Electronic Supplementary Information

Unexpected Anion Segregation Enabling High Conductivity in Argyrodite $Li_{6-x}PS_{5-x}ClBr_x$ Solid Electrolytes

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‡ Seho Yi and Taegon Jeon contributed equally to this work.

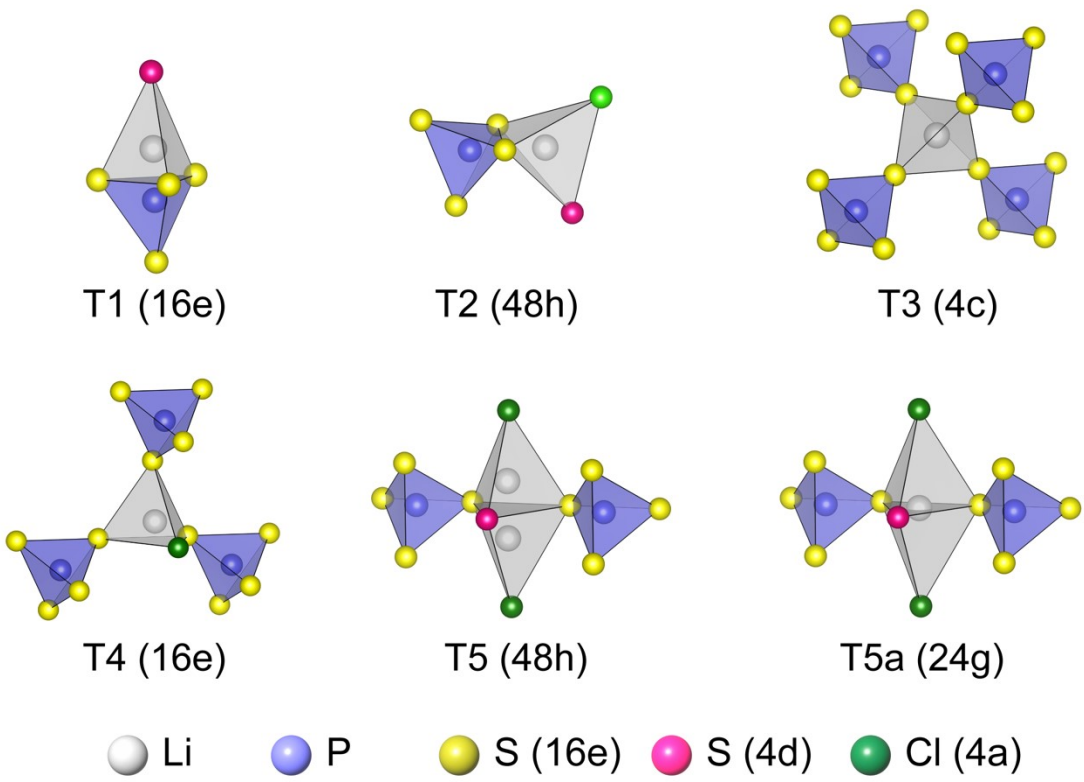

Fig. S1 Five types of LiS_4/LiS_3X tetrahedra (grey) in Li_6PS_5Cl. They share the corners, edges, and faces of neighboring PS_4 tetrahedra (violet) in different ways.

