Supplementary Materials

Computational Characterization of β-Li₃PS₄ Solid Electrolyte: From Bulk and Surfaces to Nanocrystals

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Topic S1: Bulk data

Table S1: Cell parameters and band gap of β-Li₃PS₄

β-Li₃PS₄ (Pnma)	a (Å)	b (Å)	c (Å)	E_{gap} (eV)
Experimental[1]	12.82	8.22	6.12	5.0
Theoretical[2]	12.86	7.76	6.21	2.2 – 3.7
PBE	13.03	8.13	6.29	2.70
PBE0	12.96	8.08	6.25	4.71
HSE06	12.96	8.09	6.25	3.97

Table S2: Mechanical properties of β-Li₃PS₄

	Bulk modulus	Young's modulus	Poisson ratio	c_{11}	c_{12}	c_{13}	c_{22}	c_{23}	c_{33}	c_{44}	c_{55}	c_{66}
Theooretical.[3]	21.39	28.90	0.27	47.82	15.93	17.90	36.23	10.20	28.46	12.88	9.81	12.17
Pnma	21.82	32.35	0.26	53.33	16.46	18.24	38.38	10.48	31.31	13.72	11.66	13.64
Pn2₁a	24.31	33.58	0.27	51.57	18.94	18.66	36.52	13.63	37.96	15.69	11.71	14.24

Topic S2: β-Li₃PS₄ surfaces

Table S3: Possible termination along +z of each analyzed surface. The "X" represents the termination found in the surface and the '-' the termination not found

	LiS₃	PS₃	PS₂	SLi₂	S	Li	SPLi₂	LiS₂	SPLi	LiS
(100)	-	X	-	X	-	X	-	X	-	-
(001)	X	X	-	-	-	-	X	X	-	X
(010)	-	X	-	-	-	X	-	X	-	-
(101)	-	X	-	X	X	-	X	X	-	-
(011)	-	X	X	-	-	-	X	X	X	X
(110)	X	-	X	X	-	-	-	X	-	X
(111)	X	X	X	X	-	-	-	-	X	X
(210)	-	X	X	-	-	-	-	X	X	-
(211)	X	-	X	X	-	-	X	X	-	-

Topic S3: Discussion on the choice of surface terminations

- **(001)**

In order to maintain the 4 units in the surface as in the bulk, the analyzed surfaces (001) contain 22 layers each. According to our analysis, only 2 terminations were judged to be possible candidates for the study. The surfaces are shown below. As the termination LiS_2/LiS_2 (not symmetric) presented the minor E_{surf}, it was calculated with 8 units of Li_3PS_4.
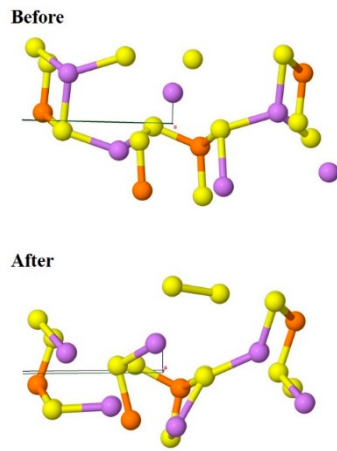
(a) $E_{surf} = 5.15$ J/m²   (b) $E_{surf} = 1.89$ J/m²
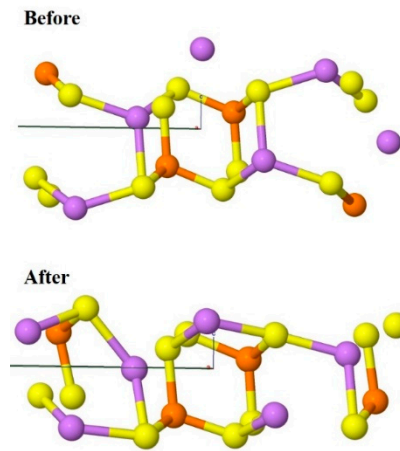
Figure S1: (a) SLi_2/SP and (b) LiS_2/LiS_2

