SUPPLEMENTARY INFORMATION

Enhanced N_2 capture and cleavage promoted by lithium nanoparticles

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Section 1. Methodology

The mechanism of N_2 capture and cleavage by lithium sub-nanoclusters and nanoparticles was studied by density functional theory (DFT) through the generalised gradient approximation (GGA) with the revised Perdew–Burke–Ernzerhof (RPBE) with Pade approximation[1] as functional and a plane-wave cut-off energy of 400 eV. Body-centred cubic (bcc) unit cell of metallic lithium, Li^0, was fully optimised with very tight convergence criteria, specifically, energy and force convergence limits equal to 10^{-5} eV/atom and |0.001| eV/Å, respectively. For this, the Brillouin zone (periodic boundary conditions) was sampled *via* the Monkhorst–Pack scheme,[2] increasing the number of *k*-points up to electronic energy differences less than |0.01| eV. Once optimised the bulk structure of bcc-Li^0, different Li^0 nanostructures of spherical shape were built and re-optimised (Γ point; *viz*. $1\times1\times1$ *k*-points) with a vacuum width of 10 Å at each side of the X, Y, and Z coordinates. For the modelling of the clean Li^0 lithium sub-nanoclusters and nanoparticles and N_2 adsorbed states, energy and force convergence limits were set to 10^{-4} eV/atom and |0.01| eV/Å, respectively. Transition states (TS) for N_2 cleavage were located using the improved DIMER (IMD) method,[3,4] increasing the cut-off for force convergence to |0.03| eV/Å. In all cases, explicit dispersion correction terms in the energy were included through the D3 method with the standard parameters programmed by Grimme and co-workers.[5,6] Free energies were calculated for gases, Li^0 sub-nanoclusters and nanoparticles, and adsorbates as explained in **Section 2** of this Supplementary Information. All optimisation and vibrational frequency (harmonic) calculations were performed throughout the facilities provided by the Vienna *Ab Initio* Simulation Package (VASP, version 5.4.4).[7–10] In this sense, minima and TSs were corroborated by the presence of none and one imaginary frequency, respectively. A series of NVT [substance (N), volume (V), and temperature (T); canonical ensemble] molecular dynamics (MD) simulations at quantum level were carried out to analyse the diffusion effects of N_2 on and within the Li_{51} nanoparticle model. All *ab initio* MD simulations were carried out at the same level of theory as the optimisations, with time steps of 0.5 fs.

Section 2. Thermochemistry

Free energy calculations have been carried out as it follows:

$$G = E + \int C_P \, dT - TS$$

where G, E, and C_P refer to the free energy, electronic energy, and heat capacity, respectively. The entropy term, S, can be expressed as the sum of the translational, rotational, vibrational, and electronic contributions as it follows:

$$S = S_t + S_r + S_v + S_e$$

Finally, intrinsic zero-point energy (ZPE) and extrinsic dispersion (D) corrections were included to obtain this expression:

$$G = E + \int C_P \, dT - T(S_t + S_r + S_v + S_e) + ZPE + D$$

For N_2 gas at standard conditions (298.15 K of temperature, 1 atm of fugacity), $S_e \approx 0$ at the fundamental electronic level. Thus, **Table S1** gathers the thermodynamic quantities for this species.

Table S1. Thermodynamic quantities, in eV, for N_2 gas at standard conditions (298.15 K, 1 atm).

Gas	***E* (+D)**	**$\int C_P$ dT**	**–T*S***	**ZPE**	***G***
$N_2(g)$	–16.24	0.09	–0.59	0.15	–16.59

In the case of clean surfaces and adsorbates, some approximations can be assumed. First and as for N_2 gas at standard conditions, $S_e \approx 0$ at the fundamental electronic level. Secondly, translational and rotational motions can be neglected, therefore, $S_t \approx 0$ and $S_r \approx 0$. In this sense, all entropy contributions come from vibrations: $S \approx S_v$. Similarly, translational and rotational contributions to the heat capacity have been neglected. Therefore, for clean surfaces and adsorbates, free energies have been calculated as to:

$$G = E + \int C_P \, dT - TS_v + ZPE + D$$

Procedurally, vibrational frequencies have been calculated for all atoms, *i.e.*, without any structural constrain for any species, metallic or not. Following this procedure, **Table S2** gathers free energies for clean surfaces and $*N_2$ adsorbates for the series of Li^0 structures studied herein as well as for slabs of flat bcc-Li^0 surfaces, the latter being computed for comparison.