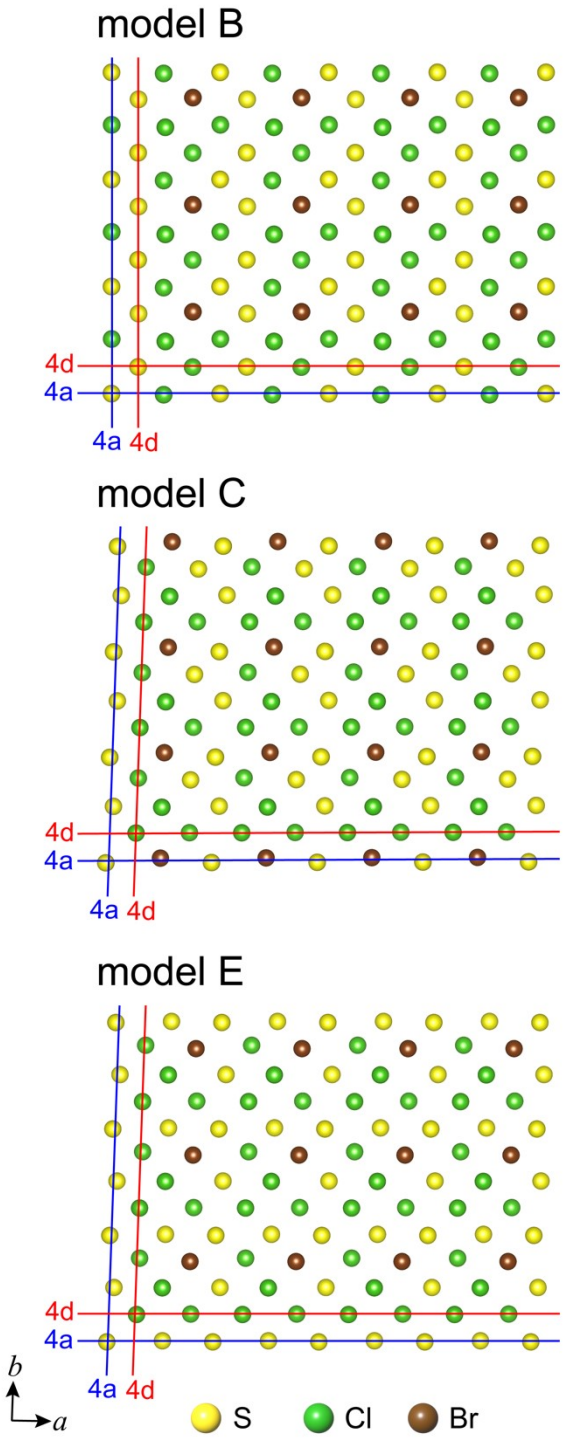

Fig. S2 S, Cl, and Br anions at the 4a/4d sites of models B, C, and E in $Li_{5.75}PS_{4.75}ClBr_{0.25}$. Li cations and PS_4 polyanions are not drawn for clarity.

