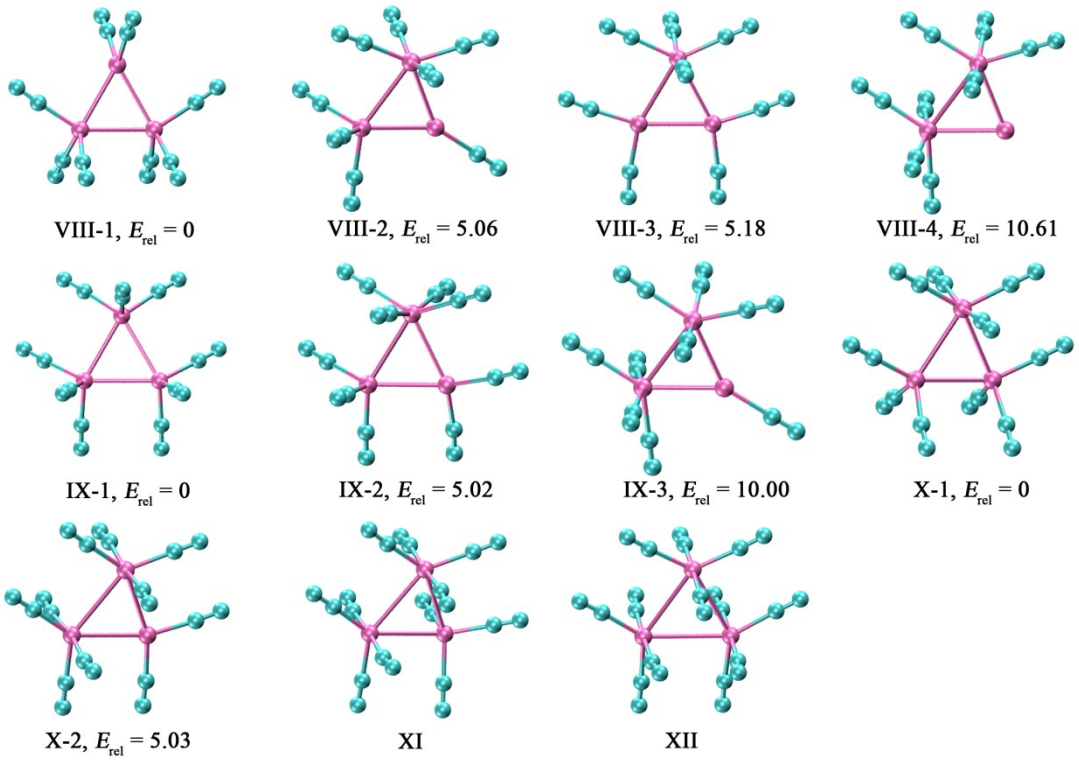

Fig. S3 Optimized low-lying structures of the $Li_3^+(N_2)_n$ (n = 8–12) complexes and their relative energies (E_{rel}, in kcal/mol) at the B3LYP/6-311+G(d) level.

