Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Influence of Diluent Concentration in Localized High Concentration Electrolytes: Elucidation of Hidden Diluent-Li^+ Interactions and Li^+ Transport Mechanism

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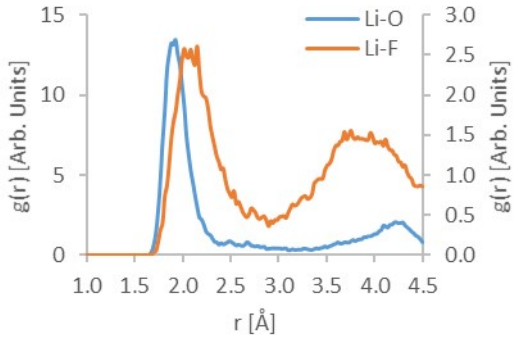
Table S1: Simulation cells for classical MD simulations without electric field

Electrolyte Formulation	Molar Ratio LiFSI:DMC:TTE	# Molecules LiFSI:DMC:TTE	Unit cell size a1 x a2 x a3 [Å]
A1	1.00:2.00:5.00	24:48:128	30.94 x 31.20 x 30.47
A2	1.00:2.16:4.31	32:64:120	31.01 x 30.90 x 31.04
A3	1.00:2.00:3.00	32:72:104	30.22 x 29.90 x 31.17
A4	1.00:2.00:2.00	48:88:88	30.14 x 30.29 x 31.31

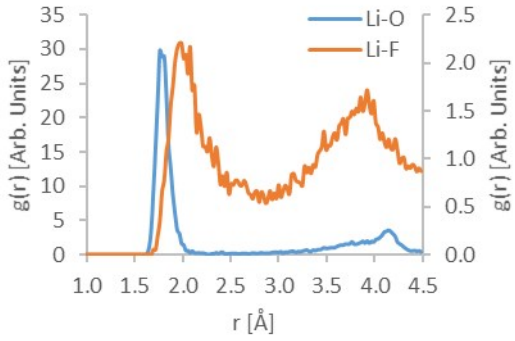
Table S2: Simulation cells for classical MD with electric field (0.4 V/Å)

Electrolyte Formulation	Molar Ratio LiFSI:DMC:TTE	Molar Ratio LiFSI:TTE	# Molecules LiFSI:DMC:TTE	Unit cell size a1 x a2 x a3 [Å]
A1	1.00:2.00:5.00	0.20	72:144:384	30.94 x 31.20 x 99.40
A2	1.00:2.16:4.31	0.23	96:192:360	31.01 x 30.90 x 101.11
A3	1.00:2.00:3.00	0.33	96:216:312	30.22 x 29.90 x 101.51
A4	1.00:2.00:2.00	0.50	144:264:264	30.14 x 30.29 x 101.92