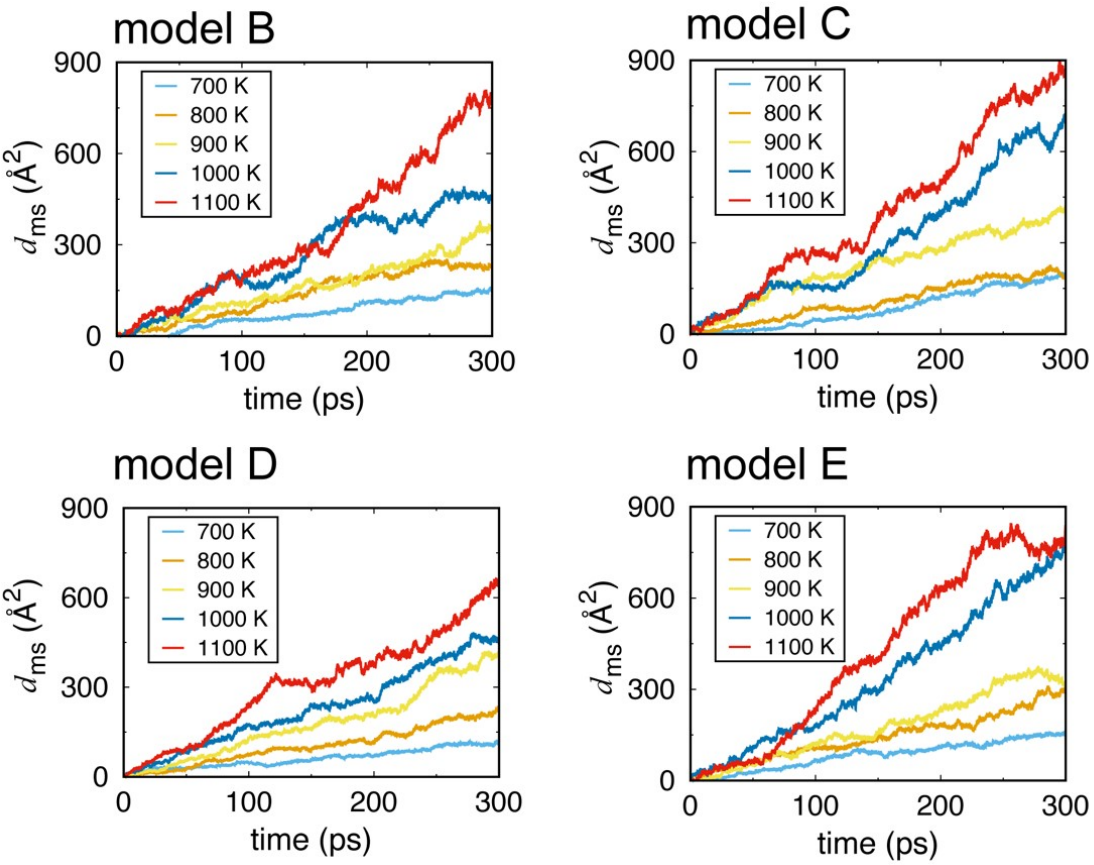

Fig. S3 Mean-square displacements (d_{ms}) of Li ions as a function of time for models B, C, D and E in $Li_{5.75}PS_{4.75}ClBr_{0.25}$.

