Electronic Supplementary Information (ESI)

Ionization energies and structures of lithium doped silicon clusters

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Supplementary Information Contains:

D) Total electronic and zero-point energies of lowest energy isomers of $Si_nLi_3^{0,+}$ (n = 5−11) and $Si_8Li_m^{0,+}$ (m = 1, 2, 4−6)

- Table SIII. Calculated AIE and VIE of the isomers of Si_8Li_m (m = 1, 2, 4−6).
- Table SIV. Total electronic and zero-point energies of lowest energy isomers of Si_nLi_3 (n = 5−11) presented in Fig. 3.
- Table SV. Total electronic and zero-point energies of lowest energy isomers of $Si_nLi_3^+$ (n = 5−11) presented in Fig. 3.
- Table SVI. Total electronic and zero-point energies of lowest energy isomers of Si_8Li_m (m = 1−6; $m \neq 3$) presented in Fig. 4.
- Table SVII. Total electronic and zero-point energies of lowest energy isomers of $Si_8Li_m^+$ (m = 1−6; $m \neq 3$) presented in Fig. 4.

A) Photoionization efficiency curves

FIG. S1. PIE curves of Si_nLi_m clusters with $m > 3$ and $n \neq 8$ that have a vertical ionization energy in the 4.68−6.24 eV range. The PIE curves of these clusters are included in the same experimental data set and do not belong to the Si_nLi_3 (n = 5−11) or Si_8Li_m ($3 \leq m \leq 6$) series. The open squares represent the experimental data, while the solid red lines represent smeared out step functions fitted to the data. The experimental VIE and the ionization thresholds are indicated by a blue and red dot, respectively.

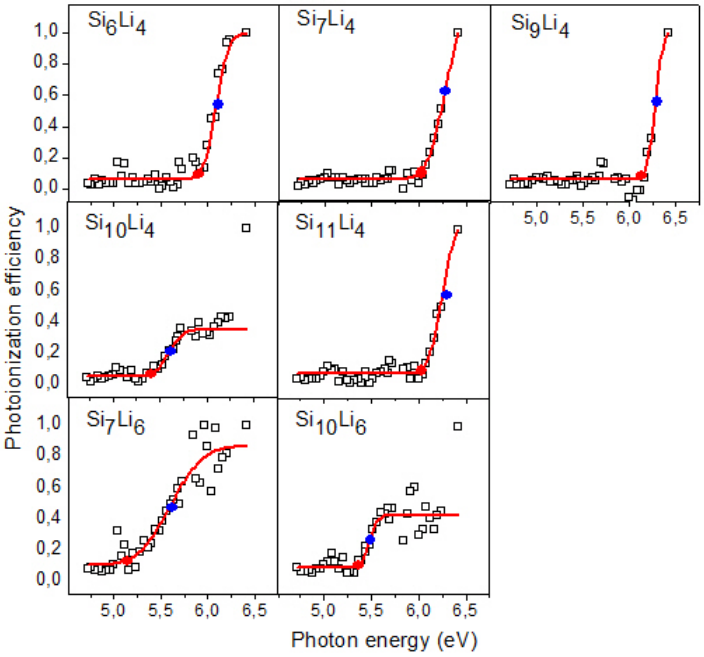
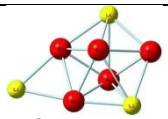
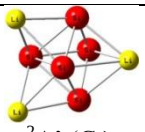
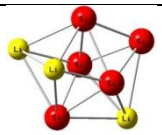
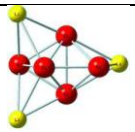
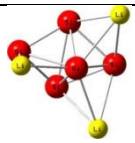
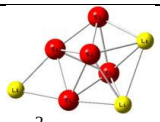
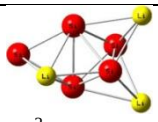
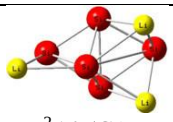
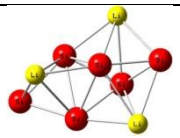
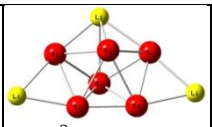
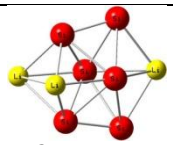
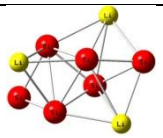
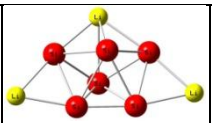
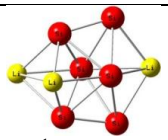
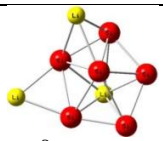
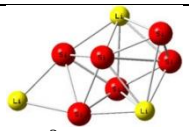
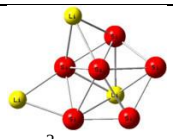
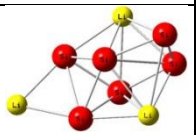
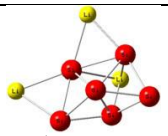
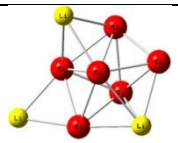
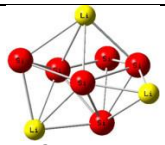
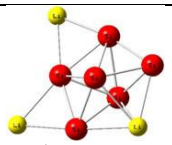


