

Supplementary Information for

Lithium Oxidation and Electrolyte Decomposition at Li-Metal/Liquid Electrolyte Interfaces

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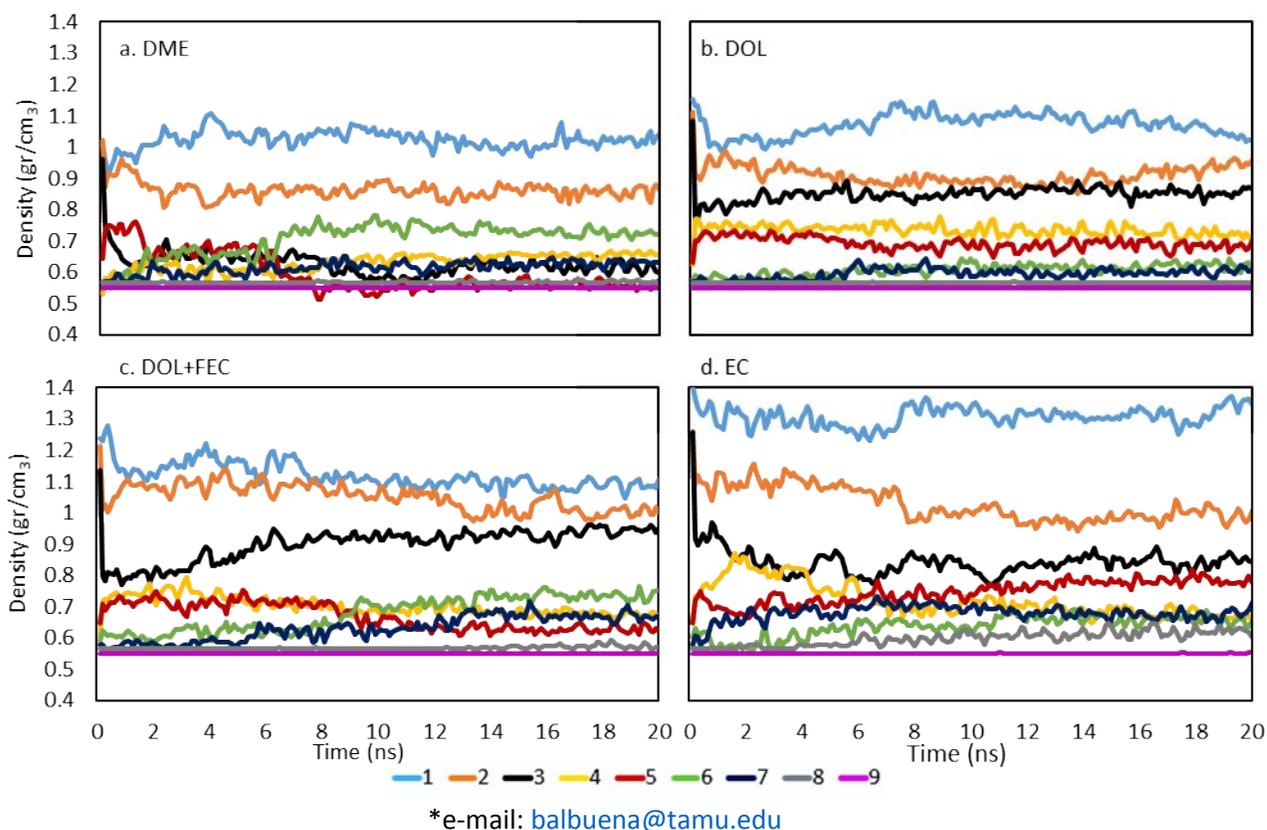


Figure S1. Total density evolution for Li slab blocks considering all species present (refer to Figure 1a for block discretization) from LiPF₆ in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC. Color code: light blue for top block 1, orange for block 2, black for block 3, yellow for block 4, red for block 5, green for block 6, dark blue for block 7, grey for block 8, and purple for bottom block 9.

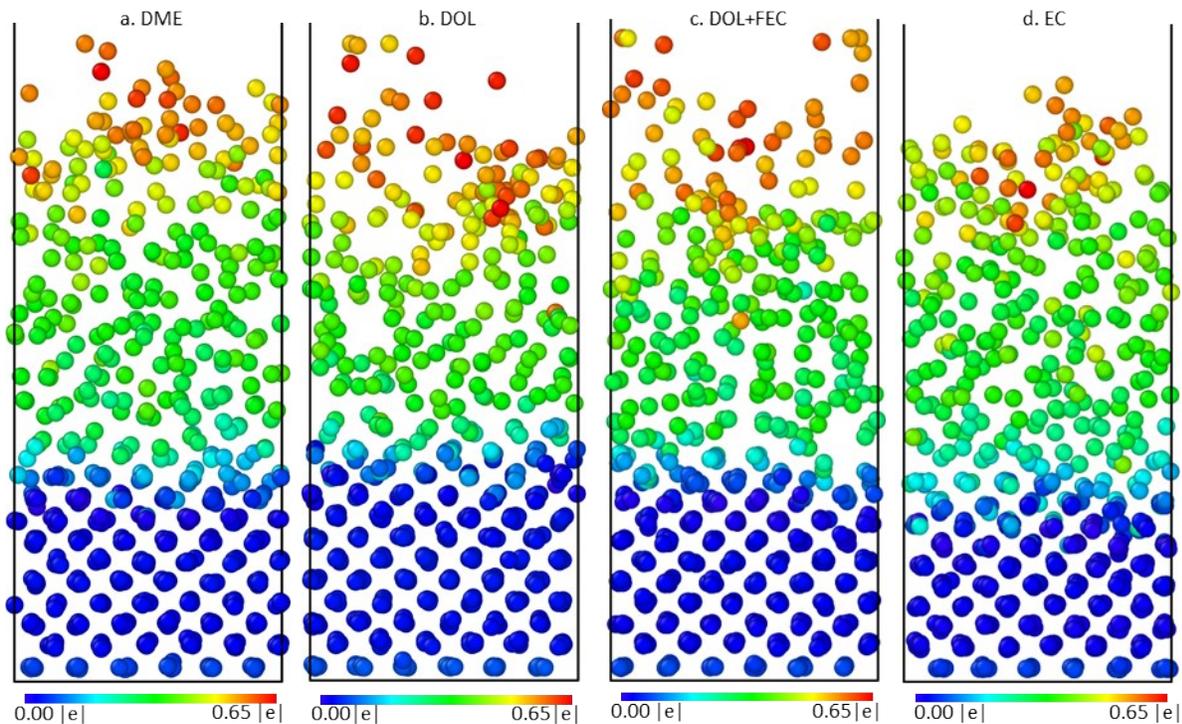


Figure S2. Final configuration reached for the Li-slab atoms expansion after 20 ns of simulation time for systems based on LiPF_6 . For (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC systems the general behavior is the same, it can be recognized the different regions (dense, nest, and disperse phase according to their average electronic charge distribution). For Figure d, the dense phase includes less bottom layers compared with the other systems, that behavior is due to the high reactivity of the EC molecules which tends to decompose and react with Li atoms. It is also the system where the knock-off mechanism is more severe due to the excess of electrons in the SEI top layers.

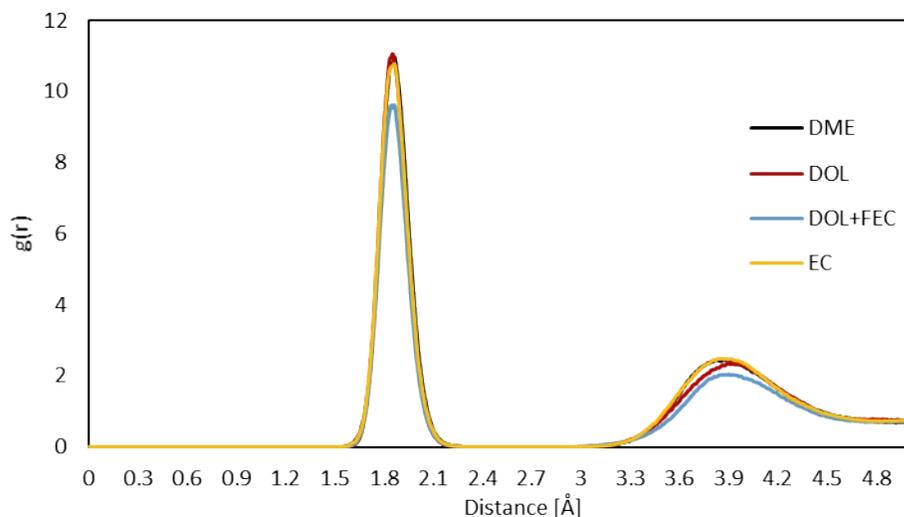


Figure S3. Pair radial distribution function (PRDF) for Li-F pair in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC, with LiPF₆. Color code: black for DME, red for DOL, light blue for mixture of DOL and FEC, and yellow for EC system.

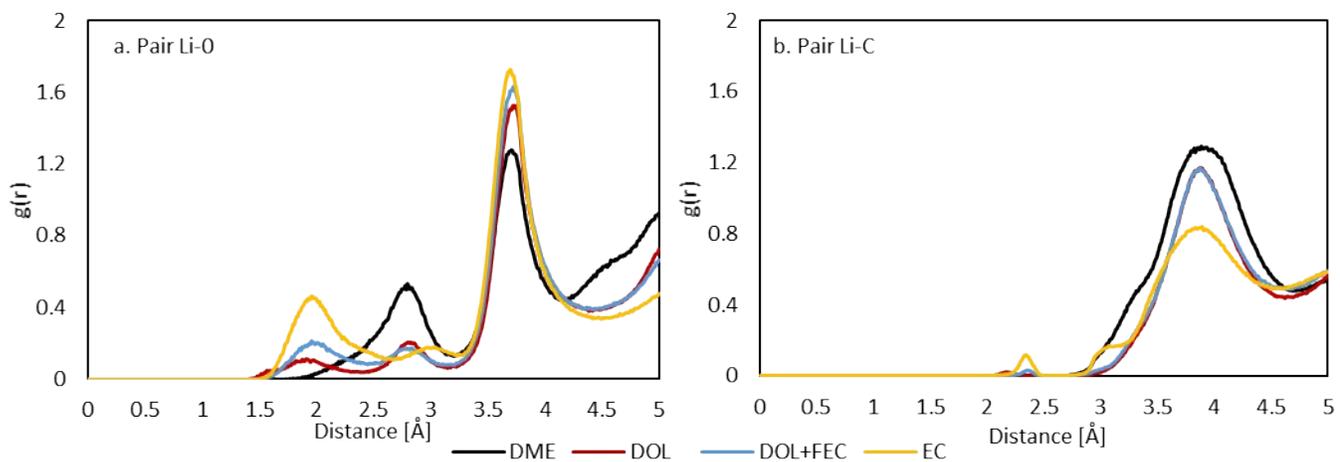


Figure S4. Pair radial distribution function (PRDF) for (a) Li-O and (b) Li-C pairs in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC, with LiPF₆. Color code: black for DME, red for DOL, light blue for mixture of DOL and FEC, and yellow for EC system.