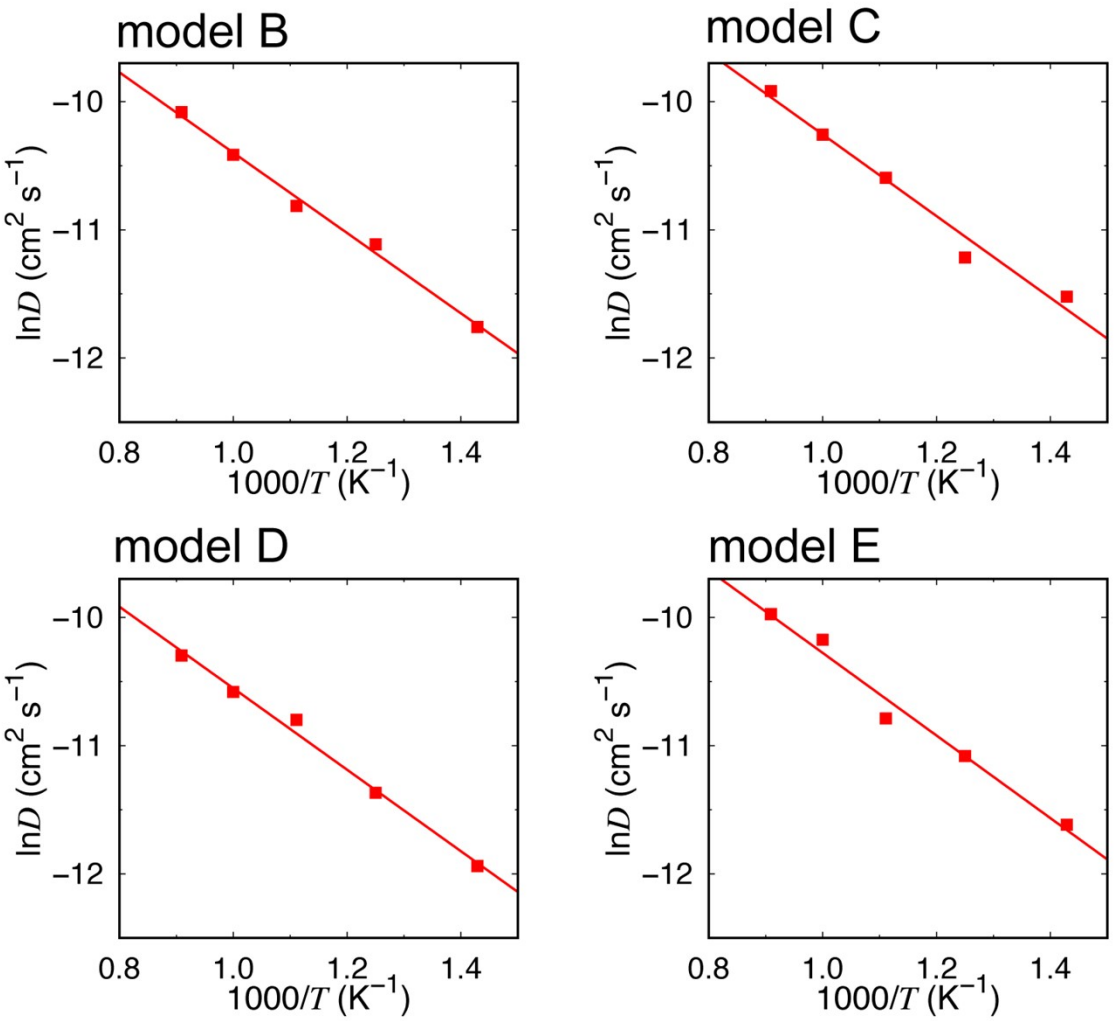

Fig. S4 Logarithmic diffusivities (ln$D$) of Li ions as a function of inverse temperature for models B, C, D, and E in $Li_{5.75}PS_{4.75}ClBr_{0.25}$.

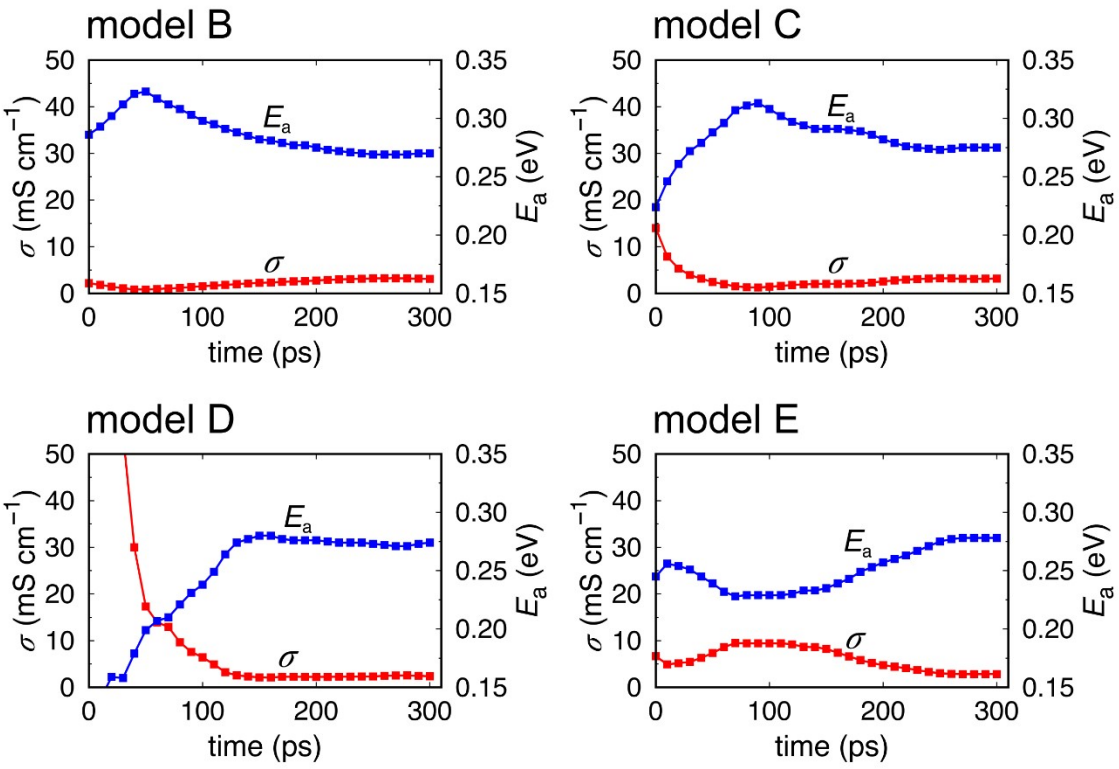

Fig. S5 Conductivity (σ) and activation energy (E_a) as a function of time for models B, C, D and E in $Li_{5.75}PS_{4.75}ClBr_{0.25}$.