Table S2. Free energies (298.15 K), in eV, for clean surfaces and $*N_2$ adsorbates.

bcc-Li^0 slab (Li_{128}), (001) surface, equivalent to (010) and (100)					
State	***G***	**State**	***G***	**State**	***G***
clean	–236.21	end-on $*N_2$	–252.72	side-on $*N_2$	–253.35

bcc-Li^0 slab (Li_{128}), (101) surface, equivalent to (110) and (011)					
State	***G***	**State**	***G***	**State**	***G***
clean	–238.99	end-on $*N_2$	–255.37	side-on $*N_2$	–255.93
Li^0 sub-nanocluster (Li_1)					
State	***G***	**State**	***G***	**State**	***G***
clean	–0.04	min. [1] $*N_2$	–16.27	min. [2] $*N_2$	–16.09
Li^0 sub-nanocluster (Li_2)					
State	***G***	**State**	***G***	**State**	***G***
clean	–1.38	min. [1] $*N_2$	–17.64	min. [2] $*N_2$	–17.67
min. [3] $*N_2$	–17.43				
Li^0 sub-nanocluster (Li_6)					
State	***G***	**State**	***G***	**State**	***G***
clean	–6.47	min. [1] $*N_2$	–23.15	min. [2] $*N_2$	–22.95
min. [3] $*N_2$	–22.90	min. [4] $*N_2$	–22.85		
Li^0 sub-nanocluster (Li_{15})					
State	***G***	**State**	***G***	**State**	***G***
clean	–19.49	min. [1] $*N_2$	–37.23	min. [2] $*N_2$	–37.17
min. [3] $*N_2$	–37.17	min. [4] $*N_2$	–36.87	min. [5] $*N_2$	–36.73
min. [6] $*N_2$	–36.72	min. [7] $*N_2$	–36.54	min. [8] $*N_2$	–36.46
min. [9] $*N_2$	–36.39	min. [10] $*N_2$	–36.11		
Li^0 sub-nanocluster (Li_{27})					
State	***G***	**State**	***G***	**State**	***G***
clean	–38.08	min. [1] $*N_2$	–57.02	min. [2] $*N_2$	–56.93
min. [3] $*N_2$	–56.87	min. [4] $*N_2$	–56.79	min. [5] $*N_2$	–56.71
min. [6] $*N_2$	–56.06	min. [7] $*N_2$	–56.11	min. [8] $*N_2$	–56.03
min. [9] $*N_2$	–55.91				
Li^0 nanoparticle (Li_{51})					
State	***G***	**State**	***G***	**State**	***G***
clean	–78.20	min. [1] $*N_2$	–97.37	min. [2] $*N_2$	–97.39
min. [3] $*N_2$	–97.26	min. [4] $*N_2$	–97.27	min. [5] $*N_2$	–97.25
min. [6] $*N_2$	–97.21	min. [7] $*N_2$	–97.09	min. [8] $*N_2$	–97.13
min. [9] $*N_2$	–96.37	min. [10] $*N_2$	–96.37	min. [11] $*N_2$	–96.50

Li^0 nanoparticle (Li_{51}), second N_2 adsorption from min. [1] described above					
State	***G***	**State**	***G***	**State**	***G***
min. [1] $*N_2$	–114.79	min. [2] $*N_2$	–114.76	min. [3] $*N_2$	–114.80
min. [4] $*N_2$	–114.65	min. [5] $*N_2$	–114.56	min. [6] $*N_2$	–114.60
min. [7] $*N_2$	–114.58	min. [8] $*N_2$	–114.47	min. [9] $*N_2$	–114.44
min. [10] $*N_2$	–114.50	min. [11] $*N_2$	–114.49	min. [12] $*N_2$	–114.42
min. [13] $*N_2$	–114.38	min. [14] $*N_2$	–114.03	min. [15] $*N_2$	–113.96
min. [16] $*N_2$	–113.91	min. [17] $*N_2$	–113.88	min. [18] $*N_2$	–113.84
min. [19] $*N_2$	–113.82				

Free energies for TSs are also shown in **Table S3**.