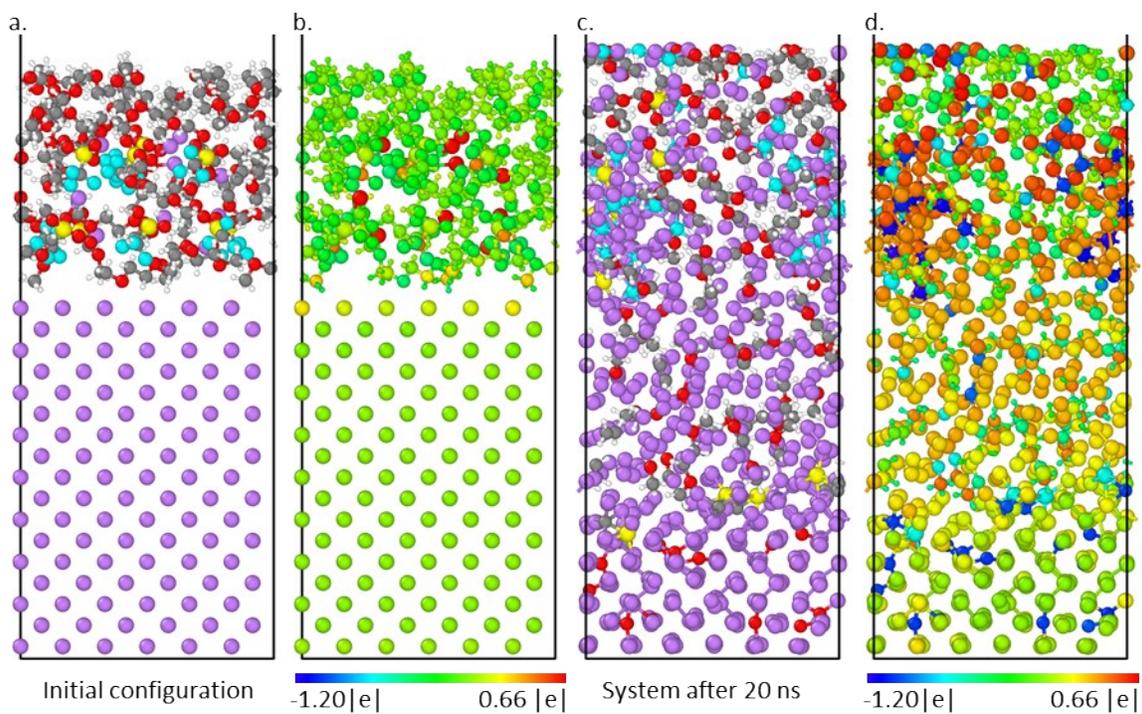


Figure S5. General representation of the system simulated with LiTF as salt. (a) initial configuration, (b) initial electronic charge distribution, (c, d) final configuration obtained at the end of simulation time and its charge distribution, with the formation of S-, C-, and O-based compounds as well as the F-based compounds forming the SEI.

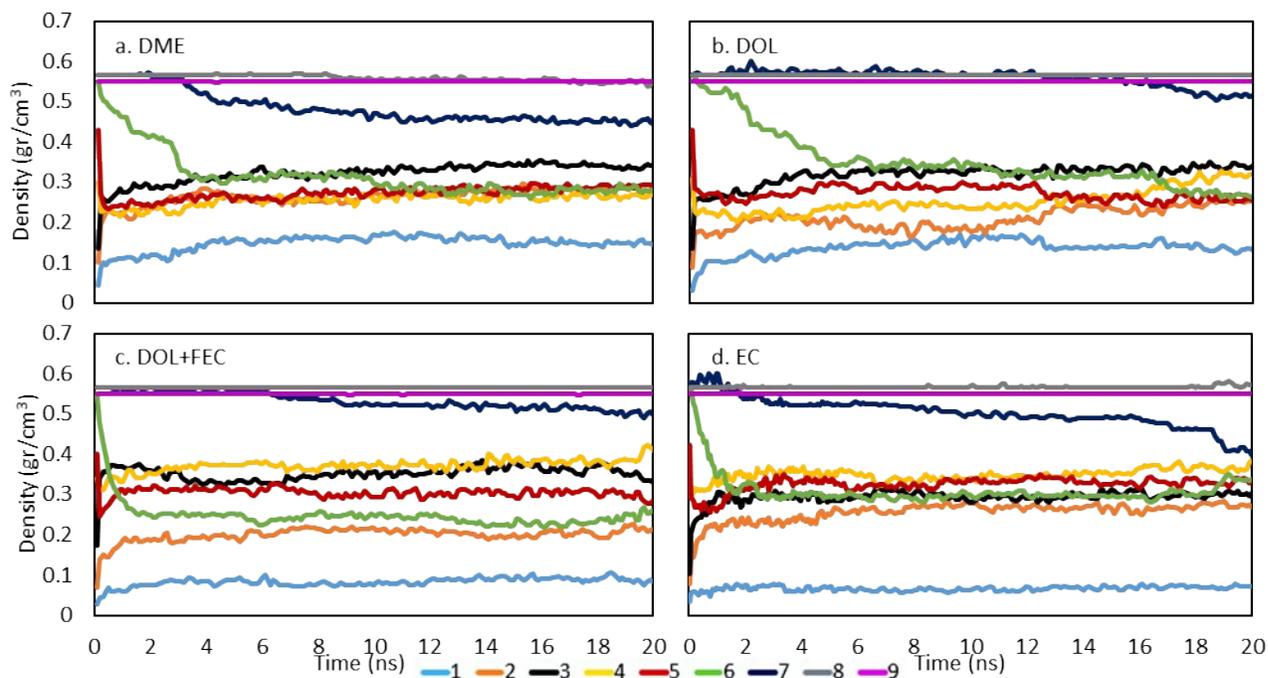


Figure S6. Li-density evolution for Li slab blocks (refer to Figure 1a for block discretization) from LiTF in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC. Color code: light blue for top block 1, orange for block 2, black for block 3, yellow for block 4, red for block 5, green for block 6, dark blue for block 7, grey for block 8, and purple for bottom block 9.

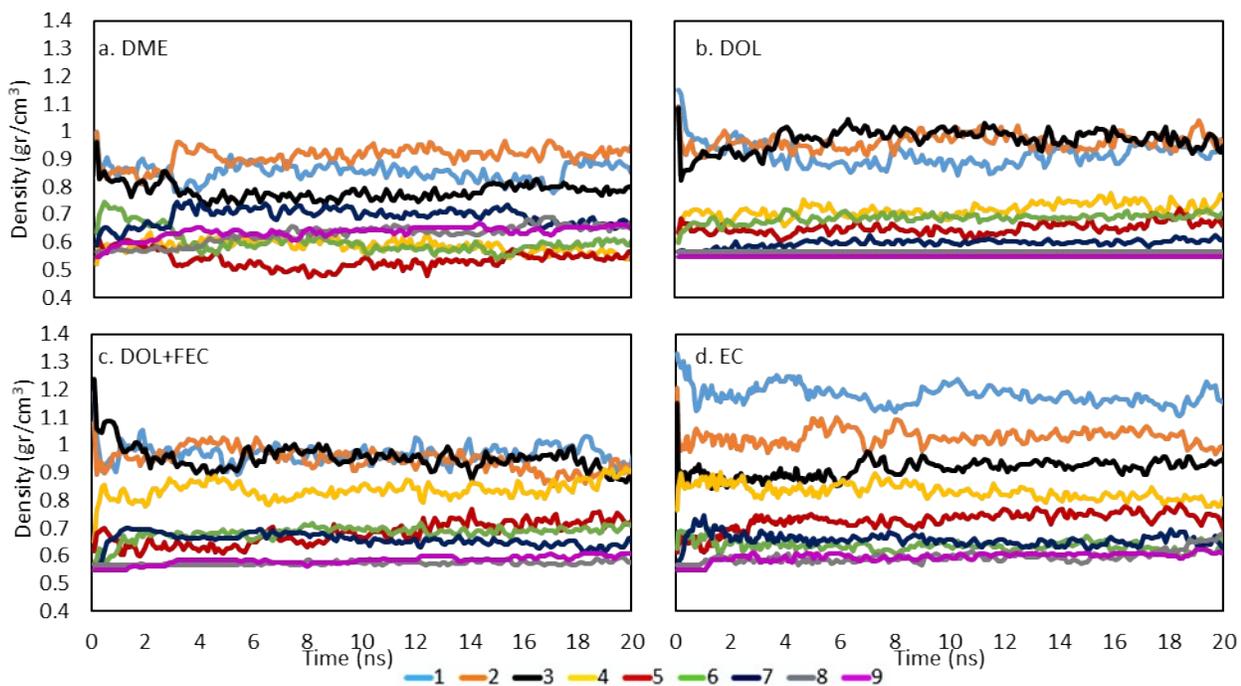


Figure S7. Total density evolution for Li slab blocks considering all species present (refer to Figure 1a for block discretization) from LiTF in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC. Color code: light blue for top block 1, orange for block 2, black for block 3, yellow for block 4, red for block 5, green for block 6, dark blue for block 7, grey for block 8, and purple for bottom block 9.

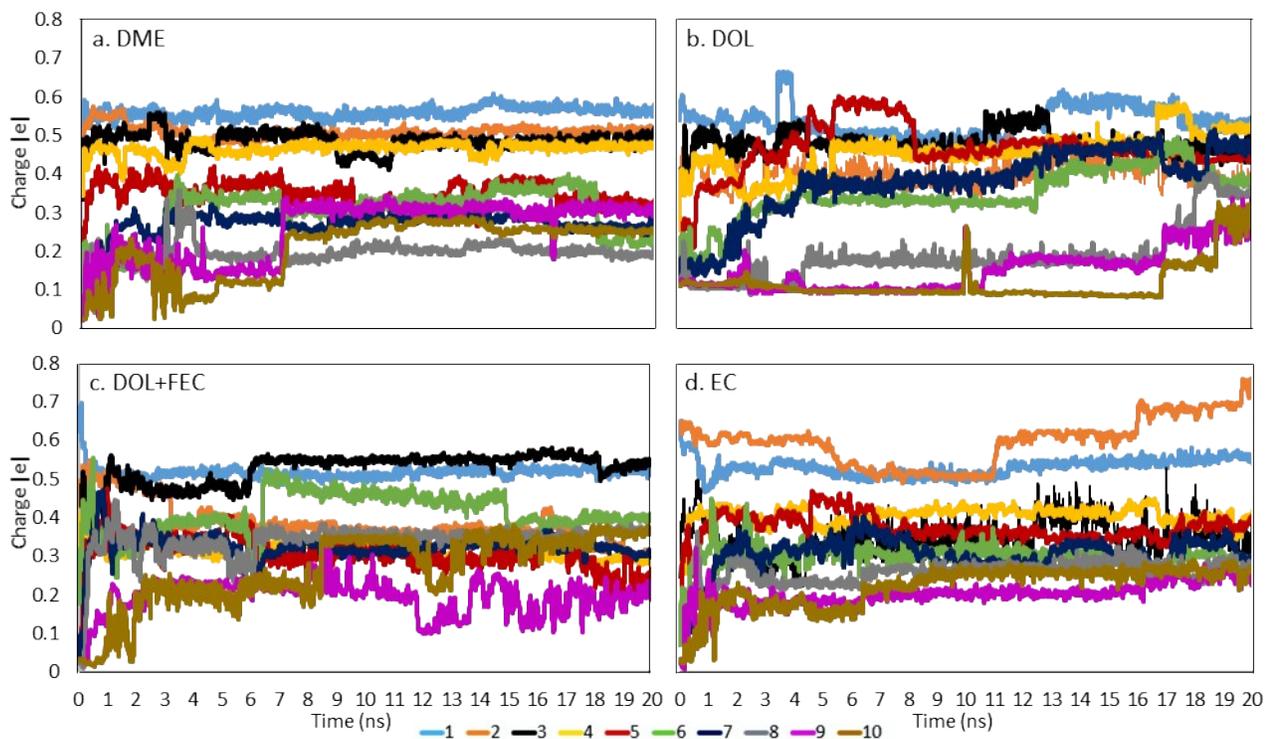


Figure S8. Charge evolution for Li-slab top layers (refer to Figure 1b for Li-slab layers numeration) from LiTF in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC. Color code: light blue for top layer 1, orange for layer 2, black for layer 3, yellow for layer 4, red for layer 5, green for layer 6, dark blue for layer 7, grey for layer 8, purple for top layer 9, and light brown for internal layer 10.