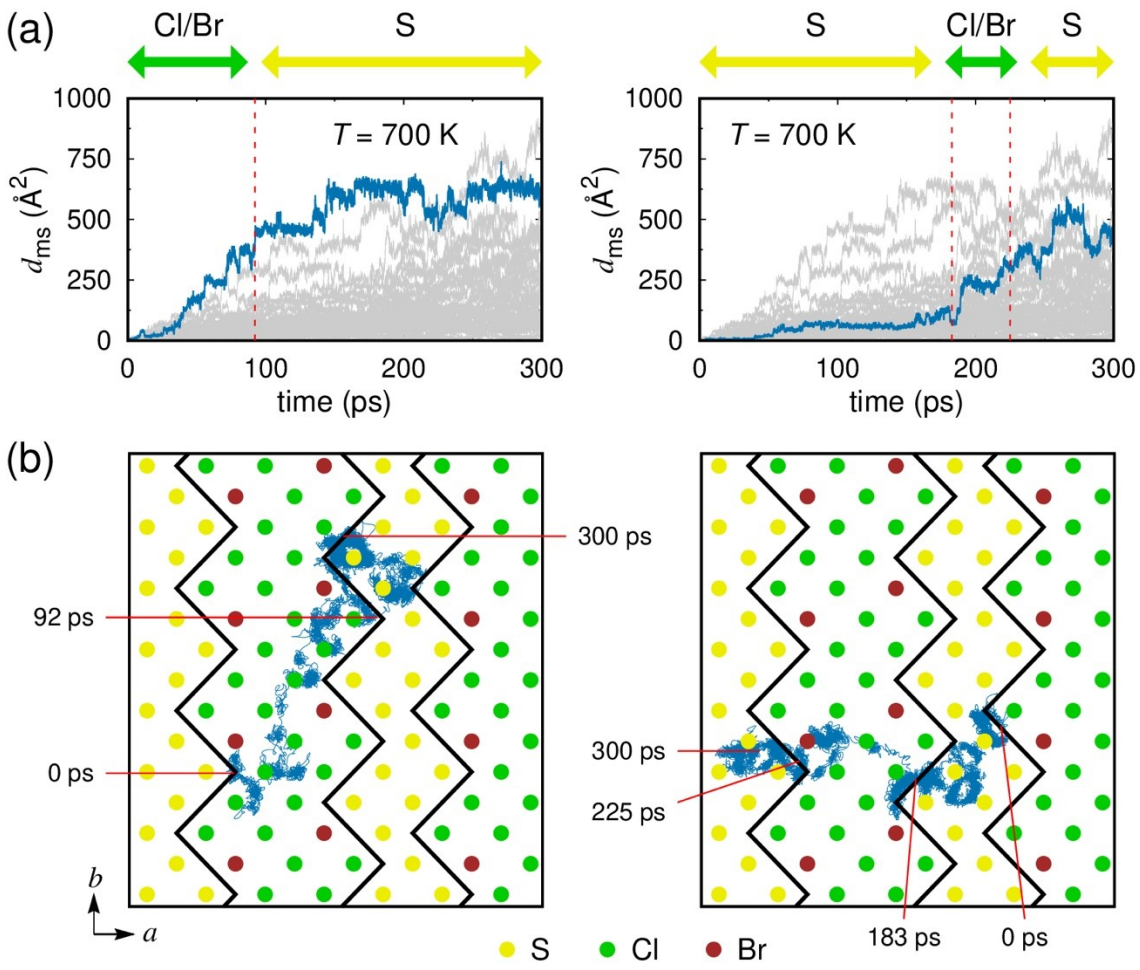

Fig. S6 (a) Mean-square displacements (d_{ms}) and (b) trajectories of two Li ions of model A in $Li_{5.75}PS_{4.75}ClBr_{0.25}$, obtained from the AIMD simulation for 300 ps at T = 700 K.

