Supplementary Information

The Solvation Structure, Transport Properties and Reduction Behavior of Carbonate-Based Electrolytes of Lithium-Ion Batteries

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Section 1. The MD simulation box

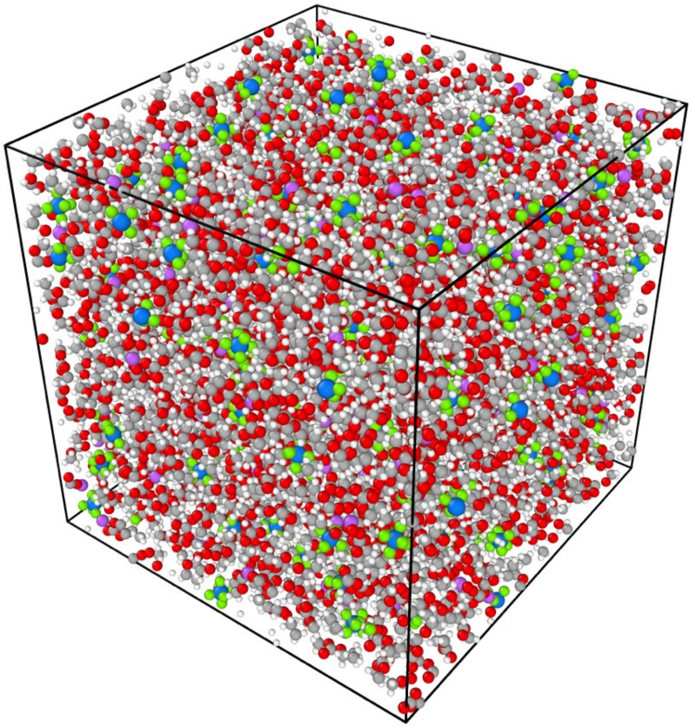


Fig. S1 The MD simulation box of the Gen2 electrolyte.

Section 2. Detailed solvation structure population

Table S1 The detailed population of species in the four electrolytes.

Electrolyte	SSIP	CIP	AGG
EC-base	90.1%±1.0%	9.2%±0.9%	0.7%±0.4%
ECF	87.5%±0.9%	11.2%±1.0%	1.3%±0.4%
Gen2	35.6%±0.9%	33.3%±1.3%	31.1%±0.8%
GenF	38.4%±2.1%	32.9%±0.8%	28.7%±1.9%

Table S2 The detailed solvent-specific solvation numbers of the four electrolytes.

Electrolyte	Solvent/salt	SSIP	CIP	AGG
EC-base	$LiPF_6$	0 (by definition)	1 (by definition)	1.487±0.068
	EC	5.897±0.003	4.715±0.013	4.216±0.099
ECF	$LiPF_6$	0 (by definition)	1 (by definition)	1.461±0.063
	EC	5.653±0.018	4.535±0.038	4.002±0.100
	FEC	0.234±0.016	0.177±0.025	0.152±0.061
Gen2	$LiPF_6$	0 (by definition)	1 (by definition)	1.416±0.019
	EC	2.642±0.027	1.492±0.020	1.199±0.017
	EMC	3.028±0.030	2.970±0.028	2.838±0.022
GenF	$LiPF_6$	0 (by definition)	1 (by definition)	1.443±0.020
	EC	2.381±0.056	1.407±0.018	1.115±0.023
	EMC	2.966±0.034	2.884±0.016	2.751±0.016
	FEC	0.331±0.022	0.201±0.032	0.140±0.015

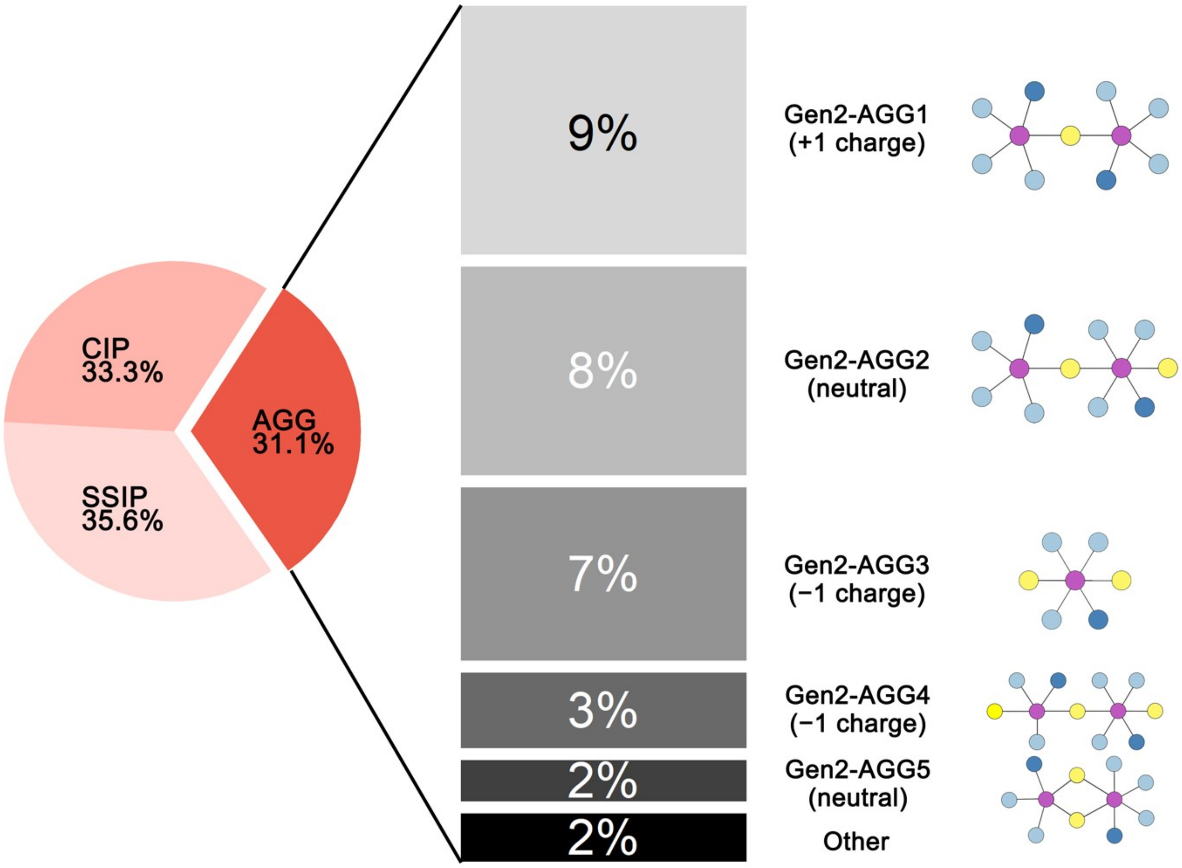


Fig. S2 AGG species in the Gen2 electrolyte.

Among the 31.4% of the AGG species, 9% are AGG1 (positive triple ions) with two Li^+ and one PF_6^-. Meanwhile, the AGG2 structure with neutral charge and the AGG3 (negative triple ions) structure account for 8% and 7%, respectively. The remaining 7% consists of AGG4, AGG5, and other larger structures. Subsequently, while the EC electrolyte has a much higher SSIP ratio than the Gen2 electrolyte, more than half of the AGG species in the Gen2 electrolyte narrow the gap of the proportion of ionically conductive solvation species.