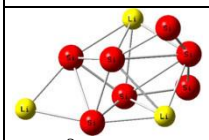
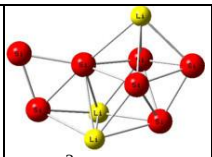
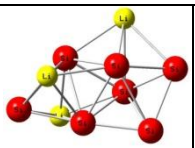
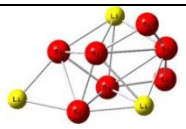
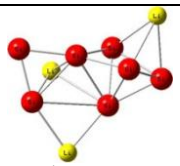
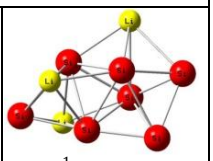
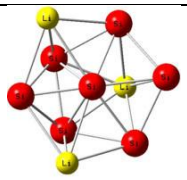
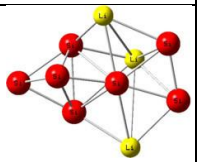
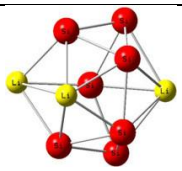
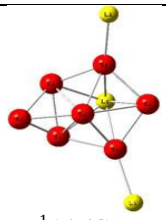
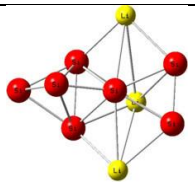
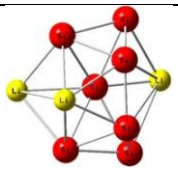
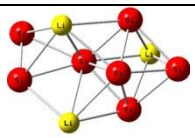
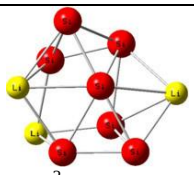
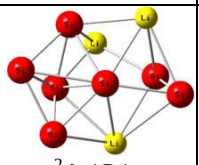
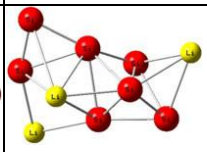
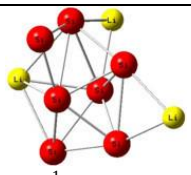
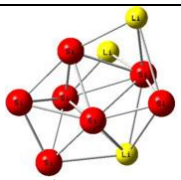
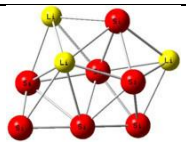
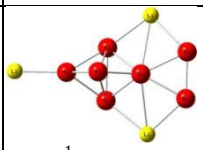
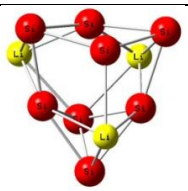
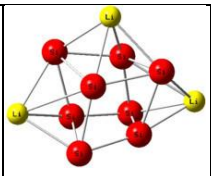
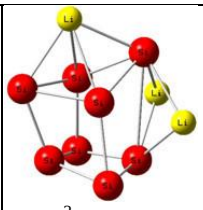
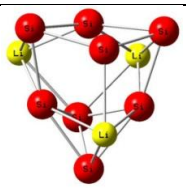
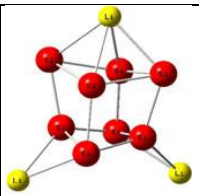
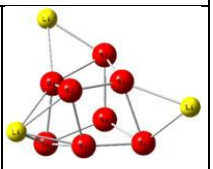
Table SI: Experimental ionization threshold and VIE of the Si_nLi_m clusters shown in Fig. S1. The standard error from the fitting procedure is given between brackets.

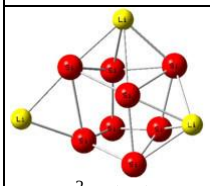
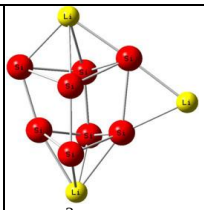
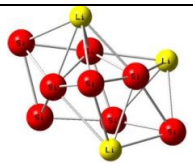
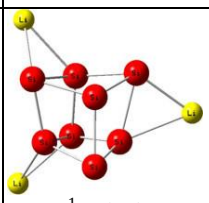
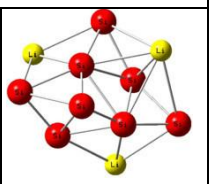
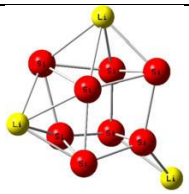
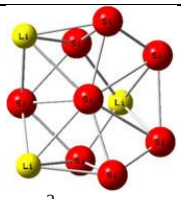
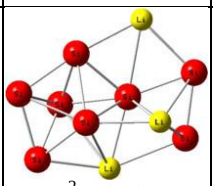
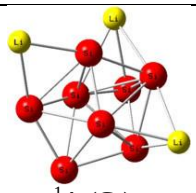
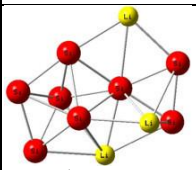
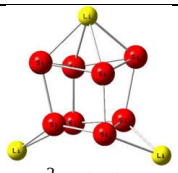
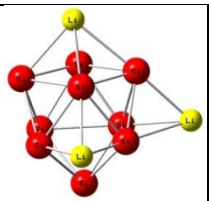
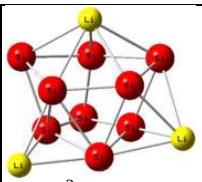
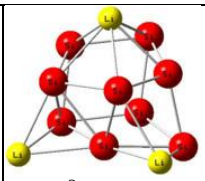
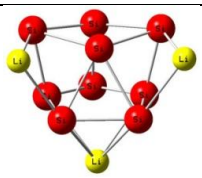
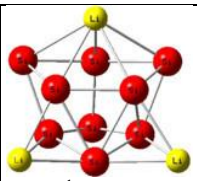
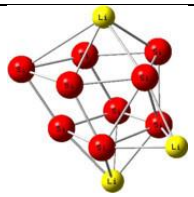
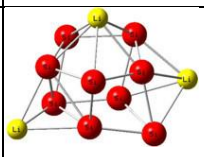
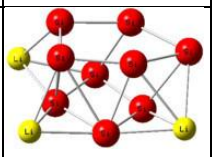
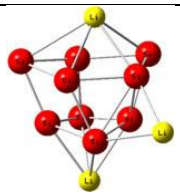
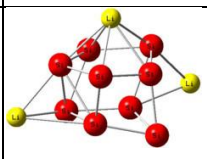
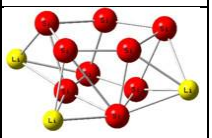
Cluster	Ionization threshold (eV)	VIE-Exp. (eV)
Si_6Li_4	5.85 (0.05)	6.09 (0.01)
Si_7Li_4	5.94 (0.07)	6.28 (0.02)
Si_9Li_4	6.12 (0.09)	6.28 (0.02)
$Si_{10}Li_4$	5.32 (0.08)	5.59 (0.02)
$Si_{11}Li_4$	5.99 (0.08)	6.25 (0.02)
Si_7Li_6	5.00 (0.22)	5.60 (0.04)
$Si_{10}Li_6$	5.32 (0.11)	5.48 (0.02)

