

## **Structures and Dynamic Properties of the LiPF<sub>6</sub> Electrolytic Solution Under Electric Fields - A Theoretical Study**

Man Liu , Peter J. Chintali, Xue-bin Huang and Ru-bo Zhang\*:

\*School of Chemistry and Chemical Engineering, Beijing Institute of Technology, South  
Street No. 5, Zhongguancun, Haidian District, 100081 Beijing, China.

Ru-bo Zhang: E-mail: [zhangrubo@bit.edu.cn](mailto:zhangrubo@bit.edu.cn); Tel: 010-62767759

## Contents:

S-1:

Partial charges from COMPASS force fields.

S-2:

Interaction binding energies between ETFEC, DTFEC and EC, DMC and DEC molecules calculated in terms of the compass force field, DFT M06-2X and DFT B3LYP methods.

S-3:

Figure S1. The plots of mean square displacement (MSD) versus time curves at different temperatures and the diffusion coefficient versus temperature.

Figure S2 Radial distribution functions of the  $\text{Li}^+ \cdots \text{O}_{\text{carbonyl}}$  with free electric field.

Figure S3. Calculated  $\text{Li}^+$  ion mean coordination number.

S-4:

The geometries of the first solvation shell of  $\text{Li}^+$  optimized by DFT

S-6:

Figure S4 Distribution of the Li-ligands clusters in the ternary and quaternary solvents.

Figure S5. Radial distribution functions of F-H and  $\text{O}_c\text{-H}$ .

Figure S6. Diffusion coefficient of  $\text{Li}^+$  in three electrolytes at 298K and 318K.

S-7:

Figure S7. The plots of density of simulated box and average molecular dipole moment  $\mu_e$  versus time under electric field.

S-8:

Figure S8. The plots of radial distribution functions between  $\text{Li}^+$  and different species, and of the mean coordination numbers of  $\text{Li}^+$  for EC-DMC-DEC-ETFEC with electric fields.

Figure S9. The plots of radial distribution functions between  $\text{Li}^+$  and different species, and of the mean coordination numbers of  $\text{Li}^+$  for EC-DMC-DEC-DTFEC with electric fields.

S-9:

Figure S10. The plots of mean-square displacement as a function of time and diffusion coefficient at different electric fields for  $\text{Li}^+$  and  $\text{PF}_6^-$ .

S-10:

Figure S11. Size and direction of the dipole moments of all the solvent molecules displayed with electric fields.

S-11:

Figure S12. Drift velocity and ion mobility of 1.0 M  $\text{Li}^+$  ion in EC under an external electric field at 318K.

Figure S13. Drift velocity and ion mobility of 0.7 M  $\text{Li}^+$  ion in EC under an external electric field at 318K.

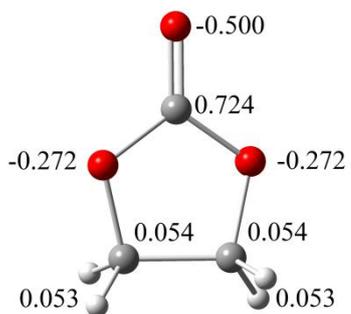
S-12:

Table S1. The mean diffusion coefficient of all the species in the solutions at different temperature.

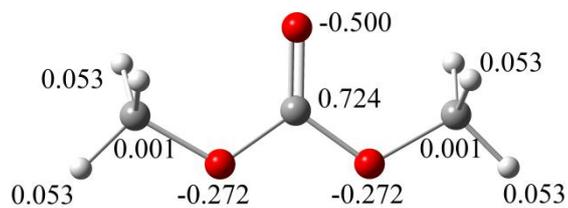
Table S2. Transference number for  $\text{Li}^+$  at varying temperatures.

S-13:

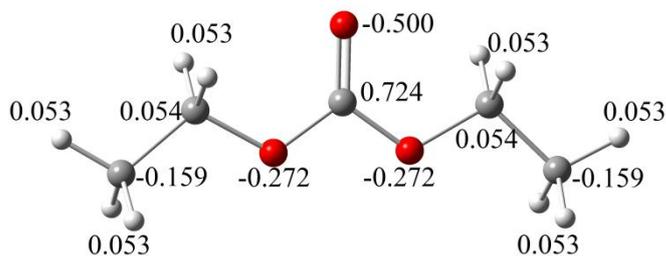
Table S3. Dipole moment of molecule under electric field; Values of  $\tilde{\beta}$  from booth model.



