

Supporting information for:

Insights into Lithium Ion Deposition on Lithium Metal Surfaces

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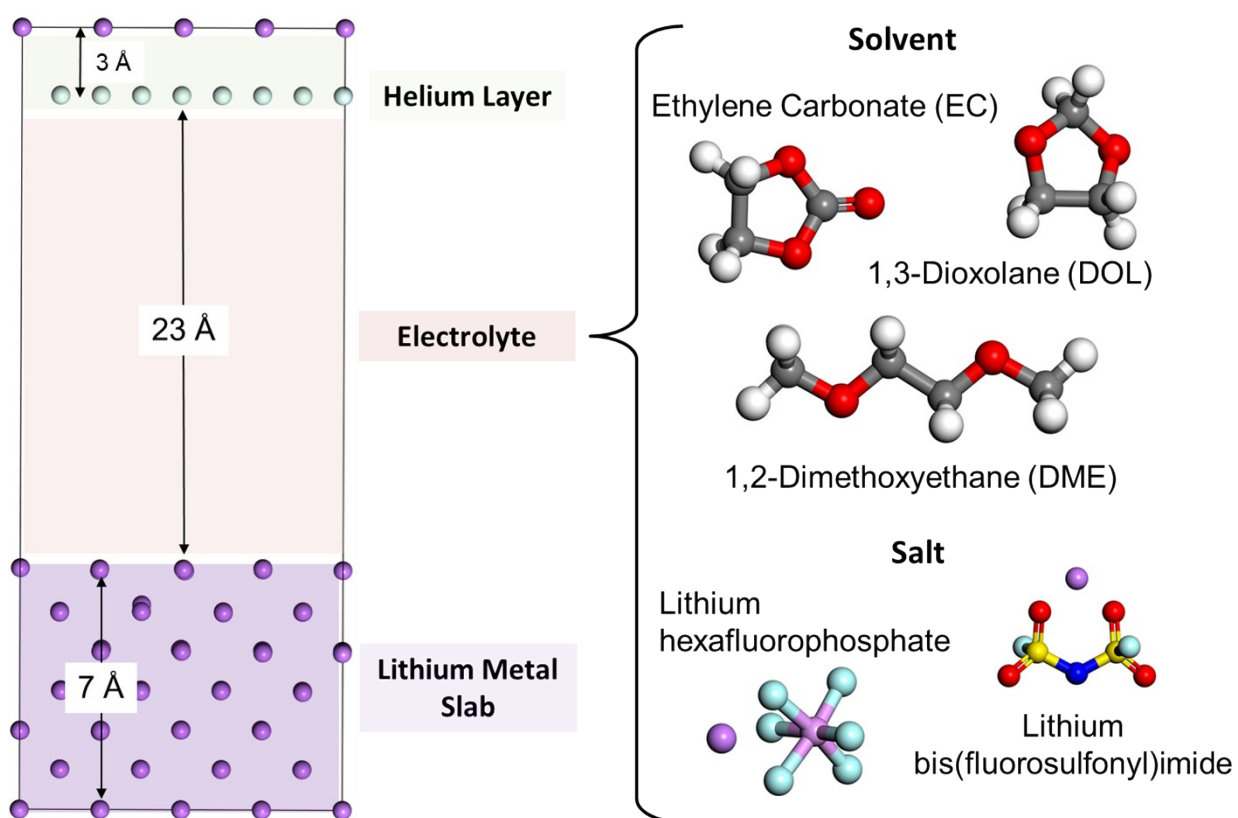


Figure S1. Simulation cell and molecular structure of solvents and salts.