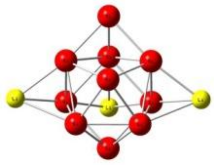
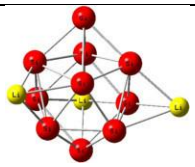
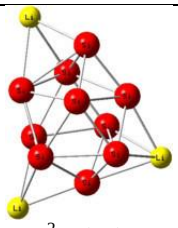
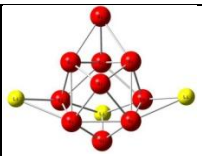
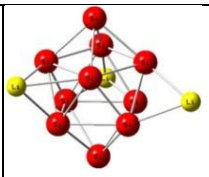
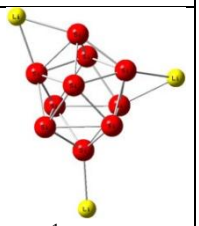
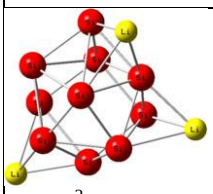
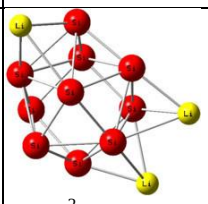
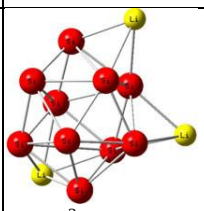
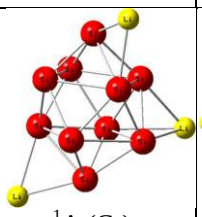
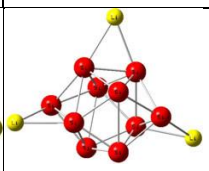
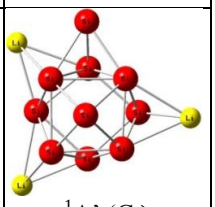
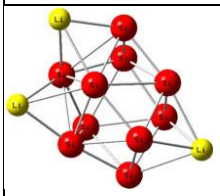
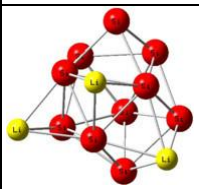
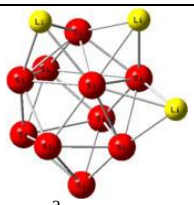
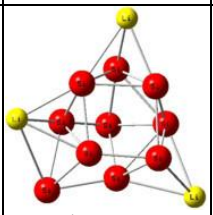
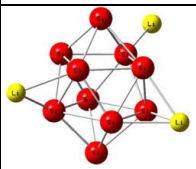
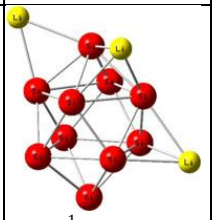
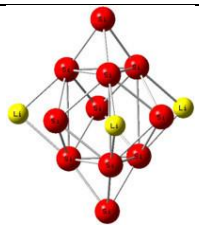
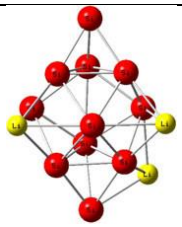
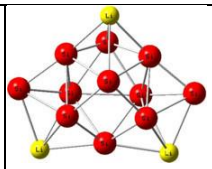
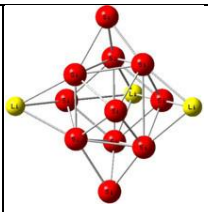
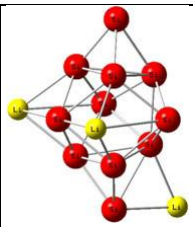
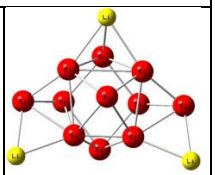
B) Shape, relative energy, and ionization energies

Figure S2. The shape, relative energy (in eV), and point group of low energetic isomers of Si_nLi_3 and $Si_nLi_3^+$ (n = 5−11) at the B3LYP/6-311+G(d,p) level.

Neutral			Cation		
Si_5Li_3					
 $^2B_2$ (C_{2v}) **0.0 eV** **5-3A^0**	 $^2A'$ (C_s) +0.23 eV **5-3B^0**	 $^2A'$ (C_s) +0.29 eV **5-3C^0**	 $^1A'$ (C_s) **0.0 eV** **5-3A$^+$, 5-3B$^+$, 5-3C$^+$, 5-3D$^+$, 5-3E$^+$**	 $^1A'$ (C_s) +0.13 eV **5-3F$^+$**	
 $^2A'$ (C_s) +0.31 eV **5-3D^0**	 $^2A'$ (C_s) +0.33 eV **5-3E^0**	 $^2A'$ (C_s) +0.47 eV **5-3F^0**			
Si_6Li_3					
 $^2A'$ (C_s) **0.0 eV** **6-3A^0**	 $^2B_1$ (C_{2v}) +0.33 eV **6-3B^0**	 $^2B_1$ (C_{2v}) +0.35 eV **6-3C^0**	 $^1A'$ (C_s) +1.03 eV **6-3A$^+$**	 $^1A_1$ (C_{2v}) **0.0 eV** **6-3B$^+$**	 $^1A_1$ (C_{2v}) +0.40 eV **6-3C$^+$, 6-3D$^+$, 6-3H$^+$**
 ^2A (C_1) +0.37 eV **6-3D^0**	 $^2A'$ (C_s) +0.37 eV **6-3E^0**	 ^2A (C_1) +0.41 eV **6-3F^0**		 $^1A'$ (C_s) +1.24 eV **6-3E$^+$**	 ^1A (C_1) +0.70 eV **6-3F$^+$**
 ^2A (C_1) +0.42 eV **6-3G^0**	 ^2A (C_1) +0.46 eV **6-3H^0**		 $^1A'$ (C_s) +0.13 eV **6-3G$^+$**		

Neutral			Cation		
Si_7Li_3					
 $^2A_2$ (C_{2v}) **0.0 eV** **7-3A^0**	 $^2A'$ (C_s) +0.05 eV **7-3B^0**	 $^2A'$ (C_s) +0.07 eV **7-3C^0**	 $^1A_1$ (C_{2v}) +0.42 eV **7-3A$^+$**	 ^1A (C_1) +0.48eV **7-3B$^+$**	 $^1A'$ (C_s) **0.0 eV** **7-3C$^+$**
 $^2A''$ (C_s) +0.08 eV **7-3D^0**	 ^2A (C_1) +0.11 eV **7-3E^0**	 $^2A''$ (C_s) +0.15 eV **7-3F^0**	 $^1A'$ (C_s) +0.71 eV **7-3D$^+$**	 $^1A'$ (C_s) +0.38 eV **7-3E$^+$**	 $^1A'$ (C_s) +1.14 eV **7-3F$^+$**
 ^2A (C_1) +0.22 eV **7-3G^0**	 ^2A (C_1) +0.25 eV **7-3H^0**	 ^2A (C_1) +0.29 eV **7-3I^0**	 ^1A (C_1) +0.48 eV **7-3G$^+$**	 ^1A (C_1) +0.47 eV **7-3H$^+$**	 ^1A (C_1) +0.54 eV **7-3I$^+$**
 ^2A (C_1) +0.30 eV **7-3J^0**			 $^1A'$ (C_s) +0.53 eV **7-3J$^+$**		
Si_8Li_3					
 $^2A'$ (C_s) **0.0 eV** **8-3A^0**	 ^2B (C_2) +0.03 eV **8-3B^0**	 $^2A'$ (C_s) +0.05 eV **8-3C^0**	 $^1A'$ (C_s) +0.23 eV **8-3A$^+$**	 ^1A (C_2) +0.004 eV **8-3B$^+$, 8-3G$^+$, 8-3J$^+$**	 ^1A (C_1) **0.0 eV** **8-3C$^+$**