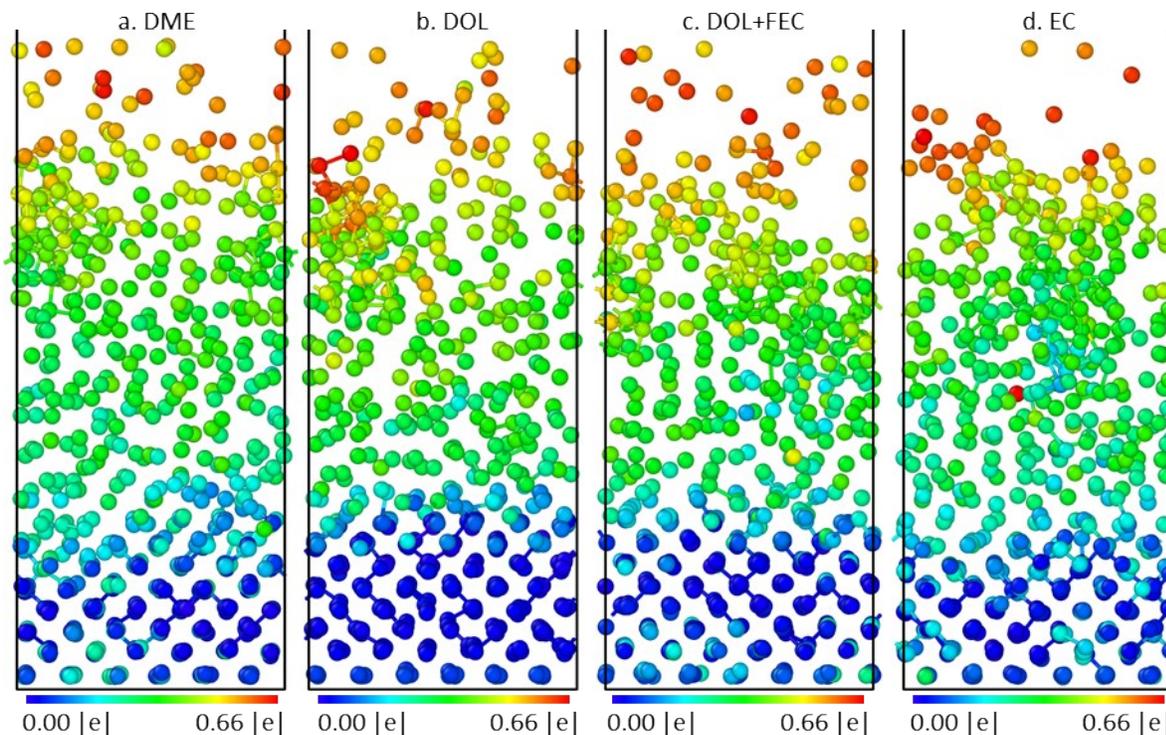


Figure S9. Final configuration reached for the Li-slab atoms expansion after 20 ns of simulation time. For (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC systems the general behavior is the same, it can be recognized the different regions according to their average electronic charge distribution. Presence of light color atoms in the bottom of the slabs corresponds to the O atoms forming lithium oxide clusters in that zone.

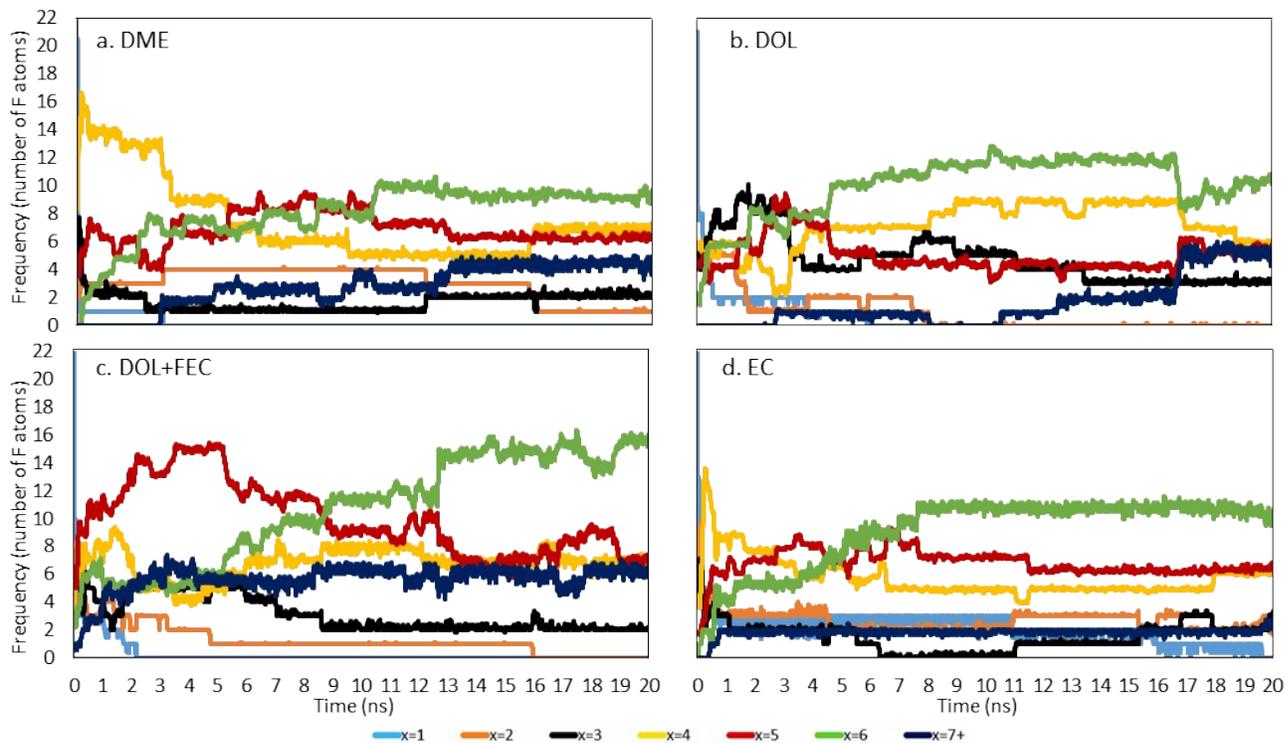


Figure S10. LixF coordination evolution for LiTF in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC. Color coding: light blue for coordination $x=1$, orange coordination $x=2$, black coordination $x=3$, yellow for coordination $x=4$, red for coordination $x=5$, green for coordination $x=6$, and dark blue for coordination $x=7$ or more.

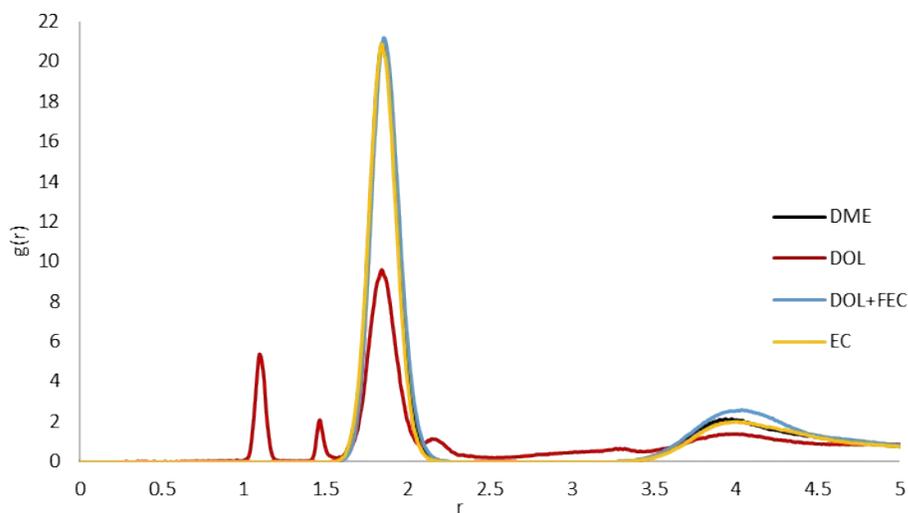


Figure S11. Pair radial distribution function (PRDF) for Li-F pair in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC, with LiTF. Color code: black for DME, red for DOL, light blue for mixture of DOL and FEC, and yellow for EC system.

