ADVANCED MATERIALS

Supporting Information

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Anharmonic Cation–Anion Coupling Dynamics Assisted Lithium-Ion Diffusion in Sulfide Solid Electrolytes

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Supplementary Information

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Table S1. The vibrational structures of the anharmonic coupling modes between the medium-low frequency Li modes and the high-frequency polyanion modes with relatively high coupling strengths (> 0.1 meV/atom) of $Li_7P_3S_{11}$. The high-frequency polyanion modes are the stretching modes. The length of arrow donates the vibrational amplitude.

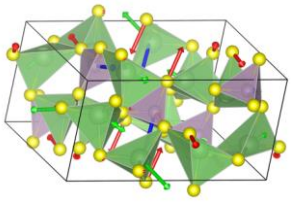
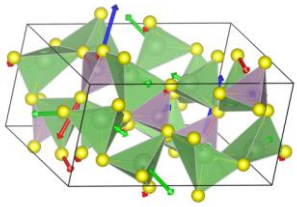
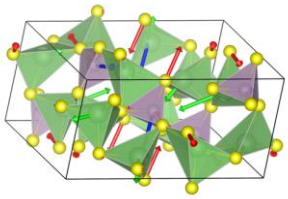
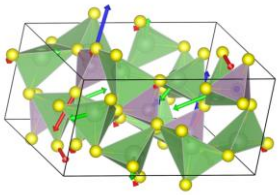
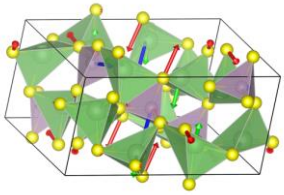
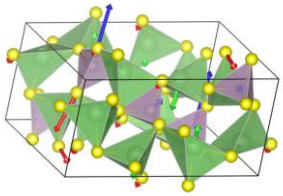
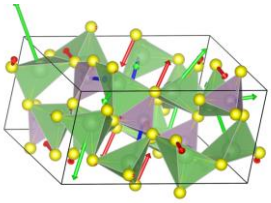
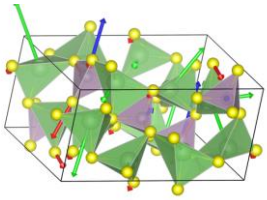
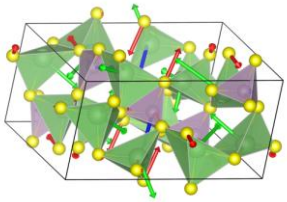
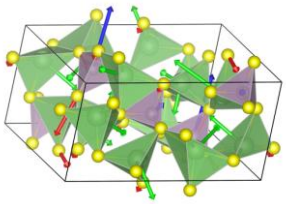
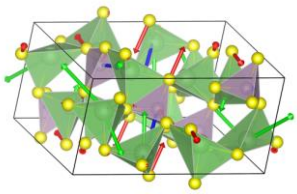
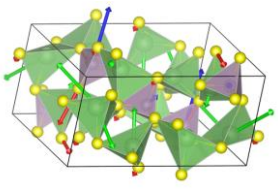
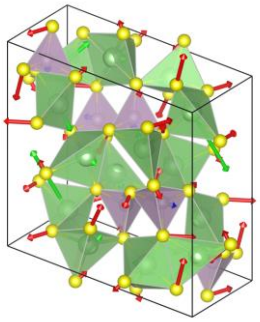
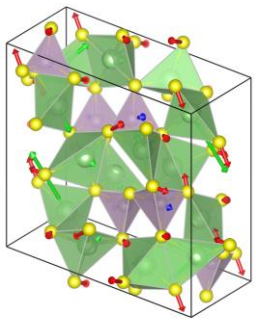
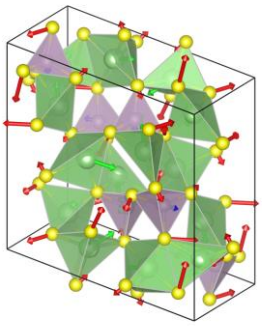
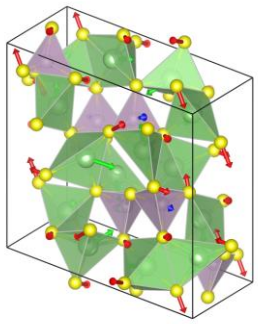
	PS_4 polyanion (17.17 THz)	PS_4 polyanion (18.15 THz)
Li ion (1.61 THz)		
Li ion (2.12 THz)		
Li ion (4.09 THz)		
Li ion (5.74 THz)		
Li ion (6.38 THz)		
Li ion (9.75 THz)		

Table S2. The vibrational structures of the anharmonic coupling modes between the high-frequency Li modes and the low-frequency polyanion modes with relatively high coupling strengths (> 0.1 meV/atom) of $Li_7P_3S_{11}$. The two low-frequency polyanion modes are the rotational modes. The length of arrow donates the vibrational amplitude.

