Supporting Information of “Superhalogen-based Lithium Superionic Conductors”

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Fig. S1 The planar configuration of the superalkali Li₃O⁺ in its gas phase.
Fig. S2 Interaction between the superalkali Li$_3$O$^+$ and the superhalogen BH$_4^-$ in a cluster model. Li$_3$O$^+$ becomes a pyramidal configuration due to the repulsion between the lone pair on the oxygen (in red) and the negative BH$_4^-$ (boron in pink and hydrogen in grey) as well as the attraction between lithium (in violet) and the negative BH$_4^-$. 

Fig. S3 Given the similar ionic radius of BH$_4^-$ compared to that of Br$^-$, we expected that Li$_3$O(BH$_4$) could be stabilized in the same cubic phase as Li$_3$OBr where BH$_4$ would occupy the Br sites. However, unlike Br atom which is spherical, BH$_4$ cluster has tetrahedral symmetry. Thus, one has to determine the precise orientation of the BH$_4$ tetrahedron. We have carried out an extensive testing with different starting orientation of BH$_4$, among which the three high-symmetry configurations are listed below: (i) an H atom of BH$_4$ pointing to the lattice center, (ii) two opposite edges of BH$_4$ tetrahedron pointing along the diagonals of the corresponding faces, and (iii) two opposite edges of BH$_4$ tetrahedron parallel to the corresponding planes of the lattice. The first configuration is the ground-state structure which lies 0.3 eV and 0.48 eV lower in energy than the other two. These are shown in the figure where the white, purple, green and red balls represent H, Li, B, O respectively. For each case, the corresponding total energy is given.
Fig. S4 (a) Low-barrier migration for an interstitial Li in Li$_3$O(BH$_4$): left and right are the initial and final configurations, respectively. The Li atoms involved in the migration are in red and migration direction is indicated by green arrows. Insets are the enlarged views of rotation of BH$_4$ cluster as the Li$^+$ ion migrates. (b) The calculated migration energy barrier as a function of distance travelled by the Li$^+$-ion.

Fig. S5 The mean square displacement (MSD) of different ions of Li$_3$O(BH$_4$) at 2000 K. H$^+$ ion also exhibits superionic conductivity at this temperature.
Symmetry operations

Following shows the operations to obtain the symmetry-related orientations in the \( T_d, D_{2d}, C_{2v} \) and \( C_{3v} \) groups. \( x(\pi/2), y(\pi/2) \) and \( z(\pi/2) \) denotes the rotation of \( \pi/2 \) about the \( x, y \) and \( z \) axes, respectively. “i” is the inversion operation.

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\begin{align*}
\text{T}_d: & \quad 1 \rightarrow 2 \\
& \quad z(\pi/2) \\
\text{D}_{2d}: & \quad 1 \rightarrow 2 \\
& \quad x(\pi/2), y(\pi/2) \\
& \quad 1 \rightarrow 3 \rightarrow 4 \\
& \quad y(\pi/2), x(\pi/2) \\
& \quad 1 \rightarrow 5 \rightarrow 6 \\
\text{C}_{2v}: & \quad 1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \\
& \quad x(\pi/2), y(\pi/2), y(\pi/2) \\
& \quad 1 \rightarrow 5 \rightarrow 6 \rightarrow 7 \rightarrow 8 \\
\text{C}_{3v}: & \quad 1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \\
& \quad i, z(\pi/2), z(\pi/2), i \\
& \quad 1 \rightarrow 5 \rightarrow 6 \rightarrow 7 \rightarrow 8 \\
& \quad y(\pi/2), x(\pi/2), x(\pi/2) \\
& \quad 1 \rightarrow 9 \rightarrow 10 \rightarrow 11 \rightarrow 12
\end{align*}
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Fig.S6 Reaction of \( \text{Li}_2\text{O} \) with \( \text{LiBH}_4 \) in both cluster (upper) and crystalline forms, where B is in pink, H in grey, Li in violet and O in red.