## **Supporting information**

# Selective Blockage of Li ion diffusion pathways in Li<sub>10</sub>SnP<sub>2</sub>S<sub>12</sub>: Insight from Nuclear Magnetic Resonance

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1. Variable temperature static <sup>7</sup>Li NMR spectra at 116.5 MHz for  $Li_{10}SnP_2S_{12}$ 



Figure S1. Variable temperature static  $^{7}Li$  NMR spectra at 116.5 MHz for  $Li_{10}SnP_{2}S_{12}$ .

### 2. 7Li Spin-Alignment Echo (SAE) NMR decay curve

The  $\tau_{\text{SAE}}$  in equation S1 denotes the decay time constant associated with the motional correlation time of Li ion migration, and  $T_{1Q}$  is a relaxation time of quadrupolar order, as well as  $\gamma_c$  is a stretched exponential factor.<sup>1, 2</sup>

$$S_2(t_m, t_p) = \left\{ A \exp\left(-\frac{t_m}{\tau_{SAE}}\right)^{\gamma_c} + B \right\} \exp\left(-\frac{t_m}{T_{1Q}}\right)$$
(S1)



**Figure S2.** <sup>7</sup>Li SAE NMR correlation functions of (a)  $Li_{10}GeP_2S_{12}$  and (b)  $Li_{10}SnP_2S_{12}$  recorded at 116.5 MHz and  $t_p = 20 \ \mu s$  at variable temperature.

3. Distances and numbers of  ${}^{31}P{}^{-7}Li$  spin pairs for  $Li_{10}SnP_2S_{12}$  compared to  $Li_{10}GeP_2S_{12}$ 

	Li4-LGPS <sup>3</sup>		Li4-LSPS <sup>4</sup>	
	Distance(Å)	Number	Distance(Å)	Number
P(1)	4.413	2	4.439	2
	4.397	2	4.430	2
P(2)	3.204	2	3.163	2

Table S1. Distances and numbers of <sup>31</sup>P-<sup>7</sup>Li(4) spin pairs for LSPS and LGPS

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