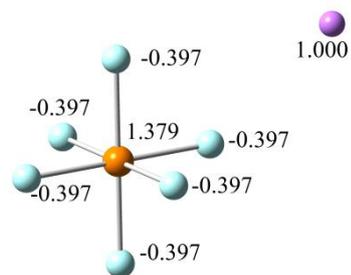
EC



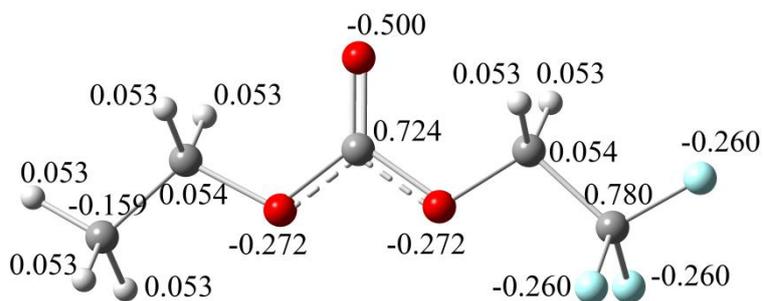
DMC



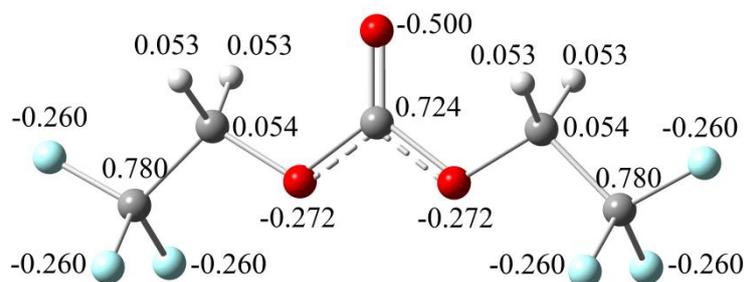
DEC



LiPF<sub>6</sub>



ETFEC



DTFEC

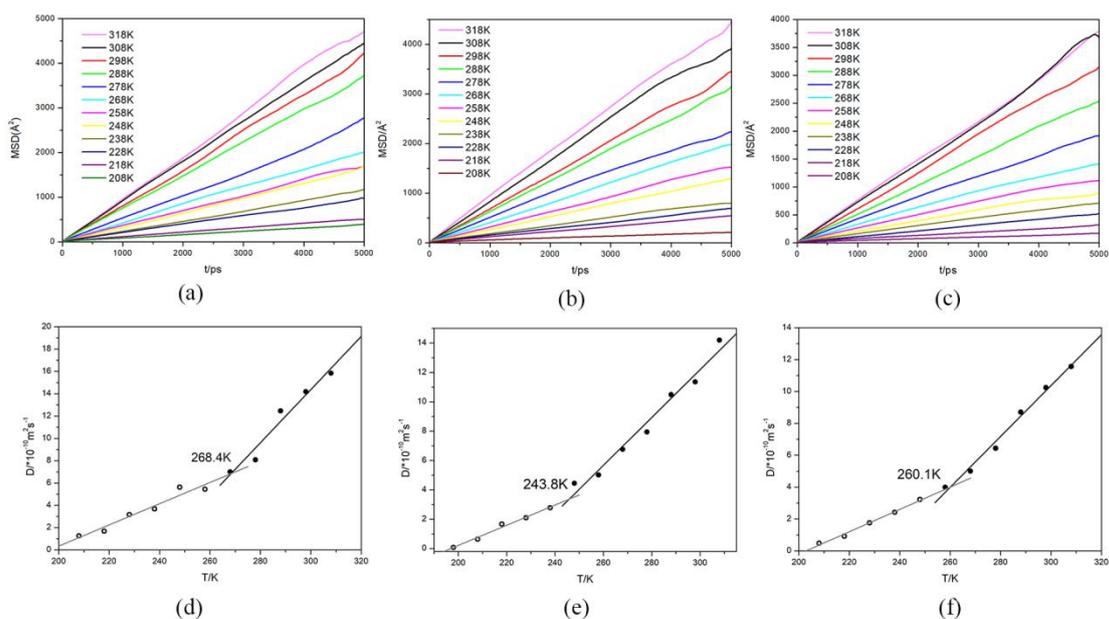
Partial charges from COMPASS force fields.