Table S3. Free energies (298.15 K), in eV, for TSs of $*N_2$ cleavage, with indication of the imaginary frequency (IF), in cm^{-1}.

bcc-Li^0 slab (Li_{128}), (001) surface, equivalent to (010) and (100)					
State	***G***	**IF**	**State**	***G***	**IF**
TS_1	–255.34	410.2 i			
bcc-Li^0 slab (Li_{128}), (101) surface, equivalent to (110) and (011)					
State	***G***	**IF**	**State**	***G***	**IF**
TS_1	–255.50	436.0 i	TS_2	–255.59	428.0 i
Li^0 nanoparticle (Li_{51})					
State	***G***	**IF**	**State**	***G***	**IF**
TS_1	–96.76	413.7 i	TS_2	–96.80	459.8 i
TS_3	–96.72	398.4 i	TS_4	–96.84	410.2 i
TS_5	–96.62	399.7 i	TS_6	–96.74	418.0 i

Note that binding free energies for N_2 adsorption, $\Delta G(*N_2)$, and free energy barriers for $*N_2$ cleavage, $\Delta G^{‡}$, have been calculated as:

$$\Delta G(*N_2) = G(*N_2) - G[N_2(g)] - G(*)$$

$$\Delta G^{‡} = G(\mathrm{TS}) - G(*N_2)$$

where $G(*N_2)$, $G[N_2(g)]$, $G(*)$, and $G(\mathrm{TS})$ refer to the free energies of adsorbed $*N_2$, N_2 gas, clean surface, and TS for N_2 cleavage, respectively, which can be found in **Tables S2** and **S3**.

Section 3. Additional figures

Below, a series of optimised structures for both minima and TSs not included in the main manuscript are shown.

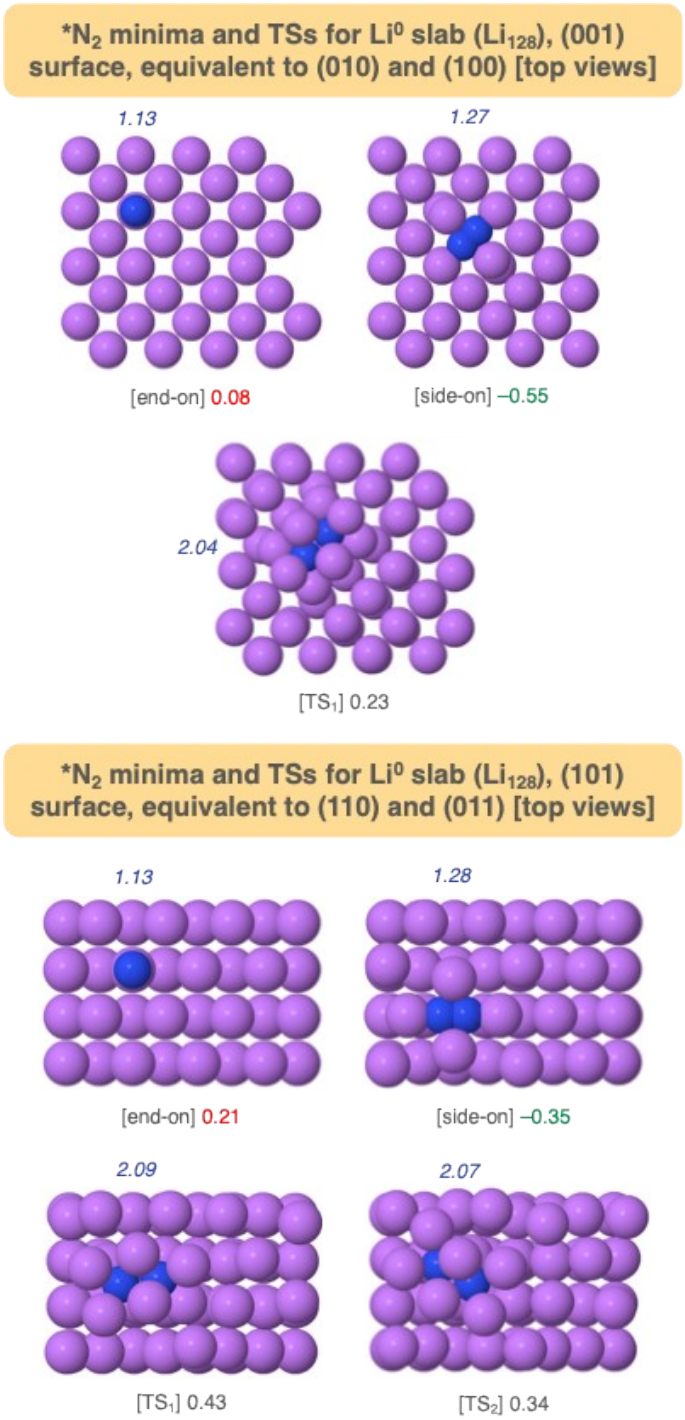

Figure S1. *N_2 minima and TSs obtained for flat bcc-Li^0 surfaces. N≡N distances (Å) are shown in *blue*. Binding free energies (eV) for *N_2 minima are shown in green (spontaneous) and red (non-spontaneous), while activation free energies (eV) for TSs corresponding to N_2 cleavage are shown in grey.