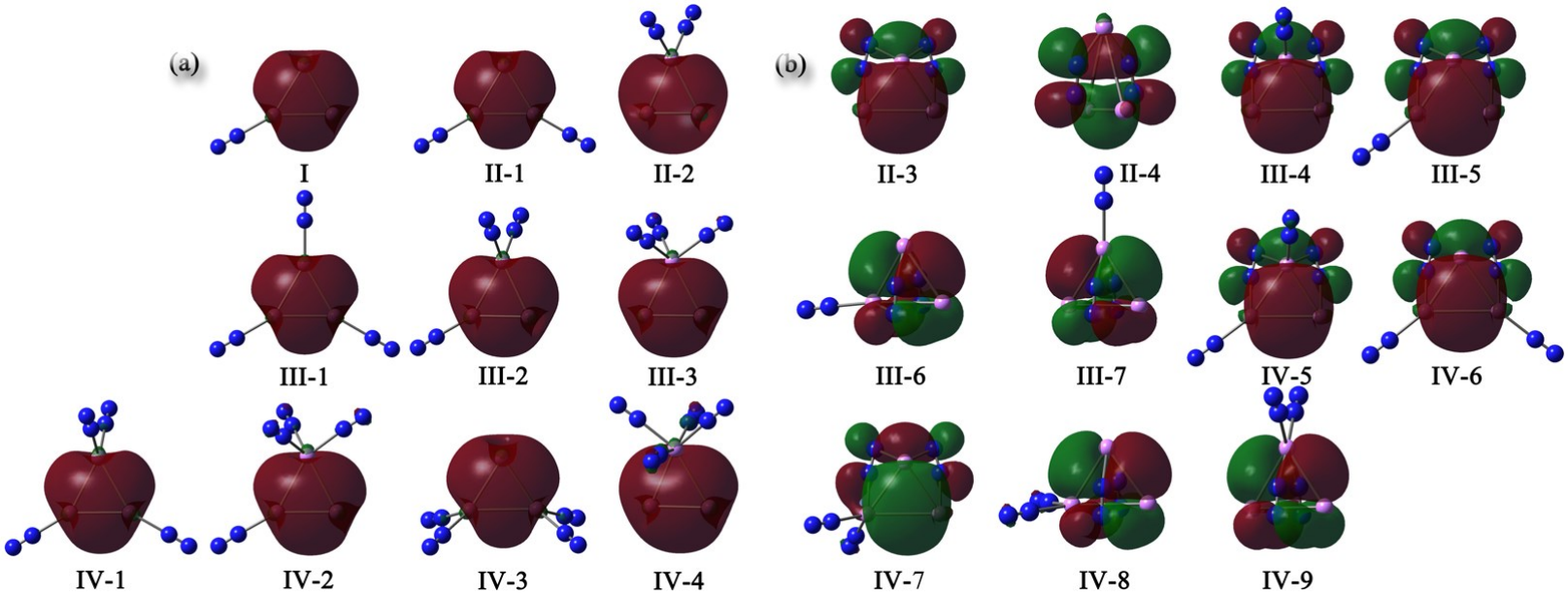

Fig. S4 The graphs of highest occupied molecular orbitals (HOMOs) of the $Li_3^+(N_2)_n$ (n = 1–4) complexes.

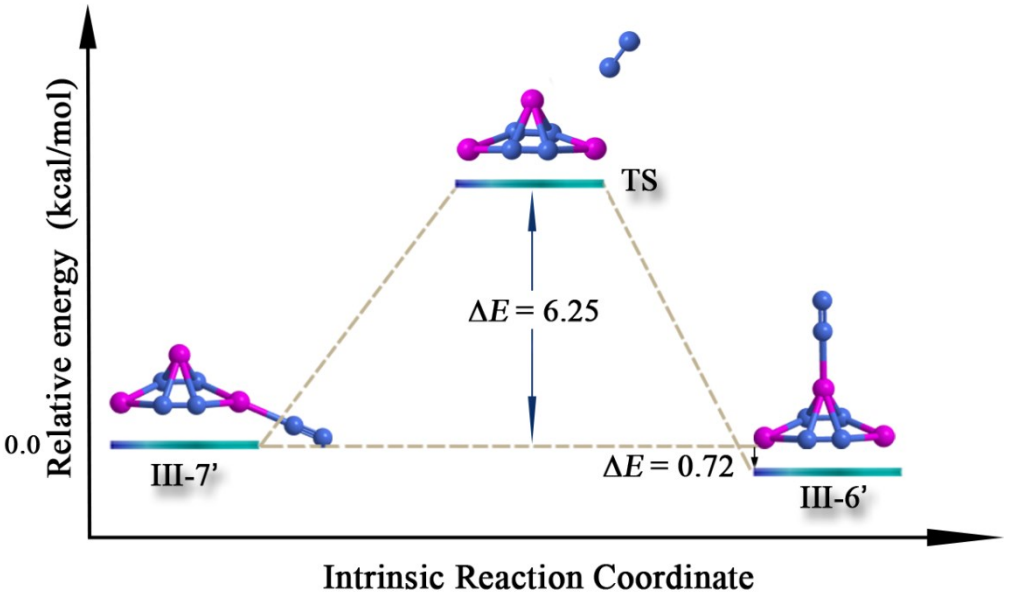

Fig. S5 Energetics (zero-point correction included) for the isomerization process of **III-7′** and **III-6′** at the MP2/6-311+G(d) level.