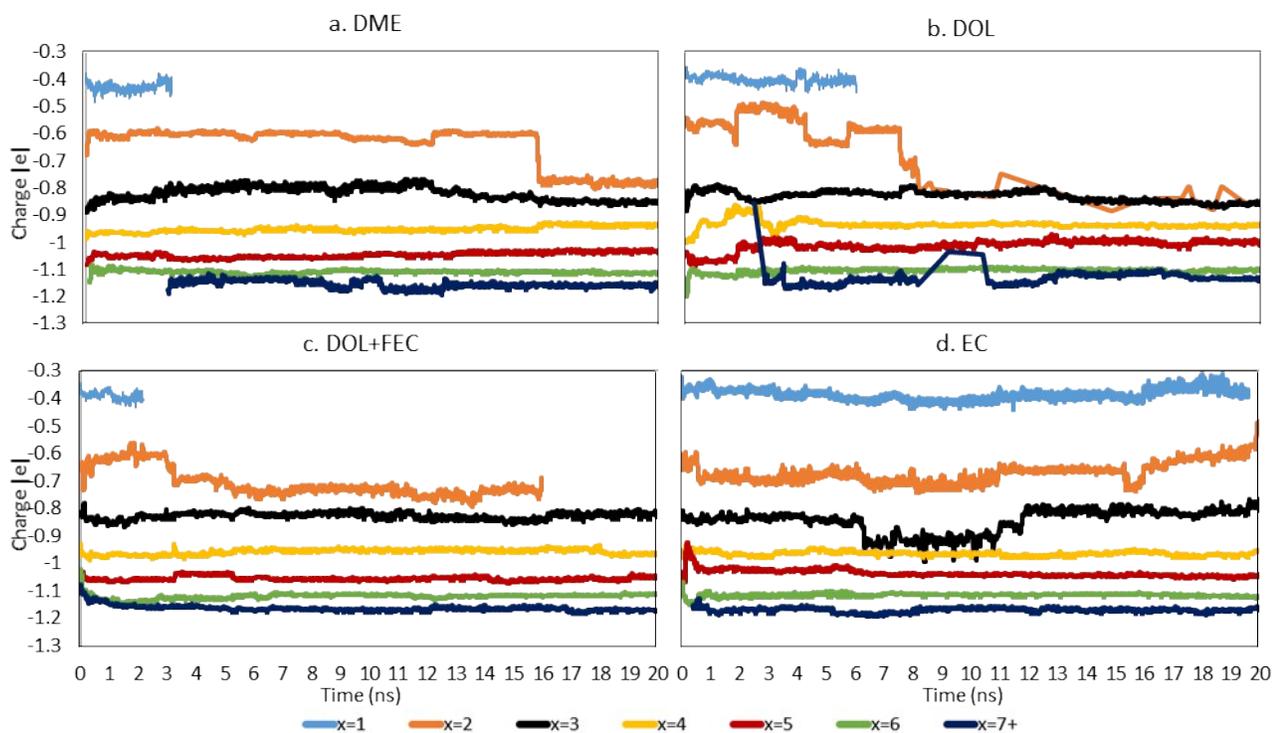


Figure S12. F atom charge evolution for Li_xF from LiTF in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC. Color code: light blue for coordination $x=1$, orange coordination $x=2$, black coordination $x=3$, yellow for coordination $x=4$, red for coordination $x=5$, green for coordination $x=6$, and dark blue for coordination $x=7$ or more.

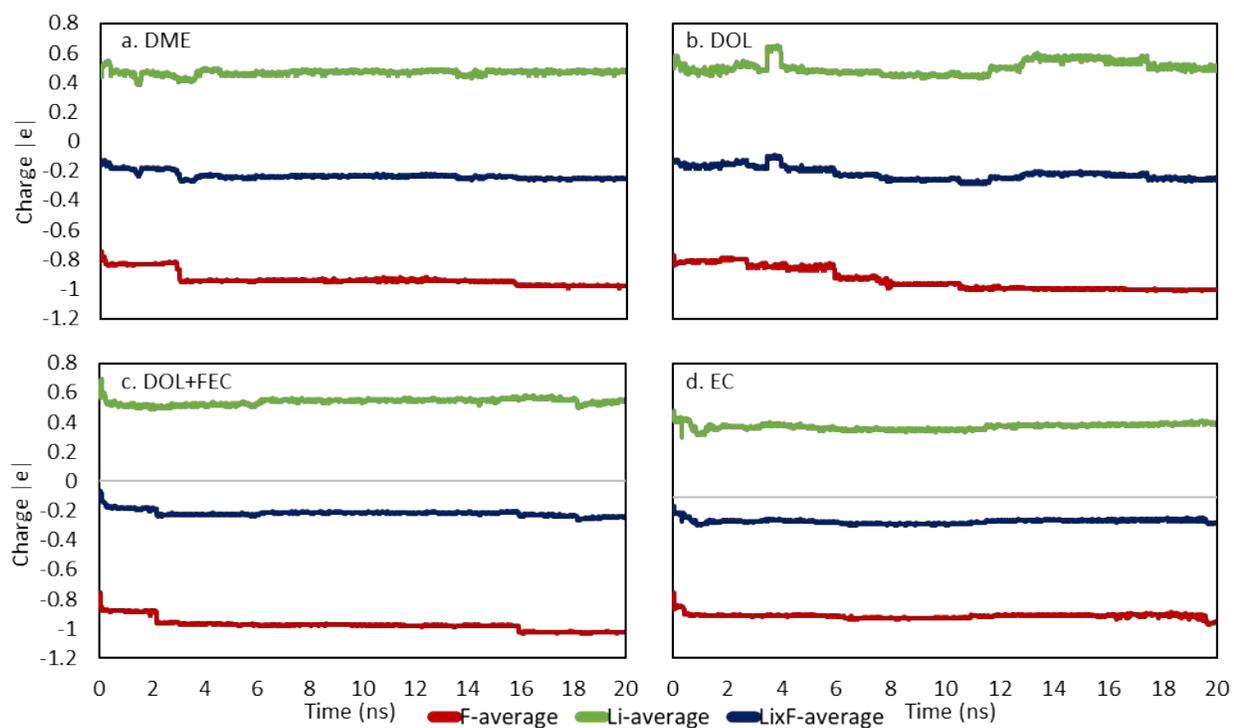


Figure S13. LixF-SEI charge evolution for SEI from LiTF in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC. Color code: red for average F charge, green for average Li charge, and blue for average SEI charge evolution.

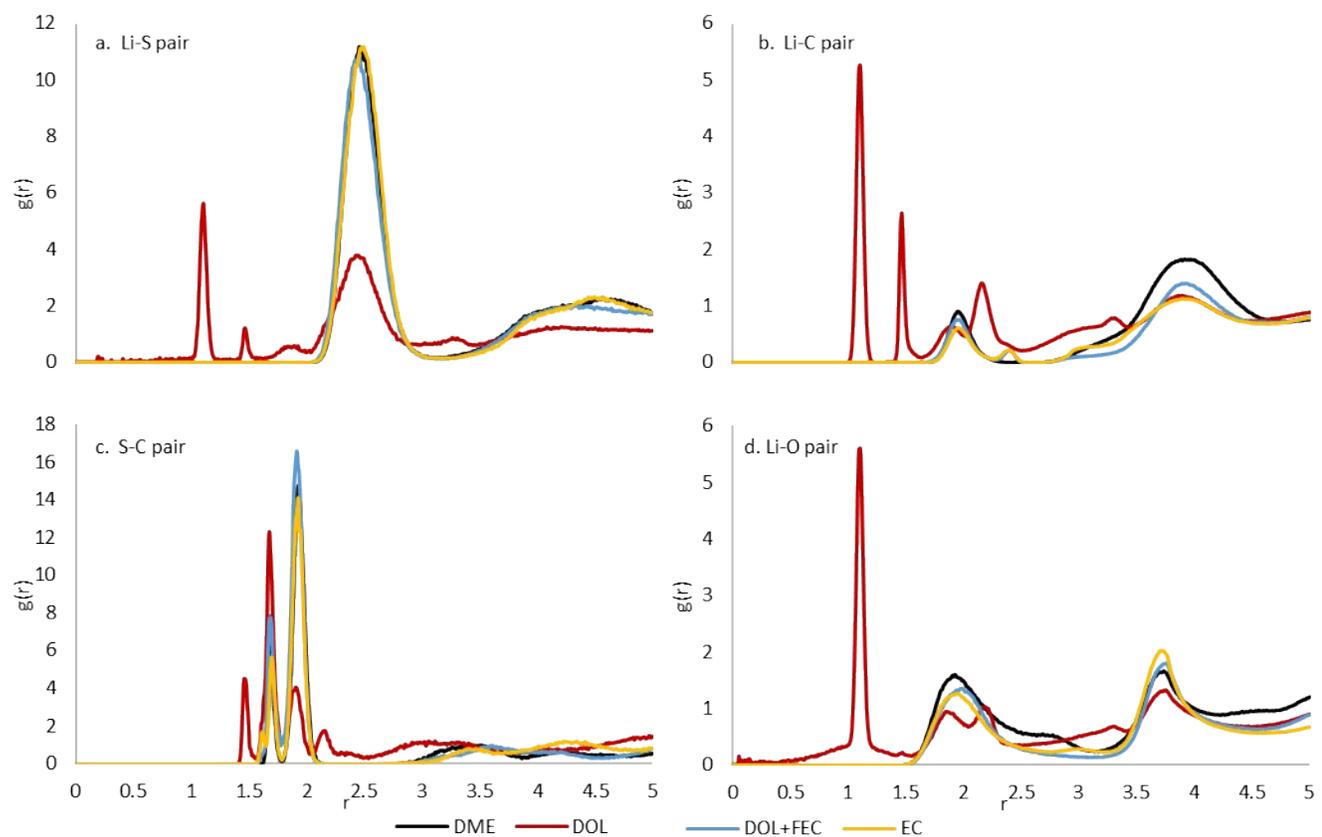


Figure S14. Pair radial distribution function (PRDF) for (a) Li-S, (b) Li-C, (c) S-C, and (d) Li-O pairs in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC, with LiTF. Color code: black for DME, red for DOL, light blue for mixture of DOL and FEC, and yellow for EC system.

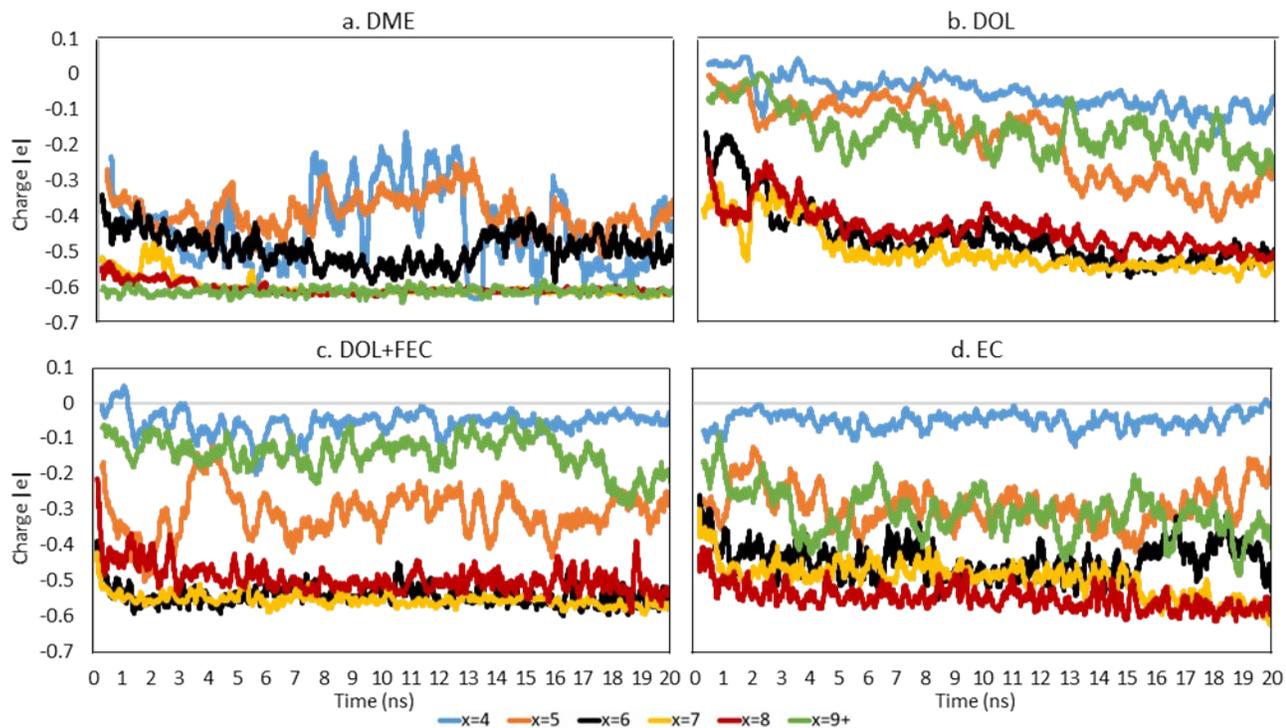


Figure S15. S atom charge evolution for ΨxS compound from LiTF in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC, where Ψ may be the S coordination with Li or C atoms. Color code: light blue for coordination x=4, orange coordination x=5, black coordination x=6, yellow for coordination x=7, red for coordination x=8, and green for coordination x=6 or more.

