Supplementary information:

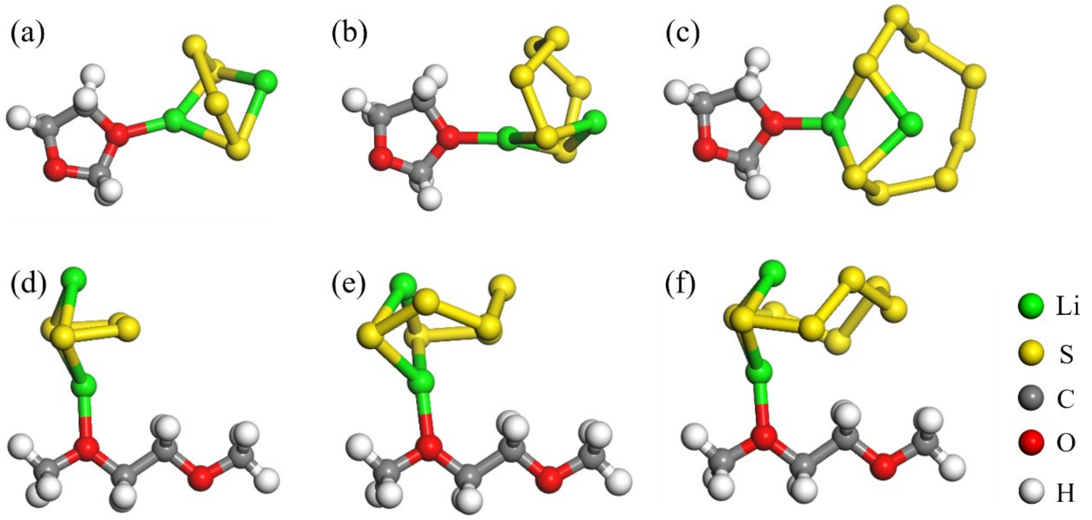

Fig. S1 The optimized structures of electrolyte solvent molecule DOL with (a) Li_2S_4, (b) Li_2S_6, (c) Li_2S_8, and DME with (d) Li_2S_4, (e) Li_2S_6, (f) Li_2S_8.

Table S1 The binding energies (in eV) between long-chain Li_2S_n clusters and electrolyte solvent molecules (DOL and DME).

Clusters	DOL				DME			
	E_b (eV) This work	E_b (eV) Ref. [1]	E_b (eV) Ref. [2]	E_b (eV) Ref.[3]	This work	E_b (eV) Ref. [1]	E_b (eV) Ref. [2]	E_b (eV) Ref.[3]
Li_2S_4	0.87	0.87	0.87	0.80	0.92	0.92	0.94	0.80
Li_2S_6	0.90	0.90	0.92	0.83	0.95	0.95	0.97	0.85
Li_2S_8	0.92	0.92	0.93	0.77	0.97	0.98	0.99	0.78

Table S2 The calculated parameters of ε-P with adsorbed Li_2S, LiS+Li or 2Li+S. The nearest distances between Li/S and P atoms (D_{AM-Li} and D_{AM-S}), the distance between Li and S atoms in adsorbed species (d_{Li-S1} and d_{Li-S2}), the longest distance between two adjacent P atoms in ε-P (d_{P-P}), the serious distance change of P-P bond in ε-P with adsorbed species (Δd_{P-P}), the P-S bond population (P_{P-S}), Mulliken atomic population of Li atoms (e_{Li1}, e_{Li2}), total Mulliken charge magnitude of S atoms (e_S) and total Mulliken charge difference of ε-P. Here, Mulliken charge difference means the difference of charge value between adsorbed case and free-standing case (Δe_{AM})(e). (In free Li_2S, d_{Li-S} = 2.094 Å; in free ε-P, d_{P-P}=2.230 Å)

ε-P	D_{AM-Li} (Å)	D_{AM-S} (Å)	d_{Li-S1} (Å)	d_{Li-S2} (Å)	d_{P-P} (Å)	Δd_{P-P} (Å)	P_{P-S}	e_{Li1}(e)	e_{Li2}(e)	e_S(e)	Δe_{AM}(e)
Li_2S	2.542	2.112	2.507	2.470	3.156	0.926	0.41	0.96	0.95	-0.83	1.08
LiS+Li	2.532	2.018	2.412	-	2.314	0.084	0.59	0.97	0.95	-0.62	1.30
2Li+S	2.543	2.112	-	-	2.262	0.032	0.33	0.98	0.97	-0.25	1.70