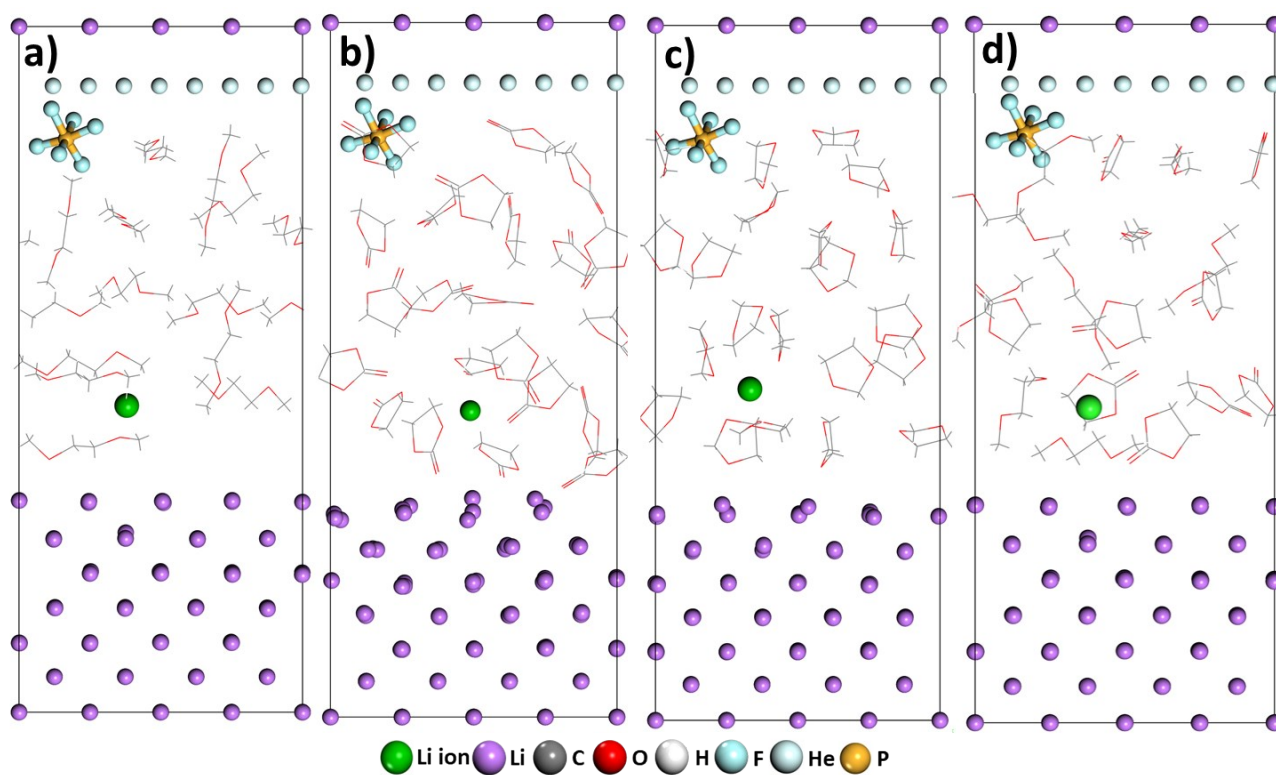


Figure S2. Initial configurations for various solvents. a) DME, b) DOL, c) EC, and d) EC-DME (1:1 v/v)

Table S1. Total number of atoms/molecules per component in the simulation cell.

	DME	EC	DOL	EC-DME
Li Metal	84	84	84	84
Solvent	14	22	21	9 - 9
Li Ion	1	1	1	1
PF₆⁻	1	1	1	1
He	16	16	16	16

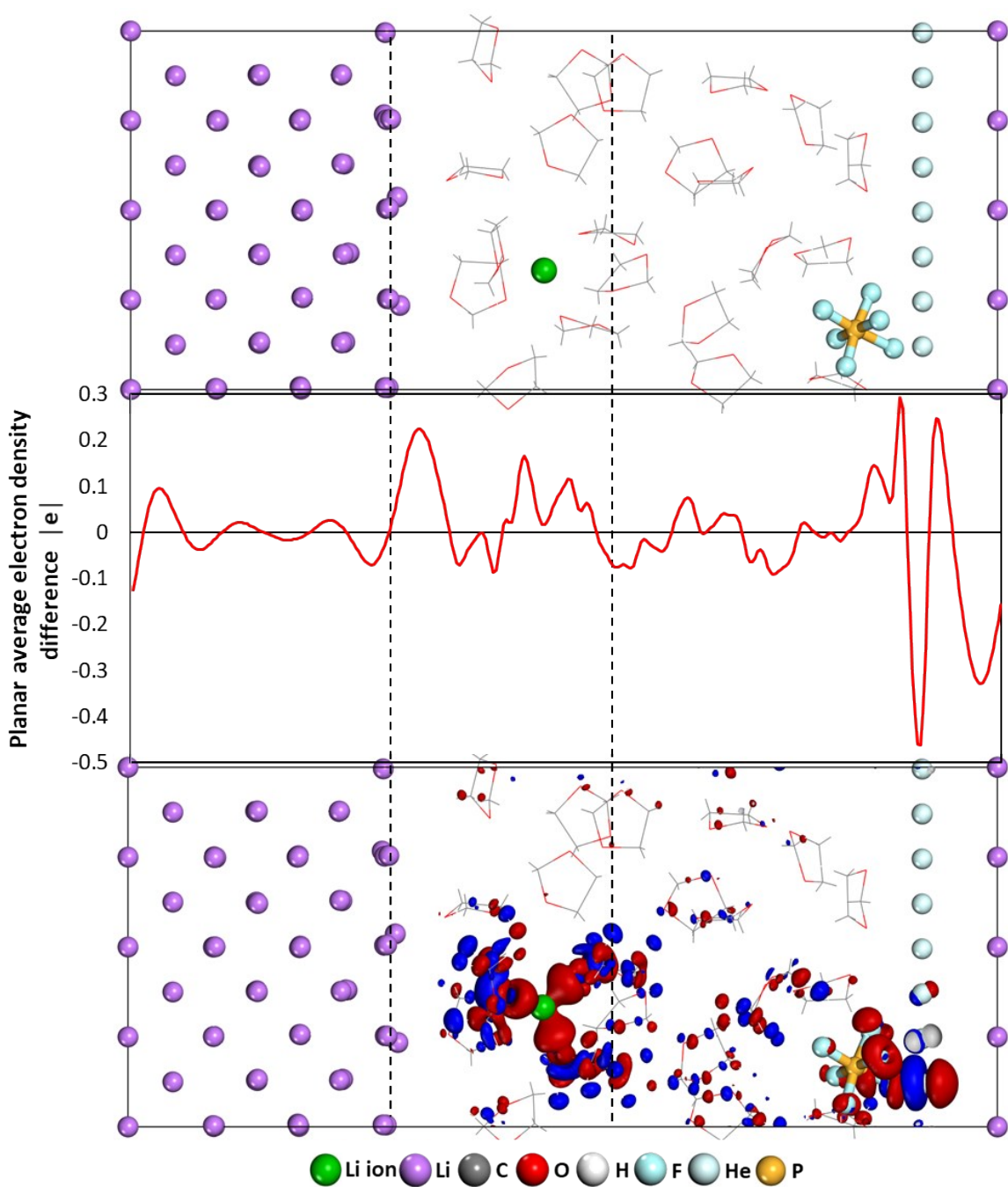


Figure S3. Cation deposition structure with DOL as solvent (Top), planar average electron density difference $\Delta\sigma(z)$ curves (middle) and charge density difference diagrams (bottom) (isosurface level = $5.0e-4$). In the charge density difference distribution diagrams, red represents the electron accumulation area, while blue is the electron depletion area. Grey areas are the cross-sections of the charge density difference.