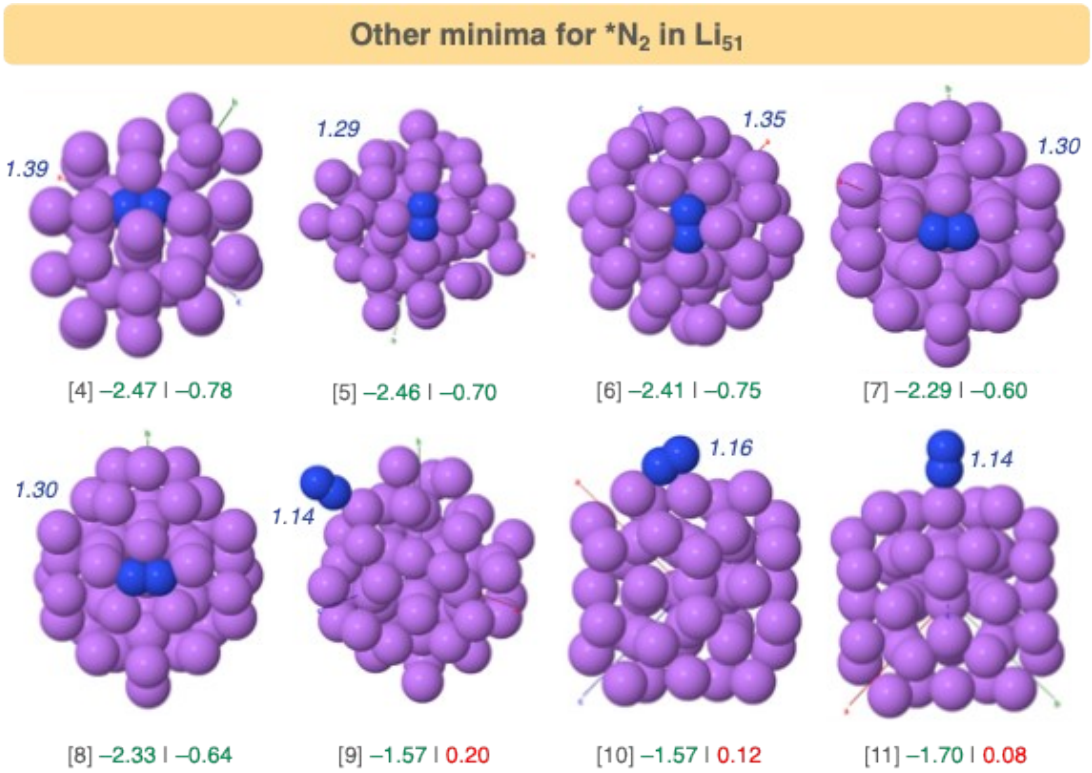

Figure S2. Other *N_2 minima for the Li_{51} nanoparticle. N≡N distances (Å) are shown in *blue*. Binding free energies (eV) are shown in green (spontaneous) and red (non-spontaneous).

