Supporting Information

$Li_4P_2Se_6$ - Structure and Properties

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General NMR Simulation Parameters

All NMR simulations were performed using the SIMPSON software (version 4), employing the simplex algorithm for fitting. The simulations were performed at a magnetic flux density of B_0 = 14.1 T using the ZCW232 powder averaging scheme with 232 crystal orientations.

^{31}P NMR Simulations:

The simulations were carried out at ν_{MAS} = 5 kHz. The spin system was defined as a two-spin ^{31}P-^{31}P system including both direct dipolar coupling (*D*) and scalar or *J*-coupling. The fitted parameters included the full chemical shift tensors defined in the principal axis system for both spins, as well as the direct coupling constant *D* and the *J*-coupling constant. The dipolar vector was assumed to be collinear with the principal axis of the chemical shift tensor constant DD. A third isolated spin was also included in the model to account for the minor Li_3PO_4 impurity observed in the experimental spectrum.

^{77}Se NMR Simulations:

The simulations were carried out at ν_{MAS} = 20 kHz. The spin system was defined as of four independent two-spin systems, each representing a ^{77}Se-^{31}P pair, including direct dipolar and scalar *J*-coupling. The fitted parameters included the ^{77}Se chemical shift tensors and the corresponding *J*-coupling constants for each Se-P pair. The direct coupling constant was set to -881 Hz corresponding to a P-Se distance of 2.195 Å. In addition an isolated spin was also considered to account for unidentified impurity at approximately 800 ppm.

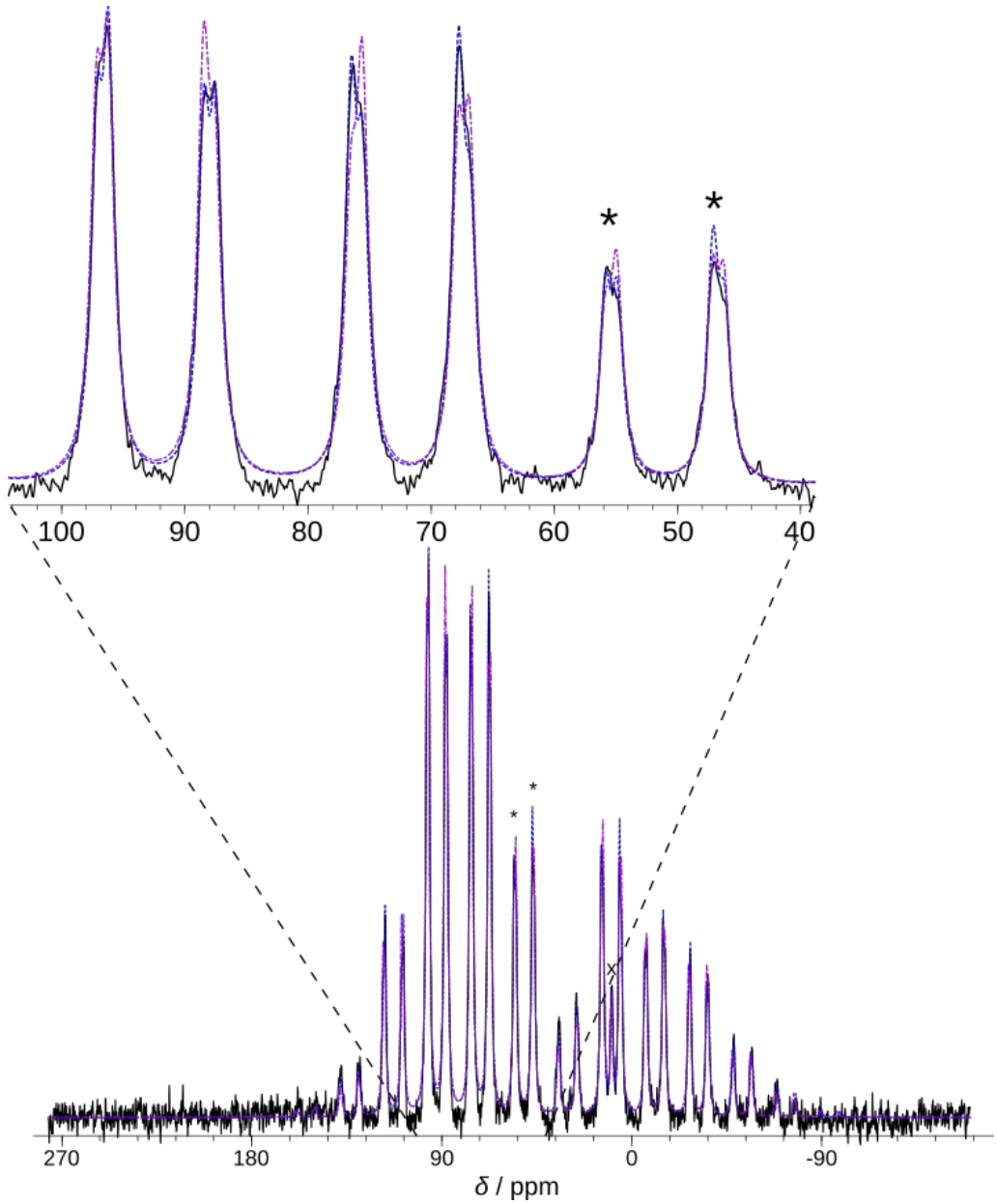

Figure S1: Comparison of experimental (solid black line) and simulated ^{31}P MAS NMR spectra with positive (dash-dot magenta line), and negative (dotted blue line) signs for the *J*-coupling. Isotropic peaks are marked with asterisks (*) and the minor impurity phase Li_3PO_4 is indicated with a cross (×). Input for files for simpson for these spectra are provided as supporting information ("simpson-NMR-inputfiles-bestfit.zip").

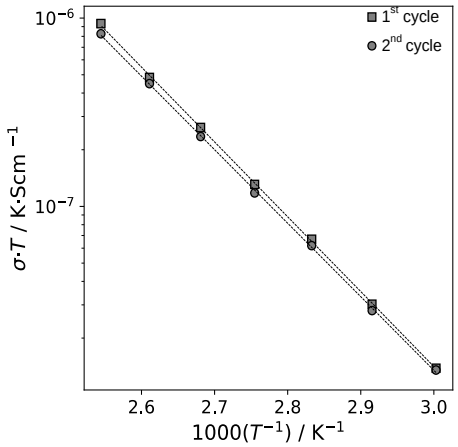

Figure S2: Plot of the product of electrical conductivity σ and temperature T versus inverse temperature for $Li_4P_2Se_6$. The results were obtained from impedance spectra in temperature range from 333 K to 393 K. Linear fits are indicated by dashed lines. The bulk conductivities are indicated by grey circle and square markers for first and second measurements cycles, respectively.

Table S1: The macroscopic conductivity at room temperature $\sigma_{298\,K}$, pre-exponential factor a_0, and activation energy E_A of $Li_4P_2Se_6$ obtained using $\sigma \cdot T = a_0 \exp(-E_A/k_B T)$

	1st cycle	2nd cycle
$\sigma_{298\,K}$ / (S · cm^{-1})	1.83(33) ·10^{-12}	1.85(44) ·10^{-12}
a_0/(S · K· cm^{-1})	1.18(1)· 10^4	6.98(1)· 10^3
E_A / eV	0.79(1)	0.78(1)