Support Information

Anion Effect on Solvation Structure and Properties of imide lithium salt based electrolytes

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Table S1 Summary of total energies and HOMO/LUMO energy levels of solvent, Li^+-solvent, and Li^+-anion-solvent complex, which are calculated using COSMO-DFT method in DMol3 with PBE as functional and DNP 4.4 as basis set.

Entry	Species	Energy (Ha)	HOMO (eV)	LUMO (eV)
1	1-(*cis*-DMC)	-343.3778474	-6.99088	-0.46014
2	2-(*trans*-DMC)	-343.3749535	-6.99061	-0.46096
3	3-Li^+-(*cis4*-DMC)	-1380.9855088	-7.71987	-1.23703
4	4-Li^+-(*cis3-trans1*-DMC)	-1380.9841970	-7.67688	-1.19757
5	5-Li^+-(*cis2-trans2*-DMC)	-1380.9823405	-7.65184	-1.18424
6	1-Li^+- (*cis2*-DMC)-(*cis*-FSI^-)	-2045.5413326	-7.59851	-1.40411
7	2-Li^+-(*cis2*-DMC)-(*trans*-FSI^-)	-2045.5400047	-7.64994	-1.53037
8	3-Li^+-(*cis3*-DMC)-(*cis*-FSI^-)	-2388.9243045	-7.24966	-1.22805
9	4-Li^+-(*cis3*-DMC)-(*trans*-FSI^-)	-2388.9219961	-7.07496	-1.17091
10	1-Li^+-(*cis2*-DMC)-(*cis*-$TFSI^-$)	-2520.8544306	-7.36748	-1.05961
11	2-Li^+-(*cis2*-DMC)-(*trans*-$TFSI^-$)	-2520.8559330	-7.53674	-1.05825
12	3-Li^+-(*cis3*-DMC)-(*cis*-$TFSI^-$)	-2864.2365804	-7.09428	-1.00709
13	4-Li^+-(*cis3*-DMC)-(*trans*-$TFSI^-$)	-2864.2373153	-7.15278	-1.01526

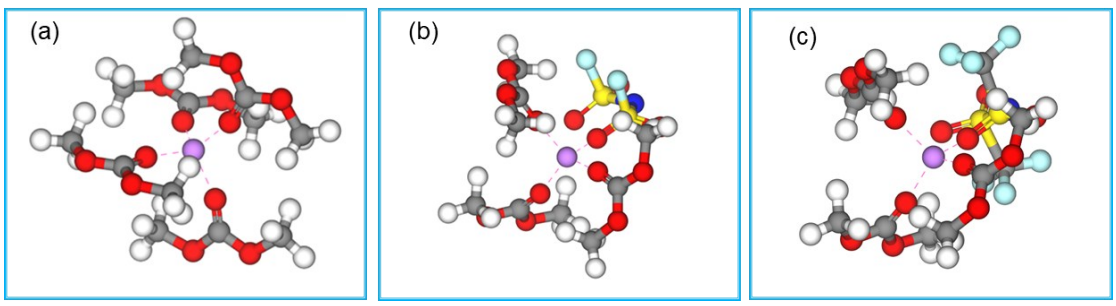

Figure S1 Optimized structures based on DFT-COSMO simulation. (a)Li^+-4DMC; (b) Li^+-2DMC-FSI^-; (c) Li^+-2DMC-$TFSI^-$. Color code: grey sphere, C; red sphere, O; white sphere, H; magenta sphere, Li. For Li^+-4DMC, the energy favorable conformation is Li^+-(*cis4*-DMC). For

Li^+-2DMC-FSI^-, the energy favorable conformation is Li^+-(*cis2*-DMC)-(*cis*-FSI^-). And for Li^+-2DMC-$TFSI^-$, the energy favorable conformation is Li^+-(*cis2*-DMC)-(*trans*-$TFSI^-$).