Neutral			Cation		
 ^2A (C_1) +0.16 eV **8-3D^0**	 $^2A'$ (C_s) +0.16 eV **8-3E^0**	 ^2A (C_1) +0.19 eV **8-3F^0**	 ^1A (C_1) +0.09 eV **8-3D$^+$, 8-3E$^+$**		 ^1A (C_1) +0.68 eV **8-3F$^+$**
 $^2A'$ (C_s) +0.27 eV **8-3G^0**	 $^2A'$ (C_s) +0.34 eV **8-3H^0**	 ^2A (C_1) +0.39 eV **8-3I^0**		 ^1A (C_1) +0.53 eV **8-3H$^+$**	 ^1A (C_1) +0.52 eV **8-3I$^+$**
 ^2A (C_2) +0.45 eV **8-3J^0**					
Si_9Li_3					
 ^2A (C_1) **0.0 eV** **9-3A^0**	 ^2A (C_1) +0.19 eV **9-3B^0**	 ^2A (C_1) +0.24 eV **9-3C^0**	 $^1A'$ (C_s) **0.0 eV** **9-3A$^+$, 9-3C$^+$**	 ^1A (C_1) +0.14 eV **9-3B$^+$**	
 ^2A (C_1) +0.26 eV **9-3D^0**	 ^2A (C_1) +0.30 eV **9-3E^0**	 ^2A (C_1) +0.59 eV **9-3F^0**	 ^1A (C_1) +0.18 eV **9-3D$^+$**	 ^1A (C_1) +0.21 eV **9-3E$^+$**	 ^1A (C_1) +0.25 eV **9-3F$^+$**

Neutral			Cation		
$Si_{10}Li_3$					
 $^2A''$ (C_s) **0.0 eV** **10-3A^0**	 ^2A (C_1) +0.08 eV **10-3B^0**	 ^2A (C_1) +0.12 eV **10-3C^0**	 $^1A'$ (C_s) +0.15 eV **10-3A$^+$**	 ^1A (C_1) **0.0 eV** **10-3B$^+$**	 ^1A (C_1) +0.13 eV **10-3C$^+$**
 ^2A (C_1) +0.14 eV **10-3D^0**	 ^2A (C_1) +0.20 eV **10-3E^0**	 ^2A (C_1) +0.27 eV **10-3F^0**	 ^1A (C_1) +0.09 eV **10-3D$^+$**	 ^1A (C_2) +0.10 eV **10-3E$^+$**	 $^1A'$ (C_s) +0.26 eV **10-3F$^+$**
 ^2A (C_1) +0.31 eV **10-3G^0**	 ^2A (C_1) +0.32 eV **10-3H^0**	 ^2A (C_1) +0.38 eV **10-3I^0**	 ^1A (C_1) +0.26 eV **10-3G$^+$**	 ^1A (C_1) +0.08 eV **10-3H$^+$**	 ^1A (C_1) +0.34 eV **10-3I$^+$**
$Si_{11}Li_3$					
 $^2B_2$ (C_{2v}) **0.0 eV** **11-3A^0**	 ^2A (C_1) +0.16 eV **11-3B^0**	 $^2A''$ (C_s) +0.22 eV **11-3C^0**	 $^1A'$ (C_s) +0.07 eV **11-3A$^+$**	 $^1A'$ (C_s) +0.11 eV **11-3B$^+$, 11-3D$^+$**	 $^1A'$ (C_s) +0.16 eV **11-3C$^+$, 11-3E$^+$, 11-3F$^+$**

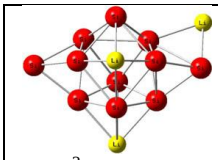
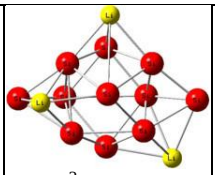
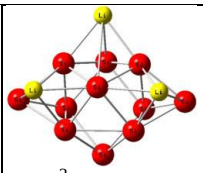
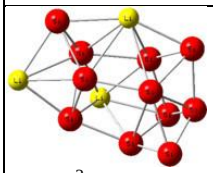
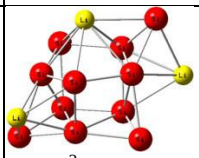
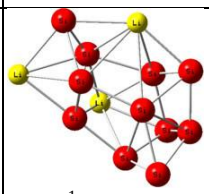
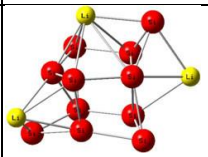
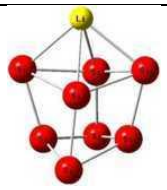
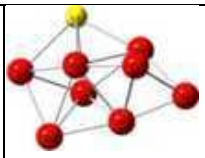
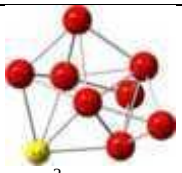
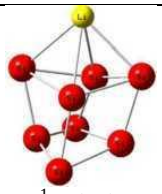
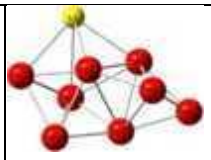
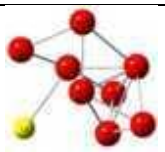
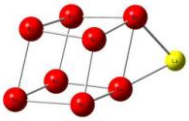
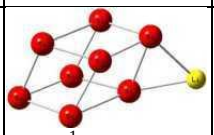
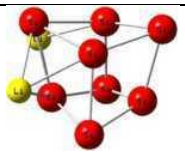
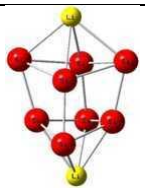
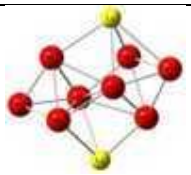
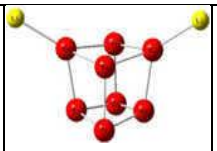
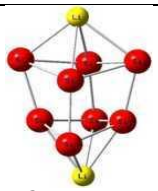
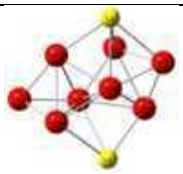
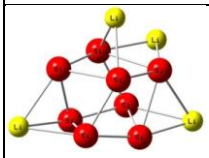
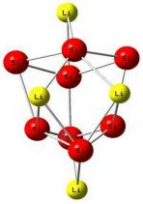
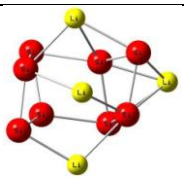
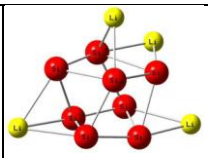
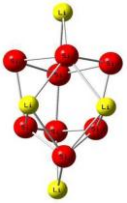
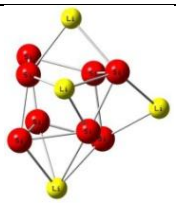
 $^2A'$ (C_s) +0.24 eV **11-3D^0**	 ^2A (C_1) +0.26 eV **11-3E^0**	 $^2A''$ (C_s) +0.35 eV **11-3F^0**			
 ^2A (C_1) +0.36 eV **11-3G^0**	 ^2A (C_1) +0.43 eV **11-3H^0**		 ^1A (C_1) +0.23 eV **11-3G$^+$**	 ^1A (C_1) **0.0 eV** **11-3H$^+$**	