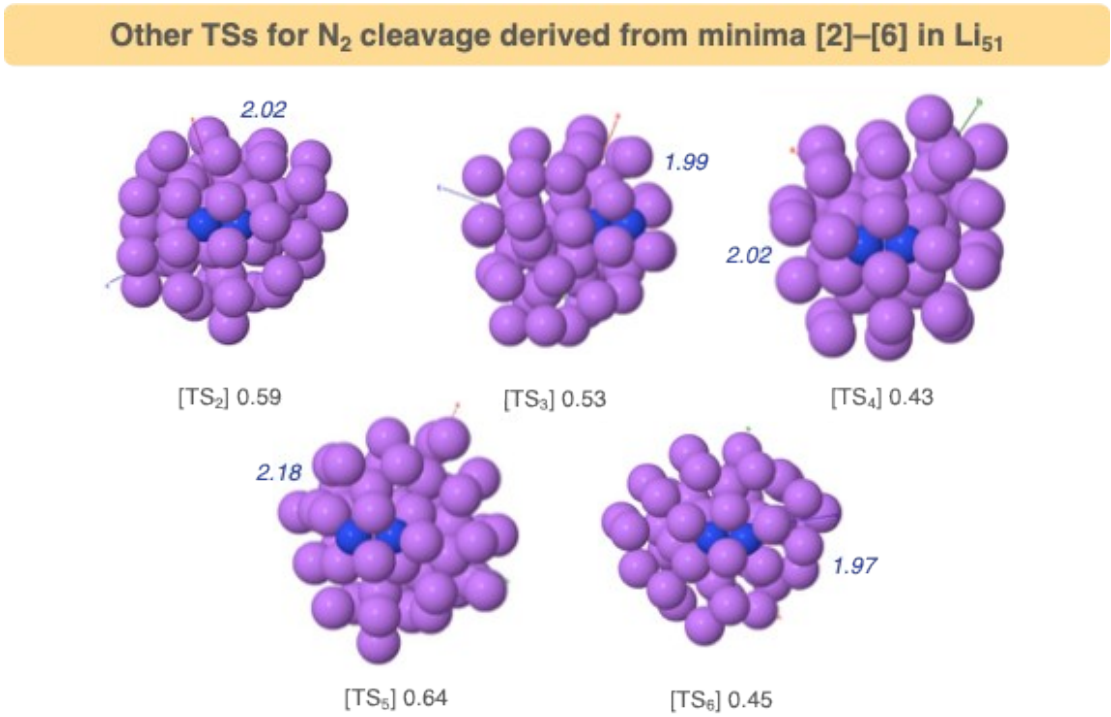

Figure S3. Other TSs for N_2 cleavage derived from minima [2]–[6] for the Li_{51} nanoparticle. N≡N distances (Å) are shown in *blue*. Activation free energies (eV) are also shown.

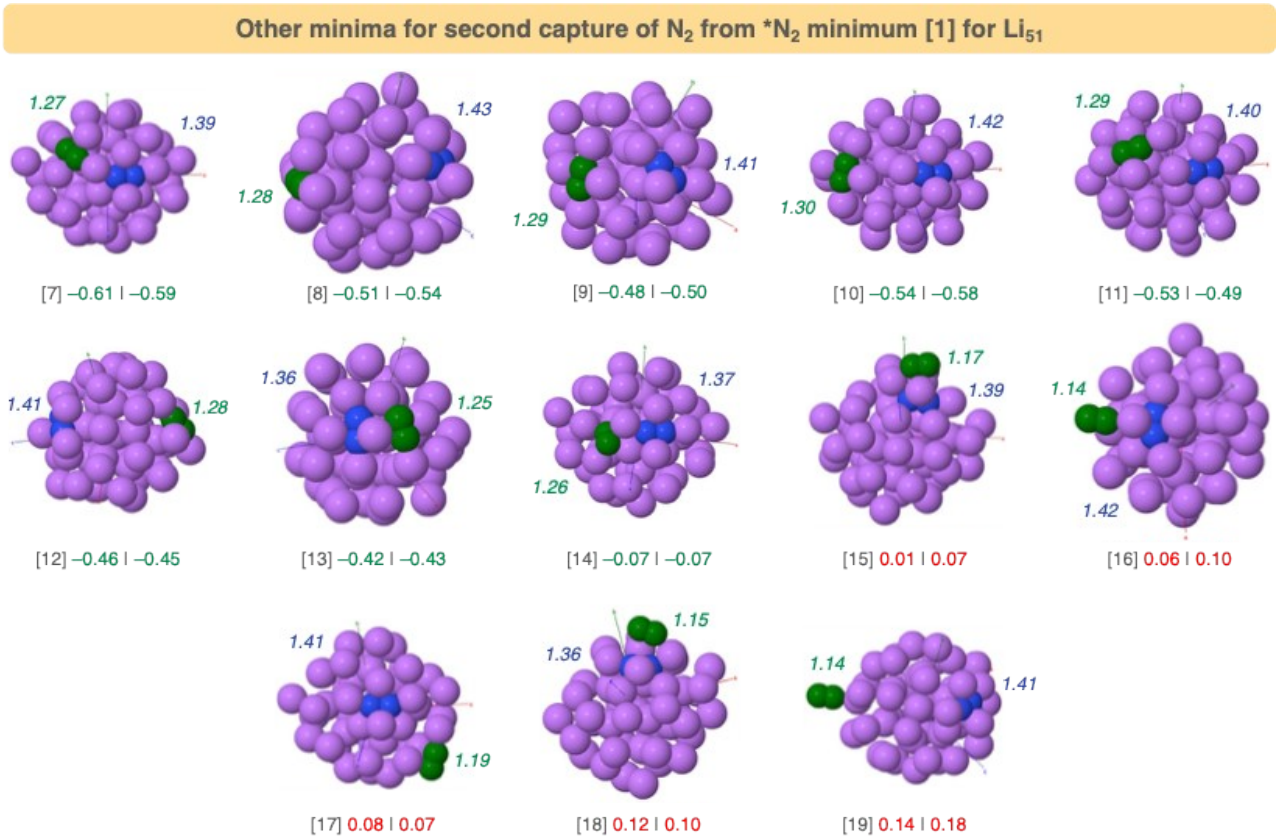

Figure S4. Other minima corresponding to a second N_2 adsorption from minimum [1] of the Li_{51} nanoparticle. N≡N distances (Å) are shown in *blue* (first *N_2) and *green* (second *N_2). Binding free energies (eV) are shown in green (spontaneous) and red (non-spontaneous).