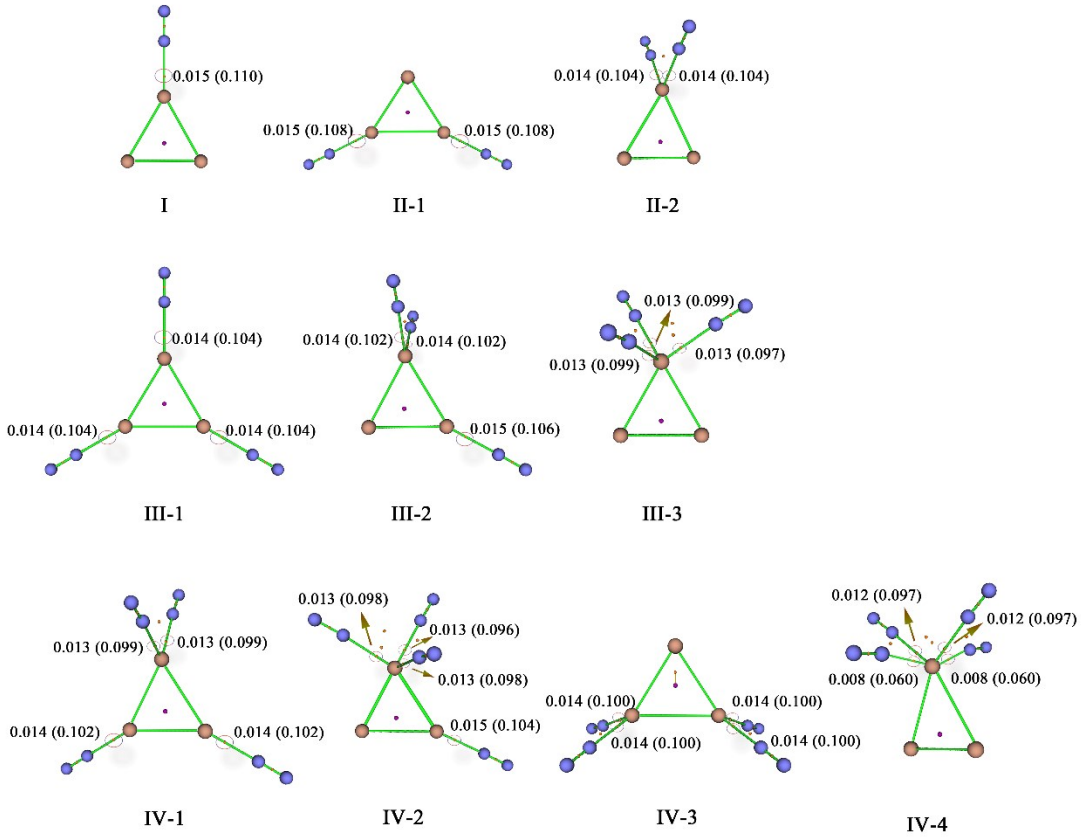

Fig. S6 Molecular graphs of the $Li_3^+(N_2)_n$ (n = 1–4) complexes and the electron density (ρ, in au) and its Laplacian ($\nabla^2\rho$ in the parentheses, in au) at the Li···N BCPs.