Section 3. The linear diffusion behavior

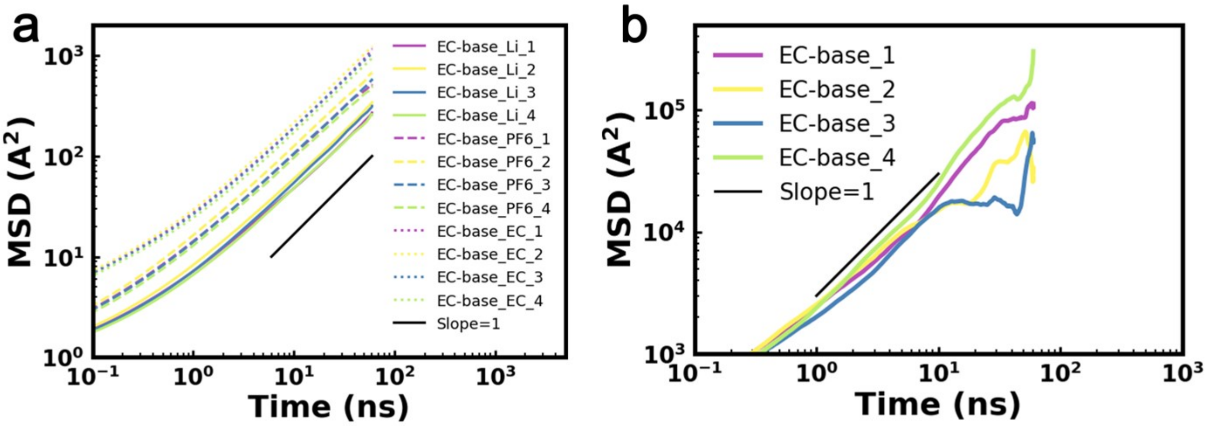


Fig. S3 The linear diffusion behavior of four duplicate runs of the EC-base electrolyte required to calculate (a) self-diffusion coefficients, and (b) ionic conductivity. A slope of one (corresponding to linear data on a log-log plot) is indicated on each plot. The effective "mean square displacement" on the y-axis of panel (b) is the quantity in angular brackets in Eq. (10).

Section 4. Sample trajectories

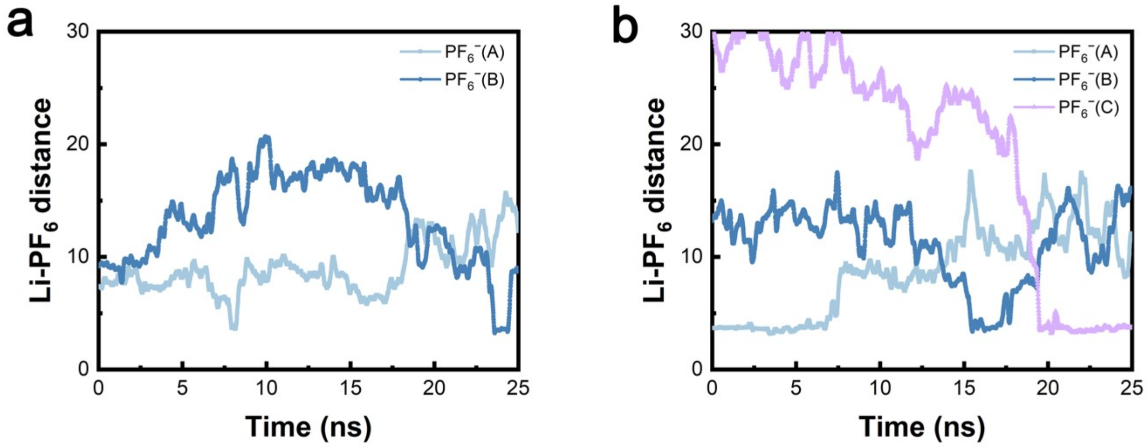
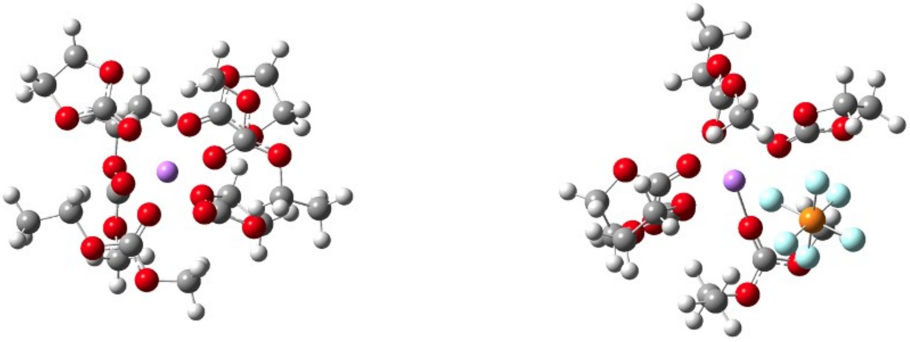


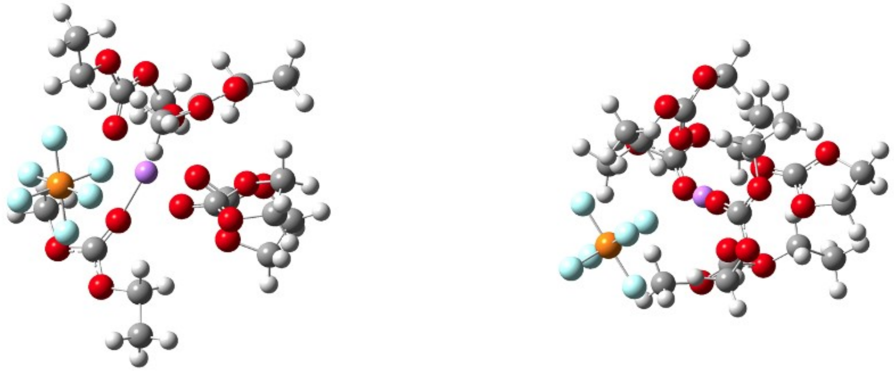
Fig. S4 Sample trajectory of Li-PF_6 coordination distance as a function of time in (a) EC-base electrolyte, and (b) Gen2 electrolyte. A cutoff distance of 5 Å is used to differentiate CIP and SSIP.

Fig. S4 presents the Li-PF_6 coordination distance as a function of time in the EC-base and Gen2 electrolyte. The two sets of trajectories are sampled from one Li^+ over a long period (25 ns) of MD simulations. The Li^+-PF_6^- pair in the Gen2 electrolyte coordinates with each other for a longer period of time.