Interaction binding energies between ETFEC, DTFEC and EC, DMC and DEC molecules calculated in terms of the compass force field, DFT M06-2X and DFT B3LYP methods.

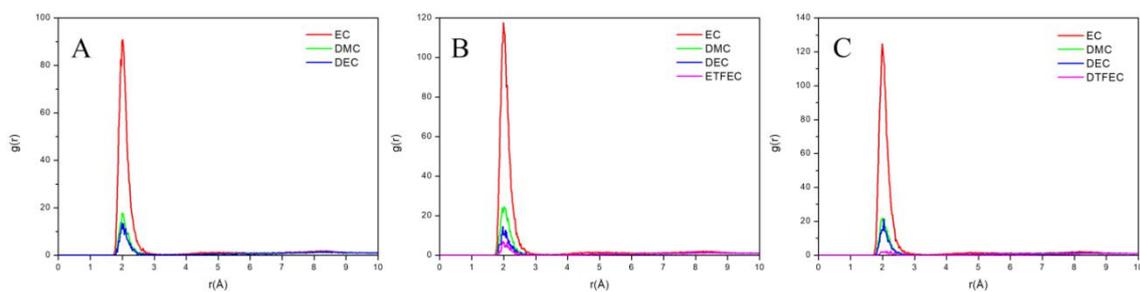
---

species	$\Delta E$ (kcal/mol)		
	COMPASS	DFT M062X/6-31+G(d,p)	DFT B3LYP/6-31+G(d,p)
ETFEC-EC	-5.29	-7.83	-3.46
ETFEC-DMC	-4.35	-4.63	-2.35
ETFEC-DEC	-3.73	-2.32	-2.79
DTFEC-EC	-2.64	-3.10	-1.40
DTFEC-DMC	-5.20	-5.81	-3.17
DTFEC-DEC	-7.63	-9.19	-3.41

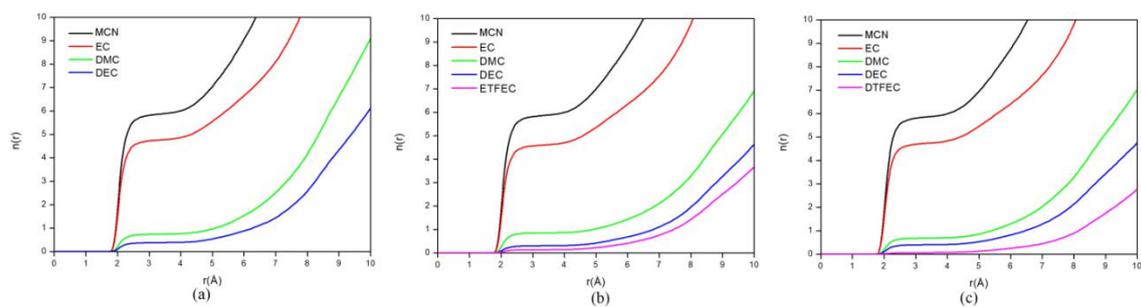
---



**Figure S1** The plots of mean square displacement (MSD) versus time curves at different temperatures (top), and of the diffusion coefficient versus temperature for (a) (d)EC-DMC-DEC (b)(e) EC-DMC-DEC-ETFEC (c) (f)EC-DMC-DEC-DTFEC