	PS_4 polyanion (4.41 THz)	PS_4 polyanion (5.53 THz)
Li ion (12.09 THz)		
Li ion (13.59 THz)		

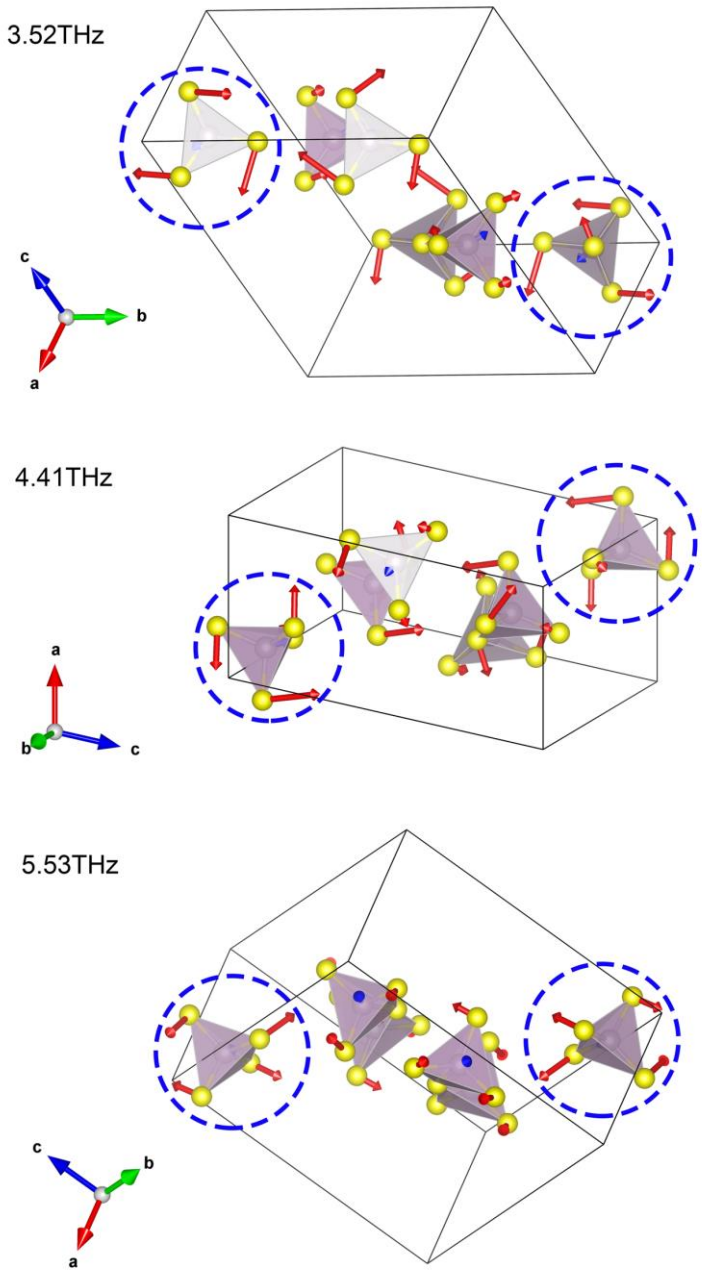
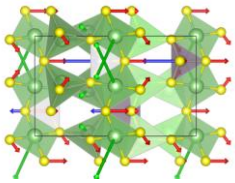
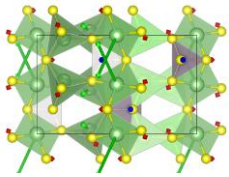
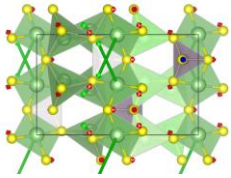
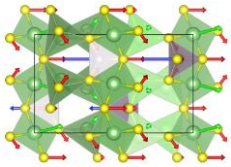
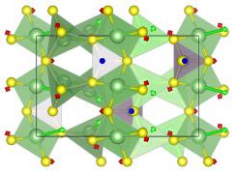
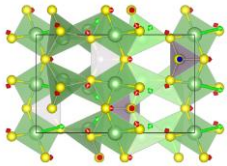
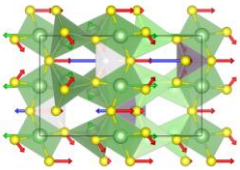
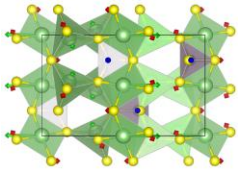
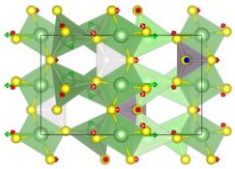