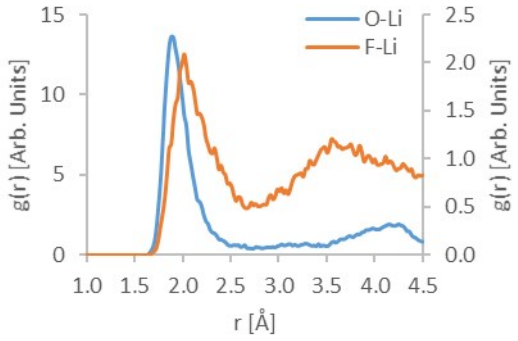
AIMD-NVT formulation A1



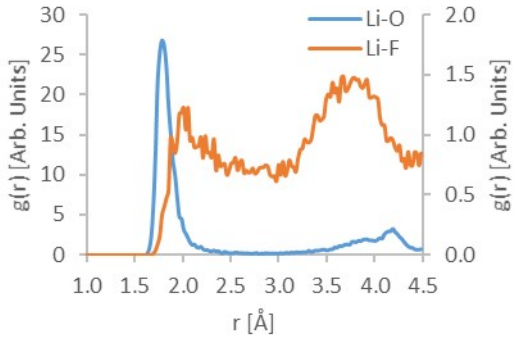
Classical MD- Formulation A1



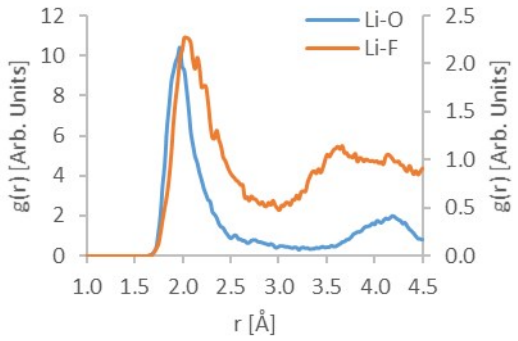
AIMD-NVT formulation A2



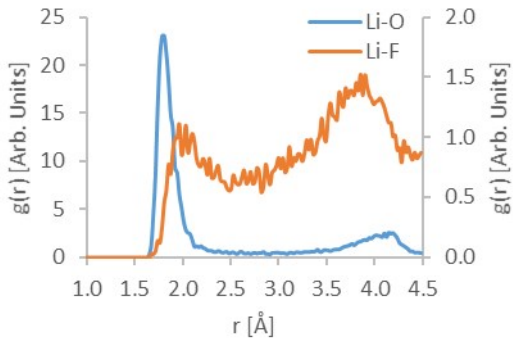
Classical MD- Formulation A2



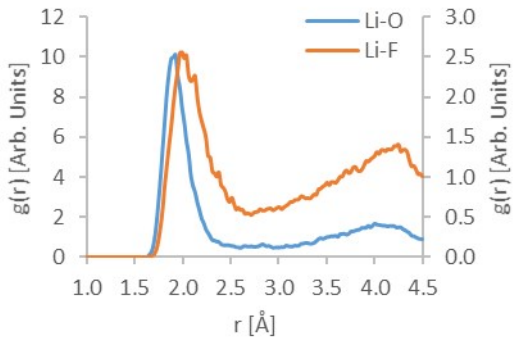
AIMD-NVT formulation A3



Classical MD- Formulation A3



AIMD-NVT formulation A4



Classical MD- Formulation A4

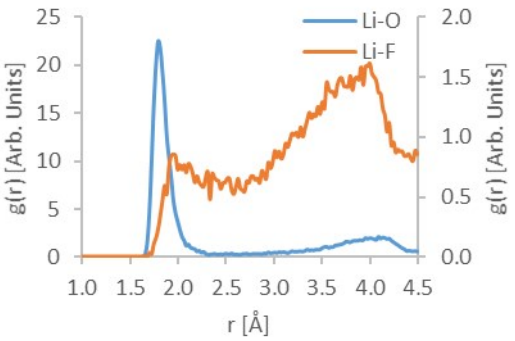


Figure S1: Partial Radial distribution function (PRDF) profiles for Li-O (left vertical axis) and Li-F (right vertical axis) interactions from AIMD-NVT and classical MD simulations.