- **(100)**

For this surface, also 22 layers correspond to 4 units of Li_3PS_4. Four terminations were analyzed (see below), as the termination denominated LiS_2/LiS_2 presented the minor E_{surf}, the surface with 8 units was calculated and the E_{surf} obtained is 0.91 J/m², i. e., 0.90 J/m² minor than the surface with 4 units.
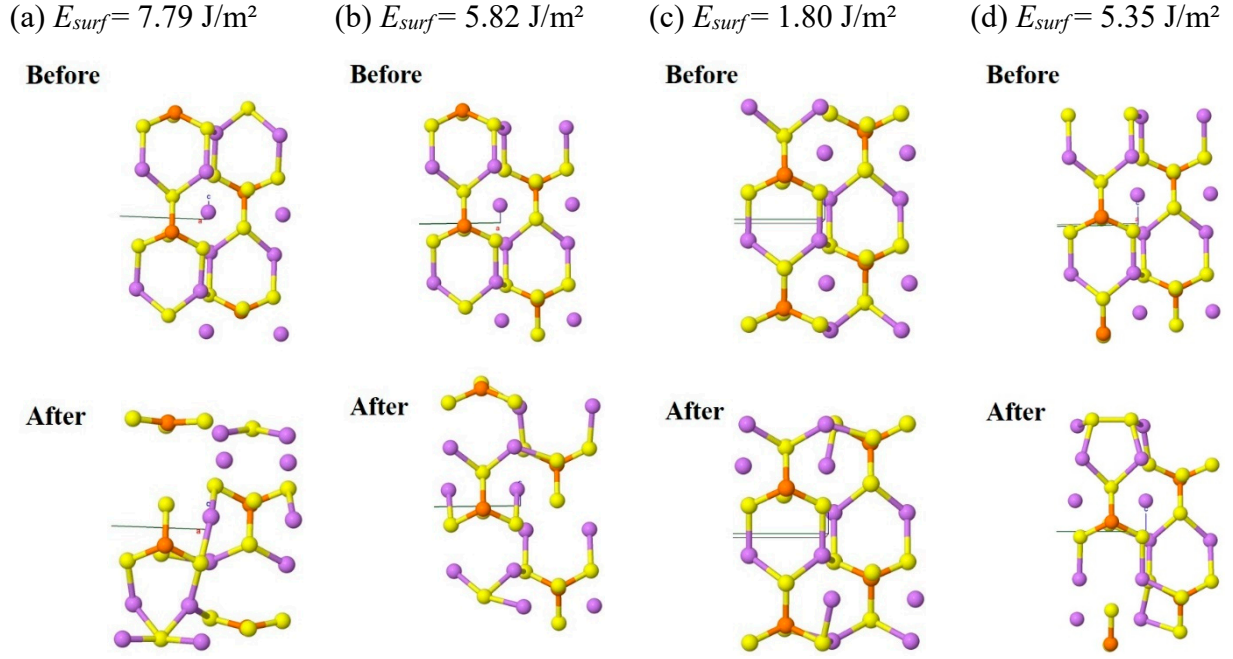
(a) E_{surf}= 7.79 J/m²   (b) E_{surf}= 5.82 J/m²   (c) E_{surf}= 1.80 J/m²   (d) E_{surf}= 5.35 J/m²

Before   Before   Before   Before

After   After   After   After

Figure S2: (a) SLi$_2$/SLi, (b) PS$_3$/SP, (c) LiS$_2$/LiS$_2$, and (d) LiS/PS

- **(010)**

Eight layers of this surface have 4 units of Li$_3$PS$_4$. This surface has only two possible terminations: LiS$_2$/Li and PS$_3$/SLi$_2$ (see below). The surface with termination LiS$_2$/Li presented the minor E_{surf} and it was calculated with 8 units of Li$_3$PS$_4$. After optimization, the E_{surf} of (010) with 8 units is 1.83 J/m² and decreases 1.20 J/m² from the E_{surf} of (010) with 4 units.
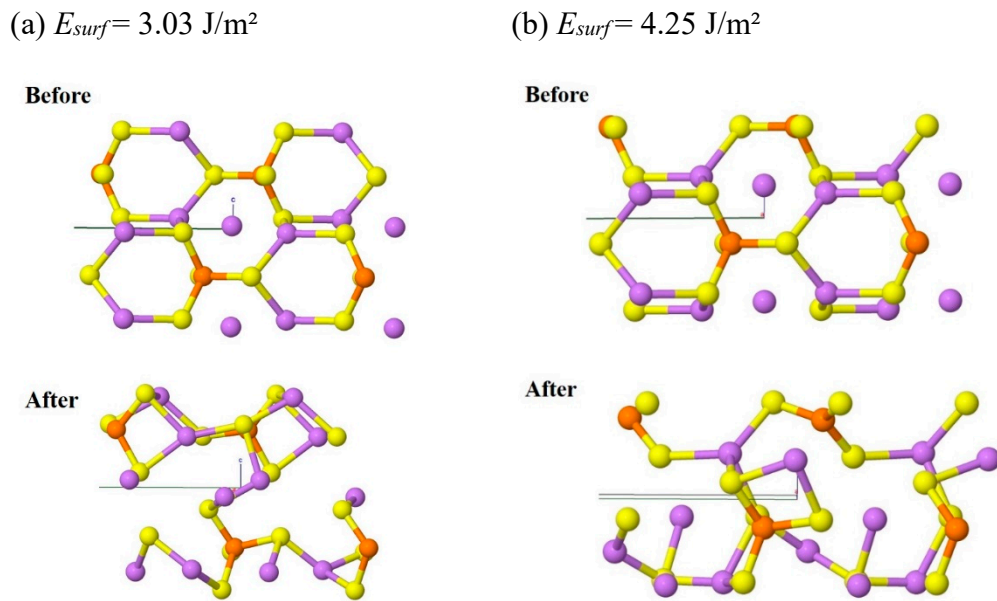
(a) E_{surf}= 3.03 J/m²   (b) E_{surf}= 4.25 J/m²