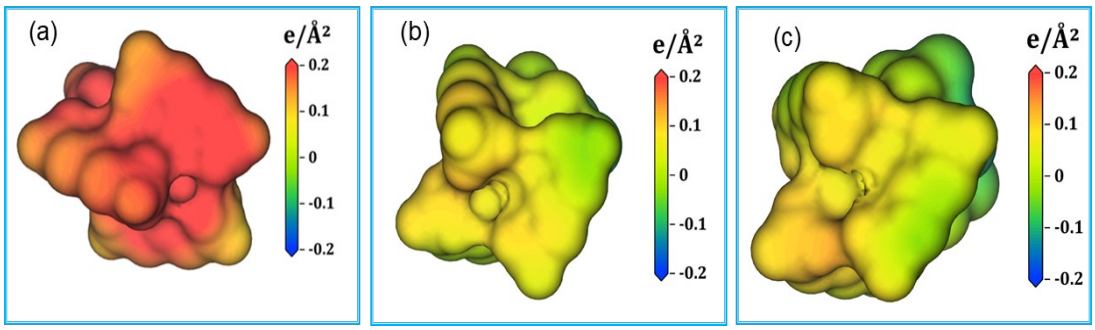

Figure S2 Surface charge distribution of different clusters. (a) Li^+-(*cis4*-DMC); (b) Li^+-(*cis2*-DMC)-(*cis*-FSI^-); (c) Li^+-(*cis2*-DMC)-(*trans*-$TFSI^-$). The structures presented are same to the ones in figure S1. It can be observed that Li^+-(*cis4*-DMC) are apparently positive in charge, while Li^+-(*cis2*-DMC)-(*cis*-FSI^-) and Li^+-(*cis2*-DMC)-(*trans*-$TFSI^-$) are apparently negative in surface charge, and the negative charge is mainly on fluorine atoms.

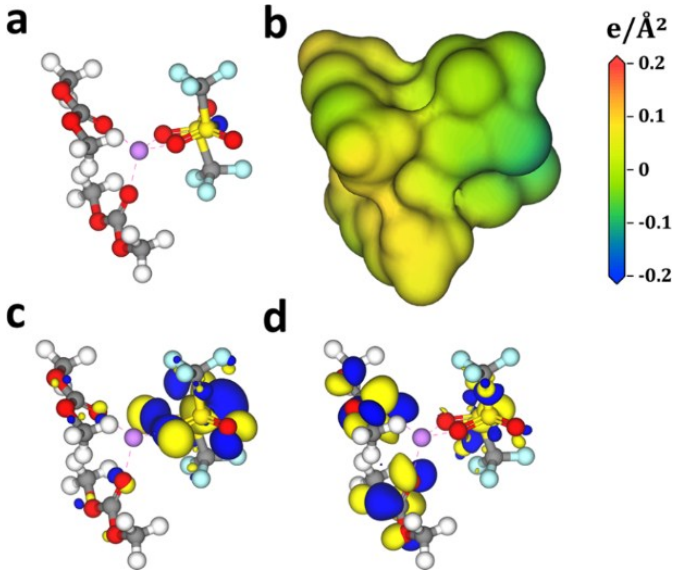

Figure S3 The structure of Li^+-2DMC-$TFSI^-$. (a) Li^+-(*cis2*-DMC)-(*trans*-$TFSI^-$), the energy favorable conformation of Li^+-2DMC-$TFSI^-$ according to DFT-COSMO simulation; (b) surface charge distribution under the environment of electrolyte; (c) HOMOs and (d) LUMOs distributions. Color code: grey sphere, C; red sphere, O; blue sphere, N; white sphere, H; yellow sphere, S; cyan sphere, F; magenta sphere, Li. The yellow and blue regions of HOMOs/LUMOs represent the positive and negative parts of orbitals, respectively. As generally HOMOs indicate the active sites to be oxidized and LUMOs indicate the active sites to be reduced, it can be inferred accordingly that $TFSI^-$ will be involved in CEI formation and DMC will be involved in SEI formation.

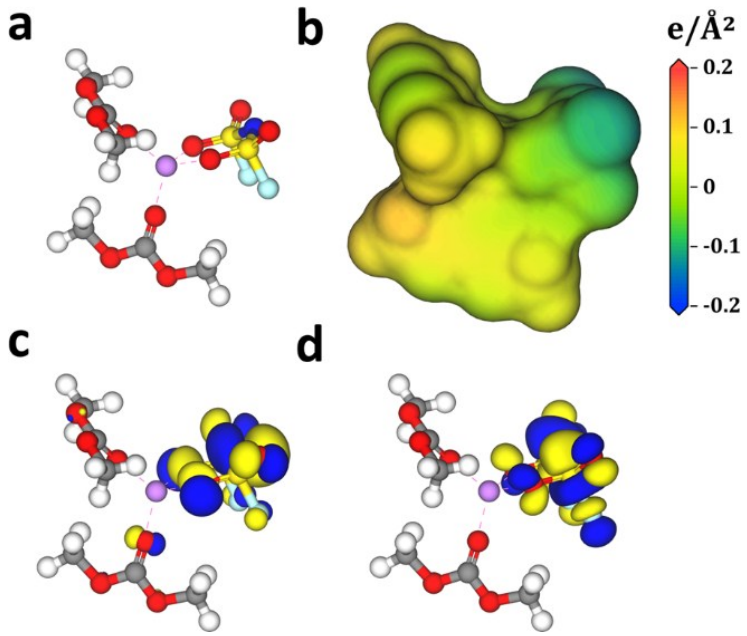

Figure S4 The structure of Li^+-2DMC-FSI^- (a) Li^+-(*cis2*-DMC)-(*cis*-FSI^-), the energy favorable conformation of Li^+-2DMC-FSI^- according to DFT-COSMO simulation; (b) surface charge distribution under the environment of electrolyte; (c) HOMOs and (d) LUMOs distributions of Li^+-(*cis2*-DMC)-(*cis*-FSI^-). Color code: grey sphere, C; red sphere, O; blue sphere, N; white sphere, H; yellow sphere, S; cyan sphere, F; magenta sphere, Li. The yellow and blue regions of HOMOs/LUMOs represent the positive and negative parts of orbitals, respectively. As generally HOMOs indicate the active sites to be oxidized and LUMOs indicate the active sites to be reduced, it can be inferred accordingly that FSI^- will be involved both in CEI formation and in SEI formation.