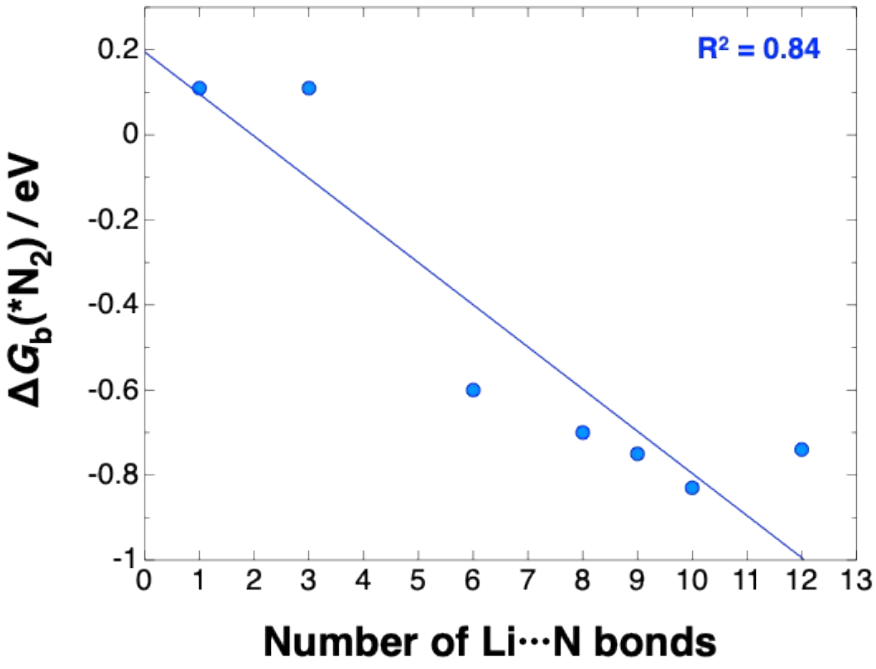

Figure S5. Average of binding free energies, ΔG_b (in eV), for *N_2 minima in Li_{27} and Li_{51} models *vs.* number of Li···N bonds with distance of 2.5 Å or less, showing correlation, *i.e.*, binding free energy becomes stronger as the number of Li···N bonds increases.