Before   Before

After   After

Figure S3: (a) LiS$_2$/Li and (b) PS$_3$/SLi$_2$

- **(101)**

The surface (101) was made with 21 layers to respect the 4 units of Li_3PS_4. Only the 4 terminations below were considered relevant. However, only the termination called LiS/LiS maintains the cluster [PS_4] integer, that is the surface with minor E_{surf}, 1.54 J/m² and it was calculated with 8 units of Li_3PS_4 which E_{surf} obtained was 8.20 J/m². Therefore, this termination's surface showed to be unstable.
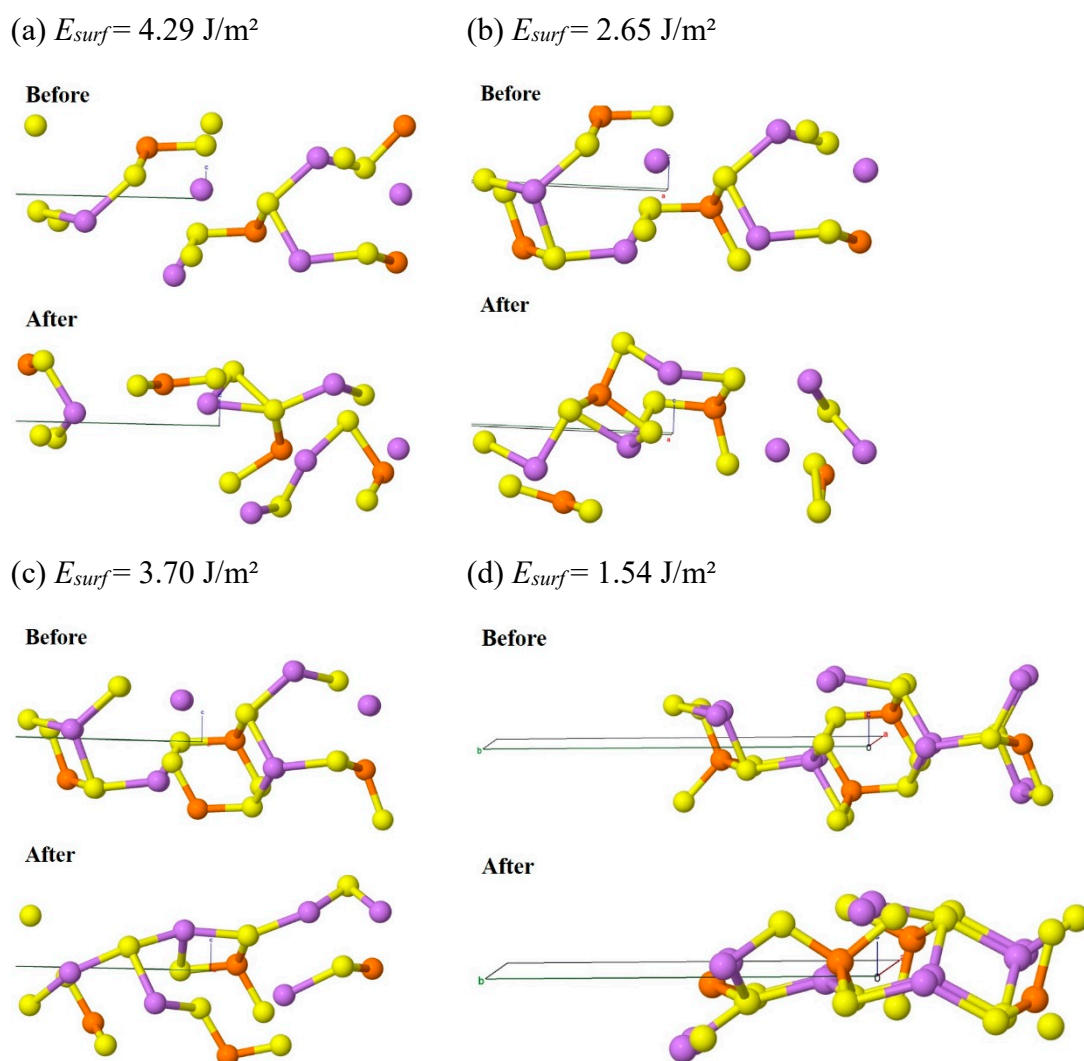
(a) E_{surf} = 4.29 J/m²