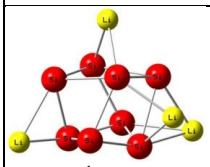
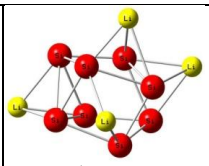
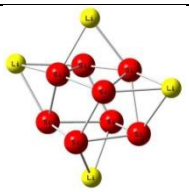
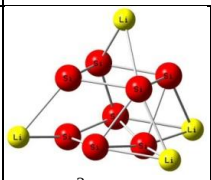
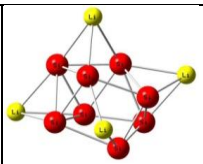
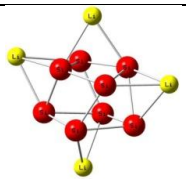
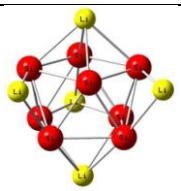
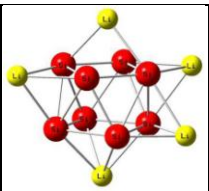
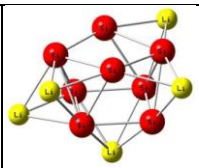
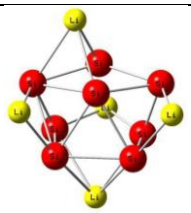
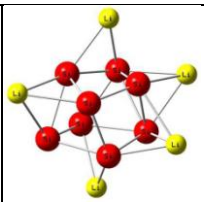
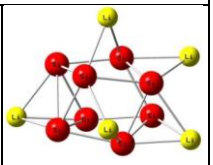
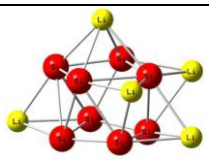
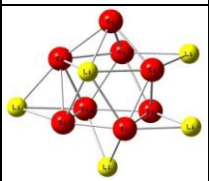
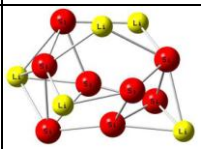
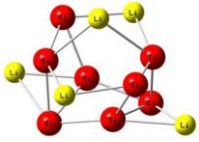
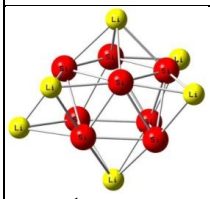
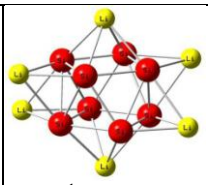
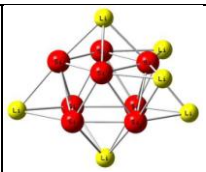
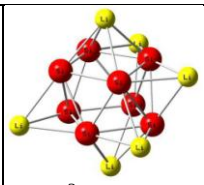
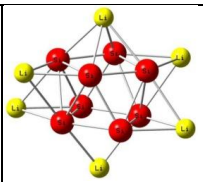
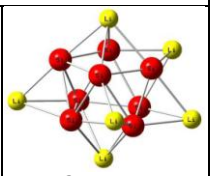
Table SII: Calculated adiabatic and vertical ionization energies for the isomers of Si_nLi_3 (n = 5–11) obtained at the B3LYP/6-311+G(d) level and the corresponding experimental values.

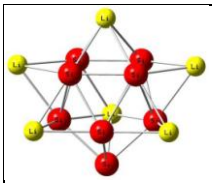
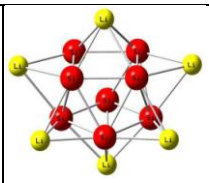
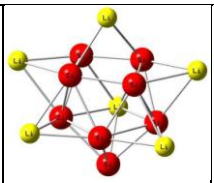
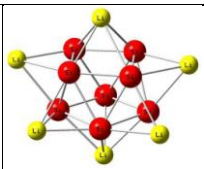
Transition	AIE (eV)	VIE (eV)	AIE exp. (eV)	VIE exp. (eV)
5-3A^0 ($^2B_2$)→ **5-3A$^+$** (^{1}A')	4.82	5.96	5.04 (0.35)	5.89 (0.09)
5-3B^0 (^{2}A')→ **5-3B$^+$** (^{1}A')	4.59	5.53		
5-3C^0 (^{2}A')→ **5-3C$^+$** (^{1}A')	4.53	5.52		
5-3D^0 (^{2}A')→ **5-3D$^+$** (^{1}A')	4.51	5.15		
5-3E^0 (^{2}A')→ **5-3E$^+$** (^{1}A')	4.49	5.64		
5-3F^0 (^{2}A')→ **5-3F$^+$** (^{1}A')	4.48	5.40		
6-3A^0 (^{2}A')→ **6-3A$^+$** (^{1}A')	5.83	6.49	4.401.07)	> 5.7
6-3B^0 ($^2B_1$)→ **6-3B$^+$** ($^1A_1$)	4.46	4.88		
6-3C^0 ($^2B_1$)→ **6-3C$^+$** ($^1A_1$)	4.85	5.18		
6-3D^0 (^{2}A)→ **6-3D$^+$** ($^1A_1$)	4.82	6.23		
6-3E^0 (^{2}A')→ **6-3E$^+$** (^{1}A')	5.66	6.06		
6-3F^0 (^{2}A)→ **6-3F$^+$** (^{1}A)	5.08	6.32		
6-3G^0 (^{2}A)→ **6-3G$^+$** (^{1}A')	4.51	5.04		
6-3H^0 (^{2}A)→ **6-3H$^+$** ($^1A_1$)	4.74	5.75		
7-3A^0 ($^2A_2$)→ **7-3A$^+$** ($^1A_1$)	5.45	5.61	4.88 (0.23)	> 5.7
7-3B^0 (^{2}A')→ **7-3B$^+$** (^{1}A)	5.46	6.08		
7-3C^0 (^{2}A'')→ **7-3C$^+$** (^{1}A')	4.95	5.29		
7-3D^0 (^{2}A'')→ **7-3D$^+$** (^{1}A')	5.66	6.05		
7-3E^0 (^{2}A)→ **7-3E$^+$** (^{1}A')	5.30	5.70		
7-3F^0 (^{2}A'')→ **7-3F$^+$** (^{1}A')	6.02	6.29		
7-3G^0 (^{2}A)→ **7-3G$^+$** (^{1}A)	5.29	6.14		
7-3H^0 (^{2}A)→ **7-3H$^+$** (^{1}A)	5.24	6.13		
7-3I^0 (^{2}A)→ **7-3I$^+$** (^{1}A)	5.27	5.91		
7-3J^0 (^{2}A)→ **7-3J$^+$** (^{1}A')	5.26	6.05		