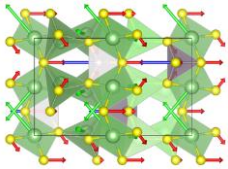
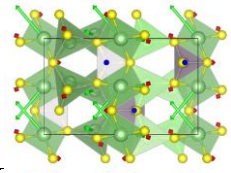
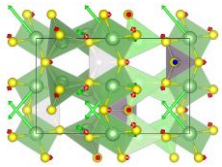
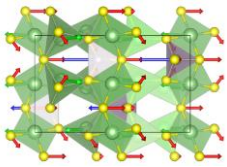
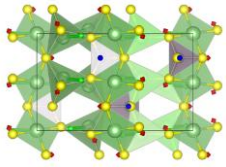
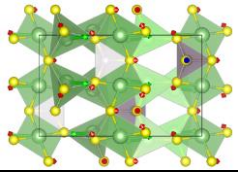
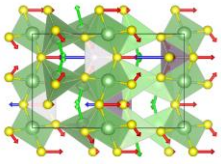
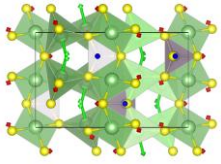
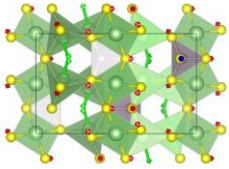
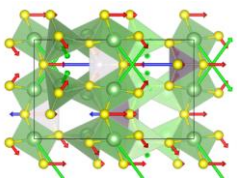
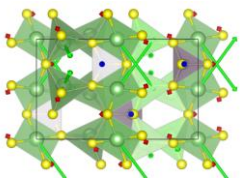
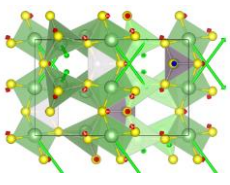