(b) E_{surf} = 2.65 J/m²

(c) E_{surf} = 3.70 J/m²

(d) E_{surf} = 1.54 J/m²

Figure S4: (a) PS_3/LiS, (b) PS_3/SPLi, (c) LiS_2/PS_2, and (d) LiS/LiS

- **(011)**

The 4 units of Li_3PS_4 are given by 16 layers of the (011) surface. Two terminations were considered relevant due to the many unbonded atoms in the other terminations (see below). The termination PS_3/Li presented the minor E_{surf} and it was calculated with 8 units of Li_3PS_4, which E_{surf} obtained was 1.50 J/m², i. e., no changes in the surface energy formation were observed by the increasing number of units.
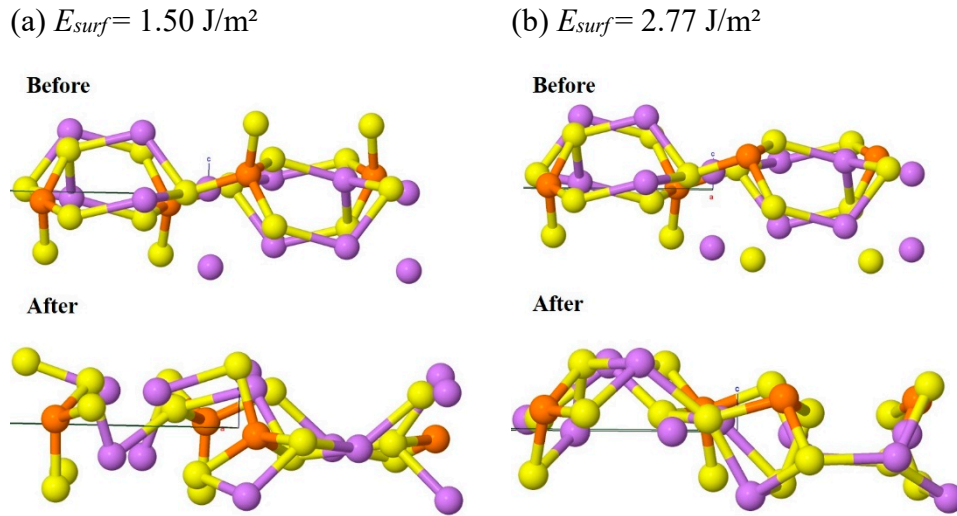
(a) E_{surf} = 1.50 J/m²   (b) E_{surf} = 2.77 J/m²

Figure S5: (a) PS_3/Li and (b) LiS_2/Li

- **(110)**

The (110) surface was initially studied with 4 units of Li_3PS_4, which is composed of 30 layers. Only 3 terminations were considered interesting for this study (see below). As the termination SLi_2/Li presented the minor E_{surf}, was calculated the surface with 8 units of Li_3PS_4, also, the termination LiS/LiS (considered symmetric) was calculated with 8 units. Both terminations with 8 units have, almost, the same E_{surf}, 2.24 and 2.27 J/m² for LiS/LiS and SLi_2/Li, respectively, a reduction of 40% and 30% concerning the 4 units models. However, the termination SLi_2/Li presented the smallest structural distortion after the optimization and kept the tetrahedron [PS_4].