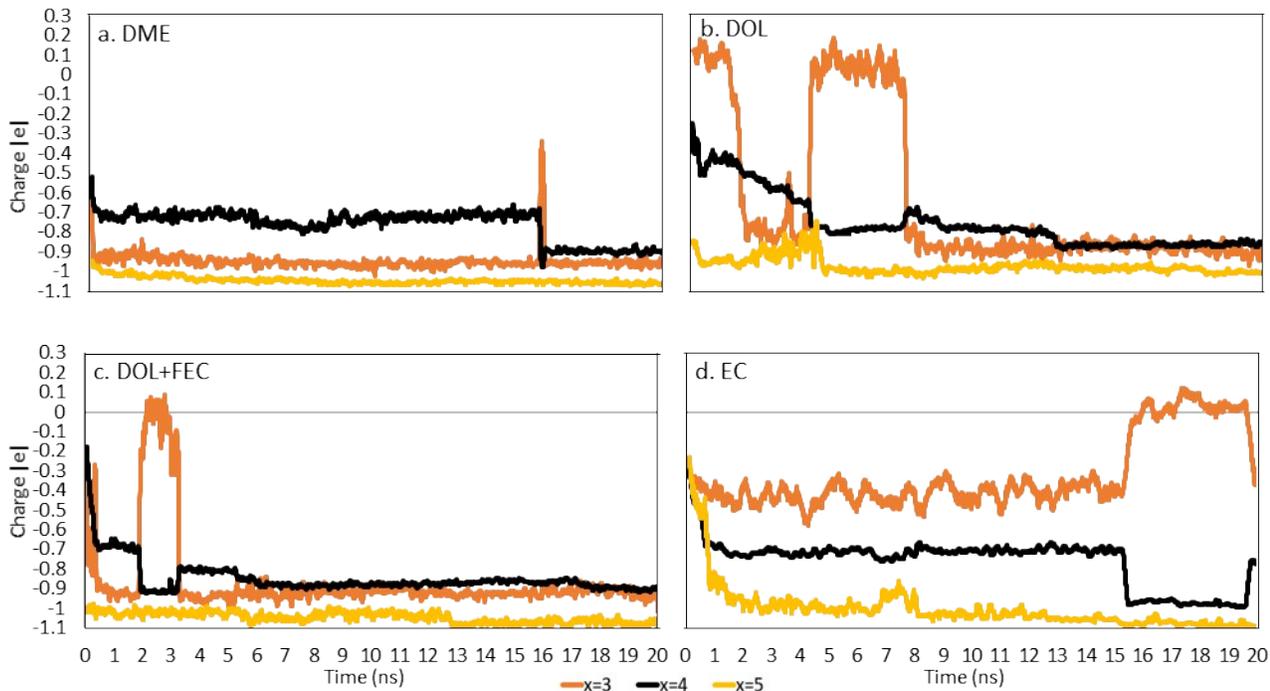
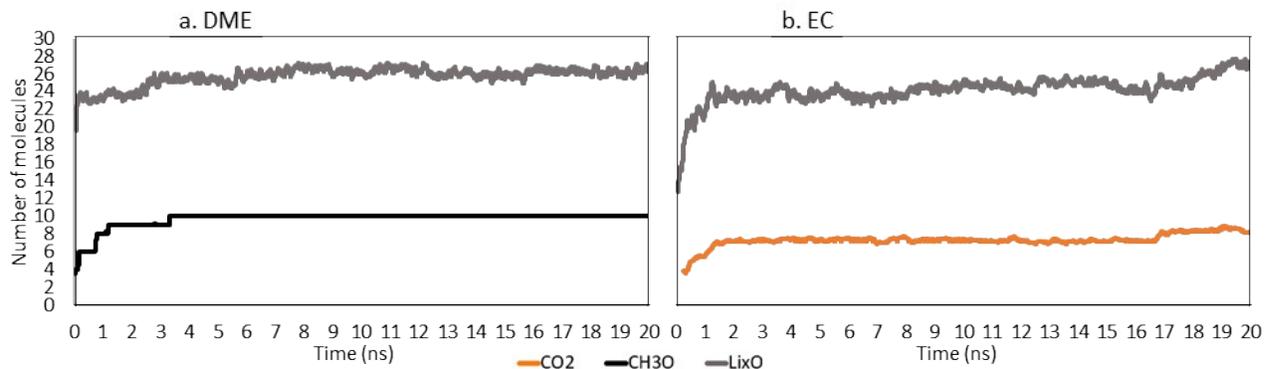


Figure S16. C atom charge evolution for $\Psi_x\text{C}$ compound from LiTF in different solvents evaluated: (a) DME, (b) DOL, (c) mix of DOL and FEC, and (d) EC, where Ψ may be the C coordination with Li or S atoms. Color



code: orange for coordination $x=3$, black for coordination $x=4$, and yellow for coordination $x=5$.

Figure S17. Formation of different organic species for the systems with (a) mixture of DOL and FEC as solvent and (b) EC as solvent. Color code: orange for carbon dioxide (CO_2), black for methoxide group (CH_3O), and gray for the total amount of lithium oxide clusters (Li_xO).

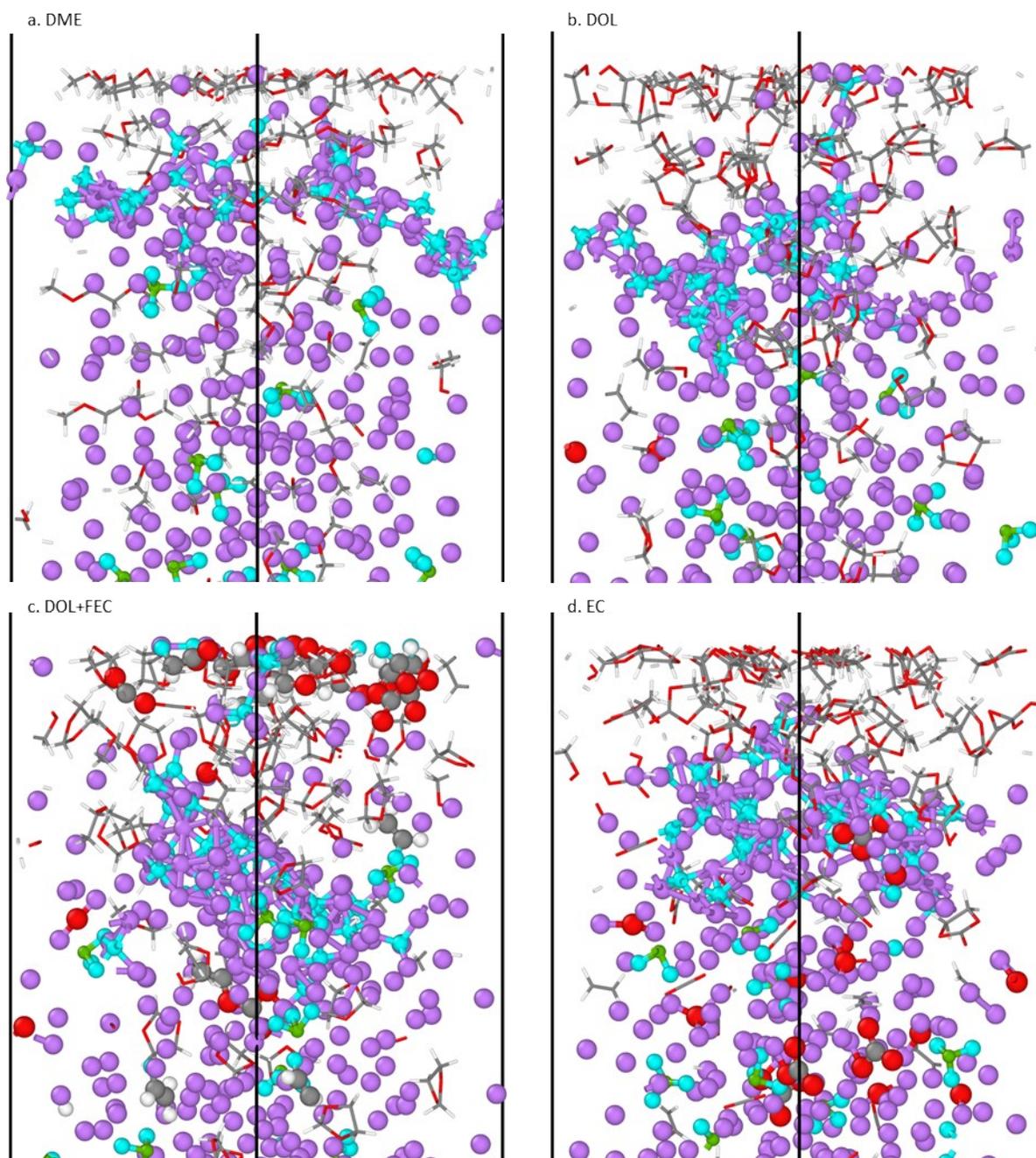


Figure S18. Orthogonal view for the SEI formed from LiPF_6 in liquid electrolyte (a) DME, (b) DOL, (c) DOL mixed with FEC, and (d) EC. Wireframe structures correspond to no-reacted electrolyte molecules and other organic compounds for better visualization. Color code: light blue for F, red for O, purple for Li, white for H, gray for C, and green for P.