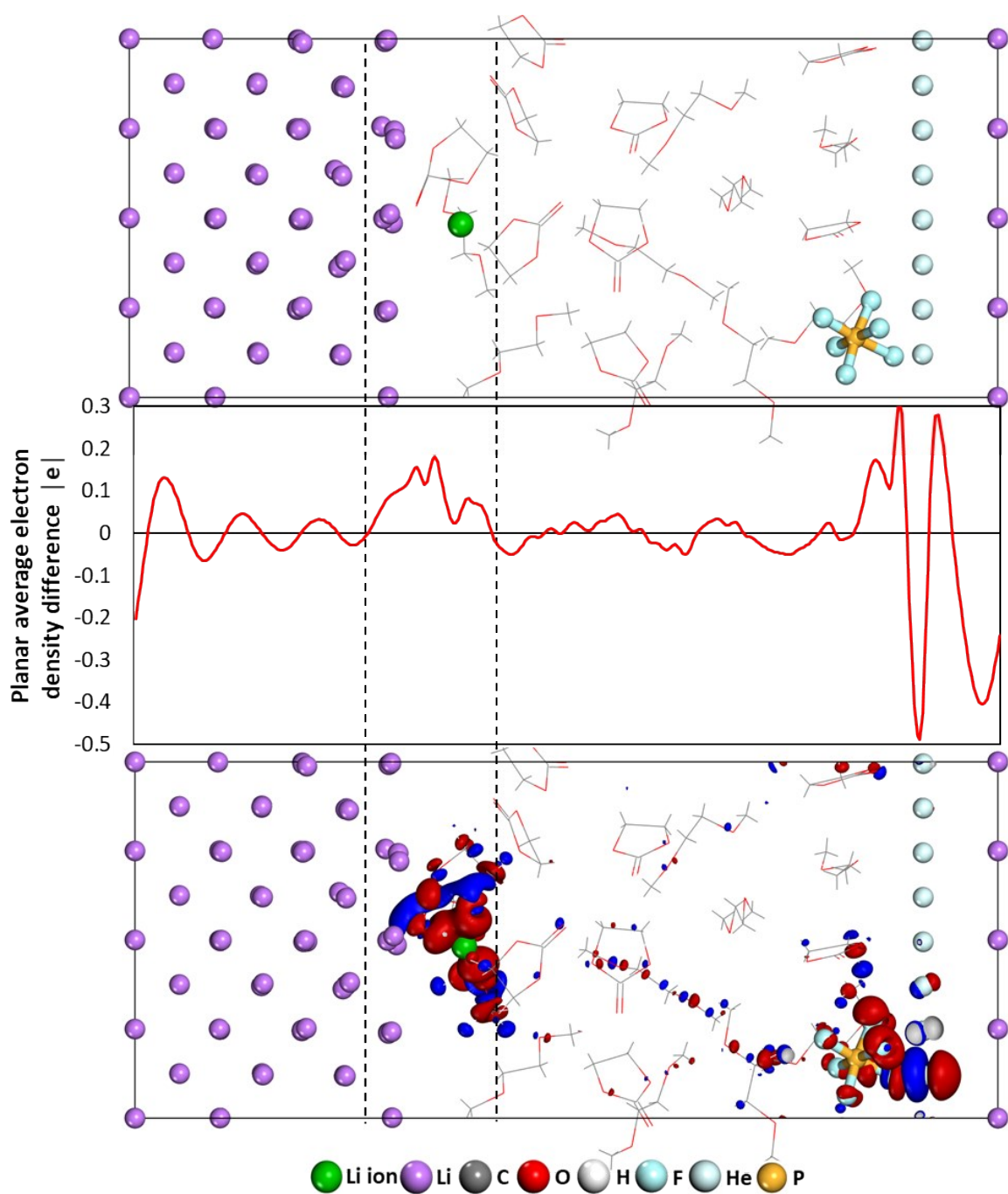
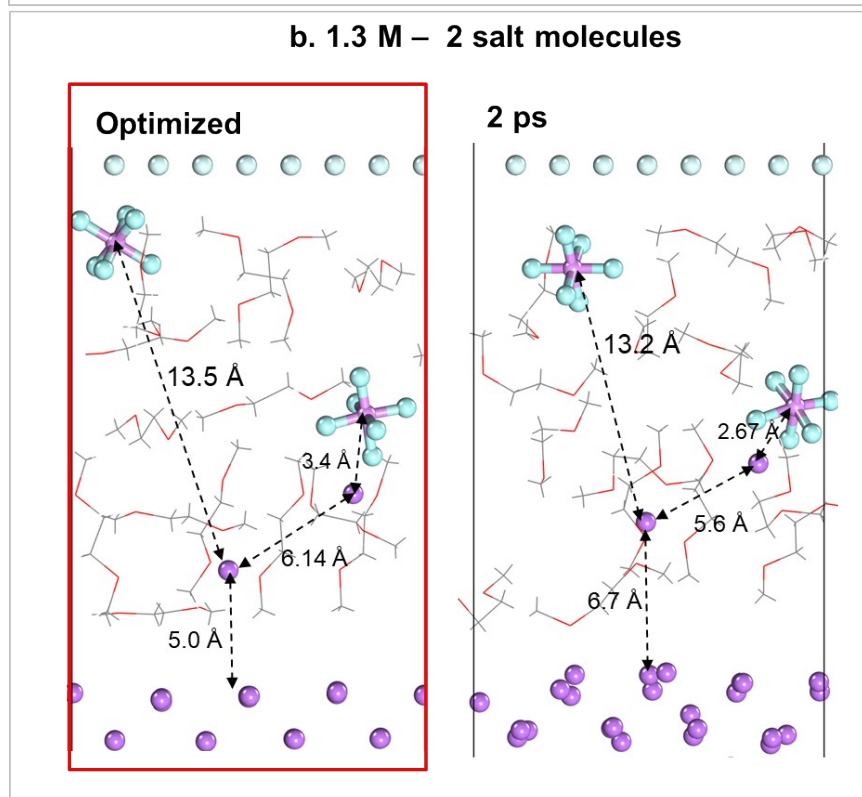