Table S2 Summary of basic physical and chemical parameters of several fluorinated non-solvents to lithium salts. HFRE shows the most applicable melting temperature and vapor pressure under room temperature among all these solvents, which ensure a reasonable temperature window in consideration of mobility and safety.

Material	**Molecular weight /g·mol^{-1}**	**Melting point /℃**	**Flashing point /℃**	**Boiling point /℃**	**Density /g·cm^{-3}**	**Viscosity /cp**	**Vapour pressure. 25.5℃/kPa**
HFME	182.06	<-40	-	51	1.39	0.8	36.1
HFPE	196.09	<-40	-	63.2	1.33	0.9	32.5
HFE	196.09	<-40	-	71	1.321	0.9	38.3
HFRE	232.07	-94.27	-	93.2	1.533	1.1	1
HFTE	332.09	-93	-	133	1.626	1.4	1.1

ETFA	142.08	-78	-1	60-62	1.194	1.2	-
MTFA	128.05	-78	-7	43-43.5	1.273	0.8	-
PFPA	192.08	-	1.7	75.5	1.353	0.9	15

HFME: 1,1,1,3,3,3-Hexafluoroisopropyl Methyl Ether, CAS No. 13171-18-1
HFPE: 2-ethoxy-1,1,1,3,3,3-hexafluoropropane, CAS No. 690-39-1
HFE: 1,1,1,2,3,3-hexafluoropropyl ethyl ether, CAS No. 380-34-7
HFRE: 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropylether, CAS No. 16627-68-2
HFTE: 1H,1H,5H-octafluoropentyl 1,1,2,2-tetrafluoroethyl Ether, CAS No. 16627-71-7
ETFA: ethyl trifluoroacetate, CAS No. 383-63-1
MTFA: methyl trifluoroacetate, CAS No. 431-47-0
PFPA: ethyl pentafluoropropionate, CAS No. 426-65-3

Table S3 Comparison of the measured residue mass and theoretical residue mass of LiFSI and LiTFSI based electrolytes with different compositions. T_d refers to the temperature where lithium salt decomposition starts.

Residue mass	LiFSI:DMC:HFRE			LiTFSI:DMC:HFRE		
	1:12:0	1:1.5:0	1:1.5:1.5	1:12:0	1:1.5:0	1:1.5:1.5
At 100 °C, measured	40%	100%	55%	44%	100%	68%
Theoretical data (the residue is Li^+:DMC≥1:4)	43%	100%	48%	47%	100%	55%
Calculated ratio	1:3.55:0	1:1.5:0	1:1.5:0.2	1:3.49:0	1:1.5	1:1.5:0.44
Right before T_d, measured	26%	52%	30%	32%	78%	55%
Theoretical data (the residue is Lithium salt)	15%	58%	28%	15%	68%	37%
Calculated ratio	1:1.58	--	1:0.16:0	1:1.67	1:0.47	1:1.52
> T_d, measured	18%	28%	20%	18%	30%	10%
Theoretical data (when the residue is LiF)	2%	8%	4%	2%	6%	3%
Theoretical data (when the residue is Li_2SO_3)	7.2%	29%	14%	7%	22%	11%

According to the DSC curves of pure DMC and HFRE, free DMC and HFRE almost totally vaporize below 100 °C. The theoretical residue mass at 100 °C is calculated setting that all the DMC are free except the DMC in solvation sheath (Li^+:DMC=1:4) in LiFSI:DMC=1:4 electrolyte and HFRE is ideally free without any interactions with DMC in solvation sheath. The theoretical mass residue right before Td is calculated on the basis that neat lithium salt is the only residue. The theoretical mass residue at the end of the decomposition is calculated based on two cases. One is that LiF is the only residue after the decomposition of LiFSI or LiTFSI, the other is that Li_2SO_3 is the only residue after the decomposition of LiFSI or LiTFSI.

Table S4 Average coulombic efficiency and capacity retention of NCM622||Li cells with different electrolytes at 25 °C after 100 cycles at 0.5C-rate. The cell with 1M LiPF6 in EC:DMC=1:1

shows the lowest capacity retention.

	Average coulombic efficiency /%	Capacity retention at the 100th cycle %
1:1.5:1.5 LiTFSI/DMC/HFRE	99.50	84.03
1:1.5:1.5 LiFSI/DMC/HFRE	99.22	89.67
1:1.5 LiTFSI/DMC	98.08	80.98
1:1.5 LiFSI/DMC	98.97	88.25
1M LiPF6 in EC:DMC=1:1	98.63	63.65