(a) $E_{surf} = 3.22$ J/m²   (b) $E_{surf} = 4.78$ J/m²

Before

After

(c) $E_{surf} = 3.67$ J/m²

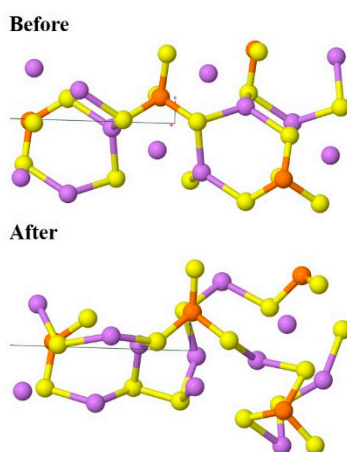**Before**

After
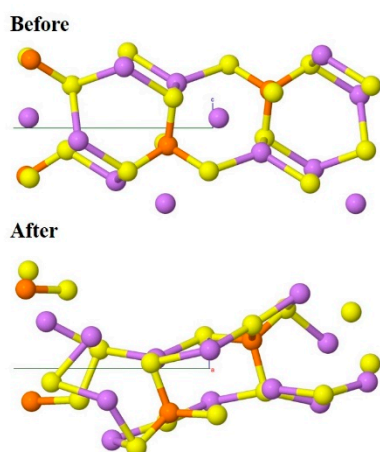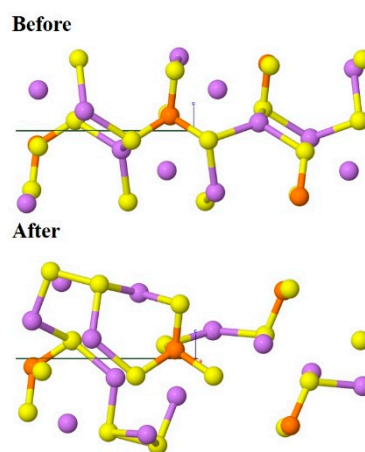
Figure S6: (a) SLi_2/Li, (b) LiS/LiS, and (c) $PS_2/SPLi$

- **(111)**

The surface (111) needs 30 layers to have 4 units of Li_3PS_4. No symmetric terminations were found for this surface. The terminations analyzed were LiS_3/LiS, PS_2/LiS_2, SLi_2/LiS_2, and Li/PS_3 (see below). The termination LiS_3/LiS presented the minor E_{surf} and it was calculated taking to account 8 units of Li_3PS_4. After full optimization, the E_{surf} is 1.60 J/m², i. e., a reduction of ~40%.