Section 5. Optimized solvation structures



Li^+-$(EMC)_3(EC)_3$ Li^+-$(EMC)_4(EC)_1$ PF_6^-



Li^+-$(EMC)_3(EC)_2$ PF_6^- Li^+-$(EMC)_2(EC)_3$ PF_6^-

Fig. S5 The optimized structures for calculating the anion–solvent exchange free energy. The red, grey, white, cyan, orange, and purple balls denote oxygen, carbon, hydrogen, fluorine, phosphorus, and lithium, respectively

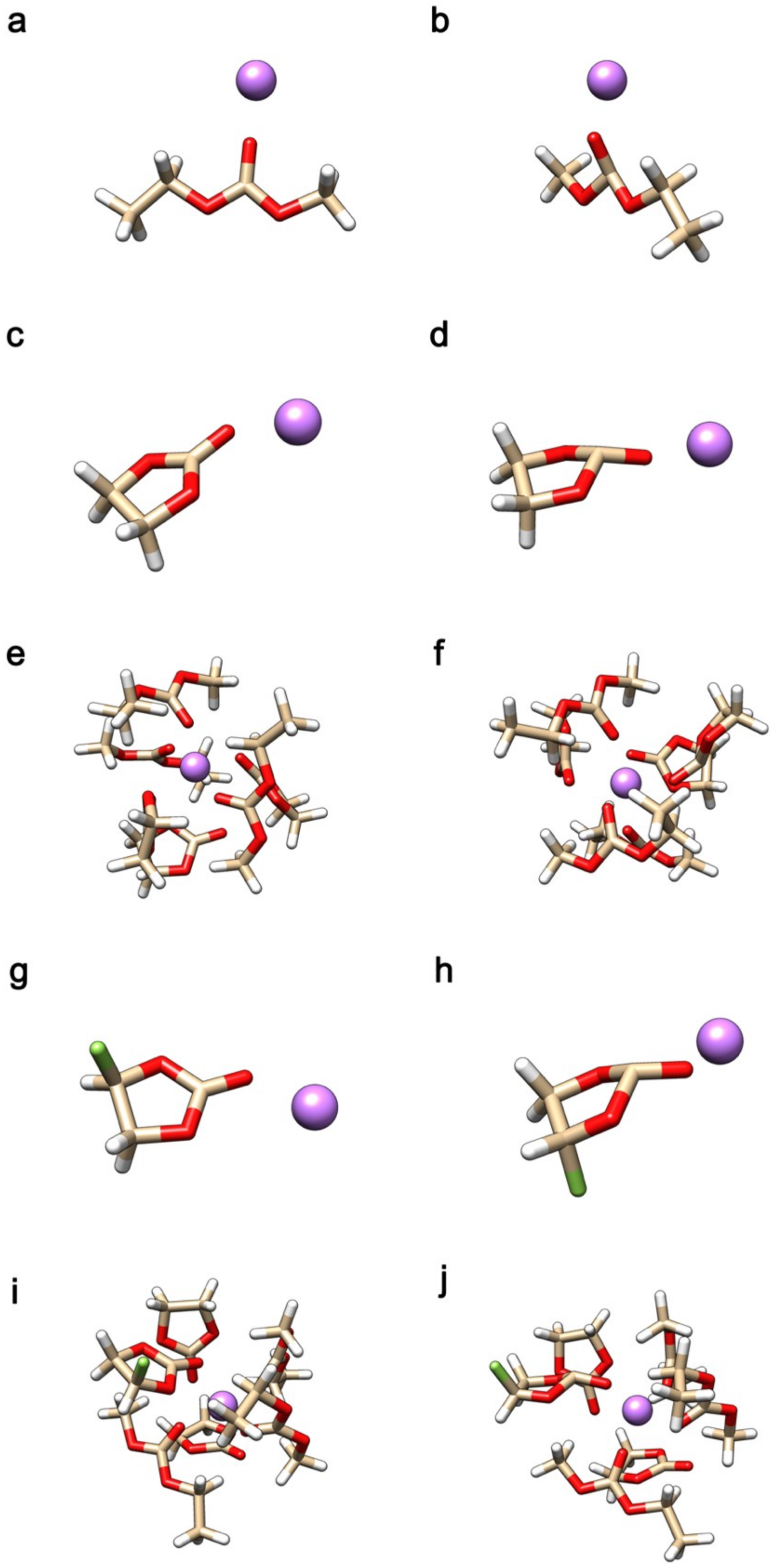


Fig. S6 The optimized geometries before and after reduction of (a) (b) Li$^+$−EMC, (c) (d) Li$^+$−EC, (e) (f) Li$^+$−(EC)$_3$(EMC)$_3$, (g) (h) Li$^+$−FEC, and (i) (j) Li$^+$−(EC)$_2$(EMC)$_3$(FEC). The red, cream, white, green, and purple colors denote oxygen, carbon, hydrogen, fluorine, and lithium, respectively.

Section 6. Binding energy decomposition

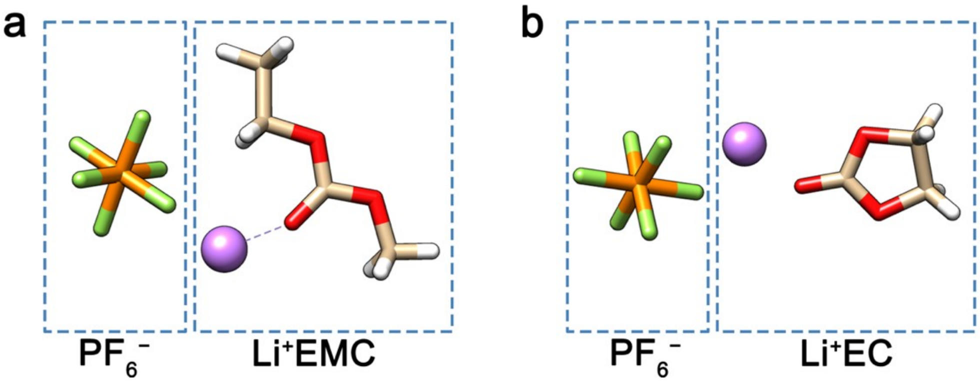


Fig. S7 Two groups of clusters (a) $[Li^+EC]\cdots[PF_6^-]$ (E_{b1}), and (b)$[Li^+EMC]\cdots[PF_6^-]$ (E_{b2}), for the binding energy decomposition using ALMO-EDA(solv). The red, cream, white, green, orange, and purple colors denote oxygen, carbon, hydrogen, fluorine, phosphorus, and lithium, respectively.

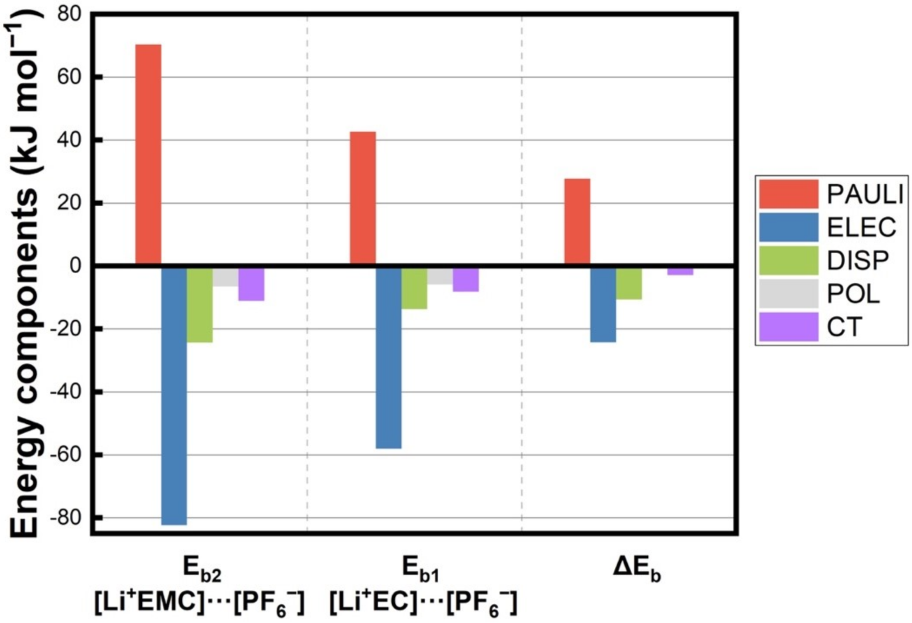


Fig. S8 The binding energy decomposition of $[Li^+EC]\cdots[PF_6^-]$ (E_{b1}), $[Li^+EMC]\cdots[PF_6^-]$ (E_{b2}) and their difference into contributions from permanent electrostatics (ELEC), Pauli repulsion (PAULI), dispersion (DISP), polarization (POL), and charge transfer (CT).