Figure S1. The low-frequency rotational modes (3.52, 4.41 and 5.53THz) of PS_4 polyanion in $Li_7P_3S_{11}$ unit cell. The Li ions are hidden to highlight the polyanion, and the red arrows donate the direction of polyanion rotation. The length of arrow donates the vibrational amplitude. For a better visualization, the rotational modes are highlighted by the blue dashed circles.

Table S3. The vibrational structures of the anharmonic coupling modes between the medium-low frequency Li modes and the high-frequency polyanion modes with relatively high coupling strengths (> 0.1 meV/atom) of Li_3PS_4. The high-frequency polyanion modes are the stretching and flexing modes. The length of arrow donates the vibrational amplitude.

	PS_4 polyanion (18.51 THz)	PS_4 polyanion (19.55 THz)	PS_4 polyanion (19.99 THz)
Li ion (4.39 THz)			
Li ion (5.94 THz)			
Li ion (6.54 THz)			
Li ion (9.58 THz)			
Li ion (10.21 THz)			
Li ion (11.06 THz)			
Li ion (11.31 THz)			

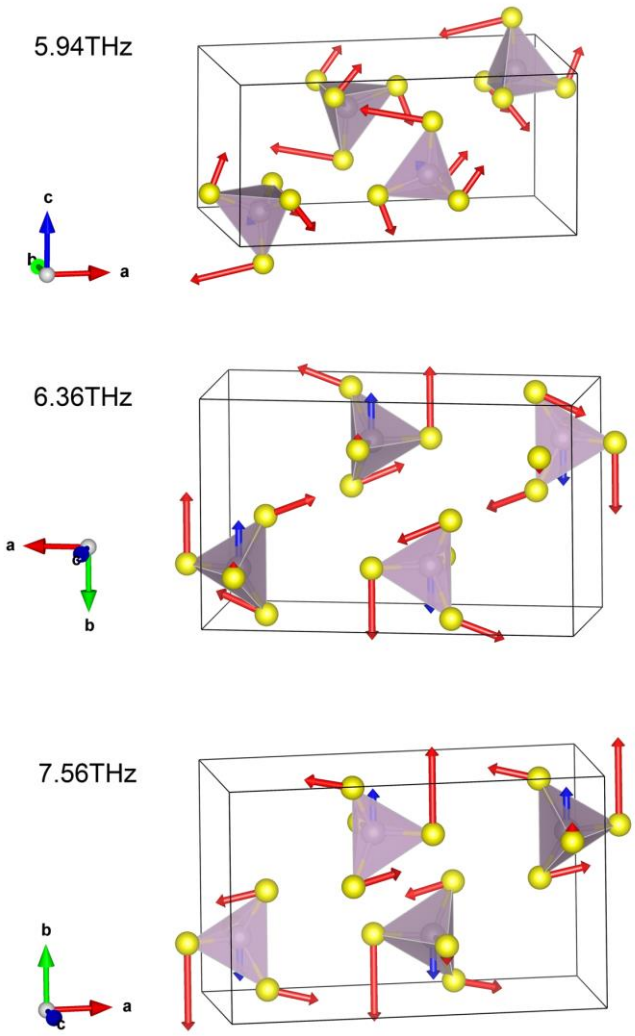


Figure S2. The low-frequency rotational modes (5.94, 6.36 and 7.56THz) of PS_4 polyanion in Li_3PS_4 unit cell. The Li ions are hidden to highlight the polyanion, and the red arrows donate the direction of polyanion rotation. The length of arrow donates the vibrational amplitude.

Table S4. The vibrational structures of the anharmonic coupling modes between the low-frequency Li modes and the high-frequency polyanion modes with relatively high coupling strengths (> 0.15 meV/atom) of Li_3YBr_6. The high-frequency polyanion modes are the stretching and flexing modes. The length of arrow donates the vibrational amplitude.

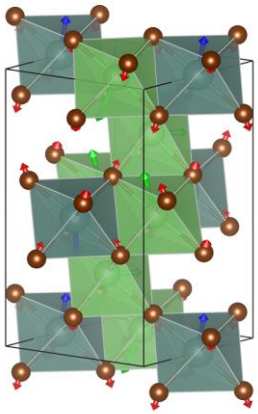
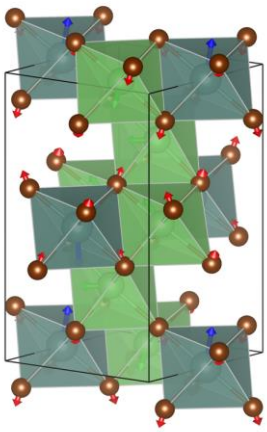
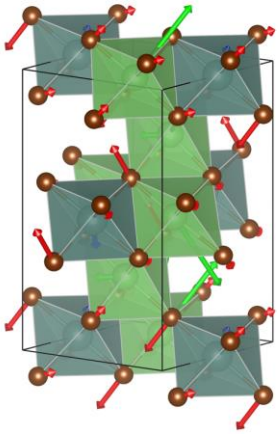
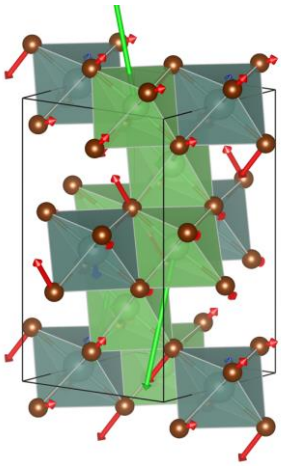
	YBr_6 polyanion (9.23 THz)
Li ion (1.90 THz)	
Li ion (1.64 THz)	

Table S5. The vibrational structures of the anharmonic coupling modes between the high-frequency Li modes and the low-frequency polyanion modes with relatively high coupling strengths (> 0.15 meV/atom) of Li_3YBr_6. The low-frequency polyanion modes are the rotational modes. The length of arrow donates the vibrational amplitude.