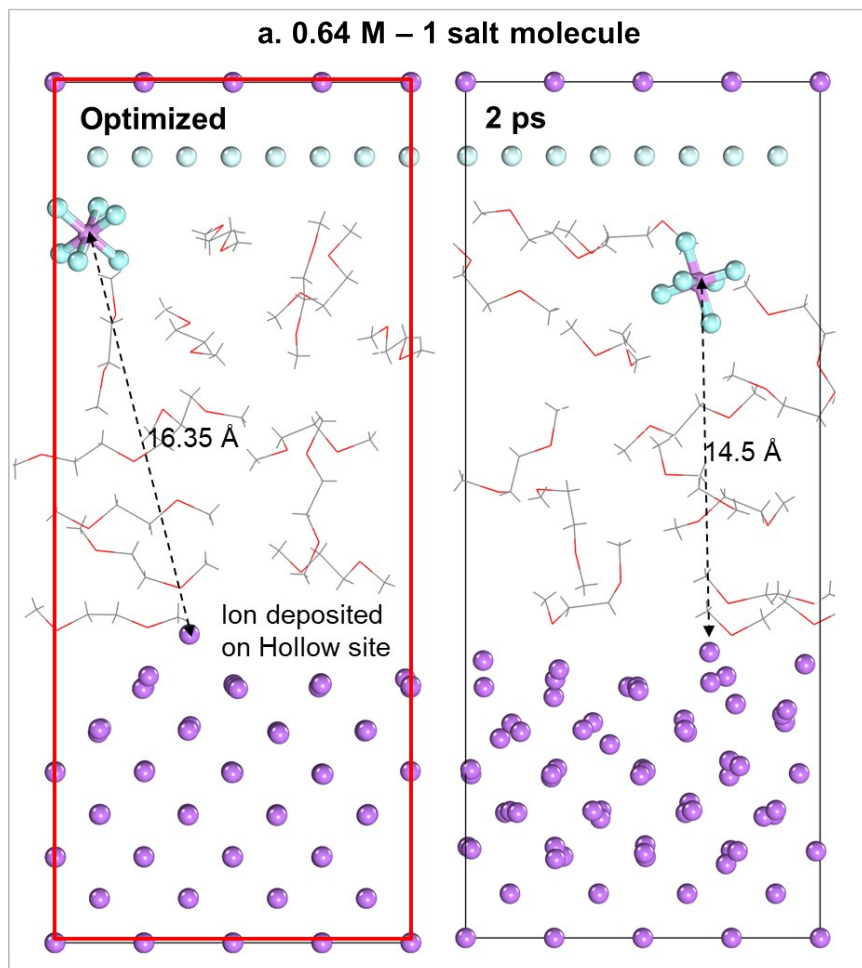
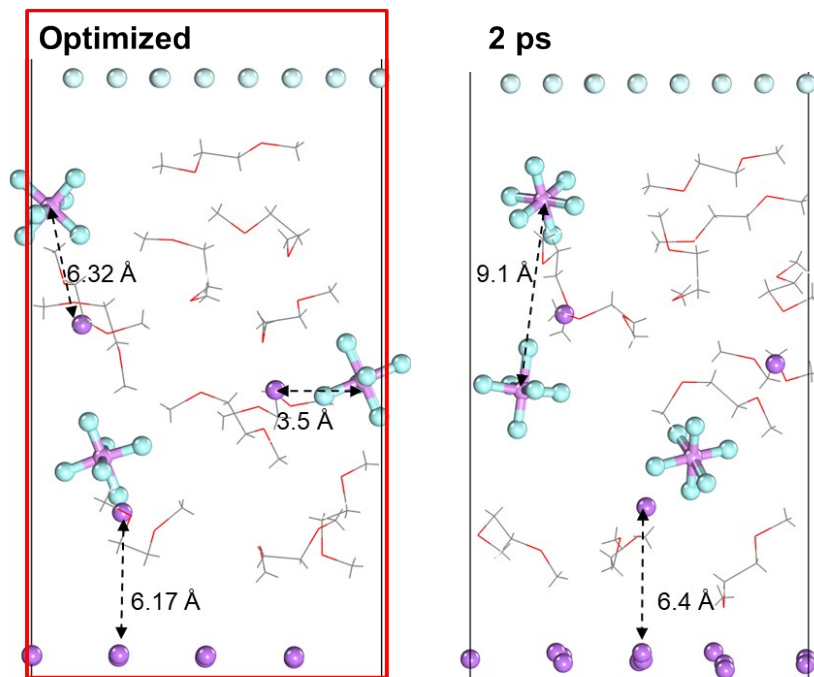