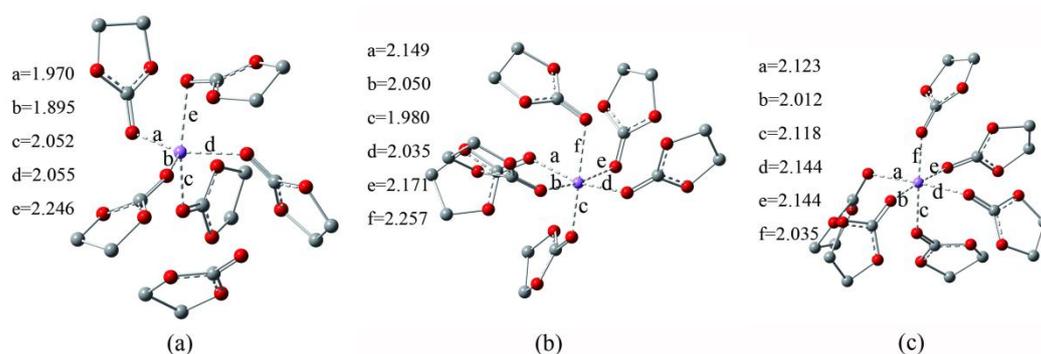


**Figure S2** Radial distribution functions of the  $\text{Li}^+\cdots\text{O}_{\text{carbonyl}}$  with free electric field.(A: EC-DMC-DEC; B: EC-DMC-DEC-ETFEC ; C: EC-DMC-DEC-DTFEC)



**Figure S3** Calculated  $\text{Li}^+$  ion mean coordination number in the EC-DMC-DEC (a) EC-DMC-DEC-ETFEC (b) EC-DMC-DEC-DTFEC (c) systems.

**Figure S4** The geometries of the first solvation shell of  $\text{Li}^+$  optimized by DFT



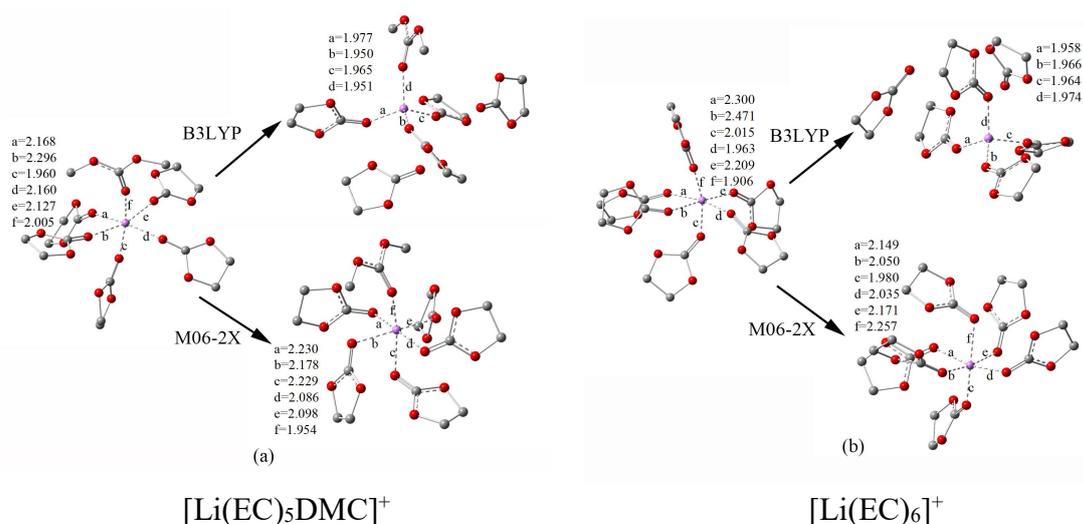
(a) Using M062X/6-31+G(d,p) in the gas phase

(b) Using M062X/6-31+G(d,p) in the bulk solvent with CPCM model and dielectric constant of 14.0

(c) Using M062X/6-31+G(d,p) in the bulk solvent with CPCM model and dielectric constant of 89.8

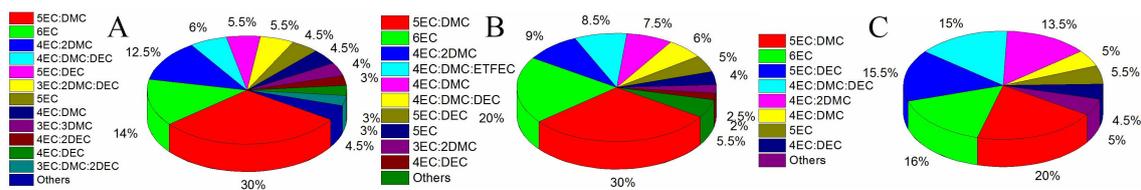
According to the above figure, we find that the octahedron conformations are obtained whether it is in the gas or in the bulk solvent. The distances of  $\text{Li}\dots\text{O}$  are almost close to 2.0 angstrom. The results show that the coordination number of 5-6 is possible from the theoretical calculations.