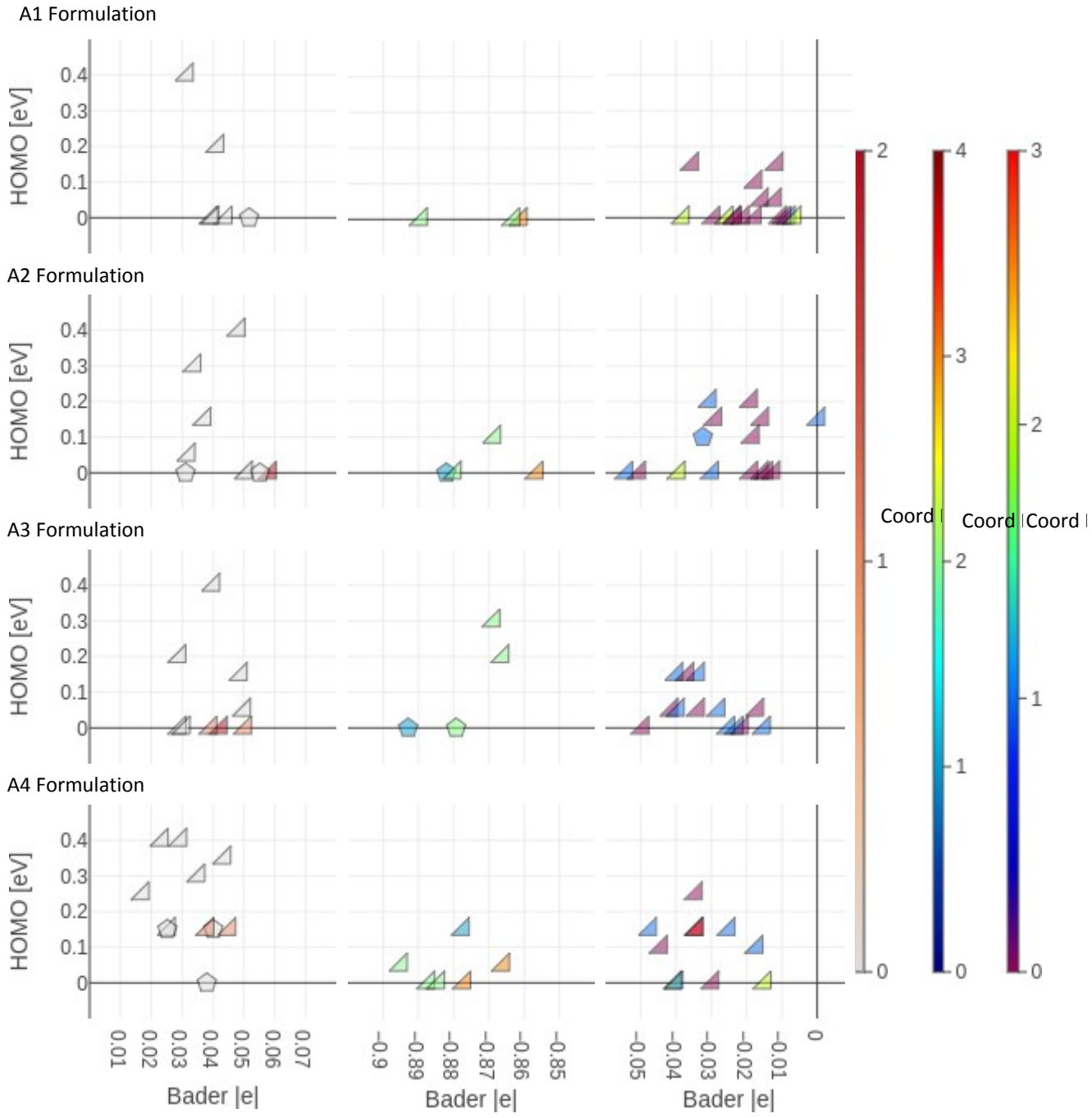


Figure S2: HOMO levels as functions of Bader electronic charges and Li-O, Li-F interactions for formulations A1, A2, A3, and A4.