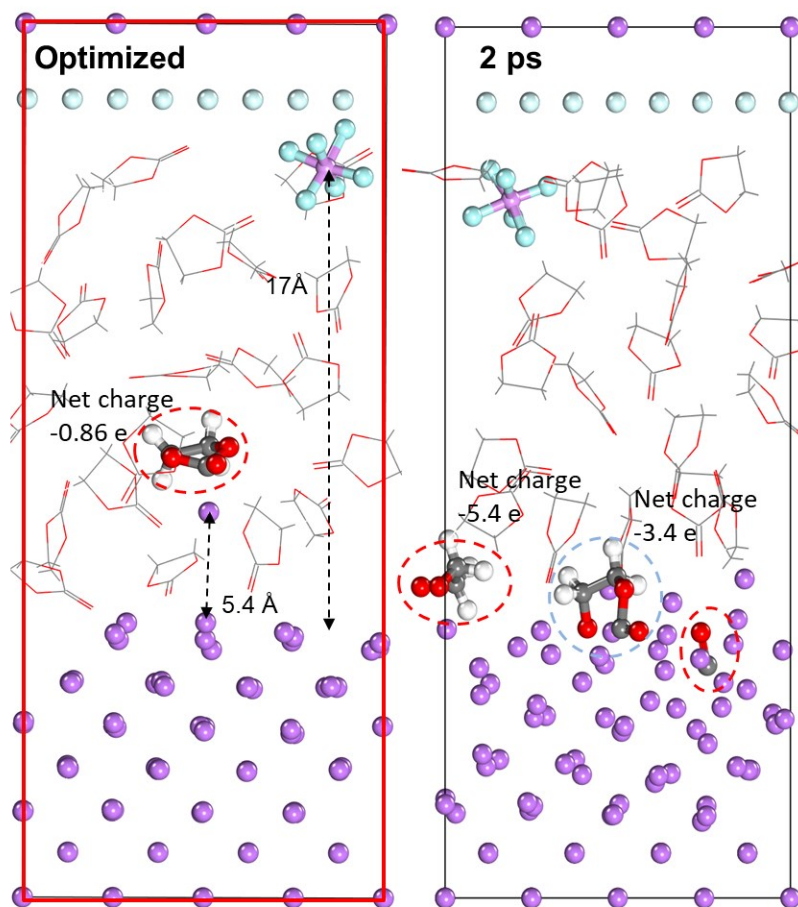
Figure S4. Cation deposition structure with a mixture of DME and EC as solvent (Top), planar average electron density difference $\Delta\sigma(z)$ curves (middle) and charge density difference diagrams (bottom) (isosurface level = $5.0e-4$). Color code same as Figure S3.