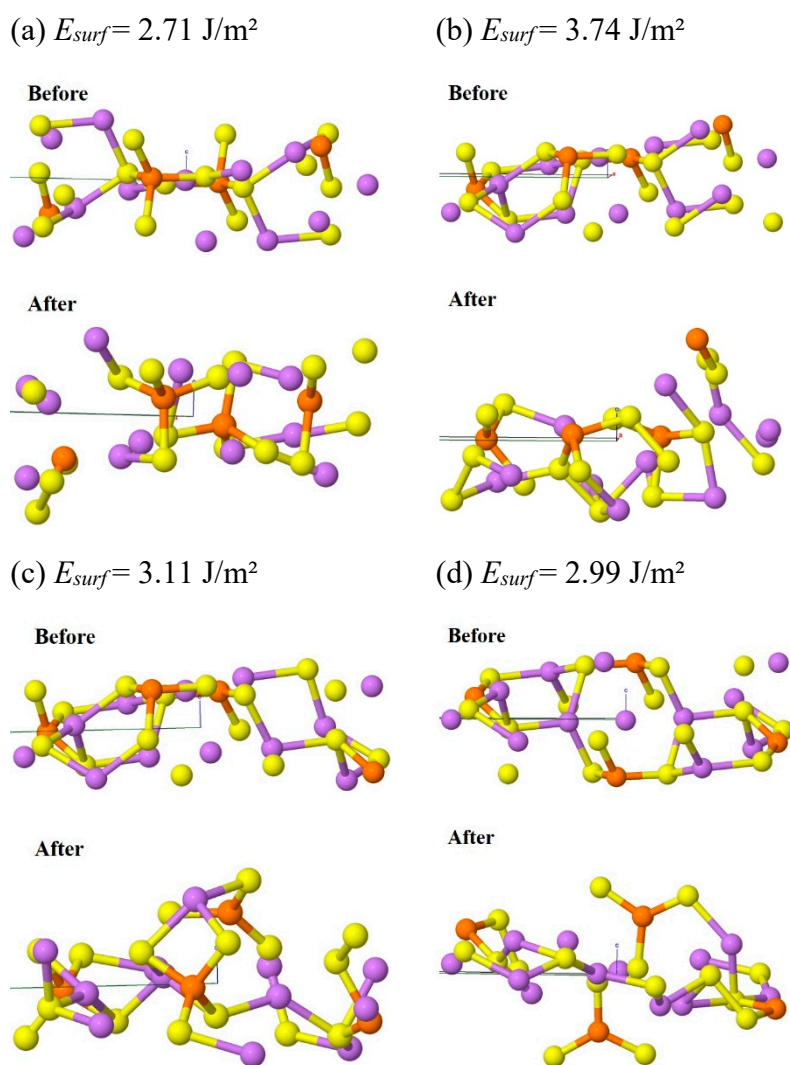(a) E_{surf}= 2.71 J/m²

(b) E_{surf}= 3.74 J/m²

Before

Before

After

After

(c) E_{surf}= 3.11 J/m²

(d) E_{surf}= 2.99 J/m²

Before

Before

After

After

Figure S7: (a) LiS_3/LiS, (b) PS_2/LiS_2, (c) SLi_2/LiS_2, and (d) Li/PS_3
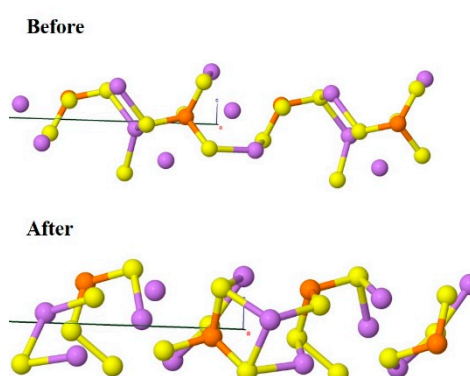
- **(210)**

The surface (210) with 16 layers is composed of 4 units of Li_3PS_4. It was seen that only 4 terminations are relevant for the present study (see below). The termination SPLi/Li presented the minor E_{surf} and it was optimized with 8 units. After optimization, it was found an $E_{surf} = 0.99$ J/m², a reduction of 41%.
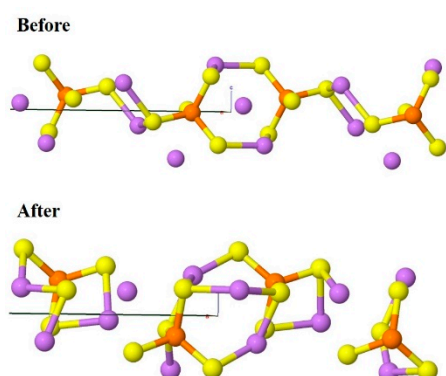
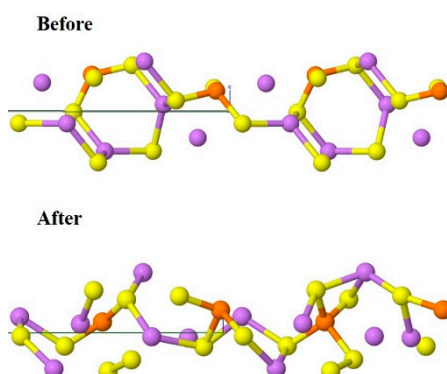(a) $E_{surf} = 1.70$ J/m² (b) $E_{surf} = 3.18$ J/m²

(c) $E_{surf} = 3.06$ J/m²

**Figure S8**: (a) SPLi/Li, (b) LiS_2/LiS, and (c) LiS_2/SLi_2

9

- **(211)**

The (211) surface was analyzed with 30 layers (4 units of Li_3PS_4). No symmetric terminations were found. The 3 relevant terminations are represented below. It was found that the termination $LiS_2/SPLi$ presents the minor E_{surf}, and a model with 8 units was also calculated. The E_{surf} of 8 units is reduced ~51%, 1.57 J/m².