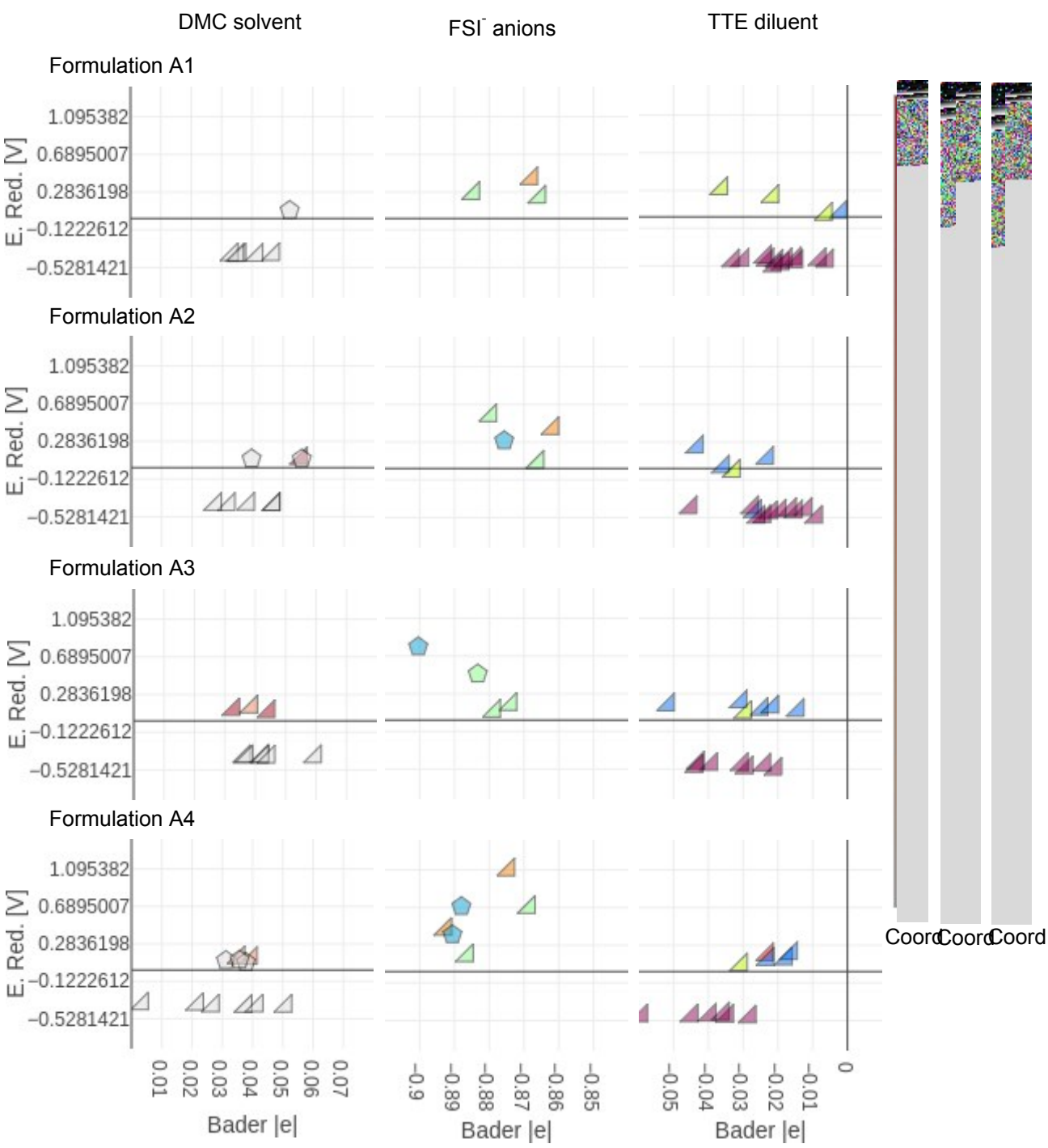


Figure S3: Reduction potentials (E. Red., in V) vs. Li/Li⁺ as functions of Bader electronic charges and Li-O, Li-F interactions for formulations A1, A2, A3, and A4. The solvent and FSI⁻ geometry configurations as found across formulations A1 to A4 .

