

## Supporting Information

### Computational details

Our calculations were performed using the plane-wave based density functional theory method as implemented in the Vienna ab initio simulation package (VASP), with the projector augmented wave pseudopotentials used to describe the interaction between the core and the valence electrons. The Perdew–Burke–Ernzerhof exchange–correlation functional was employed, and a kinetic energy cutoff of 500 eV for the plane wave basis set was used. Structural optimization was done with  $k$ -point sampling of a  $2 \times 2 \times 6$  mesh within the Monkhorst-Pack scheme. A convergence threshold of 0.05 eV/Å in force was reached for structural optimization. The ab initio molecular dynamics (AIMD) simulations were carried out within a canonical NVT ensemble by using a Nosé thermostat for temperature control. The time step was 1 fs and the a  $1 \times 1 \times 3$  mesh was used for  $k$ -point sampling in the AIMD runs. A total of 9,000 time steps were performed, in which all the configurations were collected to study the dynamics of Li<sup>+</sup>, ClO<sub>4</sub><sup>-</sup> and THFs.

The pair correlation function between Li<sup>+</sup> ions and other atoms is defined as the spherically averaged distribution of distances between each Li<sup>+</sup> ion and other atoms around it:

$$g(r) = \frac{V}{NN_{Li} \cdot 4\pi r^2 \Delta r} \sum_i^N \sum_j^{N_{Li}} \delta(r - r_{ij})$$

where  $V$  is the volume of the simulation box,  $N$  is the number of atoms,  $N_{Li}$  is the number of Li<sup>+</sup> ions, and  $\Delta r$  refers to the distance interval in the calculation.

The mean square displacement (MSD) projected on the  $c$ -axis for Li<sup>+</sup> ions is defined as  $\langle \hat{r}_c \rangle^2$ , where  $r_c$  is the displacement of Li<sup>+</sup> at time  $t$  projected onto the  $c$ -axis. The corresponding 1D diffusion coefficient along the tunnels ( $D_{1D}$ ) is calculated by linear fitting using the equation  $\langle \hat{r}_c \rangle^2 = 2Dt$ .

The rotational correlation time is obtained using the calculated orientational

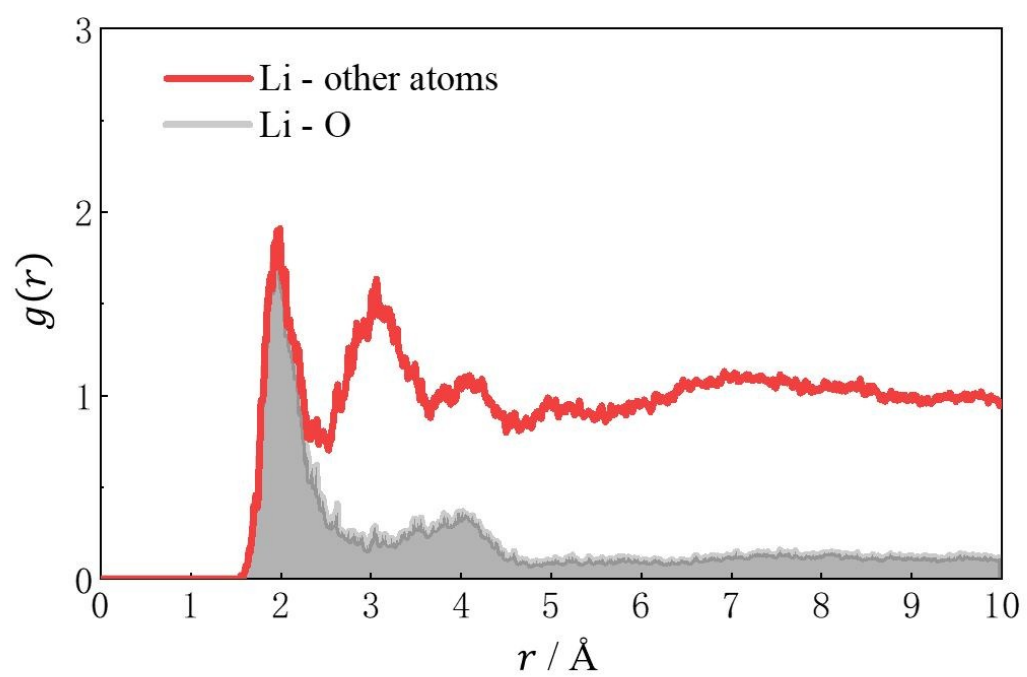
autocorrelation function from the AIMD simulation results. The orientational autocorrelation function is calculated as follow:

$$C(t) = \langle P_2(\hat{u}(t) \cdot \hat{u}(0)) \rangle$$

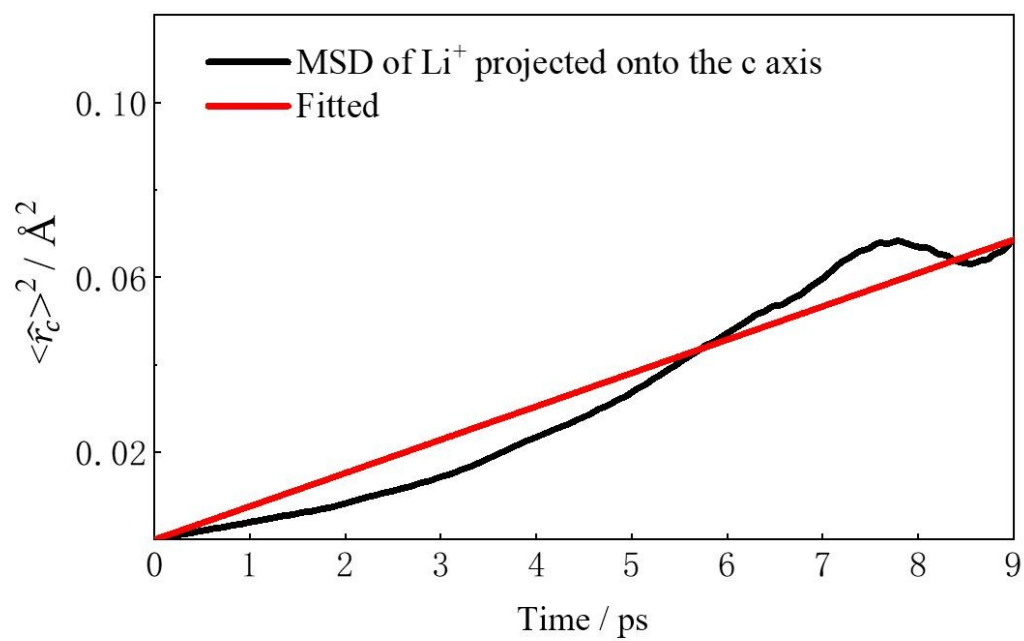
where  $\hat{u}(t)$  is the unit vector along the Cl-O bond, and  $P_2(x)$  is the second Legendre polynomial. The angular brackets denote an ensemble average. The rotational correlation time is calculated as follow:

$$\tau = \int_0^{T_{tot}} C(t) dt$$

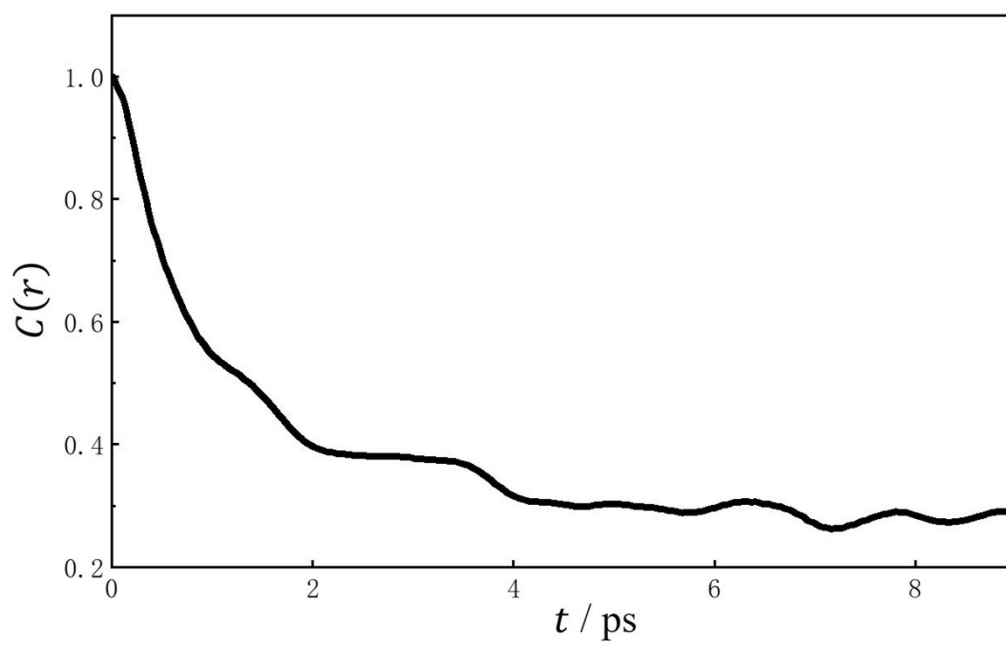
where  $T_{tot}$  is the total simulation time.