For comparison, we also used the popular B3LYP method for this study. The optimized structures are obtained with 14.0 of dielectric constant, the basis set of 6-31+G(d,p) and displayed as follows.

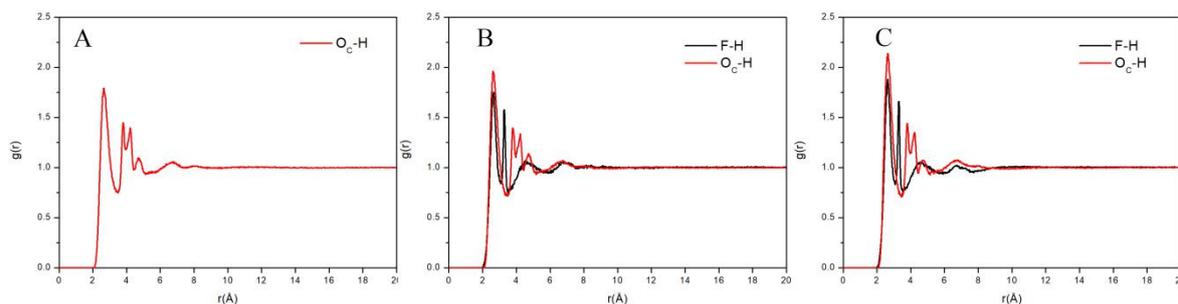


According to the results, the dispersion-absence DFT such as B3LYP always show

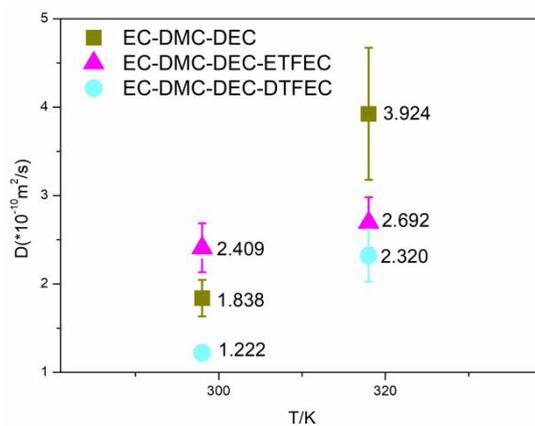
the coordination number of 4. The reliable M06-2x always shows the number of 6. Of course, MP2 method is more appreciate for this study. However, it is too expensive for me to finish the calculations. We are also expecting a new decision for the debate.