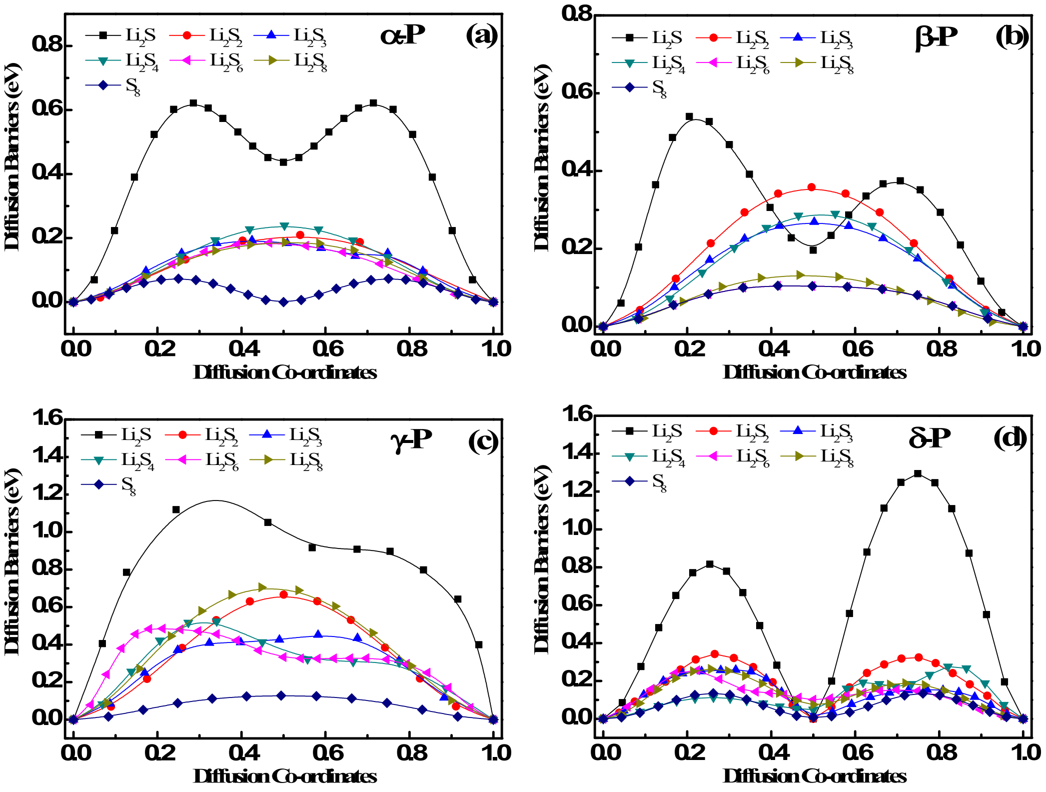

Fig. S2 Energy profiles of lithium sulfides diffusions along the directions with the lowest barriers. (a) α-P, (b) β-P, (c) γ-P, (d) δ-P.

Table S3 Diffusion energy barriers (eV) of lithium sulfides along different crystal orientations on β-P and γ-P.

Barrier (eV)	β-P[100]	β-P[010]	β-P[110]	γ-P[100]	γ-P[010]
S_8	0.069	0.132	0.137	2.957	3.19
Li_2S_8	0.127	0.161	0.178	17.456	16.446
Li_2S_6	0.104	0.134	0.197	14.198	13.226
Li_2S_4	0.285	0.385	0.498	14.303	12.075
Li_2S_3	0.268	0.269	0.374	10.417	21.36
Li_2S_2	0.358	0.394	0.426	15.369	20.459
Li_2S	0.544	0.667	0.762	28.246	30.953