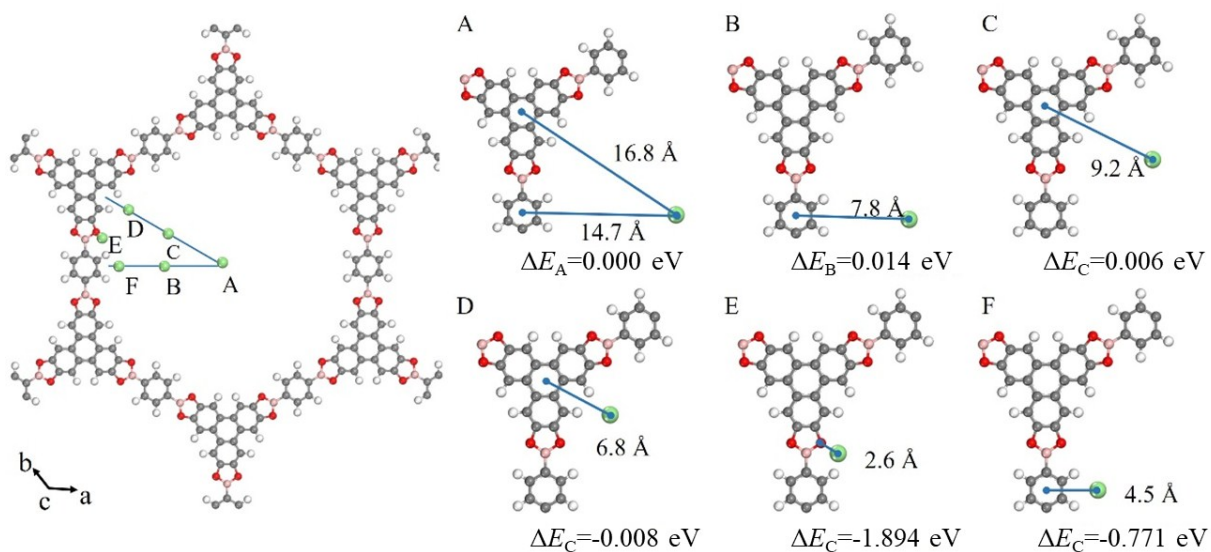
**Figure S1.** Pair correlation function between  $\text{Li}^+$  and other atoms, and the contribution from O atoms.



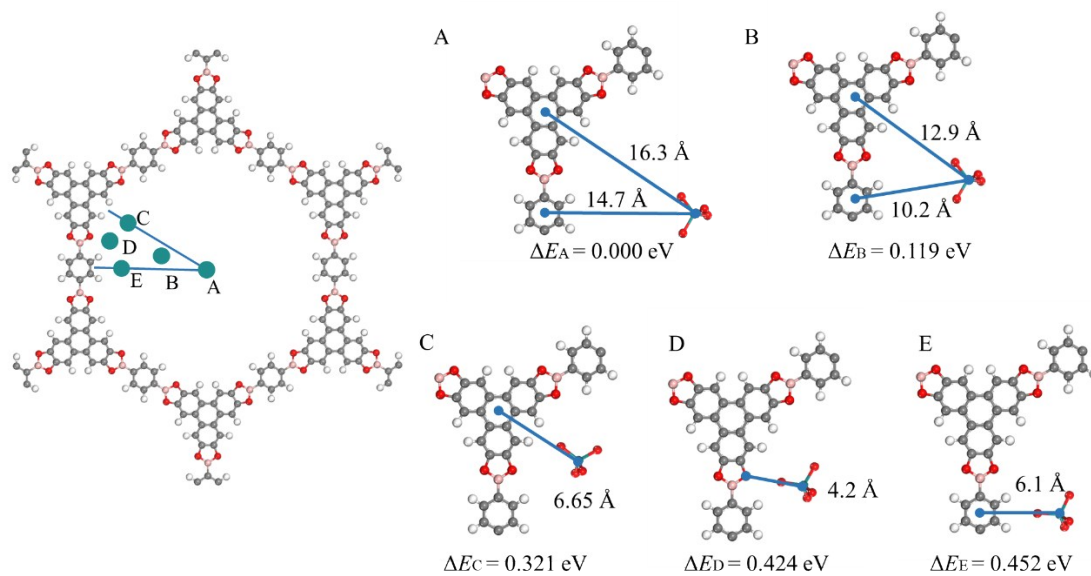
**Figure S2.** MSD projected onto the *c*-axis as a function of time for Li<sup>+</sup> ions at 300 K, and the corresponding fitted line.



**Figure S3.** The orientational autocorrelation function of Cl-O bonds.



**Figure S4.** Li fixed at different positions inside the tunnel of COF-5. The energies of Configurations B to F are referenced to Configuration A, and are here denoted by  $\Delta E$ . It is shown that configurations with sufficiently small distances between Li and the COF-5 framework ( $< 4.5 \text{ \AA}$ ) would be energetically favorable. Li at larger distances exhibits little energetic preference for any particular site.



**Figure S5.**  $\text{ClO}_4$  at different distances to the walls of COF-5. The energies of Configurations B to E are referenced to Configuration A, and are here denoted by  $\Delta E$ . It is shown that  $\text{ClO}_4$  prefers to be accommodated in the middle of the tunnels and that the energy would increase steadily when  $\text{ClO}_4$  is approaching to the walls of COF-5.