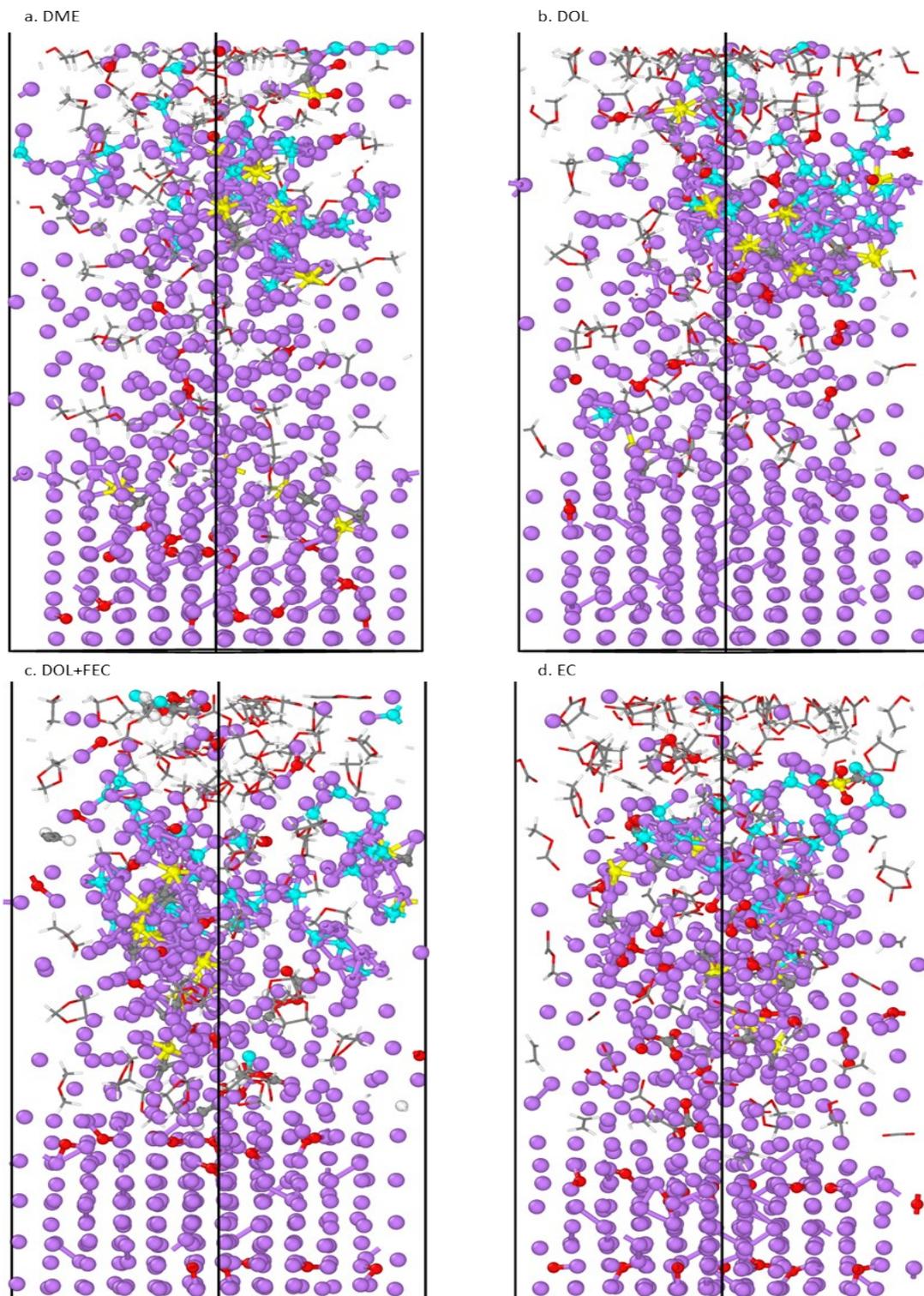


Figure S19. Orthogonal view for the SEI formed from LITF in liquid electrolyte (a) DME, (b) DOL, (c) DOL mixed with FEC, and (d) EC. Wireframe structures correspond to unreacted electrolyte molecules and other organic compounds for better visualization. Color code: light blue for F, red for O, purple for Li, white for H, gray for C, and yellow for S.

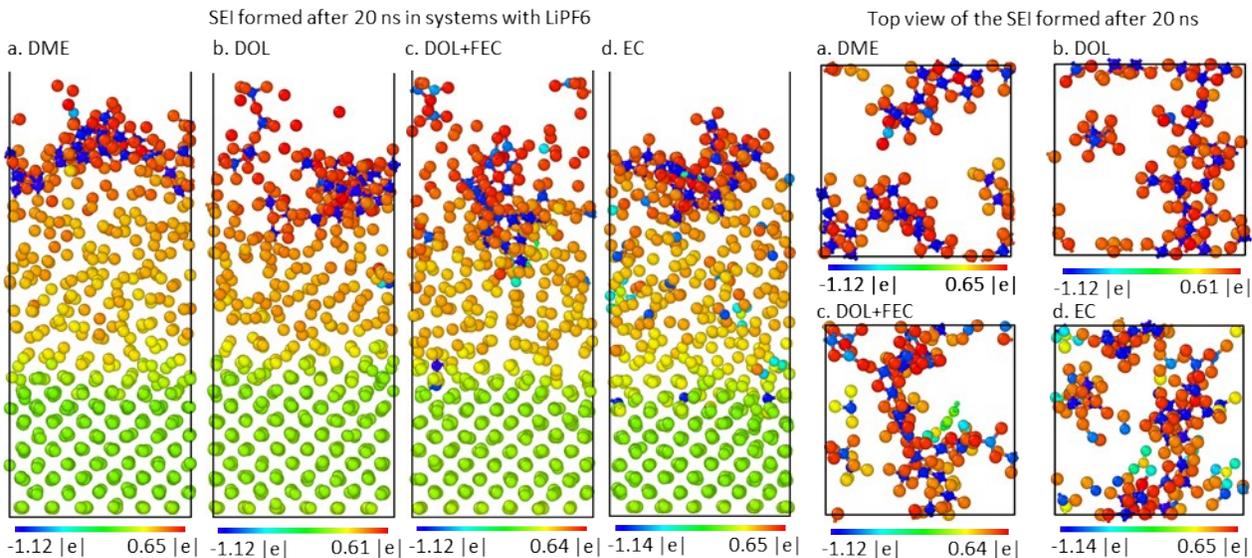
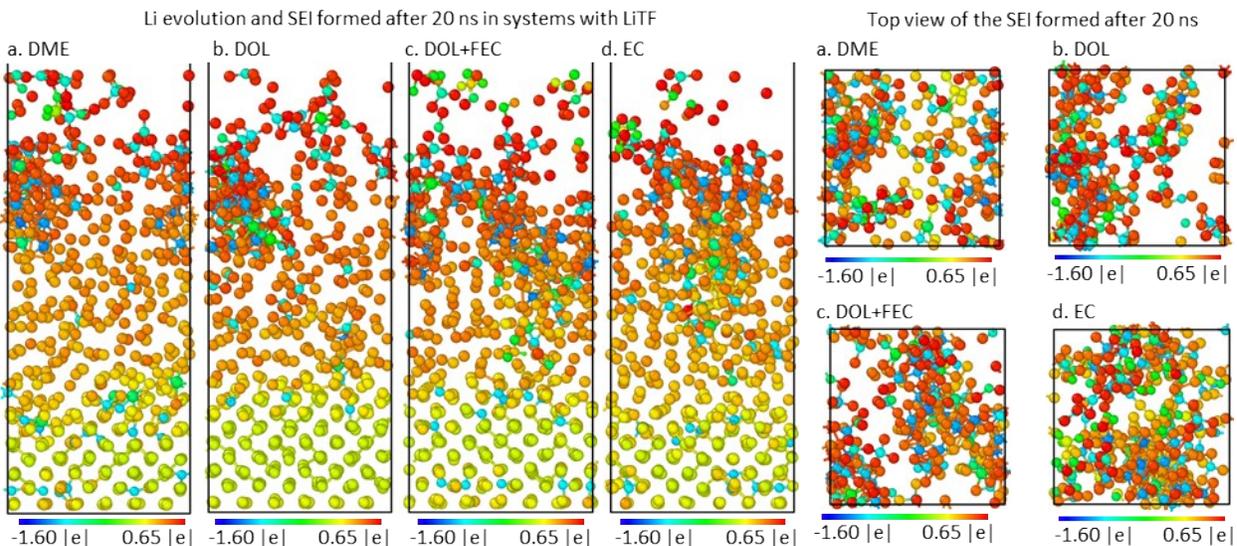


Figure S20. Electronic charge distribution for SEI formed from LiPF₆ in liquid electrolyte (a) DME, (b) DOL, (c) DOL mixed with FEC, and (d) EC. Left hand: front view of Li-slab atoms and SEI. Right hand: top view of



SEI formed.

Figure S21. Electronic charge distribution for SEI formed from LiTF in liquid electrolyte (a) DME, (b) DOL, (c) DOL mixed with FEC, and (d) EC. Left hand: front view of Li-slab atoms and SEI. Right hand: top view of SEI formed.

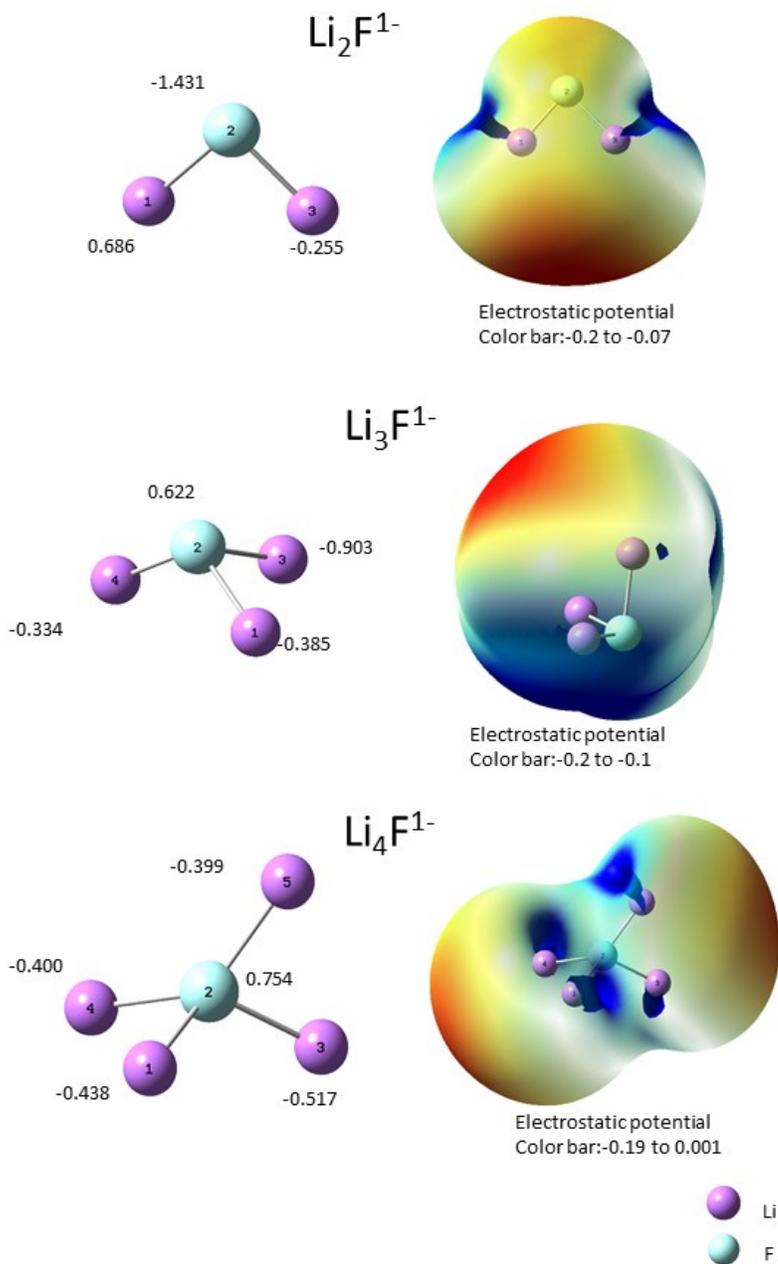


Figure S22. Optimized geometry of negatively charged LiF fragments. Charges are labeled near each atom from population analysis based on Atomic Polar Tensor (APT). Electrostatic potential surfaces are mapped onto total electron density surfaces with Iso-value = 0.0004 [electron density]. The colorbar is in units of [Energy/Charge], in this case Hartree/elementary charge. (Orange is closer to lower-bound and blue is close to upper bound)