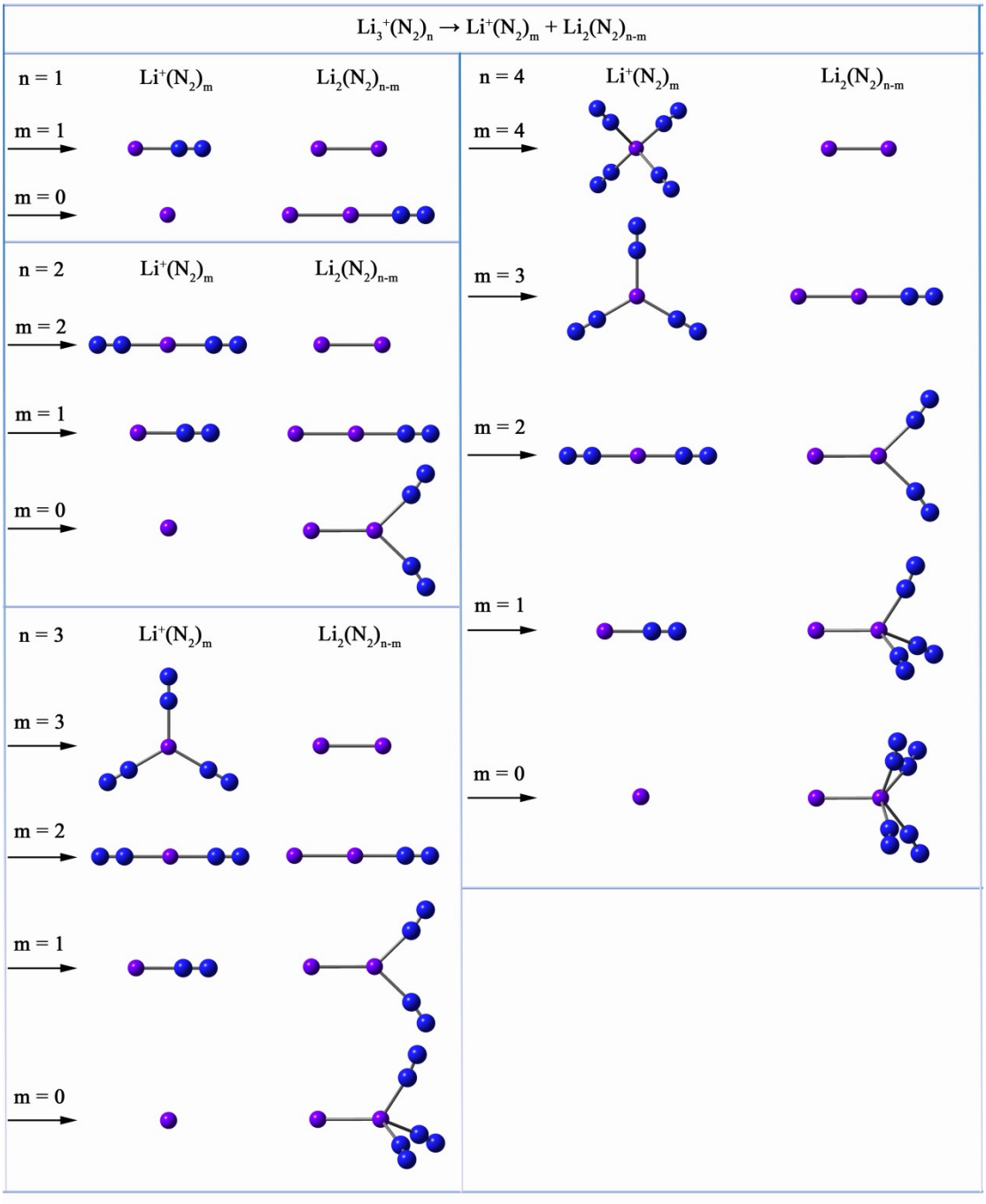

Fig. S7 Equilibrium structures of the products for the $Li_3^+(N_2)_n \rightarrow Li^+(N_2)_m + Li_2(N_2)_{n-m}$ reaction (channel 1).