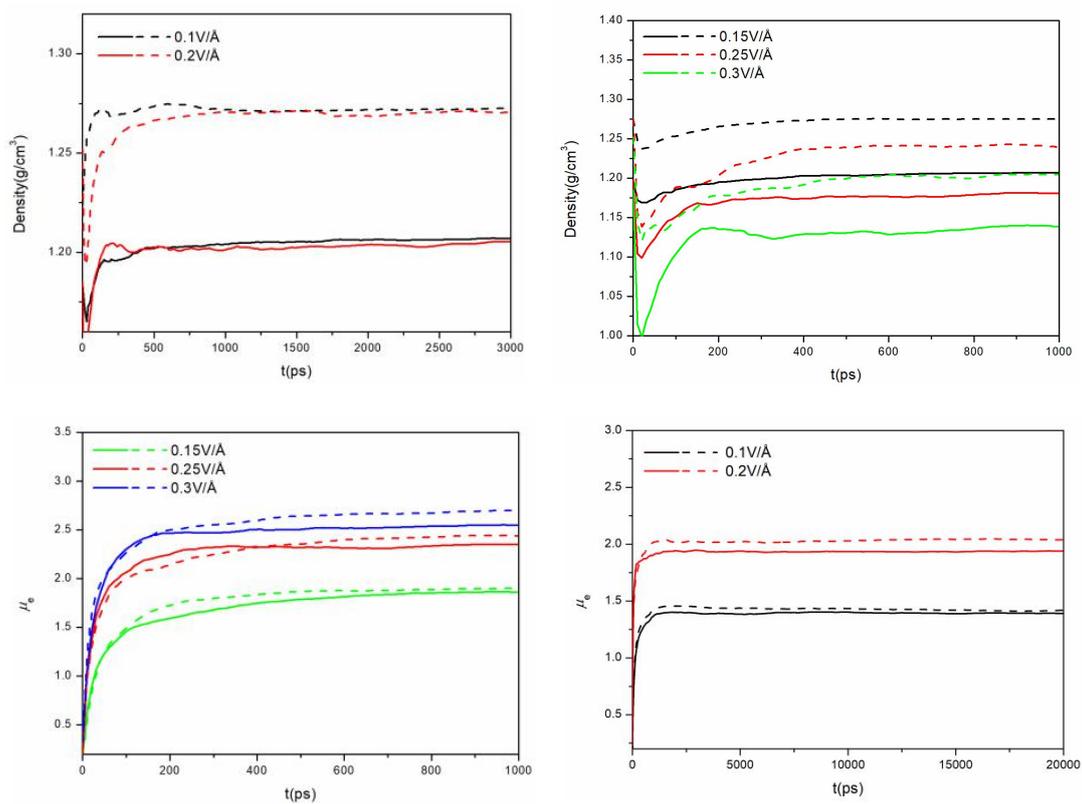
**Figure S5** Distribution of the Li-ligands clusters in the ternary and quaternary solvents. ( A: EC- DMC -DEC; B: EC- DMC- DEC- ETFEC ; C: EC- DMC- DEC- DTFEC



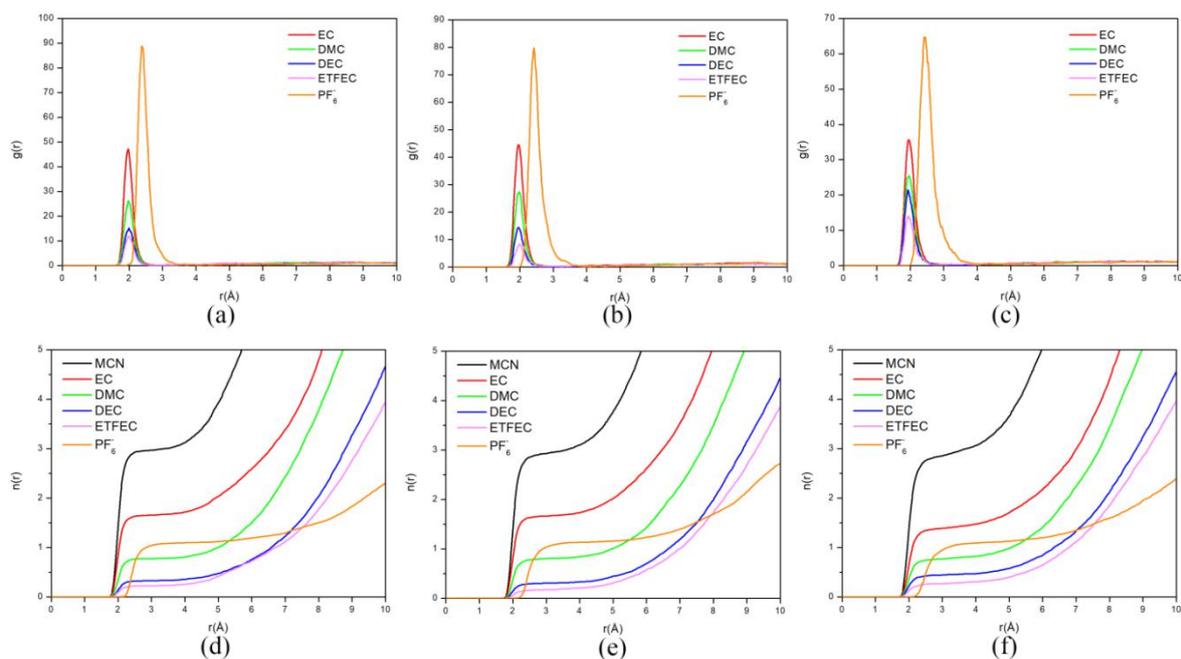
**Figure S6** Radial distribution functions of F-H and O<sub>c</sub>-H in EC-DMC-DEC(A); EC-DMC-DEC-ETFEC (B); EC-DMC-DEC-DTFEC(C)