8-3A^0 (^{2}B)→ **8-3A$^+$** (^{1}A)	5.19	5.44	5.18 (0.06)	5.40 (0.01)
8-3B^0 (^{2}B)→ **8-3B$^+$** (^{1}A)	4.94	5.26		
8-3C^0 (^{2}A')→ **8-3C$^+$** (^{1}A)	4.92	5.83		
8-3D^0 (^{2}A)→ **8-3D$^+$** (^{1}A)	4.89	5.19		
8-3E^0 (^{2}A')→ **8-3E$^+$** (^{1}A)	4.89	5.19		
8-3F^0 (^{2}A)→ **8-3F$^+$** (^{1}A)	5.46	6.00		
8-3G^0 (^{2}A')→ **8-3G$^+$** (^{1}A)	4.70	4.86		
8-3H^0 (^{2}A')→ **8-3H$^+$** (^{1}A)	5.15	5.57		
8-3I^0 (^{2}A)→ **8-3I$^+$** (^{1}A)	5.09	5.54		
8-3J^0 (^{2}A)→ **8-3J$^+$** (^{1}A)	4.52	4.78		
9-3A^0 (^{2}A)→ **9-3A$^+$** (^{1}A')	5.24	6.31	5.28 (0.26)	6.09 (0.08)
9-3B^0 (^{2}A)→ **9-3B$^+$** (^{1}A)	5.19	5.76		
9-3C^0 (^{2}A)→ **9-3C$^+$** (^{1}A')	5.00	5.60		
9-3D^0 (^{2}A)→ **9-3D$^+$** (^{1}A)	5.16	5.77		
9-3E^0 (^{2}A)→ **9-3E$^+$** (^{1}A)	5.16	5.60		
9-3F^0 (^{2}A)→ **9-3F$^+$** (^{1}A)	4.90	5.36		
10-3A^0 (^{2}A'')→ **10-3A$^+$** (^{1}A')	4.99	5.48	5.21 (0.11)	5.54 (0.02)
10-3B^0 (^{2}A)→ **10-3B$^+$** (^{1}A)	4.77	5.38		
10-3C^0 (^{2}A)→ **10-3C$^+$** (^{1}A)	4.85	5.35		
10-3D^0 (^{2}A)→ **10-3D$^+$** (^{1}A)	4.79	5.35		
10-3E^0 (^{2}A)→ **10-3E$^+$** (^{1}A)	4.75	5.44		
10-3F^0 (^{2}A)→ **10-3F$^+$** (^{1}A')	4.89	5.42		
10-3G^0 (^{2}A)→ **10-3G$^+$** (^{1}A)	4.80	5.41		
10-3H^0 (^{2}A)→ **10-3H$^+$** (^{1}A)	4.60	5.49		
10-3I^0 (^{2}A)→ **10-3I$^+$** (^{1}A)	4.81	5.39		
11-3A^0 (^{2}B$_2$)→ **11-3A$^+$** (^{1}A')	5.73	6.25	5.97 (0.19)	6.32 (0.07)
11-3B^0 (^{2}A)→ **11-3B$^+$** (^{1}A')	5.60	6.10		
11-3C^0 (^{2}A'')→ **11-3C$^+$** (^{1}A')	5.59	5.99		
11-3D^0 (^{2}A')→ **11-3D$^+$** (^{1}A')	5.53	5.93		
11-3E^0 (^{2}A)→ **11-3E$^+$** (^{1}A')	5.56	5.94		
11-3F(^{2}A)→ **11-3F$^+$** (^{1}A')	5.46	5.91		
11-3G (^{2}A)→ **11-3G$^+$** (^{1}A)	5.52	5.88		
11-3H (^{2}A)→ **11-3H$^+$** (^{1}A)	5.23	5.51		

Figure S3. The shape, relative energy (in eV), and point group of low-lying isomers of Si_8Li_m and $Si_8Li_m^+$ (m = 1, 2, 4−6) at the B3LYP/6-311+G(d,p) level.