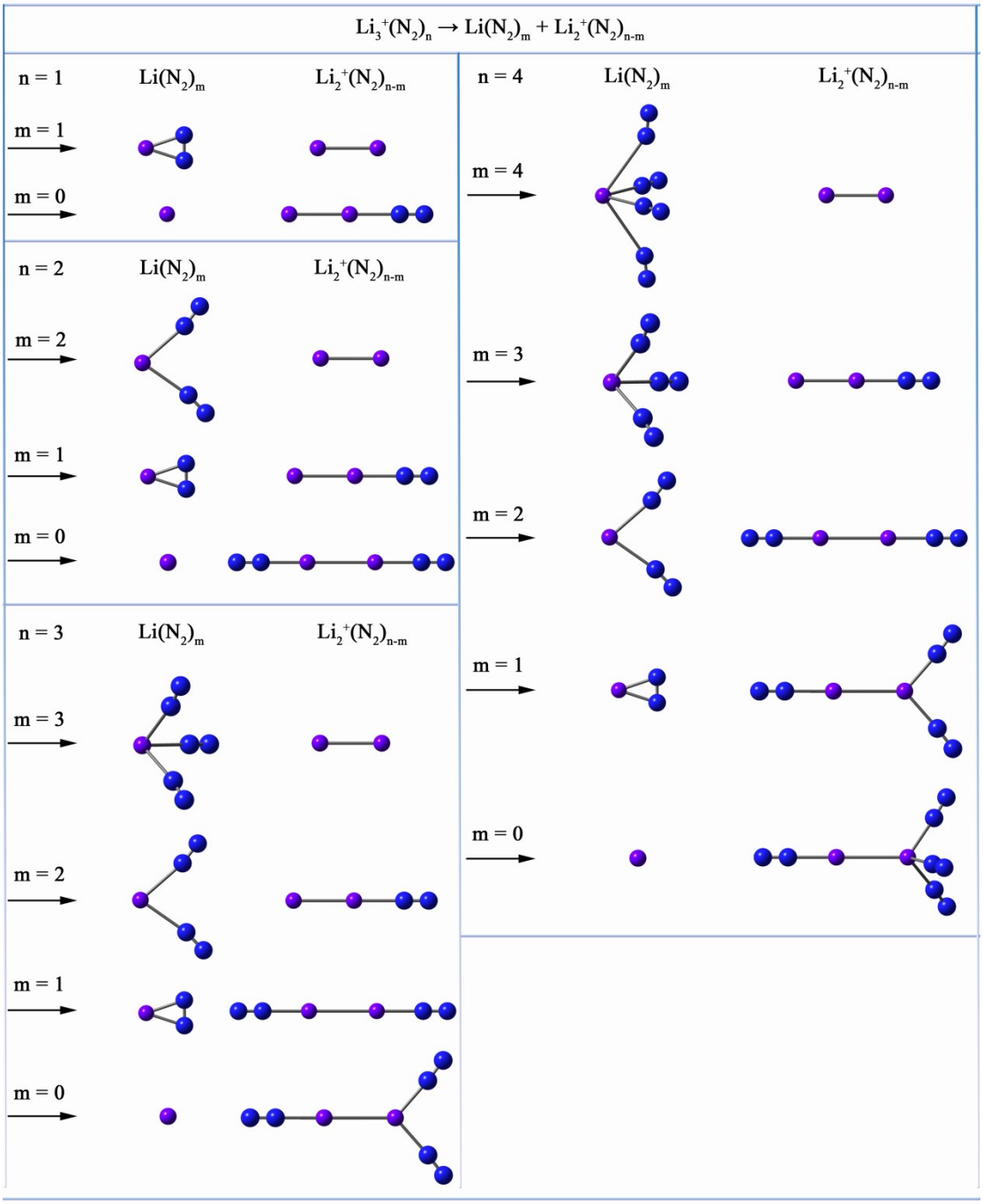

Fig. S8 Equilibrium structures of the products for the $Li_3^+(N_2)_n \rightarrow Li(N_2)_m + Li_2^+(N_2)_{n-m}$ reaction (channel 2).