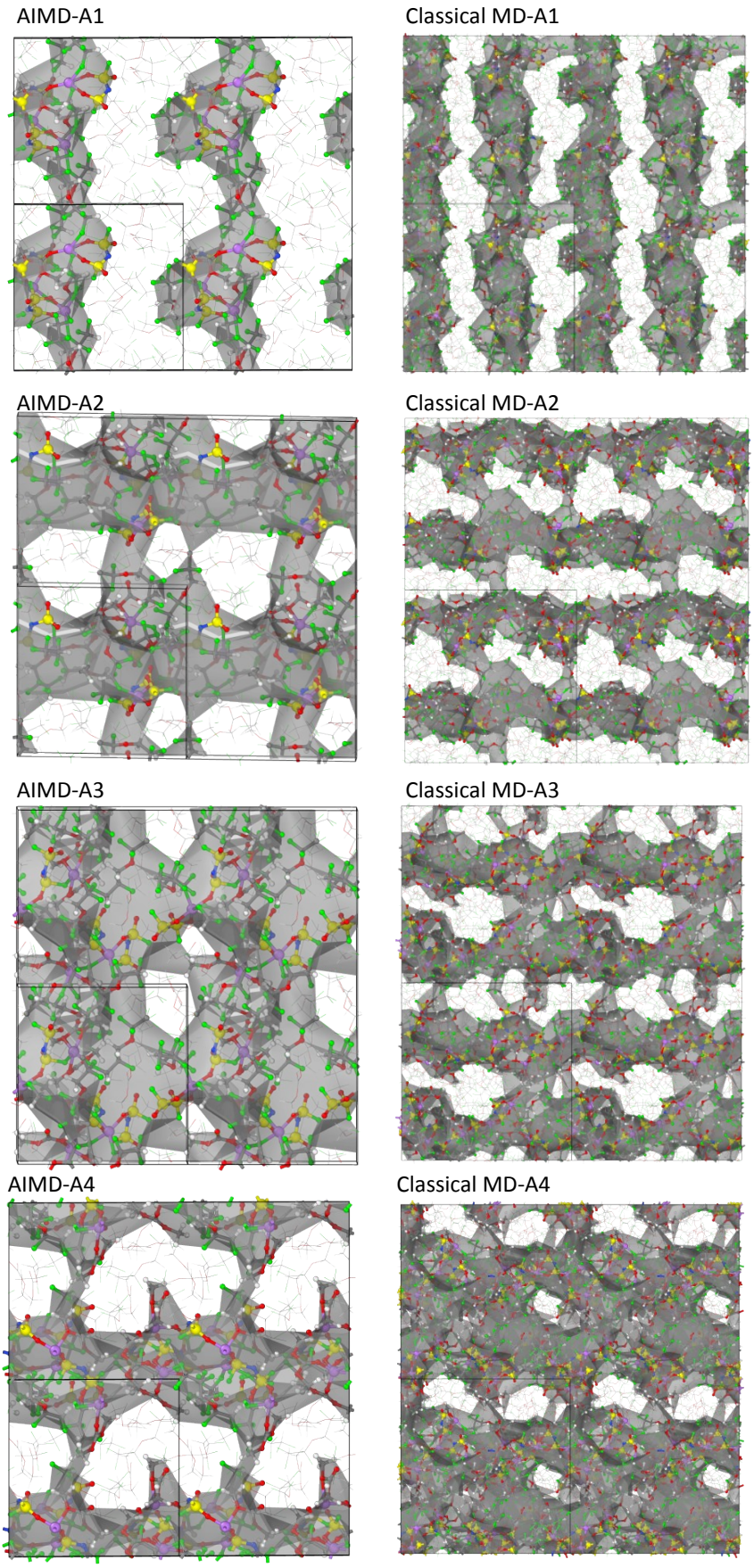
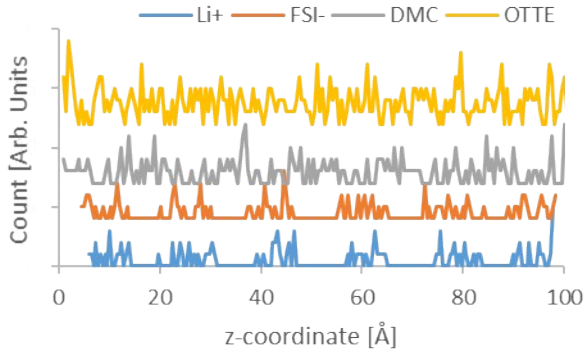