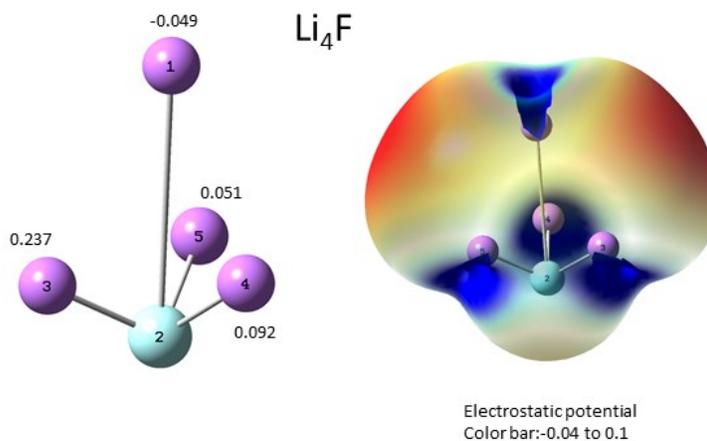
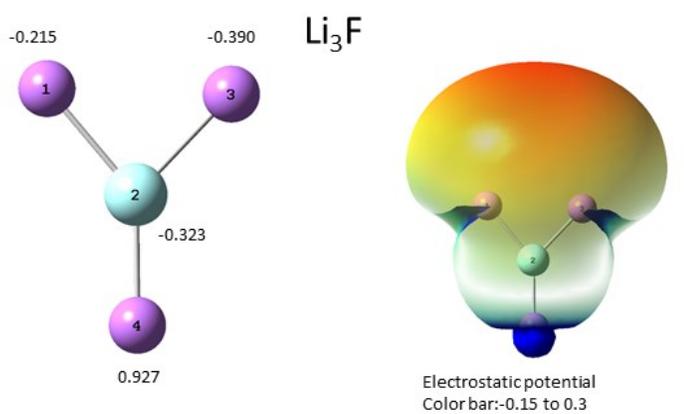
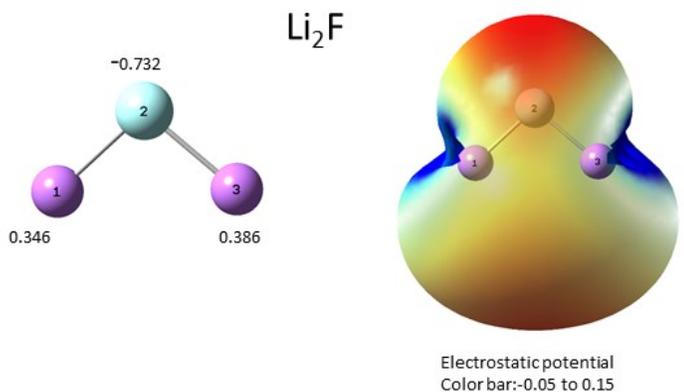


Figure S23. Optimized geometry of negatively charged LiF fragments. Charges are labeled near each atom from population analysis based on Atomic Polar Tensor (APT). Electrostatic potential surface are mapped onto total electron density surface with Iso-value = 0.0004 [electron density]. The colorbar is in units of [Energy/Charge], in this case Hartree/elementary charge. (Orange is closer to lower-bound and blue is close to upper bound)

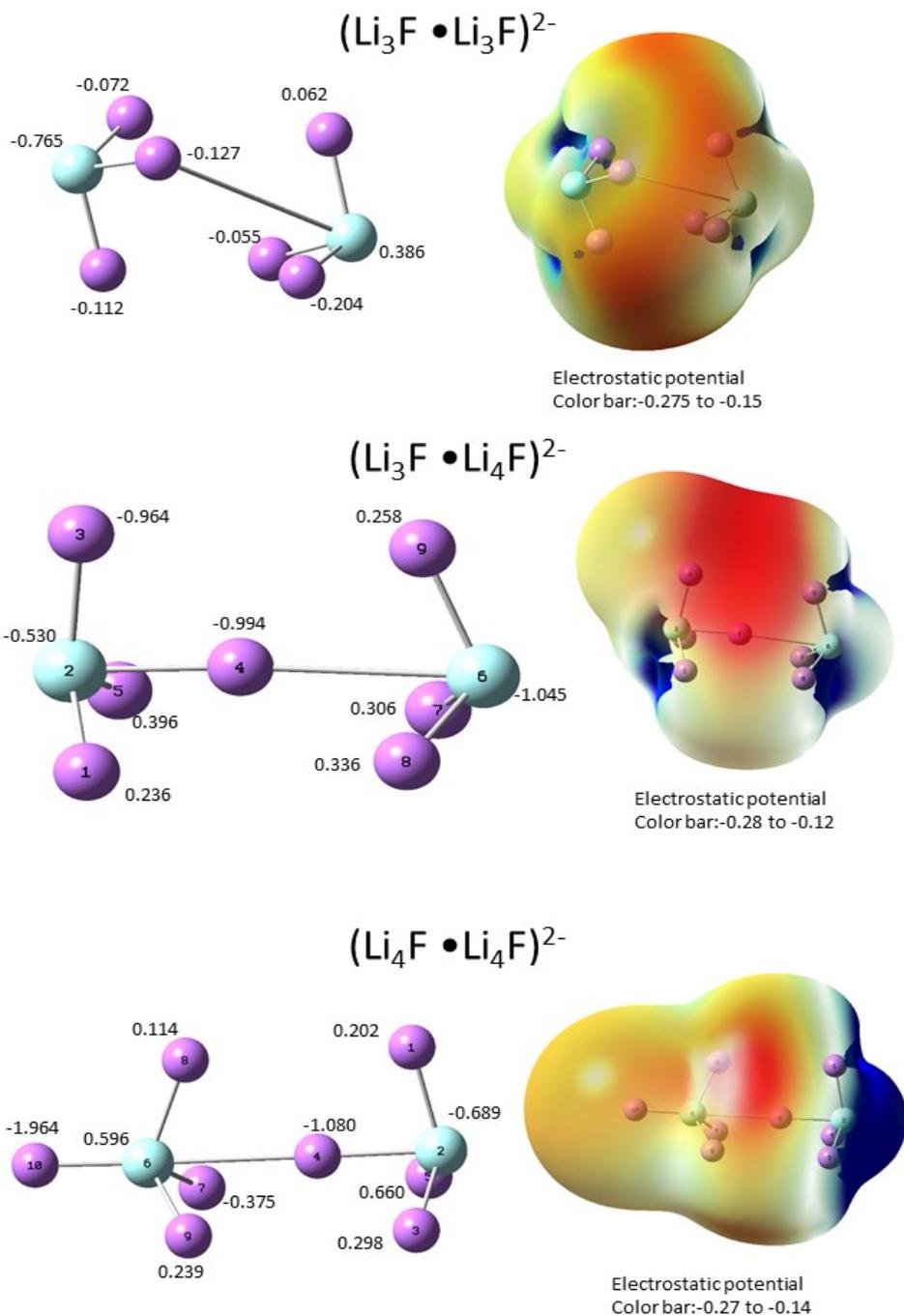
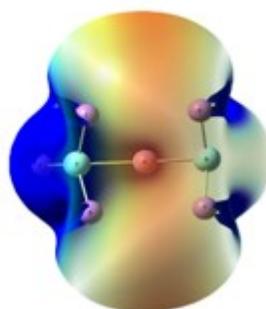
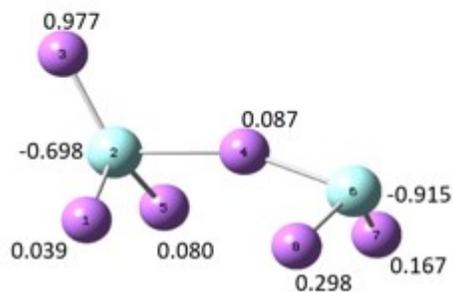
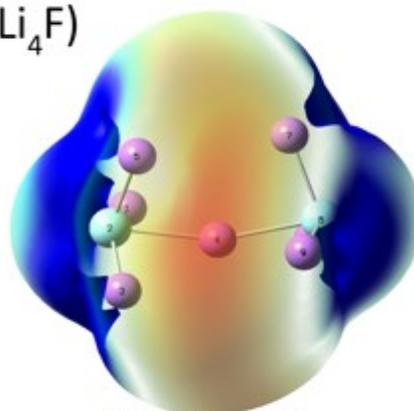
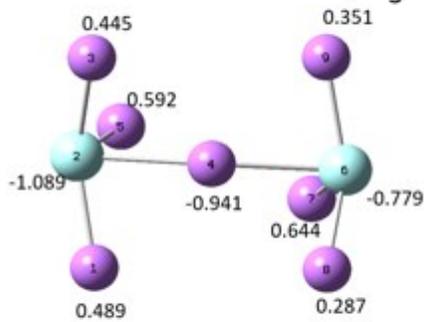


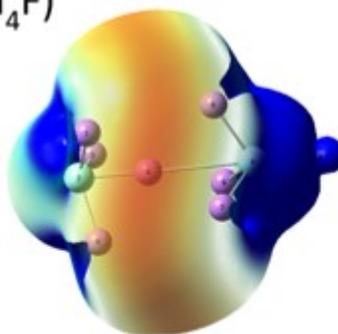
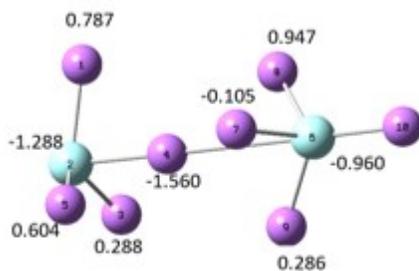
Figure S24. Geometry of (2-) charged LiF clusters. Charges are labeled near each atom from population analysis based on Atomic Polar Tensor (APT). Electrostatic potential surface are mapped onto total electron density surface with Iso-value = 0.0004 [electron density]. The colorbar is in units of [Energy/Charge], in this case Hartree/elementary charge. (Orange is closer to lower-bound and blue is close to upper bound)



Electrostatic potential
Color bar: -0.1 to 0.07



Electrostatic potential
Color bar: -0.18 to -0.07



Electrostatic potential
Color bar: -0.095 to 0.05

Figure S25. Geometry of neutral LiF clusters. Charges are labeled near each atom from population analysis based on Atomic Polar Tensor (APT). Electrostatic potential surface are mapped onto total electron density surface with Iso-value = 0.0004 [electron density]. The colorbar is in units of [Energy/Charge], in this case Hartree/elementary charge. (Orange is closer to lower-bound and blue is close to upper bound)