The ALMO-EDA(solv) was performed on the binding energy of $[Li^{+}EC]\cdots[PF_6^{-}]$ (E_{b1}) and $[Li^{+}EMC]\cdots[PF_6^{-}]$ (E_{b2}), respectively (ellipsis denotes the binding of two clusters), as shown in Fig. S7, S8. The electrostatic energy dominates the attractive terms in both E_{b1} and E_{b2}, which is consistent with the fact that ion coordination is governed by the electrostatic interaction. The difference between E_{b1} and E_{b2} ($\Delta E_b = E_{b2} - E_{b1}$) is computed to be −10.7 kJ mol^{-1}, which agrees well with the difference in the anion–solvent exchange free energy as shown in the main text, Table 1. We note that the electrostatic energy contributes 63% of the attractive terms in ΔE_b, providing a direct measurement of the energy difference of the electrostatic characterizations of EC and EMC.

Section 7. Experimental measurements raw data

Table S3 The amount of the salt and solvents used for preparing the four electrolytes for ionic conductivity measurement.

Electrolyte	$LiPF_6$ mass	EC mass	EMC volume	FEC volume
EC-base	2 g	13.80 g	-	-
ECF	2 g	12.42 g	-	1.14 ml
Gen2	2 g	3.52 g	8.17 ml	-
GenF	2 g	3.17 g	7.40 ml	0.87 ml

Table S4 Measured ionic conductivities at room temperature and corresponding corrected values at 25 °C.

Electrolyte	Measurement 1 (mS cm^{-1})	Measurement 2 (mS cm^{-1})	Corrected value at 25 °C (mS cm^{-1})
EC-base	9.964 (34.7 °C)	9.539 (30.8 °C)	8.91
ECF	8.847 (31.7 °C)	8.703 (29.8 °C)	8.33
Gen2	10.62 (33.3 °C)	10.38 (30.9 °C)	9.79
GenF	10.75 (32.3 °C)	10.55 (29.9 °C)	10.14

Section 8. Ionic conductivity calculation using the conventional method

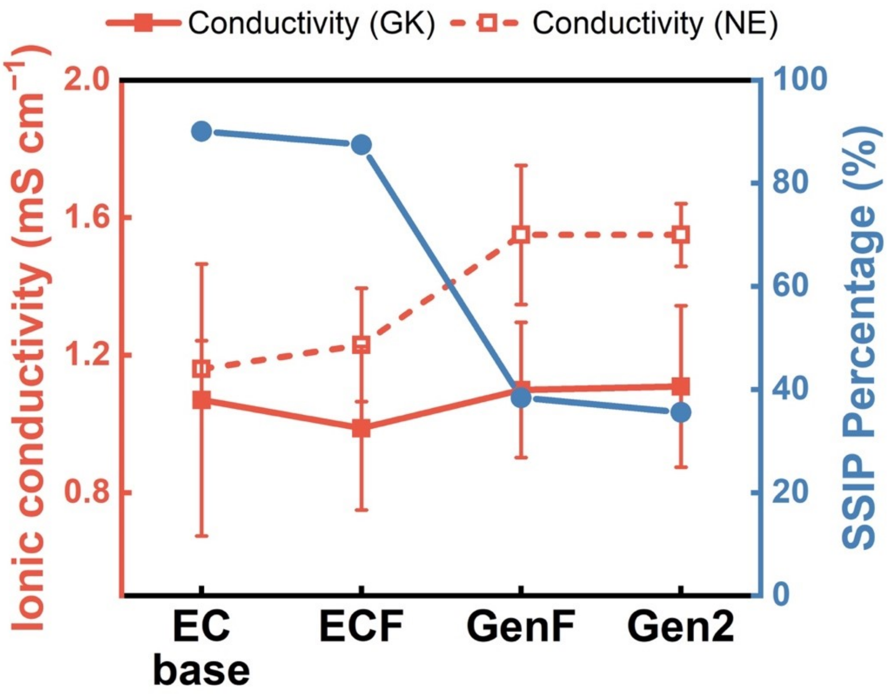


Fig. S9 The calculated ionic conductivities of the EC-base, ECF, Gen2, and GenF electrolytes using Green–Kubo relations (GK) and Nernst–Einstein equation (NE), and the corresponding ratios of solvent separated ion pair (SSIP).

The conventional approach is to assume that the anions and cations are mostly dissociated in the electrolyte, and therefore, the conductivity can be calculated using the Nernst–Einstein equation (NE) from the diffusivity of Li$^+$:

$$\sigma_{NE} = \frac{F^2}{RT}(c_+ {z_+}^2 D_+ + c_- {z_-}^2 D_-),$$

where σ_{NE} is the ionic conductivity, F is the Faraday constant, R is the gas constant, T is temperature, c_+ and c_- are the bulk molar concentrations of the cation and anion, z_+ and z_- are the charges of the cation and anion, and D_+ and D_- are the self-diffusivities of the cation and anion. Here, we compare the conductivity calculated using Green–Kubo relations (σ_{GK}, used in this work) and Nernst–Einstein equation (σ_{NE}, conventional) of the four electrolyte systems. The electrolytes are in the descending order of the corresponding percentage of solvent separated ion pair (SSIP), which reflects the degree of salt dissociation in the electrolytes. As the SSIP percentage decreases, the deviation between σ_{NE} and σ_{GK} becomes larger. For the EC-base electrolyte, where most cations are dissociated with anions to form SSIP, σ_{NE} is only 9% higher than σ_{GK}. In contrast, in the Gen2 electrolyte, where only 35.6% of Li^+ ions are fully dissociated, σ_{NE} overestimates the conductivity by more than 40%. This observation indicates that for highly associated mixed carbonate electrolytes, a rigorous calculation using Green–Kubo relations is important for obtaining a correct trend of the ionic conductivity.

Section 9. Validation of the force field

To further validate the OPLS-AA force field for the specific systems that we investigated in our MD simulations. Here, using the EC solvent as an example, we benchmarked the force field parameters against two key properties, the enthalpy of vaporization and the zero-frequency permittivity, which are both experimentally available.