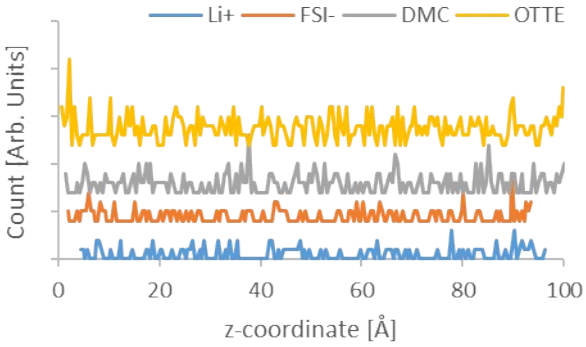
Figure S4: Grey-colored polyhedral construction drawn for all formulations around interconnected networks from AIMD-NVT and Classical MD simulations.

A1 formulation

Initial Frame

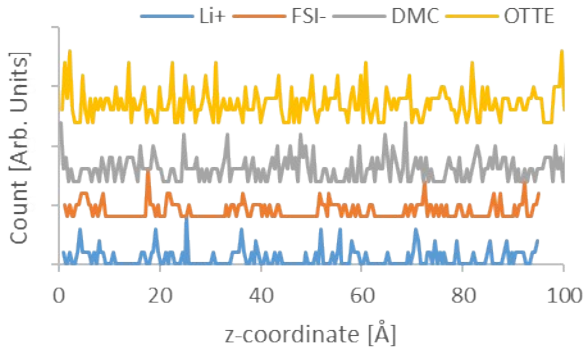


Frame @ 1.67 ns

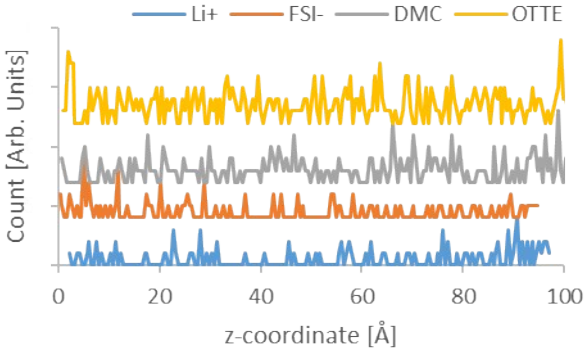


A3 formulation

Initial Frame

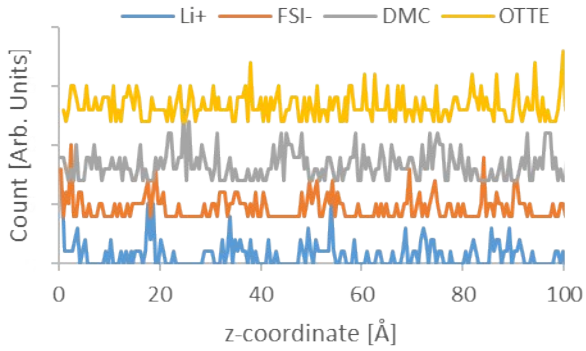


Frame @ 1.67 ns



A4 formulation

Initial Frame



Frame @ 1.80 ns

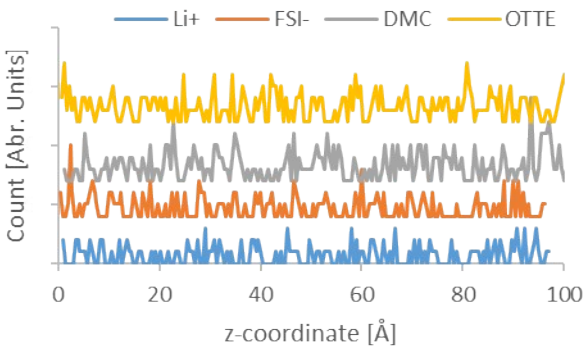


Figure S5: Concentration profiles before and after applying electric field (0.4 V/Å): Formulations P1, P4, and P5.