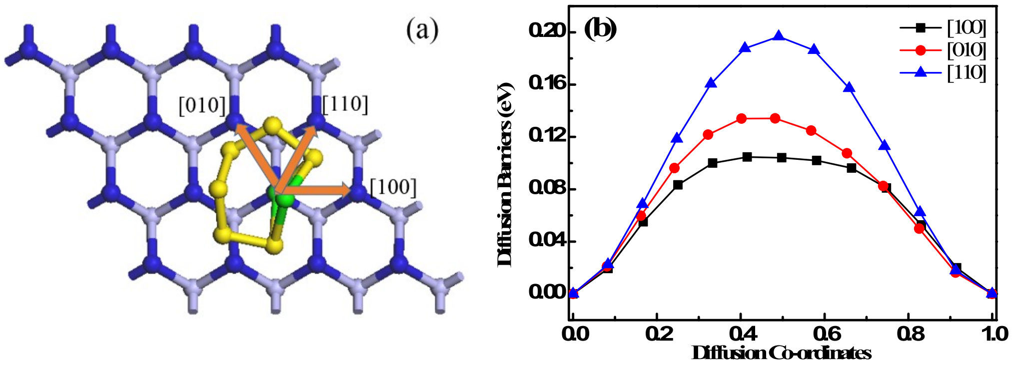

Fig. S3 Non-equivalent [100], [010] and [110] diffusion directions for Li_2S_6 on β-P. The energy profiles with different barriers along [100], [010] and [110] directions for Li_2S_6 diffusion on β-P.

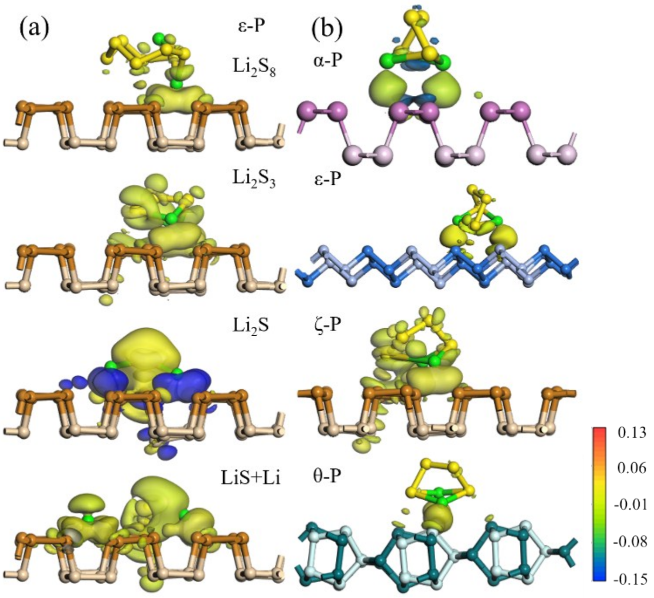

Fig. S4 (a) Electron density difference between Li_2S_8, Li_2S_3, Li_2S and LiS+Li species and ε-P AM; (b) Electron density difference between Li_2S_4 and various AMs, α-P, ε-P, ζ-P and θ-P. The charge transfer is defined as the charge difference between before and after Li_2S_n cluster is absorbed on AM, and can be expressed as $\Delta\rho = \rho(AM + Li_2S_n) - \rho(AM) - \rho(Li_2S_n)$, where $\rho(AM + Li_2S_n)$, $\rho(AM)$, and $\rho(Li_2S_n)$ are the charge densities for bound system, pristine AM and Li_2S_n cluster, respectively. Here, blue (yellow) is the spatial regions gain (loss) in charge. The isosurface level is set as 0.01 e Å^{-3}.