(a) E_{surf} = 3.62 J/m²

(b) E_{surf} = 3.04 J/m²

Before

Before

After

After

(c) E_{surf} = 4.27 J/m²
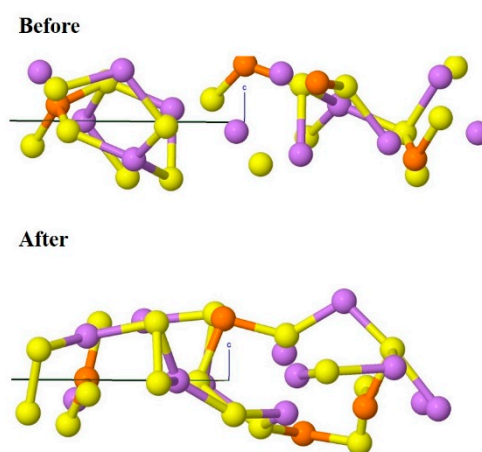
Before

After
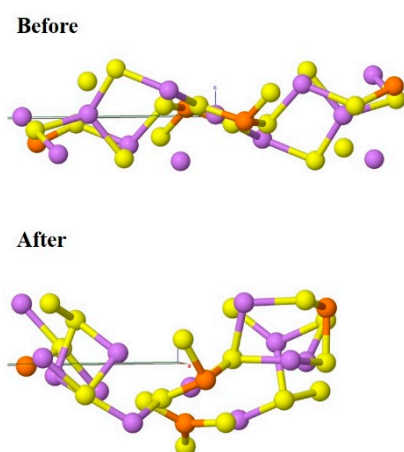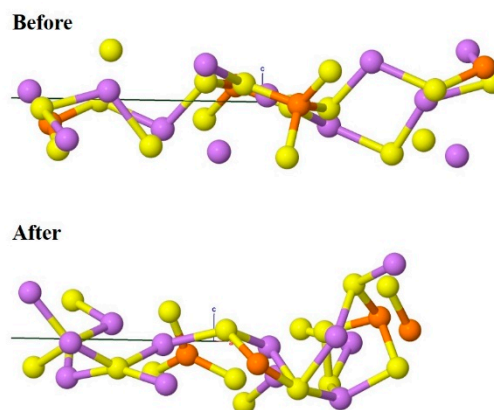
Figure S9: (a) SLi_2/LiS, (b) $LiS_2/SPLi$, and (c) PS_2/LiS

Table S4: Hirshfield charges of β-Li$_3$PS$_4$ bulk and 8-unit surfaces for the surface (indicated by *) and internal atoms.

|	Li$_1$	Li*$_1$	Li$_2$	Li*$_2$	P	P*	S$_1$	S*$_1$	S$_2$	S*$_2$	S$_3$	S*$_3$
bulk	**1.007**	**1.007**	**1.011**	**1.011**	**1.573**	**1.573**	**-1.147**	**-1.147**	**-1.272**	**-1.272**	**-1.034**	**-1.034**
(001)	1.006	1.004	1.008	0.993	1.580	1.127	-1.150	-1.023	-1.249	-1.206	-1.059	-1.176
(100)	1.007	1.003	1.010	1.008	1.575	1.498	-1.149	-1.130	-1.268	-1.297	-1.033	-1.020
(010)	1.006	0.979	1.008	1.011	1.611	1.500	-1.174	-0.945	-1.239	-1.253	-1.033	-1.035
(011)	1.009	1.001	1.013	1.012	1.566	1.588	-1.226	-0.974	-1.261	-1.022	-1.183	-0.836
(110)	1.009	1.001	1.009	1.008	1.410	1.024	-1.161	-0.706	-1.273	-1.154	-1.187	-0.799
(111)	1.005	0.959	1.009	1.009	1.657	0.605	-1.158	-0.948	-1.304	-1.192	-1.078	-0.973
(210)	1.009	0.972	1.011	1.002	1.565	1.549	-1.177	-1.006	-1.246	-1.180	-1.107	-1.001
(211)	1.007	1.002	1.016	1.013	1.508	0.569	-1.130	-0.971	-1.229	-2.004	-1.098	-0.530

(a)

(b)