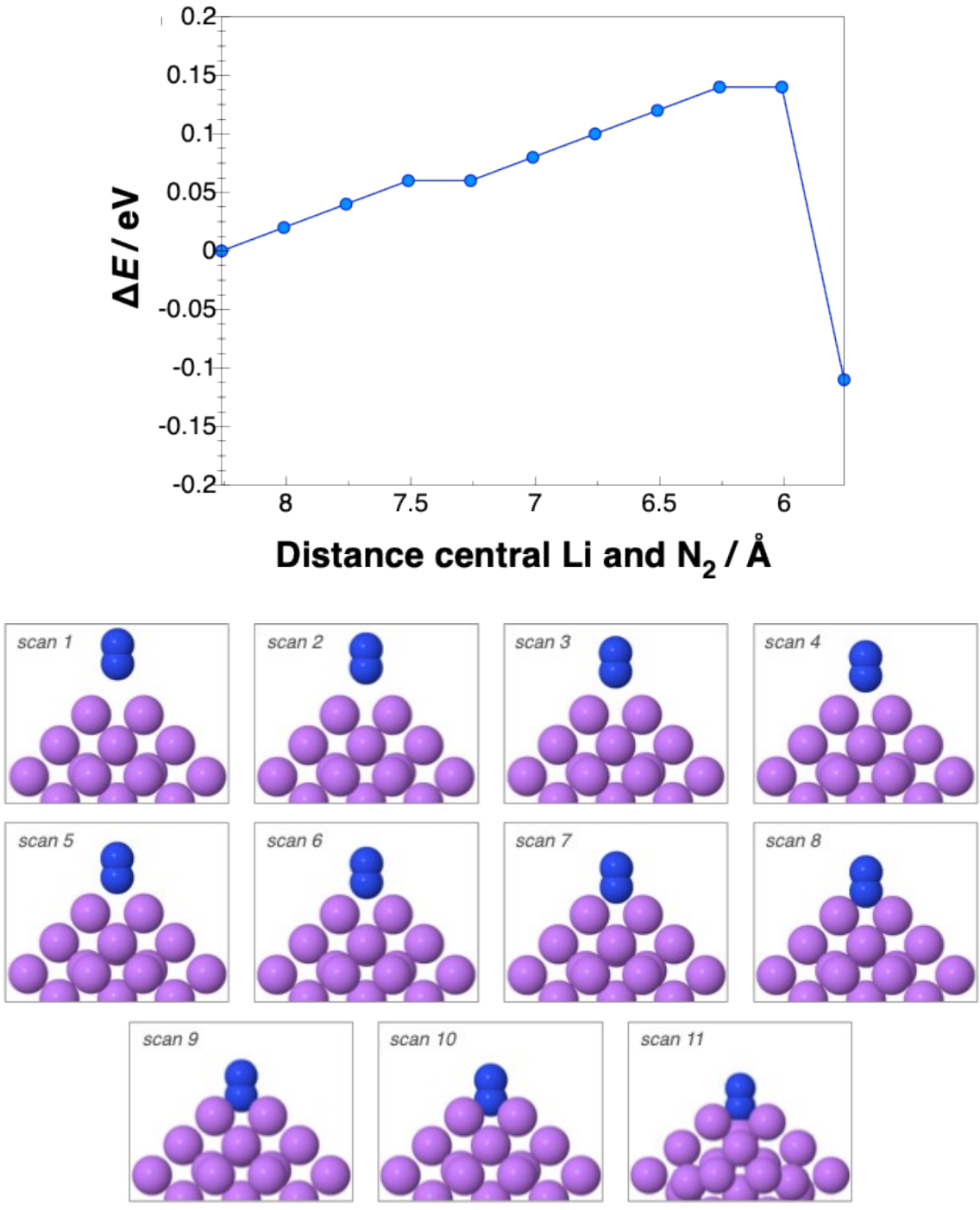

Figure S6. Electronic energy profile (eV) for the constrained approach of N_2 towards the Li_{51} nanoparticle. The Li–N distance between the central Li atom and the N_2 molecule (Å) was constrained while all other coordinates were fully relaxed. Optimised structures along the approach coordinate are also shown. Note: force convergence criterion was set to |0.02| eV/Å for these calculations.

Section 4. Optimised XYZ coordinates (in Å) for symmetrical Li^0 nanostructures

	Li_1		
Li	10.00000000	10.00000000	10.00000000
a	20.00000000	0.00000000	0.00000000
b	0.00000000	20.00000000	0.00000000
c	0.00000000	0.00000000	20.00000000
	Li_2		
Li	10.05961937	10.00000000	10.00000000
Li	13.45038063	10.00000000	10.00000000
a	23.51000000	0.00000000	0.00000000
b	0.00000000	20.00000000	0.00000000
c	0.00000000	0.00000000	20.00000000
	Li_6		
Li	13.54033234	13.54033234	11.75500000
Li	11.75450000	11.75450000	10.42204331
Li	9.96866766	9.96866766	11.75500000
Li	11.75450000	11.75450000	13.08795669
Li	13.54033234	9.96866766	11.75500000
Li	9.96866766	13.54033234	11.75500000
a	23.50900000	0.00000000	0.00000000
b	0.00000000	23.50900000	0.00000000
c	0.00000000	0.00000000	23.51000000
	Li_{15}		
Li	13.50900000	13.50900000	13.50900000
Li	15.15601767	15.15601767	15.15601767
Li	11.86198233	11.86198233	11.86198233
Li	15.15601767	11.86198233	11.86198233
Li	11.86198233	15.15601767	11.86198233
Li	13.50900000	13.50900000	9.89314690
Li	15.15601767	15.15601767	11.86198233
Li	11.86198233	11.86198233	15.15601767
Li	13.50900000	9.89314690	13.50900000
Li	15.15601767	11.86198233	15.15601767
Li	9.89314690	13.50900000	13.50900000
Li	11.86198233	15.15601767	15.15601767
Li	17.12485310	13.50900000	13.50900000
Li	13.50900000	17.12485310	13.50900000
Li	13.50900000	13.50900000	17.12485310
a	27.01800000	0.00000000	0.00000000
b	0.00000000	27.01800000	0.00000000
c	0.00000000	0.00000000	27.01800000
	Li_{27}		
Li	13.50900000	13.50900000	13.50900000
Li	15.15970972	15.15970972	15.15970972
Li	11.85829028	11.85829028	11.85829028
Li	13.50900000	10.18273322	10.18273322
Li	15.15970972	11.85829028	11.85829028
Li	10.18273322	13.50900000	10.18273322
Li	11.85829028	15.15970972	11.85829028
Li	13.50900000	13.50900000	9.99814680
Li	15.15970972	15.15970972	11.85829028
Li	16.83526678	13.50900000	10.18273322
Li	13.50900000	16.83526678	10.18273322
Li	10.18273322	10.18273322	13.50900000
Li	11.85829028	11.85829028	15.15970972