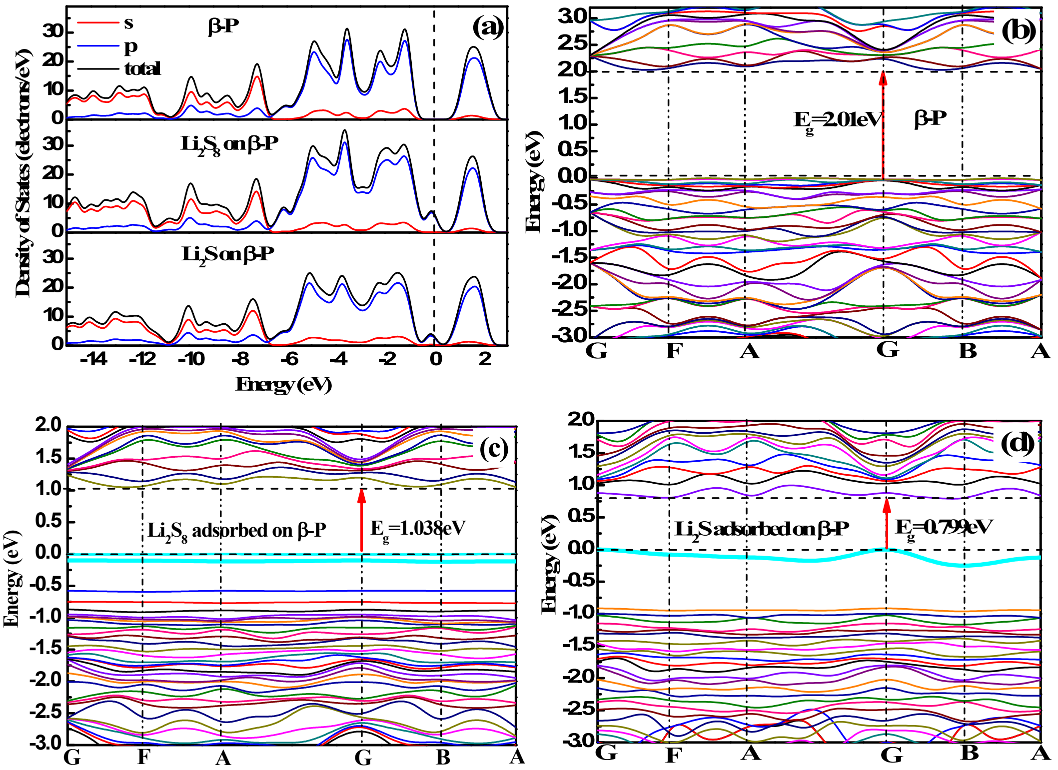

Fig. S5 (a) Atomic partial density of states (PDOS) for pristine β-P and β-P with adsorbed Li_2S_8 or Li_2S; (b) Band structure of pristine β-P; (c) Band structure of β-P with adsorbed Li_2S_8; (d) Band structure of β-P with adsorbed Li_2S.

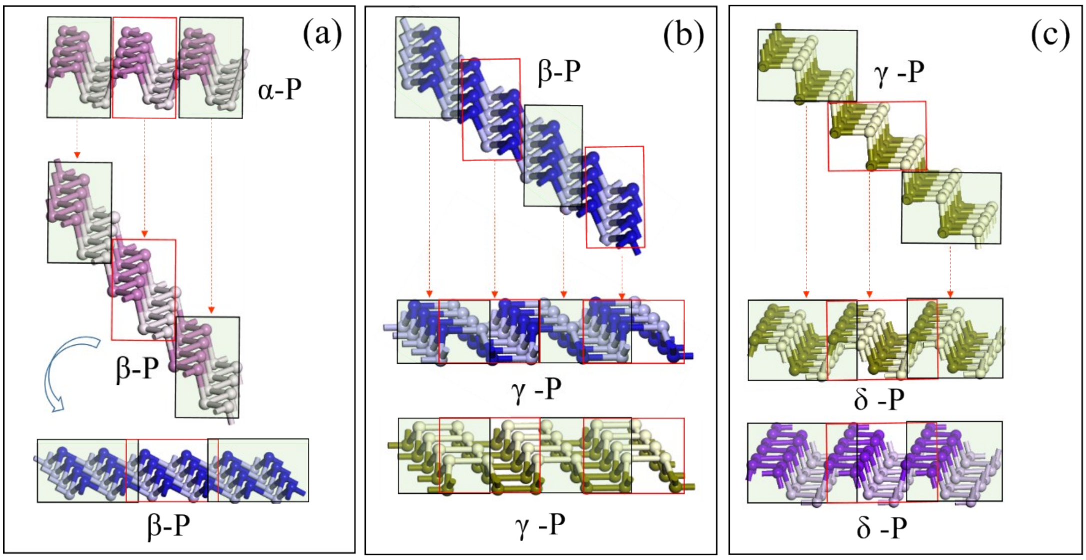

Fig. S6 Schematic diagrams of the conversions by embedding an array of dislocations, with the corresponding structural units highlighted by shaded regions and arrows. (a) from α-P to β-P, (b) from β-P to γ-P, (c) from γ-P to δ-P.

References:

[1] L.-C. Yin, J. Liang, G.-M. Zhou, F. Li, R. Saito and H.-M. Cheng, 2016, *Nano Energy*, 25: 203-210.
[2] T. Li, C. He and W. Zhang, 2020, *Energy Storage Materials*, 25: 866-875.
[3] Y. Qie, J. Liu, S. Wang, S. Gong and Q. Sun, 2018, *Carbon*, 129: 38-44.