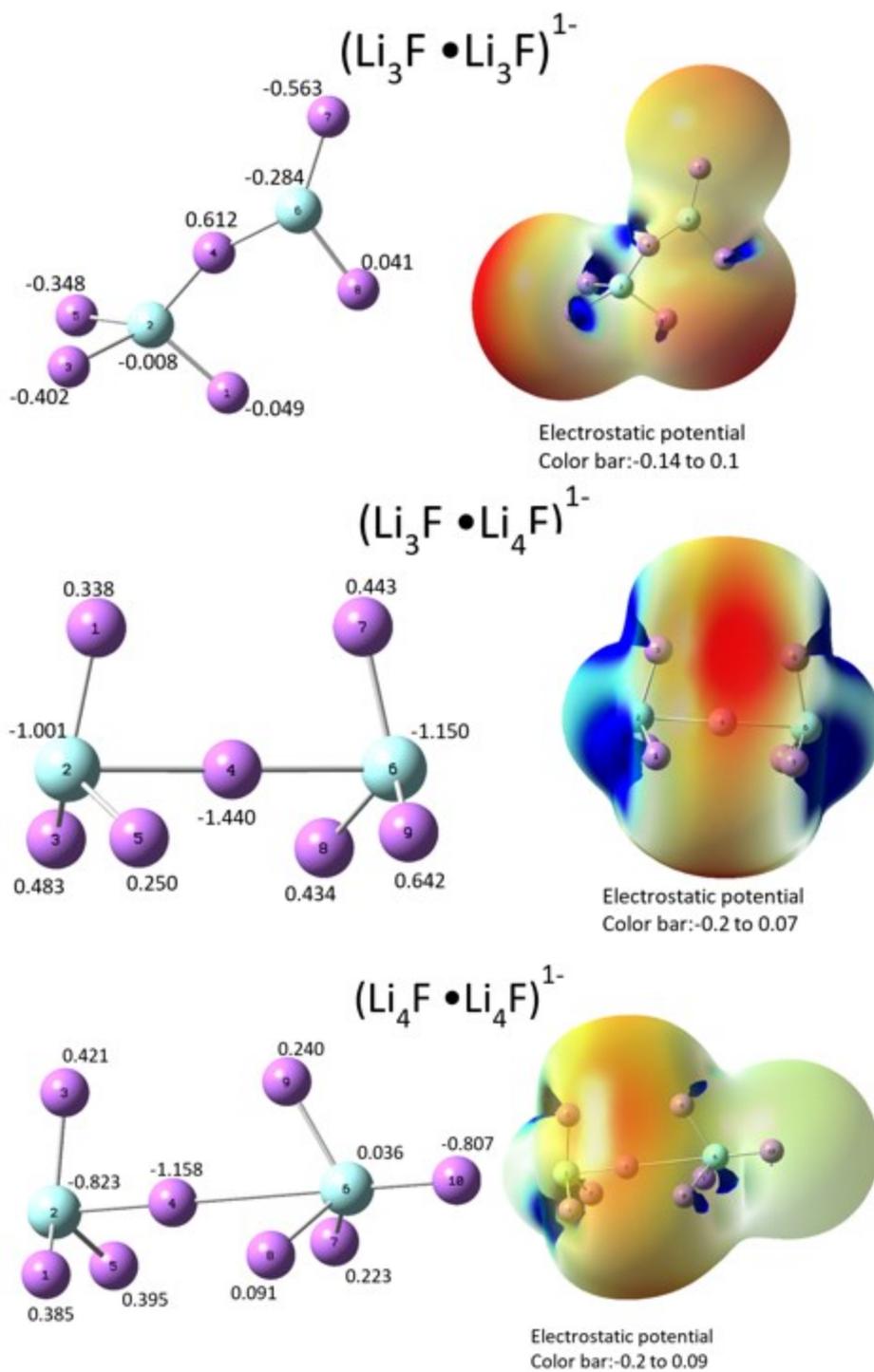


Figure S26. Geometry of (1-) charged LiF clusters. Charges are labeled near each atom from population analysis based on Atomic Polar Tensor (APT). Electrostatic potential surface are mapped onto total electron density surface with Iso-value = 0.0004 [electron density]. The colorbar is in units of [Energy/Charge], in this case Hartree/elementary charge. (Orange is closer to lower-bound and blue is close to upper bound)

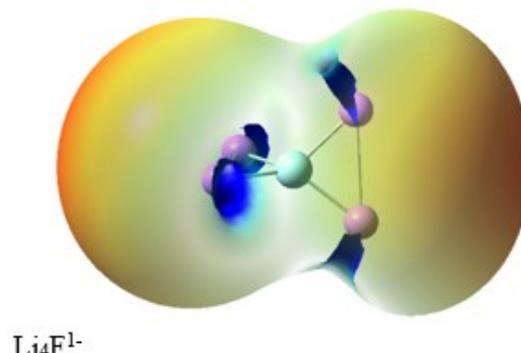
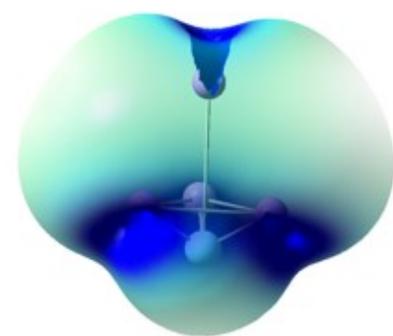
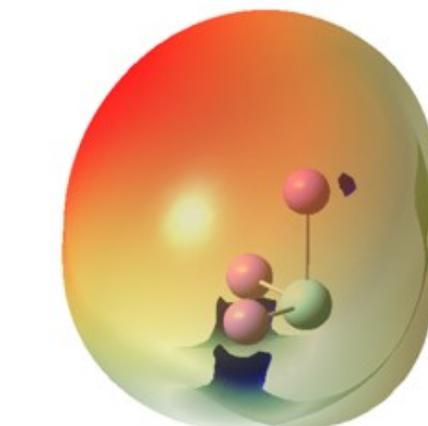
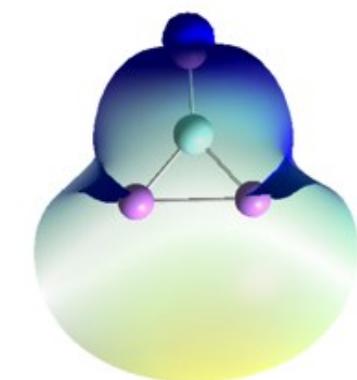
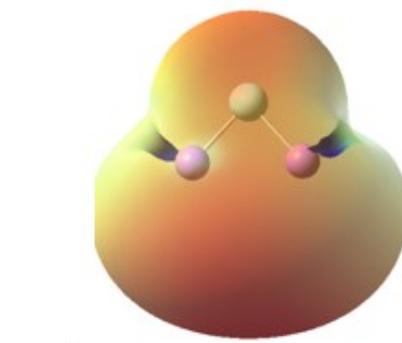
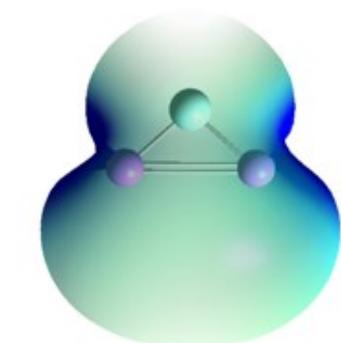


Figure S27. Electrostatic potential surface of Li_xF fragments with uniform colorbar(-0.2 to 0.1 hartree/e) mapped on total electron density surface with a Iso-value = 0.0004 [electron density].

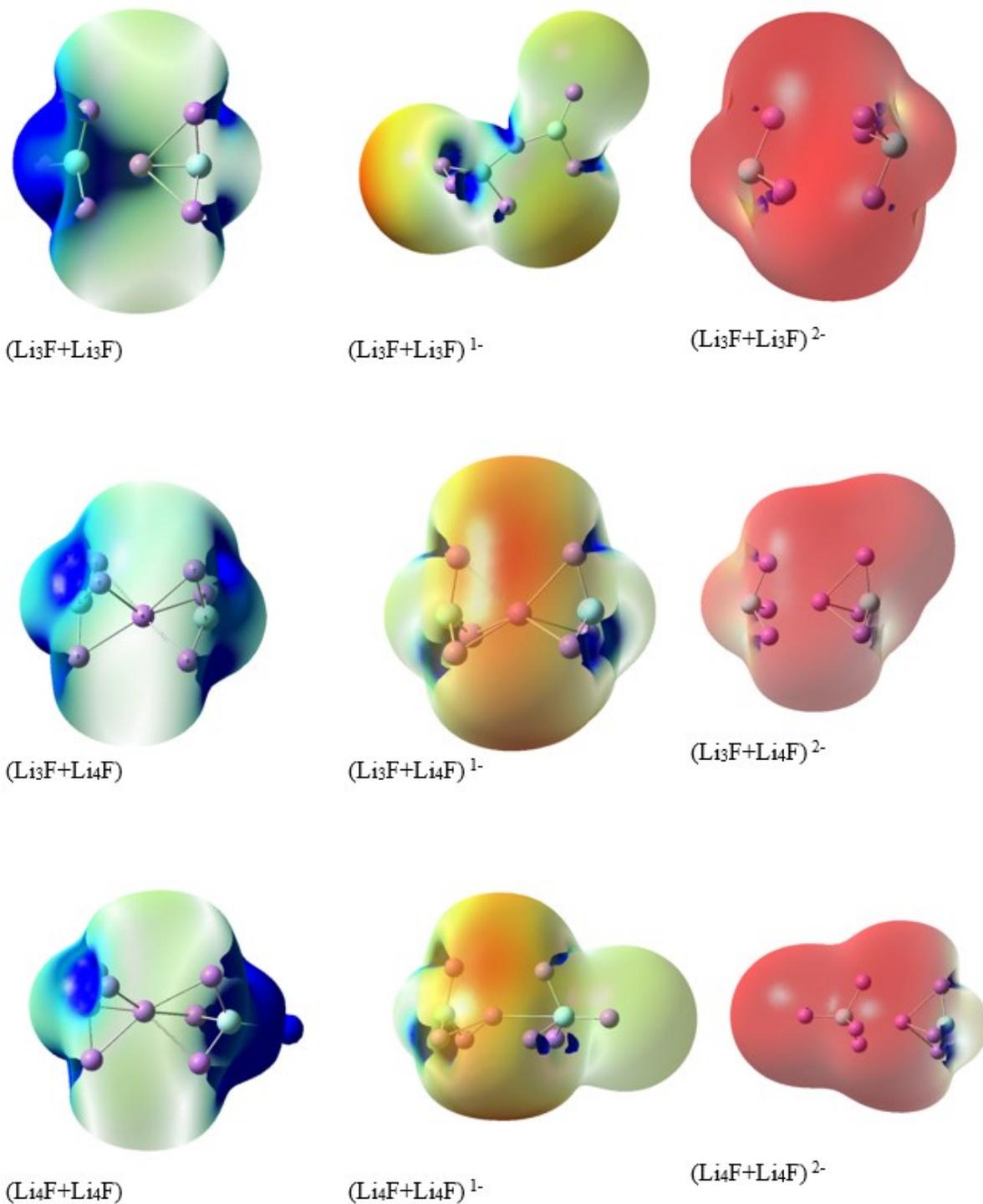


Figure S28. Electrostatic potential surface of Li_xF clusters with uniform colorbar(-0.2 to 0.1 hartree/e) mapped on total electron density surface with a Iso-value = 0.0004 [electron density]