Li	13.50900000	9.99814680	13.50900000
Li	15.15970972	11.85829028	15.15970972
Li	16.83526678	10.18273322	13.50900000
Li	9.99814680	13.50900000	13.50900000
Li	11.85829028	15.15970972	15.15970972
Li	17.01985320	13.50900000	13.50900000
Li	10.18273322	16.83526678	13.50900000
Li	13.50900000	17.01985320	13.50900000
Li	16.83526678	16.83526678	13.50900000
Li	13.50900000	10.18273322	16.83526678
Li	10.18273322	13.50900000	16.83526678
Li	13.50900000	13.50900000	17.01985320
Li	16.83526678	13.50900000	16.83526678
Li	13.50900000	16.83526678	16.83526678
a	27.01800000	0.00000000	0.00000000
b	0.00000000	27.01800000	0.00000000
c	0.00000000	0.00000000	27.01800000
	Li_{51}		
Li	15.26400000	15.26400000	15.26400000
Li	17.04448190	17.04448190	17.04448190
Li	13.72600775	13.72600775	10.00392904
Li	16.80199225	13.72600775	10.00392904
Li	13.72600775	16.80199225	10.00392904
Li	16.80199225	16.80199225	10.00392904
Li	13.72600775	10.00392904	13.72600775
Li	16.80199225	10.00392904	13.72600775
Li	10.00392904	13.72600775	13.72600775
Li	13.48351810	13.48351810	13.48351810
Li	15.26400000	11.86557631	11.86557631
Li	17.04448190	13.48351810	13.48351810
Li	20.52407096	13.72600775	13.72600775
Li	10.00392904	16.80199225	13.72600775
Li	11.86557631	15.26400000	11.86557631
Li	13.48351810	17.04448190	13.48351810
Li	15.26400000	15.26400000	11.85870306
Li	17.04448190	17.04448190	13.48351810
Li	18.66242369	15.26400000	11.86557631
Li	20.52407096	16.80199225	13.72600775
Li	13.72600775	20.52407096	13.72600775
Li	15.26400000	18.66242369	11.86557631
Li	16.80199225	20.52407096	13.72600775
Li	13.72600775	10.00392904	16.80199225
Li	16.80199225	10.00392904	16.80199225
Li	10.00392904	13.72600775	16.80199225
Li	11.86557631	11.86557631	15.26400000
Li	13.48351810	13.48351810	17.04448190
Li	15.26400000	11.85870306	15.26400000
Li	17.04448190	13.48351810	17.04448190
Li	18.66242369	11.86557631	15.26400000
Li	20.52407096	13.72600775	16.80199225
Li	10.00392904	16.80199225	16.80199225
Li	11.85870306	15.26400000	15.26400000
Li	13.48351810	17.04448190	17.04448190
Li	18.66929694	15.26400000	15.26400000
Li	20.52407096	16.80199225	16.80199225
Li	11.86557631	18.66242369	15.26400000

Li	13.72600775	20.52407096	16.80199225
Li	15.26400000	18.66929694	15.26400000
Li	16.80199225	20.52407096	16.80199225
Li	18.66242369	18.66242369	15.26400000
Li	13.72600775	13.72600775	20.52407096
Li	15.26400000	11.86557631	18.66242369
Li	16.80199225	13.72600775	20.52407096
Li	11.86557631	15.26400000	18.66242369
Li	13.72600775	16.80199225	20.52407096
Li	15.26400000	15.26400000	18.66929694
Li	16.80199225	16.80199225	20.52407096
Li	18.66242369	15.26400000	18.66242369
Li	15.26400000	18.66242369	18.66242369
a	30.52800000	0.00000000	0.00000000
b	0.00000000	30.52800000	0.00000000
c	0.00000000	0.00000000	30.52800000

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