The enthalpy of vaporization can be calculated by

$$\Delta H_{vap} = \Delta H_{gas} - \Delta H_{liquid} = E_{total}^{gas} - E_{total}^{liquid} + RT$$

where, E_{total}^{liquid} is the total potential energy or internal energy of the liquid. It was obtained from NPT simulation of the bulk liquid. An average pressure of 1 bar was applied. E_{total}^{gas} is the internal energy of the gas phase. E_{total}^{gas} was obtained by doing NVT simulation of single molecule in vacuum. PV-work term was calculated using the RT term by assuming noninteracting ideal state for the gas phase. A value of 62.39 kJ mol^{-1} (313 K) for enthalpy of vaporization was obtained using simulations, which is close to the experimental value of 60.3 kJ mol^{-1} (383 K).[1]

The zero-frequency permittivity can be calculated via the fluctuation dissipation theorem (FDT) according to the following relationship[2, 3]

$$\varepsilon_r = 1 + \frac{\langle M^2 \rangle - \langle M \rangle^2}{3VT\varepsilon_0 k_\mathrm{B}}$$

where M is the dipole moment of the system and ε0 is the permittivity of free space. A value of ε 88.1 (313 K) was obtained for EC, which agrees well with the experimental value of 89.8 (298 K).[4]

Therefore, we have shown that the OPLS-AA force field utilized in this work can effectively reproduce the key experimental properties of the bulk solvents.

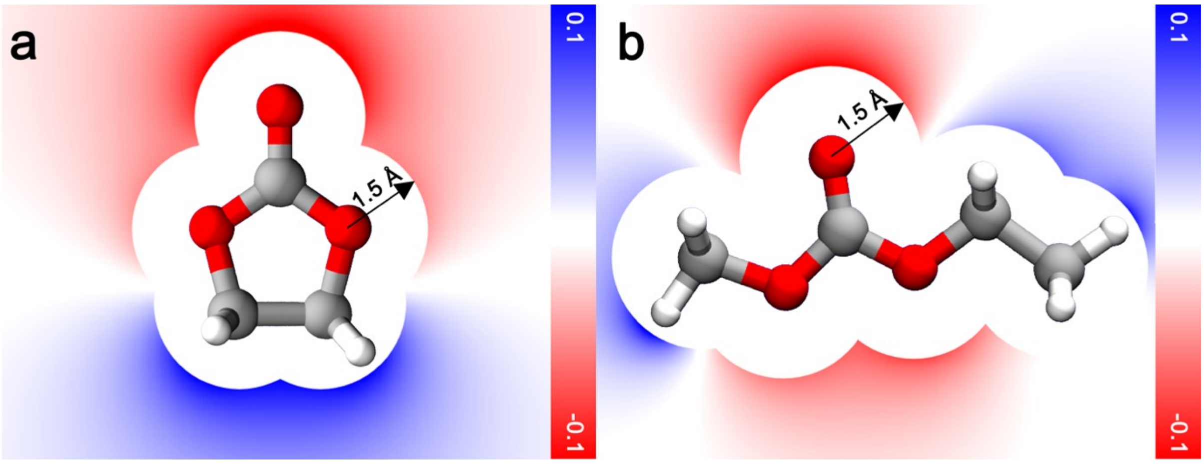


Fig. S10 The electrostatic potential contour maps of (a) EC, (b) EMC calculated from the fitted RESP charges in the chosen molecular dynamics force field. The electrostatic potential is truncated with a cutoff distance of 1.5 Å to avoid infinite potential values at point charge centers. The slice is across the carbonyl plane. Red, blue, and white colors represent the least positive (or most negative), most positive and intermediate electrostatic potential, respectively. The color bar shows the values of the electrostatic potential in volts. The connections between atoms represent chemical bonding or Li^+ coordination.

The validity of the force field is further assessed by comparing the electrostatic potential contour maps of EC and EMC obtained from quantum chemistry and the fitted RESP charges. Using the fitted RESP charges, the electrostatic potential at point i can be calculated by:

$$V_i = \sum_j \frac{kq_j}{\varepsilon r_{ij}}$$

where V_i is the electrostatic potential at point i, q_j is the partial charge of each atom in the molecule, k is the Coulomb constant, r_{ij} is the distance between point i and atom j, ε is the dielectric constant of the electrolyte where a value of 20.493 is used to match the quantum chemical calculation.

Comparing Fig. S10 with main text Fig. 3a, b, the electrostatic potential calculated from the quantum chemistry and partial charges of the MD force field are almost identical. This observation illustrates that our fitted RESP partial charges can effectively reproduce the actual electrostatic potential as obtained from quantum chemistry. In addition, the result further validates the OPLS-AA force field utilized in our MD simulation.

Section 10. Force field data of EC, EMC, FEC, and LiPF_6

EC:

```
LAMMPS data file

5 atom types
5 bond types
7 angle types
11 dihedral types
1 improper types

10 atoms
10 bonds
17 angles
28 dihedrals
1 impropers

-1.000000   54.000000 xlo xhi
-1.000000   54.000000 ylo yhi
-1.000000   54.000000 zlo zhi

Masses

   1   12.010  #       EC    c
   2   16.000  #       EC    o
   3   16.000  #       EC   os
   4   12.010  #       EC   c3
   5    1.008  #       EC   h1

Pair Coeffs #lj/coul

   1    0.1050000 3.750  #       EC    c    #OPLS-AA Charifson 1990
   2    0.2100000 2.960  #       EC    o    #OPLS-AA Charifson 1990
   3    0.1700000 3.000  #       EC   os    #OPLS-AA Charifson 1990
   4    0.0660000 3.500  #       EC   c3    #OPLS-AA Charifson 1990
   5    0.0150000 2.420  #       EC   h1    #OPLS-AA Charifson 1990

Bond Coeffs #harmonic

1     570.0000 1.229            #C=O URA,GUA,CYT,AA KOLLMAN 1986 & EC  from silva 2007
2     214.0000 1.327            #C-OS J.Comp.Chem.1990,11,1181 SKF8
3     320.0000 1.410            #C3-OS propylene carbonate D JORG ###
4     268.0000 1.529            #C3-C3 propylene carbonate D JORG JCAS 1996
5     340.0000 1.090            #C3-H propylene carbonate D JORG JCAS 1996

Angle Coeffs #harmonic

1     83.00000 116.90           #c-os-c3 silva 2007 Charifson 1990
2     83.00000 123.40           #o-c-os silva 2007 Charifson 1990
3     92.60000 111.55           #os-c-os DAMM 1997
4     50.00000 109.50           #o-c3-c3 DAMM 1997
5     35.00000 109.50           #os-c3-H DAMM 1997
6     37.50000 110.70           #c3-c3-H JACS 1996
7     33.00000 107.80           #H-c3-H 1996

Dihedral Coeffs #harmonic

1     3.200000 -1 2  #O-C-OS-C3        JPCB 2004, 2016
2     1.400000 -1 1  #O-C-OS-C3        JPCB 2004, 2016
3     2.700000 -1 2  #OS-C-OS-C3       JPCB 2004, 2016
4    0.3830000 1 3   #C3-C3-OS-C 1-3   JPCB 2004, 2016
5    0.8000000 -1 1  #C3-C3-OS-C 1-3   JPCB 2004, 2016
6    0.3830000 1 3   #H-C3-OS-C        JPCB 2004, 2016
7    0.1750000 1 2   #OS-C3-C3-OS 1-3  JPCB 2004, 2016
8     0.469000 1 5   #OS-C3-C3-OS 1-3  JPCB 2004, 2016
9            0 1 3   #
10    0.2500000 1 1  #OS-C3-C3-H       JPCB 2004, 2016
11    0.1560000 1 3  #H-C3-C3-H        JPCB 2004, 2016

Improper Coeffs #cvff

1     10.50000 -1 2  #KOLLMAN 1986
```

```
Atoms

1  1  1  0.8610  25.3353  36.0967  46.2987  #  C
2  1  2  -0.5510  25.6553  34.9559  46.1423  #  O
3  1  3  -0.3740  26.0742  37.1733  45.9053  #  OS
4  1  3  -0.3740  24.1809  36.5074  46.8945  #  OS
5  1  4  0.0680  25.4706  38.3808  46.4063  #  C3
6  1  4  0.0680  24.0455  37.9343  46.7532  #  C3
7  1  5  0.0755  25.5157  39.1424  45.6203  #  H
8  1  5  0.0755  26.0369  38.7157  47.2849  #  H
9  1  5  0.0755  23.3272  38.1385  45.9479  #  H
10  1  5  0.0755  23.6719  38.3423  47.6983  #  H

Bonds

1 1 1 2
2 2 1 3
3 2 1 4
4 3 3 5
5 3 4 6
6 4 5 6
7 5 5 7
8 5 5 8
9 5 6 9
10 5 10 6

Angles

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4 2 2 1 4
5 3 3 1 4
6 4 3 5 6
7 5 3 5 7
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10 5 4 6 9
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13 6 10 6 5
14 6 6 5 7
15 6 6 5 8
16 7 7 5 8
17 7 10 6 9

Dihedrals

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15 7 3 5 6 4
16 8 3 5 6 4
17 9 7 5 6 4
18 10 7 5 6 4
19 9 8 5 6 4
20 10 8 5 6 4
21 9 3 5 6 9
22 10 3 5 6 9
23 11 7 5 6 9
24 11 8 5 6 9
25 9 3 5 6 10
26 10 3 5 6 10
27 11 7 5 6 10
28 11 8 5 6 10

Impropers
```

```
1 1 2 3 1 4
```