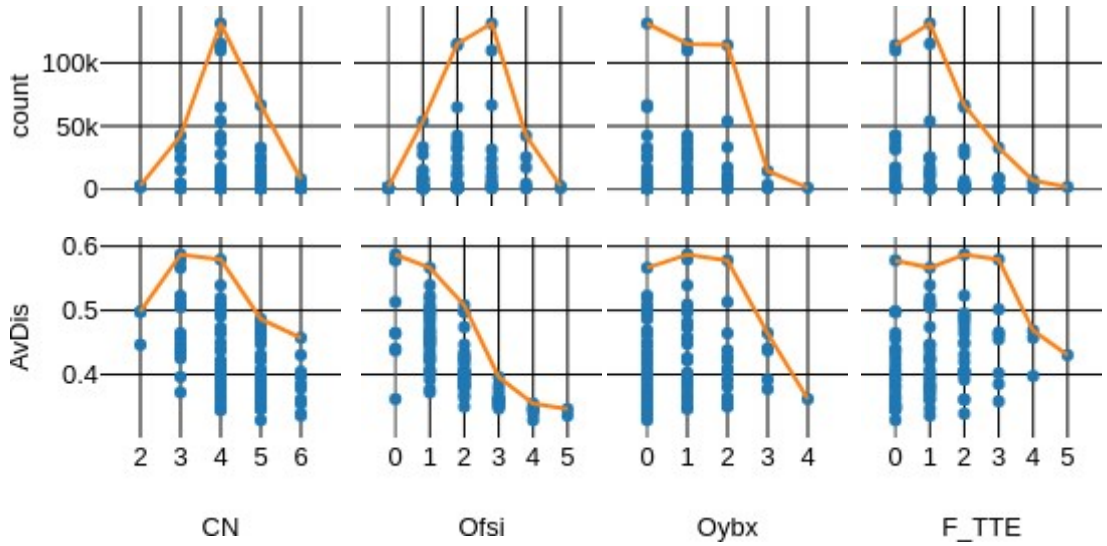


Figure S6: Solvation shells computed in formulation P1 for all Li^+ ions for every step of the simulation: Average Li+ displacement between two consecutive frames (0.125 ps) and number of times the solvation shells repeats throughout the simulation (count) vs. global coordination number (CN), Li^+ coordination with FSI- anions (Ofsi), carbonyl oxygen atoms (Cybx), and TTE molecules (F_TTE)