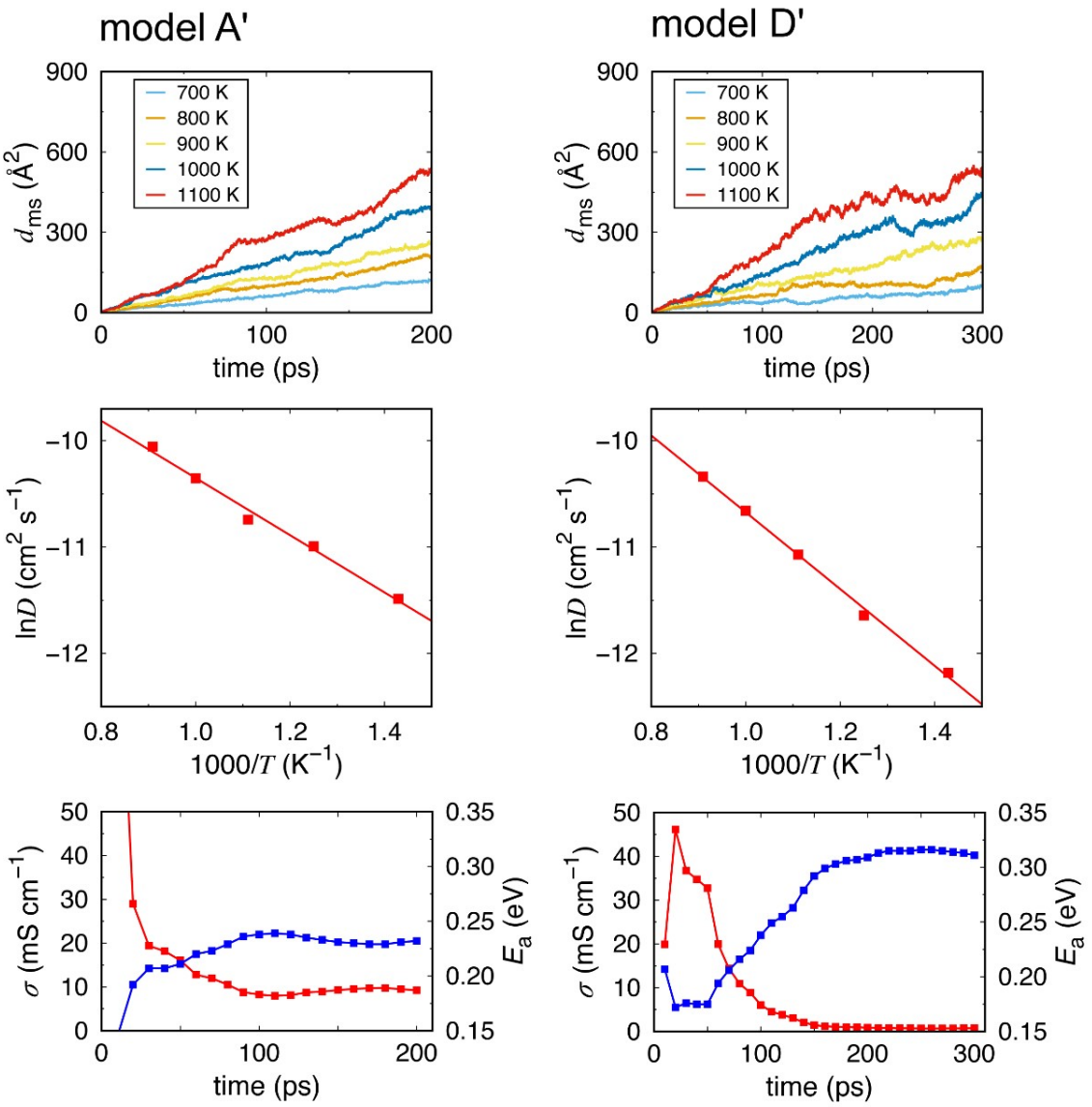

Fig. S7 Mean-square displacements (d_{ms}), logarithmic diffusivities (ln$D$), and conductivity (σ) and activation energy (E_a) of models A′ and D′ in $Li_{5.75}PS_{4.75}Cl_{1.25}$.