EMC:

```
LAMMPS data file
# 100 EMC molecules

6 atom types
6 bond types
9 angle types
9 dihedral types
1 improper types

15 atoms
14 bonds
23 angles
25 dihedrals
1 impropers

-0.5000000 57.000000  xlo xhi
-0.5000000 57.000000  ylo yhi
-0.5000000 57.000000  zlo zhi

Masses

1   12.010  # c EMC
2   16.000  # os EMC
3   16.000  # o EMC
4   12.010  # c3 EMC
5    1.008  # h1 EMC
6    1.008  # hc EMC

Pair Coeffs #lj/coil

1 0.1050000 3.750  #       EC    c    #OPLS-AA Charifson 1990
2 0.1700000 3.000  #       EC   os    #OPLS-AA Charifson 1990
3 0.2100000 2.960  #       EC    o    #OPLS-AA Charifson 1990
4 0.0660000 3.500  #       EC   c3    #OPLS-AA Charifson 1990
5 0.0150000 2.420  #       EC   h1    #OPLS-AA Charifson 1990
6 0.0150000 2.420  #       EC   hc    #OPLS-AA Charifson 1990

Bond Coeffs #harmonic

1 214.0000 1.327  # harmonic EMC c os
2 570.0000 1.229  # harmonic EMC c o
3 320.0000 1.410  # harmonic EMC c3 os
4 268.0000 1.529  # harmonic EMC c3 c3
5 340.0000 1.090  # harmonic EMC c3 h1
6 340.0000 1.090  # harmonic EMC c3 hc

Angle Coeffs #harmonic

1 83.00000 116.90  # harmonic EMC c os c3
2 92.60000 111.55  # harmonic EMC os c os
3 83.00000 123.40  # harmonic EMC o c os
4 50.00000 109.50  # harmonic EMC c3 c3 os
5 35.00000 109.50  # harmonic EMC h1 c3 os
6 37.50000 110.70  # harmonic EMC c3 c3 hc
7 37.50000 110.70  # harmonic EMC c3 c3 h1
8 33.00000 107.80  # harmonic EMC h1 c3 h1
9 33.00000 107.80  # harmonic EMC hc c3 hc

Dihedral Coeffs #harmonic

1 2.700000 -1 2  # harm EMC os c os c3
2 3.200000 -1 2  # harm EMC o c os c3
3 1.400000 -1 1  # harm EMC o c os c3
4 0.3830000 1 3  # harm EMC c3 c3 os c
5 0.8000000 -1 1  # harm EMC c3 c3 os c
6 0.3830000 1 3  # harm EMC h1 c3 os c
7 0.0  1 3  # harm EMC hc c3 c3 os
8 0.2500000 1 1  # harm EMC hc c3 c3 os
9 0.1560000 1 3  # harm EMC h1 c3 c3 hc
```

```
Improper Coeffs #cvff

1 10.50000 -1  2  # cvff EMC o os c os

Atoms

1       1       1       1.0244  -11.3015        10.713  -2.2545 #       c       C1      EMC     1
2       1       2       -0.5687 -10.6025        9.564   -2.4405 #       os      O1      EMC     1
3       1       2       -0.3841 -11.8245        11.305  -3.3575 #       os      O2      EMC     1
4       1       3       -0.6241 -11.4665        11.185  -1.1625 #       o       O3      EMC     1
5       1       4       0.5401  -9.6155 9.467   -3.5035 #       c3      C2      EMC     1
6       1       4       -0.053  -12.2335        10.519  -4.4935 #       c3      C3      EMC     1
7       1       4       -0.296  -8.3535 8.862   -2.9195 #       c3      C4      EMC     1
8       1       5       -0.065  -9.4245 10.467  -3.9145 #       h1      H1      EMC     1
9       1       5       -0.065  -10.0245        8.83    -4.2985 #       h1      H2      EMC     1
10      1       5       0.0851  -13.1515        10.986  -4.8635 #       h1      H3      EMC     1
11      1       5       0.0851  -12.4365        9.481   -4.2045 #       h1      H4      EMC     1
12      1       5       0.0851  -11.4675        10.549  -5.2785 #       h1      H5      EMC     1
13      1       6       0.0787  -7.9365 9.507   -2.1355 #       hc      H6      EMC     1
14      1       6       0.0787  -7.6025 8.741   -3.7125 #       hc      H7      EMC     1
15      1       6       0.0787  -8.5625 7.875   -2.4855 #       hc      H8      EMC     1

Bonds

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2 1 1 3  # EMC 1 C1 O2
3 2 1 4  # EMC 1 C1 O3
4 3 5 2  # EMC 1 C2 O1
5 3 6 3  # EMC 1 C3 O2
6 4 5 7  # EMC 1 C2 C4
7 5 5 8  # EMC 1 C2 H1
8 5 5 9  # EMC 1 C2 H2
9 5 6 10  # EMC 1 C3 H3
10 5 6 11  # EMC 1 C3 H4
11 5 6 12  # EMC 1 C3 H5
12 6 7 13  # EMC 1 C4 H6
13 6 7 14  # EMC 1 C4 H7
14 6 7 15  # EMC 1 C4 H8

Angles

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2 1 1 3 6  # EMC 1 C1 O2 C3
3 2 2 1 3  # EMC 1 O1 C1 O2
4 3 2 1 4  # EMC 1 O1 C1 O3
5 4 7 5 2  # EMC 1 C4 C2 O1
6 5 8 5 2  # EMC 1 H1 C2 O1
7 5 9 5 2  # EMC 1 H2 C2 O1
8 3 3 1 4  # EMC 1 O2 C1 O3
9 5 10 6 3  # EMC 1 H3 C3 O2
10 5 11 6 3  # EMC 1 H4 C3 O2
11 5 12 6 3  # EMC 1 H5 C3 O2
12 6 5 7 13  # EMC 1 C2 C4 H6
13 6 5 7 14  # EMC 1 C2 C4 H7
14 6 5 7 15  # EMC 1 C2 C4 H8
15 7 7 5 8  # EMC 1 C4 C2 H1
16 7 7 5 9  # EMC 1 C4 C2 H2
17 8 8 5 9  # EMC 1 H1 C2 H2
18 8 10 6 11  # EMC 1 H3 C3 H4
19 8 10 6 12  # EMC 1 H3 C3 H5
20 8 11 6 12  # EMC 1 H4 C3 H5
21 9 13 7 14  # EMC 1 H6 C4 H7
22 9 13 7 15  # EMC 1 H6 C4 H8
23 9 14 7 15  # EMC 1 H7 C4 H8

Dihedrals

1 1 3 1 2 5  # EMC 1 O2 C1 O1 C2
2 2 4 1 2 5  # EMC 1 O3 C1 O1 C2
3 3 4 1 2 5  # EMC 1 O3 C1 O1 C2
4 1 2 1 3 6  # EMC 1 O1 C1 O2 C3
5 2 4 1 3 6  # EMC 1 O3 C1 O2 C3
6 3 4 1 3 6  # EMC 1 O3 C1 O2 C3
7 4 7 5 2 1  # EMC 1 C4 C2 O1 C1
8 5 7 5 2 1  # EMC 1 C4 C2 O1 C1
9 6 8 5 2 1  # EMC 1 H1 C2 O1 C1
10 6 9 5 2 1  # EMC 1 H2 C2 O1 C1
11 6 10 6 3 1  # EMC 1 H3 C3 O2 C1
```

```
12 6 11 6 3 1  # EMC 1 H4 C3 O2 C1
13 6 12 6 3 1  # EMC 1 H5 C3 O2 C1
14 7 2 5 7 13  # EMC 1 O1 C2 C4 H6
15 8 2 5 7 13  # EMC 1 O1 C2 C4 H6
16 9 8 5 7 13  # EMC 1 H1 C2 C4 H6
17 9 9 5 7 13  # EMC 1 H2 C2 C4 H6
18 7 2 5 7 14  # EMC 1 O1 C2 C4 H7
19 8 2 5 7 14  # EMC 1 O1 C2 C4 H7
20 9 8 5 7 14  # EMC 1 H1 C2 C4 H7
21 9 9 5 7 14  # EMC 1 H2 C2 C4 H7
22 7 2 5 7 15  # EMC 1 O1 C2 C4 H8
23 8 2 5 7 15  # EMC 1 O1 C2 C4 H8
24 9 8 5 7 15  # EMC 1 H1 C2 C4 H8
25 9 9 5 7 15  # EMC 1 H2 C2 C4 H8

Impropers

1 1 4 3 1 2  # EMC 1 O3 O2 C1 O1
```