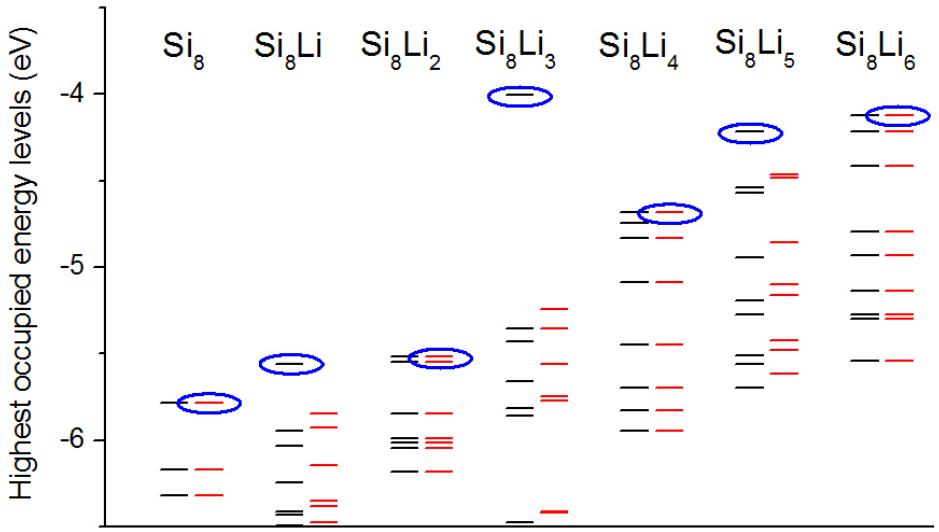
Neutral			Cation		
Si_8Li					
 $^2A''$ (C_s) **0.0 eV** **8-1A^0**	 ^2A (C_1) +0.25 eV **8-1B^0**	 ^2A (C_1) +0.35 eV **8-1C^0**	 ^1A (C_1) +0.28 eV **8-1A$^+$**	 ^1A (C_1) +0.03 eV **8-1B$^+$**	 ^1A (C_1) +0.44 eV **8-1C$^+$**
 ^2A (C_1) +0.64 eV **8-1D^0**			 ^1A (C_1) **0.0 eV** **8-1D$^+$**		
Si_8Li_2					
 $^1A'$ (C_s) **0.0 eV** **8-2A^0**	 $^1A_1$ (D_{2d}) +0.03 eV **8-2B^0**	 ^1A (C_1) +0.61 eV **8-2C^0**	 $^2A'$ (C_s) +0.35 eV **8-2A$^+$**	 $^2A_2$ (D_{2d}) **0.0 eV** **8-2B$^+$**	 ^2A (C_1) +0.23 eV **8-2C$^+$**
Si_8Li_4					
 ^1A (C_1) **0.0 eV** **8-4A^0**	 $^1A'$ (C_s) +0.00 eV **8-4B^0**	 ^1A (C_1) +0.03 eV **8-4C^0**	 ^2A (C_1) +0.05 eV **8-4A$^+$**	 $^2A''$ (C_s) +0.39 eV **8-4B$^+$**	 ^2A (C_1) **0.0 eV** **8-4C$^+$**

Neutral			Cation		
					
^{1}A C_1 +0.05 eV **8-4D^0**	^{1}A C_1 +0.05 eV **8-4E^0**	^{1}A C_1 +0.11 eV **8-4F^0**	^{2}A C_1 +0.01 eV **8-4D$^+$**	^{2}A C_1 +0.08 eV **8-4E$^+$**	^{2}A C_1 +0.11 eV **8-4F$^+$**
Si_8Li_5					
					
^{2}A' (C_s) **0.0 eV** **8-5A^0**	^{2}A (C_1) +0.10 eV **8-5B^0**	^{2}A (C_1) +0.25 eV **8-5C^0**	^{1}A (C_1) +0.15 eV **8-5A$^+$**	^{1}A (C_1) +0.12 eV **8-5B$^+$**	^{1}A (C_1) **0.0 eV** **8-5C$^+$, 8-5D$^+$**
					
^{2}A (C_1) +0.28 eV **8-5D^0**	^{2}A (C_1) +0.32 eV **8-5E^0**	^{2}A (C_1) +0.38 eV **8-5F^0**		^{1}A (C_1) +0.50 eV **8-5E$^+$**	^{1}A (C_2) +0.03 eV **8-5F$^+$**
Si_8Li_6					
					
^{1}A' (C_s) **0.0 eV** **8-6A^0**	^{1}A (D_2) +0.01 eV **8-6B^0**	^{1}A' (C_s) +0.03 eV **8-6C^0**	^{2}A (C_1) **0.0 eV** **8-6A$^+$**	^{2}B (C_2) +0.12 eV **8-6B$^+$**	^{2}A (C_1) +0.03 eV **8-6C$^+$**

					
$^1A'$ (C_s) +0.05 eV **8-6D^0**	$^1A'$ (C_s) +0.06 eV **8-6E^0**		^2A (C_1) +0.30 eV **8-6D$^+$**	^2A (C_1) +0.16 eV **8-6E$^+$**	

C) Energy levels

Figure S4. Energy levels of the highest occupied molecular orbitals of Si_8Li_m (m = 0−6). Spin up electrons are represented by black and red lines, respectively. The HOMO level, which can be seen as a proxy for the opposite of the ionization energy, is surrounded by a blue circle.



D) Total electronic and zero-point energies

Table SIII: Calculated adiabatic and vertical ionization energies for the isomers of Si_8Li_m (m = 1, 2, 4−6) obtained at the B3LYP/6-311+G(d) level and the corresponding experimental values.

Transition	AIE (eV)	VIE (eV)	AIE exp. (eV)	VIE exp. (eV)
8-1A^0 (^{2}A")→ **8-1A$^+$**(^{1}A)	7.12	6.60	< 6.42	
8-1B^0 (^{2}A)→ **8-1B$^+$**(^{1}A)	6.43	6.10		
8-1C^0 (^{2}A)→ **8-1C$^+$**(^{1}A)	6.83	6.41		
8-1D^0 (^{2}A)→ **8-1D$^+$**(^{1}A)	6.05	5.68		
8-2A^0 (^{1}A')→ **8-2A$^+$**(^{2}A')	7.03	6.87	6.42−7.89	
8-2B^0 ($^1A_1$)→ **8-2B$^+$**($^2A_2$)	6.74	6.49		
8-2C^0 (^{1}A)→ **8-2C$^+$**(^{2}A)	6.67	6.21		
8-4A^0 (^{1}A)→ **8-4A$^+$** (^{2}A)	5.70	6.05	5.85 (0.11)	6.23 (0.03)
8-4B^0 (^{1}A')→ **8-4B$^+$** (^{2}A")	6.05	6.11		
8-4C^0 (^{1}A)→ **8-4C$^+$** (^{2}A)	5.63	6.32		
8-4D^0 (^{1}A)→ **8-4D$^+$** (^{2}A)	5.61	6.01		
8-4E^0 (^{1}A)→ **8-4E$^+$** (^{2}A)	5.69	6.01		
8-4F^0 (^{1}A)→ **8-4F$^+$** (^{2}A)	5.58	5.91		
8-5A^0 (^{2}A')→ **8-5A$^+$** (^{1}A)	5.00	5.57	5.27 (1.31)	> 6.0
8-5B^0 (^{2}A)→ **8-5B$^+$** (^{1}A)	4.86	5.54		
8-5C^0 (^{2}A)→ **8-5C$^+$** (^{1}A)	4.60	5.20		
8-5D^0 (^{2}A)→ **8-5D$^+$** (^{1}A)	4.57	5.23		
8-5E^0 (^{2}A)→ **8-5E$^+$** (^{1}A)	5.02	5.67		
8-5F^0 (^{2}A)→ **8-5F$^+$** (^{1}A)	4.49	5.07		
8-6A^0 (^{1}A')→ **8-6A$^+$** (^{2}A)	5.11	5.42	5.25 (0.21)	5.56 (0.05)
8-6B^0 (^{1}A)→ **8-6B$^+$** (^{2}A)	5.21	5.47		
8-6C^0 (^{1}A')→ **8-6C$^+$** (^{2}A)	5.08	5.43		
8-6D^0 (^{1}A')→ **8-6D$^+$** (^{2}A)	5.35	5.73		
8-6E^0 (^{1}A')→ **8-6E$^+$** (^{2}A)	5.21	5.52		