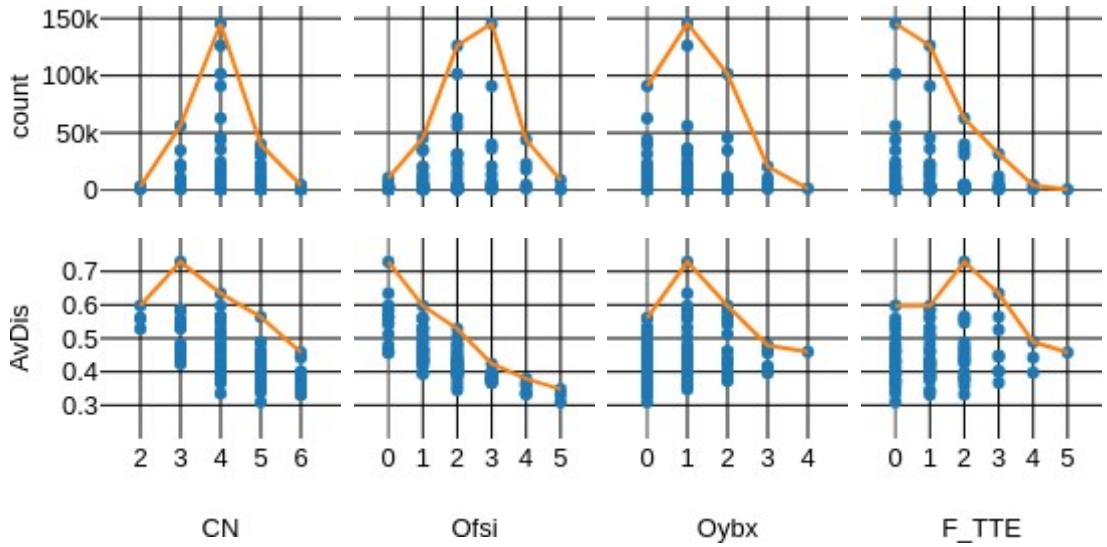


Figure S7: Solvation shells computed in formulation P4 for all Li^+ ions for every step of the simulation: Average Li+ displacement between two consecutive frames (0.125 ps) and number of times the solvation shells repeats throughout the simulation (count) vs. global coordination number (CN), Li^+ coordination with FSI- anions (Ofsi), carbonyl oxygen atoms (Cybx), and TTE molecules (F_TTE)

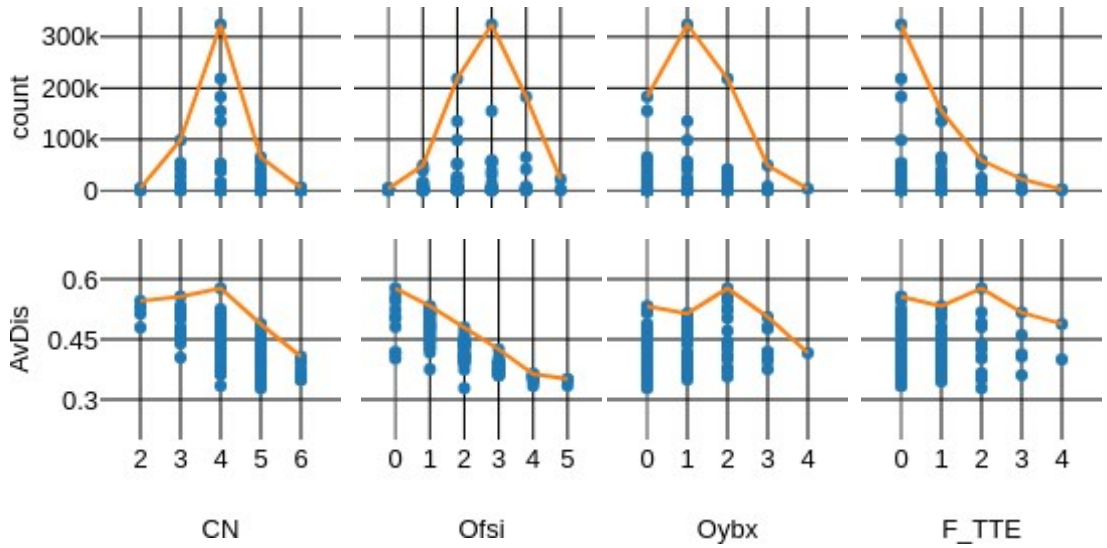


Figure S8: Solvation shells computed in formulation P5 for all Li^+ ions for every step of the simulation: Average Li+ displacement between two consecutive frames (0.125 ps) and number of times the solvation shells repeats throughout the simulation (count) vs. global coordination number (CN), Li^+ coordination with FSI- anions (Ofsi), carbonyl oxygen atoms (Cybx), and TTE molecules (F_TTE)