FEC:

```
LAMMPS data file

7 atom types
10 bond types
17 angle types
28 dihedral types
1 improper types

10 atoms
10 bonds
17 angles
28 dihedrals
1 impropers

-1.000000   54.000000 xlo xhi
-1.000000   54.000000 ylo yhi
-1.000000   54.000000 zlo zhi

Masses

1   12.010  #C3/Cf
2    1.008  #Hf
3  16.000  #O3/Of
4  12.010  #C
5  16.000  #O
6   1.008  #Hc
7  19.000  #F

Pair Coeffs #lj/coul

1    0.0660000 3.500  #            C3/Cf Cornell 1995
2   0.0150000 2.420  #            Hf Cornell 1995
3   0.1700000 3.000  #            o3/Of Cornell 1995
4   0.1050000 3.750  #            c Cornell 1995
5   0.2100000 2.960  #            o Cornell 1995
6   0.0150000 2.420  #            Hc Cornell 1995
7   0.0610000 3.118  #            F Cornell 1995

Bond Coeffs #harmonic

1    3.31700000e+02    1.09610000e+00  #Cf-Hf
2    3.08600000e+02    1.43160000e+00  #Cf-Of
3    3.00900000e+02    1.53750000e+00  #Cf-C3
4   3.56900000e+02    1.34970000e+00  #Cf-F
5   3.90800000e+02    1.35840000e+00  #C-Of
6   6.37700000e+02    1.21830000e+00  #C=O
7   3.90800000e+02    1.35840000e+00  #C-O3
8   3.08600000e+02    1.43160000e+00  #O3-C3
9   3.30600000e+02    1.09690000e+00  #C3-Hc
10   3.30600000e+02    1.09690000e+00 #C3-Hc

Angle Coeffs #harmonic

1    6.32800000e+01    1.15980050e+02  #Cf-Of-C
2    6.80000000e+01    1.07970050e+02  #Cf-C3-O3
3    4.63900000e+01    1.09560050e+02  #Cf-C3-Hc
4    4.63900000e+01    1.09560050e+02  #Cf-C3-Hc
5    5.08500000e+01    1.09580050e+02  #Hf-Cf-Of
6    4.62500000e+01    1.10220050e+02  #Hf-Cf-C3
7    5.11500000e+01    1.08790050e+02  #Hf-Cf-F
8    6.80000000e+01    1.07970050e+02  #Of-Cf-C3
9    7.07600000e+01    1.10580050e+02  #Of-Cf-F
10    7.53200000e+01    1.23250050e+02 #Of-C-O
11    7.56200000e+01    1.11290050e+02 #Of-C-O3
12    6.32800000e+01    1.15980050e+02 #C-O3-C3
13    7.53200000e+01    1.23250050e+02 #O-C-O3
14    5.08000000e+01    1.09780050e+02 #O3-C3-Hc
15    5.08000000e+01    1.09780050e+02 #O3-C3-Hc
16    6.61100000e+01    1.09240050e+02 #C3-Cf-F
17    3.92400000e+01    1.08460050e+02 #Hc-C3-Hc

Dihedral Coeffs  #hybrid harmonic charmm multi/harmonic

1 charmm    2.70000000e+00     2    180     0         #Cf-Of-C-O
2 charmm    1.40000000e+00     1    180     0         #Cf-Of-C-O
```

```
3 charmm    2.70000000e+00     2    180     0        #Cf-Of-C-O3
4 charmm    8.00000000e-01     1    180     0        #Cf-C3-O3-C
5 multi/harmonic     3.82999522e-01      -1.14899857e+00     0.00000000e+00      1.53199809e+00
0.00000000e+00    #Cf-C3-O3-C
6 multi/harmonic     3.83334130e-01      -1.15000239e+00     0.00000000e+00      1.53333652e+00
0.00000000e+00    #Hf-Cf-Of-C
7 multi/harmonic     1.55554493e-01      -4.66663480e-01     0.00000000e+00      6.22217973e-01
0.00000000e+00    #Hf-Cf-C3-O3
8 multi/harmonic     1.55554493e-01      -4.66663480e-01     0.00000000e+00      6.22217973e-01
0.00000000e+00    #Hf-Cf-C3-Hc
9 multi/harmonic     1.55554493e-01      -4.66663480e-01     0.00000000e+00      6.22217973e-01
0.00000000e+00    #Hf-Cf-C3-Hc
10 multi/harmonic     0.00000000e+00      0.00000000e+00     2.35000000e+00      0.00000000e+00
0.00000000e+00    #Of-Cf-C3-O3
11 multi/harmonic     1.44000956e-01      -4.32002868e-01     0.00000000e+00      5.76003824e-01
0.00000000e+00    #Of-Cf-C3-O3
12 multi/harmonic     2.50000000e-01      2.50000000e-01     0.00000000e+00      0.00000000e+00
0.00000000e+00    #Of-Cf-C3-Hc
13 multi/harmonic     0.00000000e+00      0.00000000e+00     0.00000000e+00      0.00000000e+00
0.00000000e+00    #Of-Cf-C3-Hc
14 multi/harmonic     0.00000000e+00      0.00000000e+00     0.00000000e+00      0.00000000e+00
0.00000000e+00    #Of-Cf-C3-Hc
15 multi/harmonic     2.50000000e-01      2.50000000e-01     0.00000000e+00      0.00000000e+00
0.00000000e+00    #Of-Cf-C3-Hc
16 charmm    2.70000000e+00     2    180     0        #Of-C-O3-C3
17 multi/harmonic     3.83334130e-01      -1.15000239e+00     0.00000000e+00      1.53333652e+00
0.00000000e+00    #C-O3-C3-Hc
18 multi/harmonic     3.83334130e-01      -1.15000239e+00     0.00000000e+00      1.53333652e+00
0.00000000e+00    #C-O3-C3-Hc
19 charmm    1.40000000e+00     1    180     0        #O-C-O3-C3
20 charmm    2.70000000e+00     2    180     0        #O-C-O3-C3
21 charmm    8.00000000e-01     1    180     0        #C3-Cf-Of-C
22 multi/harmonic     3.82999522e-01      -1.14899857e+00     0.00000000e+00      1.53199809e+00
0.00000000e+00    #C3-Cf-Of-C
23 multi/harmonic     3.83334130e-01      -1.15000239e+00     0.00000000e+00      1.53333652e+00
0.00000000e+00    #F-Cf-Of-C
24 multi/harmonic     1.55554493e-01      -4.66663480e-01     0.00000000e+00      6.22217973e-01
0.00000000e+00    #F-Cf-C3-O3
25 multi/harmonic     0.00000000e+00      0.00000000e+00     0.00000000e+00      0.00000000e+00
0.00000000e+00    #F-Cf-C3-Hc
26 multi/harmonic     1.90000000e-01      1.90000000e-01     0.00000000e+00      0.00000000e+00
0.00000000e+00    #F-Cf-C3-Hc
27 multi/harmonic     0.00000000e+00      0.00000000e+00     0.00000000e+00      0.00000000e+00
0.00000000e+00    #F-Cf-C3-Hc
28 multi/harmonic     1.90000000e-01      1.90000000e-01     0.00000000e+00      0.00000000e+00
0.00000000e+00    #F-Cf-C3-Hc

Improper Coeffs #cvff

1     10.50000 -1 2  #KOLLMAN 1986

Atoms

1  1  1  0.3295  36.9107  9.7016  35.3263  #  Cf
2  1  2  0.0807  35.9476  9.4597  34.8637  #  Hf
3  1  3  -0.3541  36.7006  10.1823  36.6245  #  Of
4  1  4  0.816  37.5785  11.215  36.8947  #  C
5  1  5  -0.5091  37.7111  11.7216  37.9638  #  O
6  1  3  -0.3316  38.237  11.5641  35.761  #  O3
7  1  1  -0.0061  37.7358  10.7989  34.653  #  C3
8  1  6  0.1038  38.5793  10.387  34.0898  #  Hc
9  1  6  0.1038  37.122  11.4493  34.0166  #  Hc
10  1  7  -0.2329  37.6408  8.5204  35.3921  #  F

Bonds

1 1 1 2
2 2 1 3
3 3 1 7
4 4 1 10
5 5 3 4
6 6 4 5
7 7 4 6
8 8 6 7
9 9 7 8
10 10 7 9

Angles
```

```
1 1 1 3 4
2 2 1 7 6
3 3 1 7 8
4 4 1 7 9
5 5 2 1 3
6 6 2 1 7
7 7 2 1 10
8 8 3 1 7
9 9 3 1 10
10 10 3 4 5
11 11 3 4 6
12 12 4 6 7
13 13 5 4 6
14 14 6 7 8
15 15 6 7 9
16 16 7 1 10
17 17 8 7 9

Dihedrals

1 1 1 3 4 5
2 2 1 3 4 5
3 3 1 3 4 6
4 4 1 7 6 4
5 5 1 7 6 4
6 6 2 1 3 4
7 7 2 1 7 6
8 8 2 1 7 8
9 9 2 1 7 9
10 10 3 1 7 6
11 11 3 1 7 6
12 12 3 1 7 8
13 13 3 1 7 8
14 14 3 1 7 9
15 15 3 1 7 9
16 16 3 4 6 7
17 17 4 6 7 8
18 18 4 6 7 9
19 19 5 4 6 7
20 20 5 4 6 7
21 21 7 1 3 4
22 22 7 1 3 4
23 23 10 1 3 4
24 24 10 1 7 6
25 25 10 1 7 8
26 26 10 1 7 8
27 27 10 1 7 9
28 28 10 1 7 9

Impropers

1 1 5 4 3 6
```