Table SIV. Total electronic (E), zero-point (ZPE), and relative (RE) energies of the low-lying isomers of Si_nLi_3 (n = 5−11) presented in Fig. 3 at the B3LYP/6-311+G(d,p) level.

Isomers[a)]	E (a.u.)	ZPE (a.u.)	E+ZPE (eV)	RE (eV)
5-3A^0	-1470.195978	0.011725	-40006.06581	0
5-3B^0	-1470.187644	0.011702	-40005.83967	0.23
6-3A^0	-1759.71088	0.0135	-47884.18136	0
6-3B^0	-1759.698328	0.01339	-47883.84261	0.33
7-3A^0	-2049.21921	0.014569	-55762.1371	0
7-3B^0	-2049.21672	0.014789	-55762.06336	0.07
8-3A^0	-2338.739707	0.016417	-63640.40268	0
8-3B^0	-2338.73889	0.016696	-63640.37284	0.03
9-3A^0	-2628.2758	0.017935	-71519.1014	0
9-3B^0	-2628.2696	0.01892	-71518.9072	0.19
10-3A^0	-2917.781809	0.0197017	-79396.97537	0
10-3B^0	-2917.778765	0.0194843	-79396.89844	0.08
11-3A^0	-3207.308891	0.0218481	-87275.41208	0
11-3H^0	-3207.293234	0.0219372	-87274.98361	0.43

[a)] Shape and symmetry of the isomers are given in the text.

Table SV. Total electronic (E), zero-point (ZPE), and relative (RE) energies of the low-lying isomers of $Si_nLi_3^+$ (n = 5−11) presented in Fig. 3 at the B3LYP/6-311+G(d,p) level.

Isomers[a)]	E (a.u.)	ZPE (a.u.)	E+ZPE (eV)	RE (eV)
5-3A$^+$	-1470.017848	0.010702	-40001.24647	0
6-3A$^+$	-1759.495803	0.01259	-47878.35342	1.03
6-3B$^+$	-1759.534205	0.01321	-47879.38147	0
7-3A$^+$	-2049.01867	0.014193	-55756.69029	0.42
7-3C$^+$	-2049.03433	0.014419	-55757.11014	0
8-3A$^+$	-2338.548279	0.015773	-63635.2111	0.23
8-3C$^+$	-2338.55676	0.016707	-63635.4165	0
9-3A$^+$	-2628.083647	0.018307	-71513.86279	0
9-3B$^+$	-2628.078154	0.018026	-71513.72097	0.14
10-3A$^+$	-2917.597673	0.0190946	-79391.98124	0.15
10-3B$^+$	-2917.602631	0.018596	-79392.12973	0
11-3A$^+$	-3207.097325	0.0207633	-87269.68457	0.07
11-3H$^+$	-3207.100833	0.0215519	-87269.75856	0

[a)] Shape and symmetry of the isomers are given in the text.

Table SVI. Total electronic (E), zero-point (ZPE), and relative (RE) energies of the low-lying isomers of Si_8Li_m (m = 1−6; $m \neq 3$) presented in Fig. 4 at the B3LYP/6-311+G(d,p) level.

Isomers[a)]	E (a.u.)	ZPE (a.u.)	E+ZPE (eV)	RE (eV)
8-1A^0	-2323.611683	0.013126	-63228.83449	0
8-1D^0	-2323.588063	0.012884	-63228.19835	0.64
8-2A^0	-2331.20106	0.015963	-63435.2765	0
8-2B^0	-2331.19986	0.015911	-63435.245	0.03
8-4A^0	-2346.313899	0.0193028	-63846.43003	0
8-4B^0	-2346.313768	0.0189685	-63846.43557	0
8-4C^0	-2346.312643	0.0189779	-63846.4047	0.03
8-5A^0	-2353.87186	0.0204823	-64052.06214	0
8-5C^0	-2353.862986	0.0207271	-64051.81401	0.25
8-6A^0	-2361.449813	0.0234128	-64258.19063	0
8-6B^0	-2361.449354	0.0234732	-64258.1765	0.01
8-6C^0	-2361.448832	0.0234466	-64258.16303	0.03

[a)] Shape and symmetry of the isomers are given in the text.

Table SVII. Total electronic (E), zero-point (ZPE), and relative (RE) energies of the low-lying isomers of $Si_8Li_m^+$ (m = 1−6; $m \neq 3$) presented in Fig. 4 at the B3LYP/6-311+G(d,p) level.

Isomers	E (a.u.)	ZPE (a.u.)	E+ZPE (eV)	RE (eV)
8-1A$^+$	-2323.368515	0.0124789	-63222.2351	0.28
8-1D$^+$	-2323.378881	0.0125459	-63222.51536	0
8-2A$^+$	-2330.947314	0.0144997	-63428.4114	0.35
8-2B$^+$	-2330.959716	0.0140782	-63428.7603	0
8-4A$^+$	-2346.102655	0.0175824	-63840.72857	0.05
8-4B$^+$	-2346.090177	0.0177053	-63840.38568	0.39
8-4C$^+$	-2346.104471	0.01762	-63840.77695	0
8-5A$^+$	-2353.686839	0.019126	-64047.06434	0.15
8-5B$^+$	-2353.692896	0.019638	-64047.21523	0
8-6A$^+$	-2361.259831	0.0212069	-64253.08094	0
8-6B$^+$	-2361.255668	0.0213439	-64252.96394	0.12
8-6C$^+$	-2361.258791	0.0213935	-64253.04756	0.03