	YBr_6 polyanion (1.90 THz)
Li ion (4.62 THz)	
Li ion (9.23 THz)	

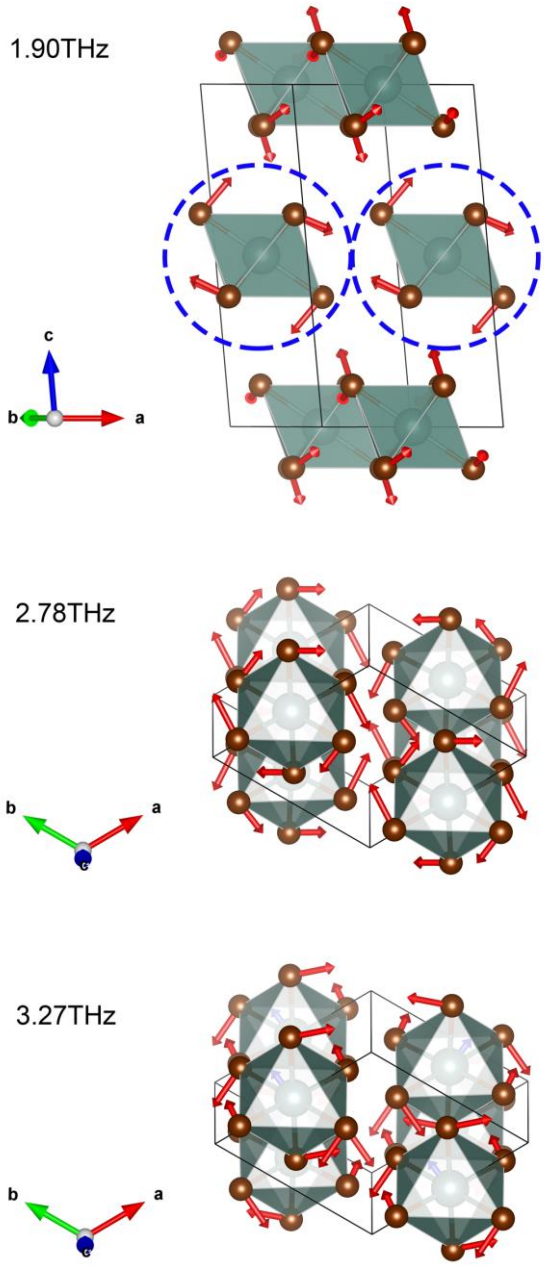


Figure S3. The low-frequency rotational modes (1.90, 2.78 and 3.27 THz) of YBr_6 polyanion in Li_3YBr_6 unit cell. The Li ions are hidden to highlight the polyanion, and the red arrows donate the direction of polyanion rotation. The length of arrow donates the vibrational amplitude. For a better visualization, the rotational modes are highlighted by the blue dashed circles.

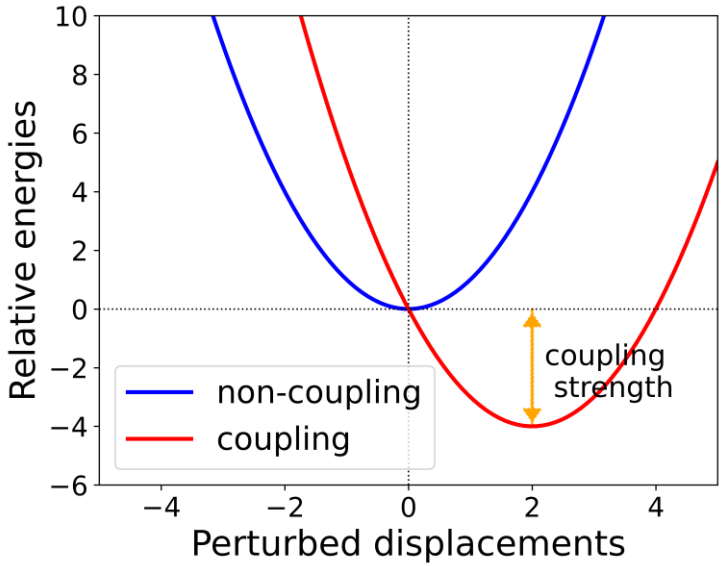


Figure S4. Schematic diagram of energy potentials of the cation-polyanion phonons with the frozen polyanion mode and different perturbed Li amplitude, where the anharmonic coupling strength is also labelled.