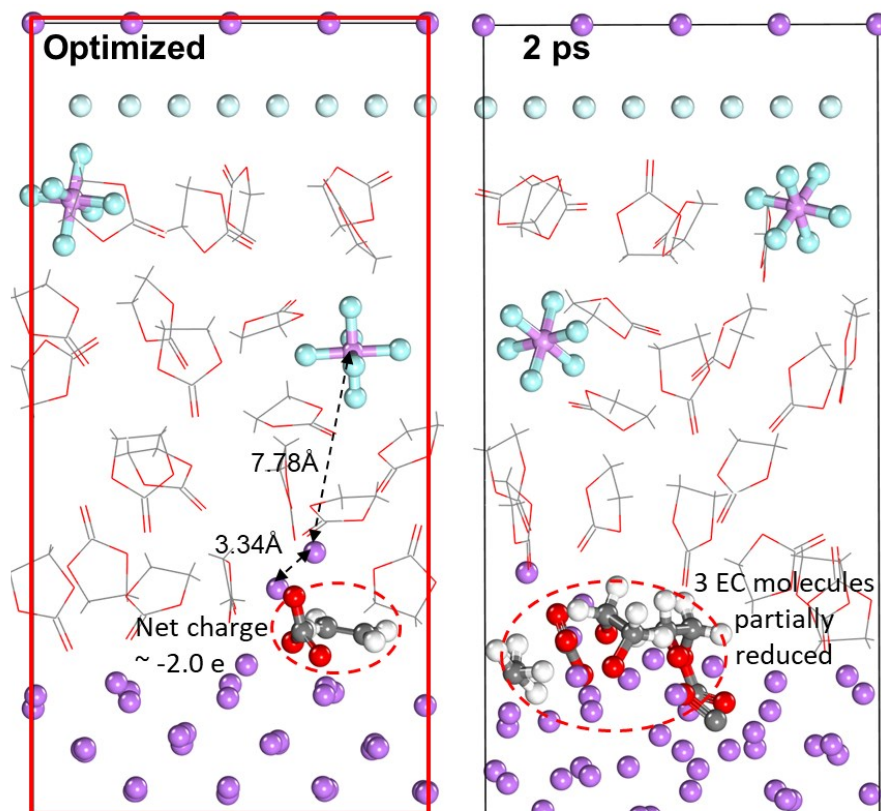
c. 2 M – 3 salt molecules



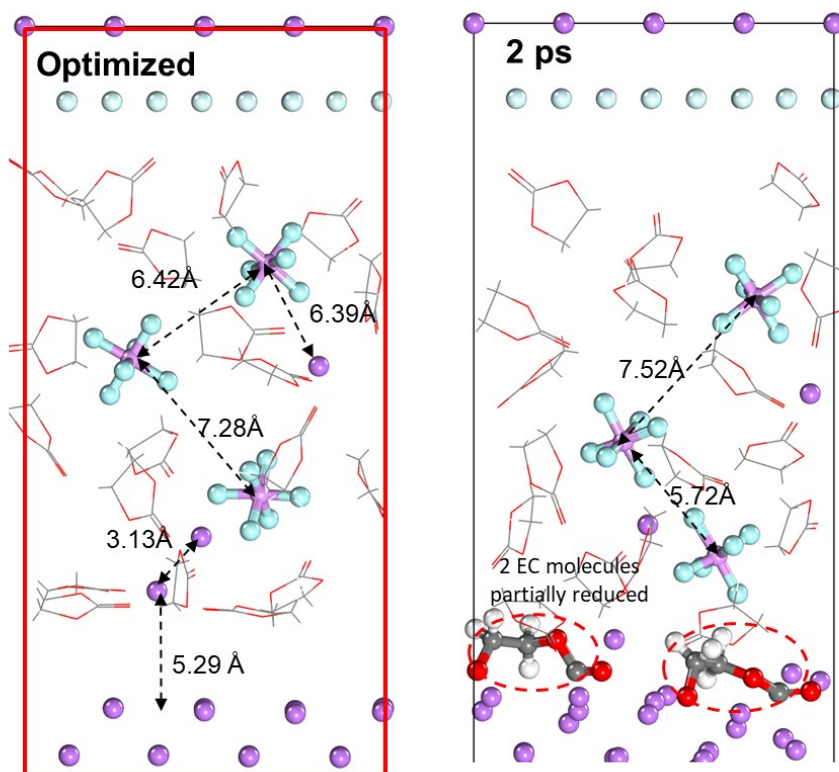
d. 0.64 M – 1 salt molecule

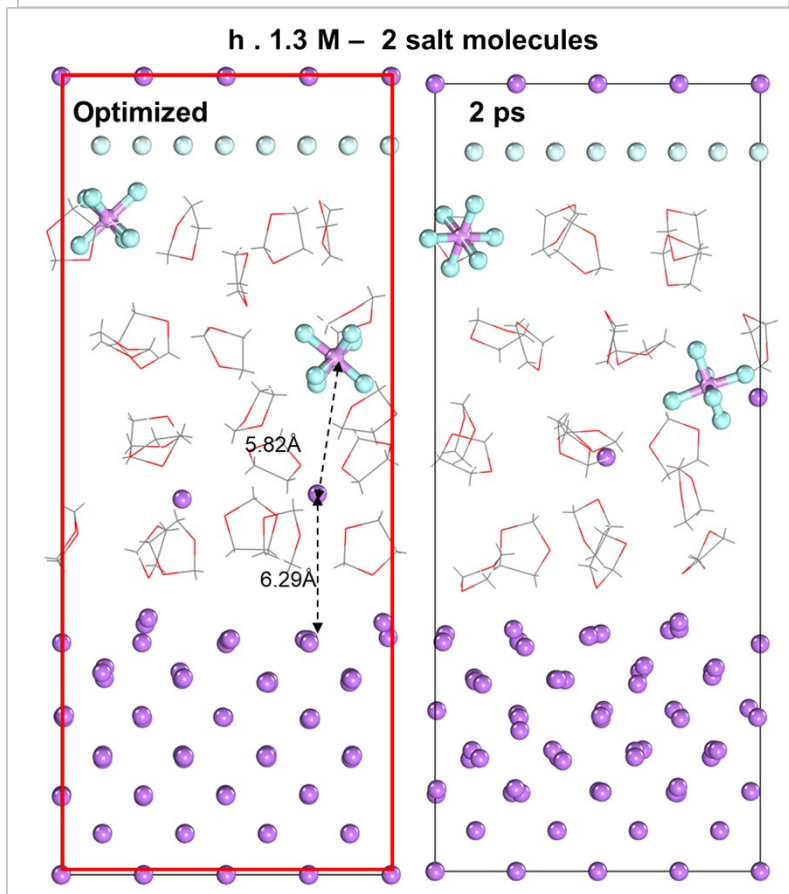
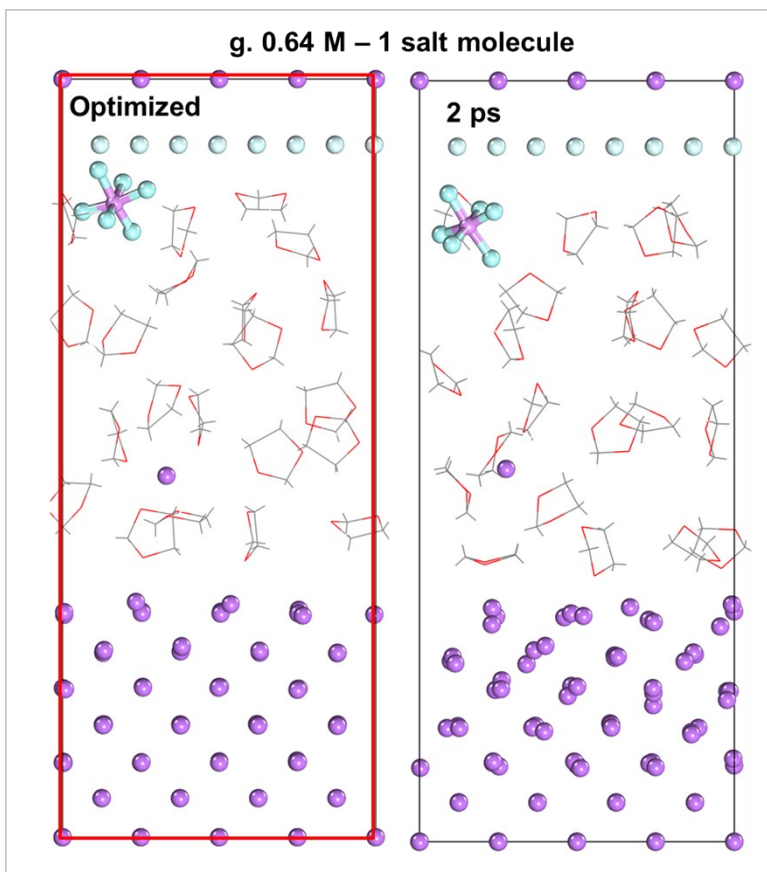