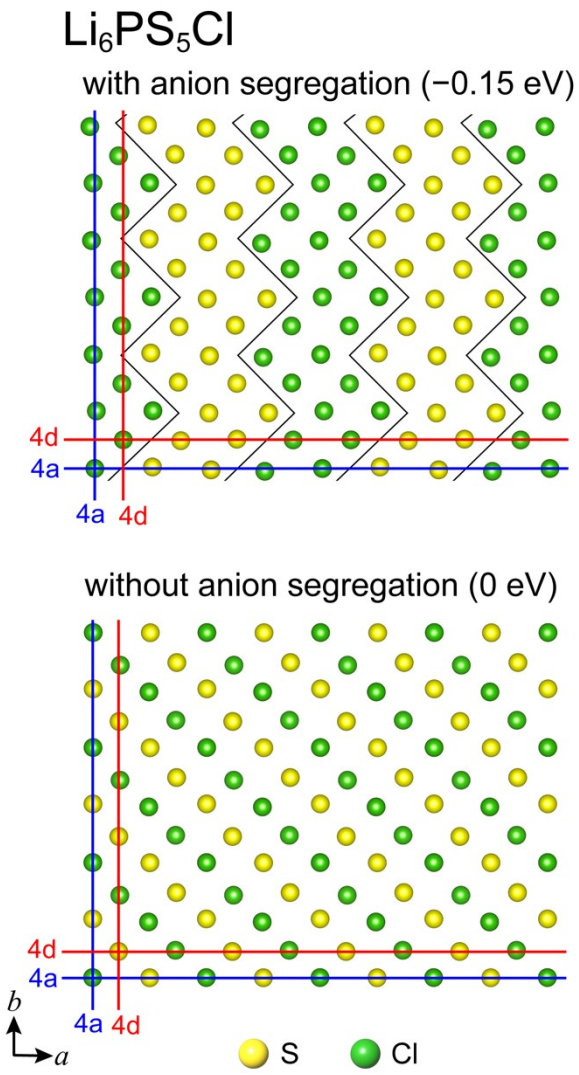

Fig. S8 S and Cl anions at 4a/4d sites in two Li_6PS_5Cl structures with and without anion segregation. The Li_6PS_5Cl structure without anion segregation was obtained from ref. 1. Li cations and PS_4 polyanions are not drawn for clarity.

Table S1 Lattice parameters of models A, B, C, D, and E in $Li_{5.75}PS_{4.75}ClBr_{0.25}$. The 2 × 1 × 1 tetragonal unit cell was used for model A, and the 1 × 1 × 1 cubic unit cell was used for models B, C, D, and E. Volumes are given per 1 × 1 × 1 unit cell.

Model	*a* (Å)	*b* (Å)	*c* (Å)	*α* (deg)	*β* (deg)	*γ* (deg)	Volume (Å^3)
A	19.49	9.81	9.74	90.8	90.2	90.9	930.5
B	9.82	9.70	9.69	89.5	90.6	89.9	923.3
C	9.73	9.73	9.80	90.8	90.0	87.7	926.6
D	9.95	9.66	9.73	90.1	90.7	90.8	934.6
E	9.78	9.84	9.71	90.7	90.0	88.4	933.5

Table S2 Diffusion properties of models A′ and D′ in $Li_{5.75}PS_{4.75}Cl_{1.25}$. D_0 is the pre-exponential factor, D is the diffusivity at T = 300 K, E_a is the activation energy, and σ is the conductivity at T = 300 K.

Model	D_0 (cm^2 s^{-1})	D (cm^2 s^{-1})	E_a (eV)	σ (mS cm^{-1})
A′	4.7×10^{-4}	6.0×10^{-8}	0.23	9.2
D′	8.6×10^{-4}	5.1×10^{-9}	0.31	0.8

References

1 T. Jeon, G. H. Cha and S. C. Jung, *J. Mater. Chem. A*, 2024, **12**, 993–1002.