$LiPF_6$:

```
LAMMPS data file
# 1 LiPF6

3 atom types
1 bond types
2 angle types
0 dihedral types
0 improper types

8 atoms
6 bonds
15 angles
0 dihedrals
0 impropers

  -1.000000   54.000000 xlo xhi
  -1.000000   54.000000 ylo yhi
  -1.000000   54.000000 zlo zhi

Masses

   1   30.970  #       P
   2   19.000  #       F
   3    6.940  #       Li

Pair Coeffs

   1    0.2000000 3.740  #       P          # JPCB 2004, 2038
   2    0.0610000 3.118  #       F          # JPCB 2004, 2038
   3    0.0005000 2.870  #       Li         # JCTC 2006

Bond Coeffs

1     370.4589 1.606            # JPCB 2004, 16893

Angle Coeffs

1     139.2209 90.00            # JPCB 2004, 16893
2     34.77535 180.00           # JPCB 2004, 16893

Atoms

1  1  1  1.34  17.1391  34.1549  40.1795  #  P
2  1  2  -0.39  17.8305  33.6172  38.8406  #  F
3  1  2  -0.39  15.8117  33.3359  39.823  #  F
4  1  2  -0.39  16.5735  35.4198  39.3794  #  F
5  1  2  -0.39  16.4477  34.6927  41.5185  #  F
6  1  2  -0.39  18.4666  34.974  40.536  #  F
7  1  2  -0.39  17.7047  32.89  40.9796  #  F
8  1  3  1  16.0126  34.0688  37.8399  #  Li

Bonds

1 1 1 2
2 1 1 3
3 1 1 4
4 1 1 5
5 1 1 6
6 1 1 7

Angles

1 2 2 1 5
2 2 3 1 6
3 2 4 1 7
4 1 2 1 3
5 1 2 1 4
6 1 2 1 6
7 1 2 1 7
8 1 5 1 3
9 1 5 1 4
10 1 5 1 6
11 1 5 1 7
12 1 3 1 4
13 1 4 1 6
```

```
14 1 6 1 7
15 1 7 1 3
```

References

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