e. 1.3 M – 2 salt molecules



f. 2 M – 3 salt molecules





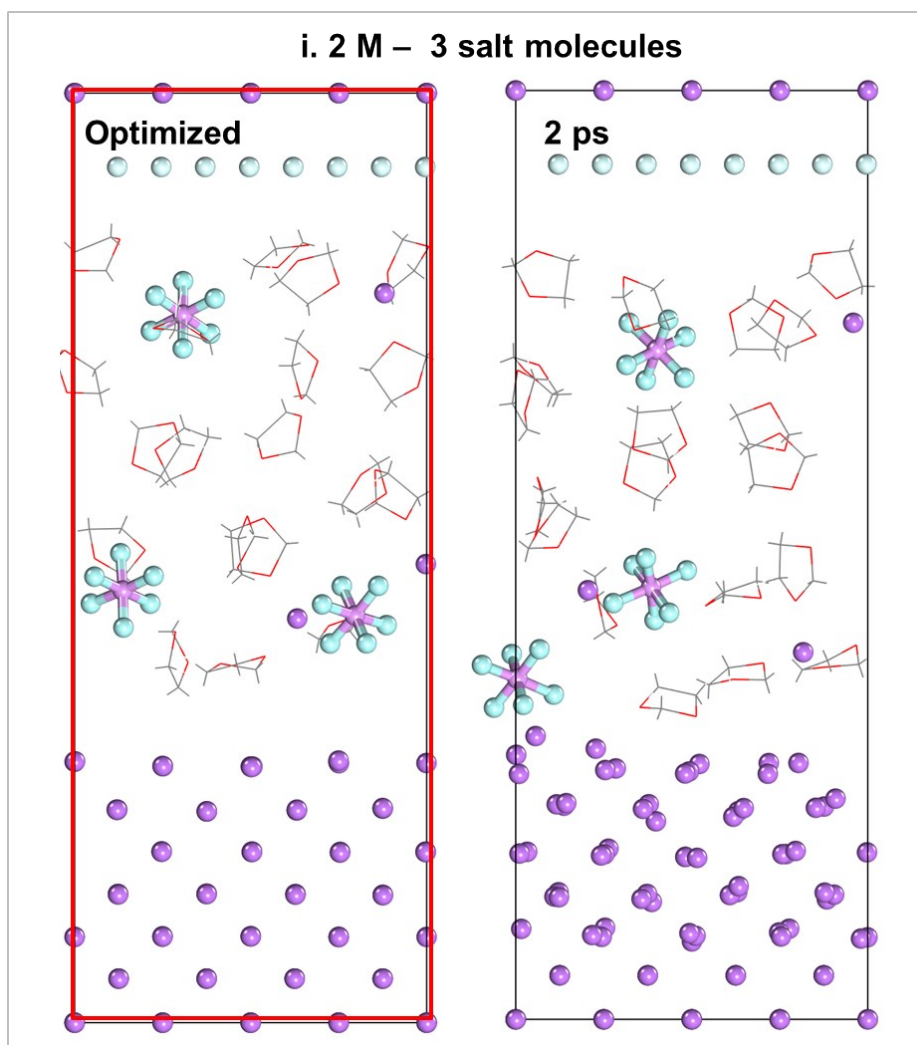


Figure S5. Optimized and dynamic snapshot of structures at different salt concentrations in solvent DME (a - c), EC (d - f), and DOL (g - i). Net charge for structures within the red box are shown in Figure 7.