(c)
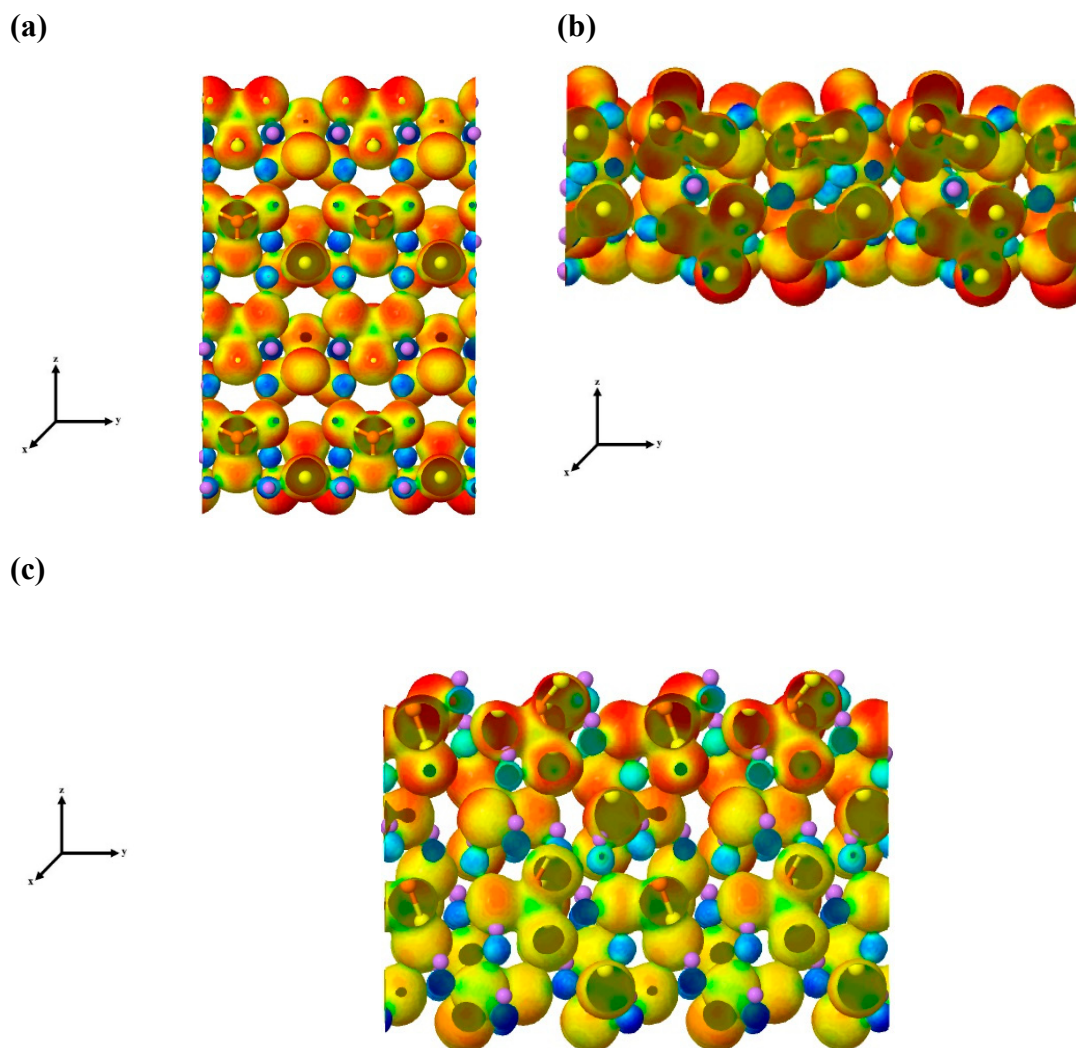
Figure S10: Three-dimensional maps of the electronic charge density superimposed to the electrostatic potential of β-Li₃PS₄ surfaces along z-direction: (a) (100), (b) (210), and (c) (011). The spheres in purple, orange, yellow, and black are related to the lithium, phosphor, and sulfur atoms. The scale maps range from negative (-) in blue to positive (+) in red.

References

1. Homma, K. *et al.* Crystal structure and phase transitions of the lithium ionic conductor Li3PS4. *Solid State Ionics* **182**, 53–58 (2011).

2. Lepley, N. D., Holzwarth, N. A. W. & Du, Y. A. Structures, Li+ Mobilities, and Interfacial Properties of Solid Electrolytes Li3PS4 and Li3PO4 from First Principles. *Phys. Rev. B* **88**, 104103 (2013).

3. Yang, Y. *et al.* Elastic Properties, Defect Thermodynamics, Electrochemical Window, Phase Stability, and Li+ Mobility of Li3PS4: Insights from First-Principles Calculations. *ACS Appl. Mater. Interfaces* **8**, 25229–25242 (2016).