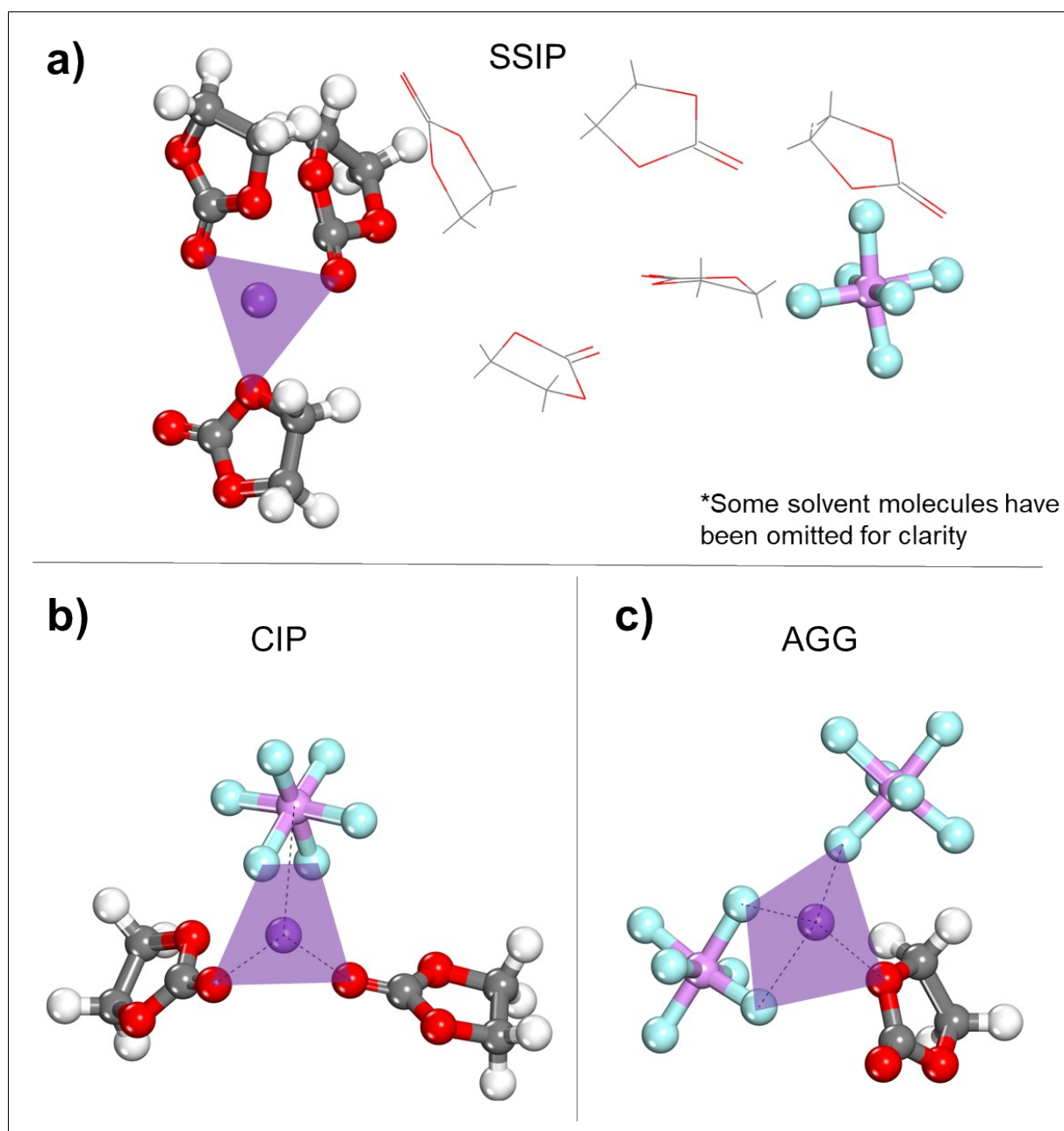


Figure S6. Close up solvated structures found in systems containing EC solvent shown in Figure S5 (d - f). a. Solvent-separated ion pairs (SSIP) found in 0.64 M after optimization. b. Contact ion pair (CIP) found in 2M after optimization c. Cation-anion aggregates (AGG) found in 2M in EC after 2 ps in a dynamic simulation.

Explanation about Figure 10 construction. Figure 10 (main text) describes the evolution of the solvation shell through the elemental analysis of the atoms that are close to the lithium ion during the diffusion and deposition pathway. This type of plot can be

obtained for all systems and reveals the structure of the liquid surrounding the travelling cation. The first step is the calculation of the radial distribution function [1] that is the local density of a given element (normalized by the bulk density) as a function of their interatomic distance, r . The first peak in Figures S7 a, b and c represents the density of solvent or anion molecules surrounding the cation in the first shell. The following minimum marks the end of the initial solvation shell (represented by the black arrow in Figure S7) of the corresponding elemental pair.

The table shown in Figure S7d has the summary of the values (in Å) used as the end of the first solvation shell for each Li-X pair.

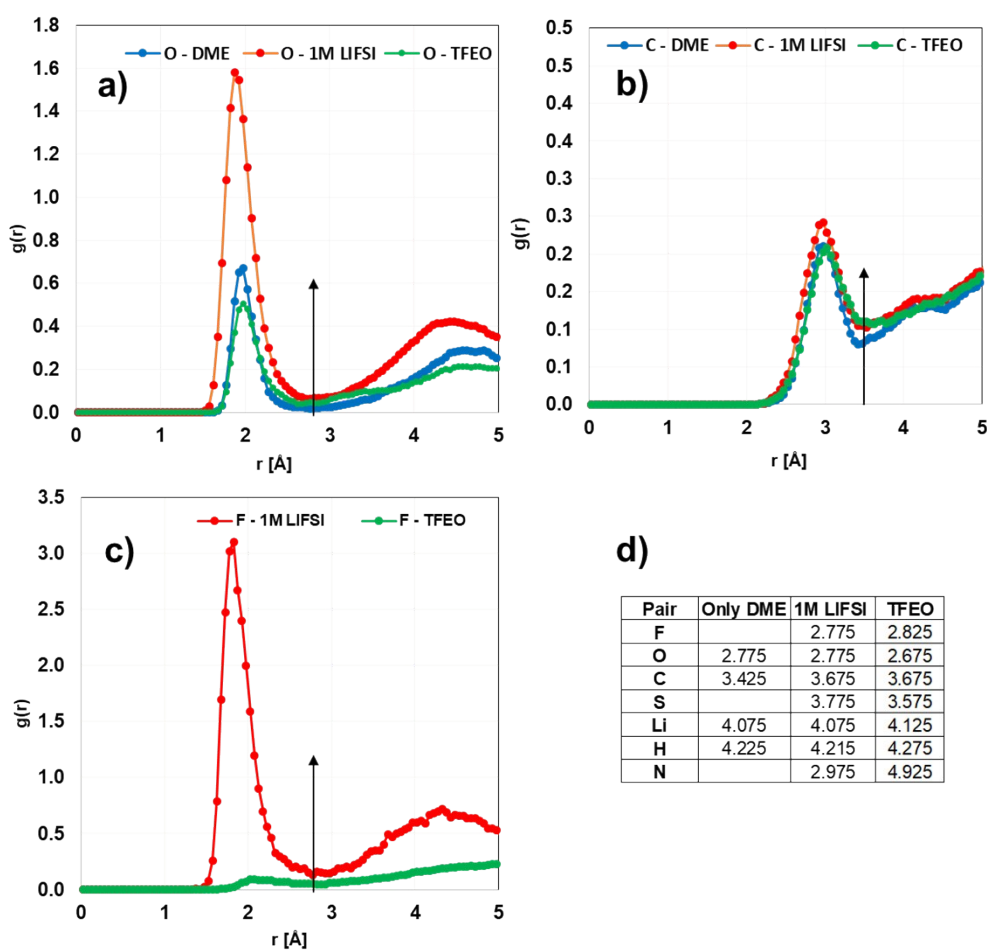


Figure S7. Radial distribution function for different pairs of atoms. a) Pair Li ion – Oxygen b) Pair Li ion – Carbon c) Pair Li atom –Fluorine d) Summary of the values (in Å) used for the end of the solvation shell.

References Cited

1. Allen, M.P. and D.J. Tildesley, *Computer Simulation of Liquids*. 1990, Oxford: Oxford University Press.