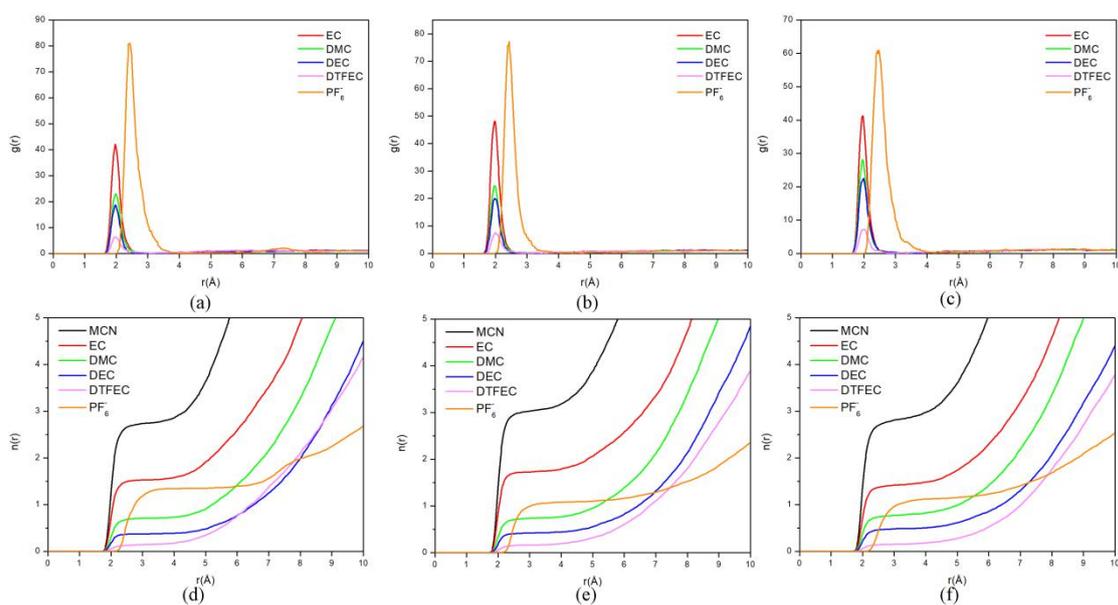
**Figure S7** Diffusion coefficient of Li<sup>+</sup> in three electrolytes at 298K and 318K.



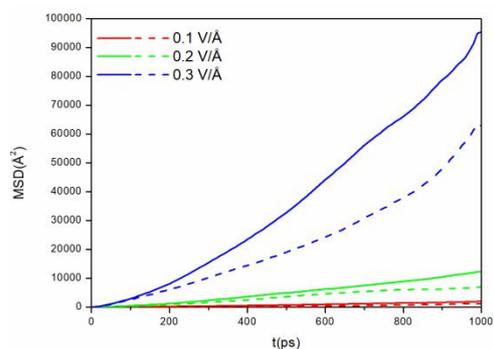
**Figure S8.** The plots of density of simulated box and average molecular dipole moment  $\mu_e$  versus time under electric field.(The full line is EC-DMC-DEC-ETFEC, dashed line is EC-DMC-DEC-DTFEC)



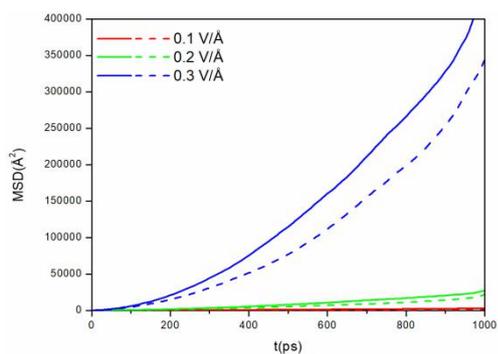
**Figure S9.** The plots of radial distribution functions between  $\text{Li}^+$  and different species(top), and of the mean coordination numbers of  $\text{Li}^+$  for EC-DMC-DEC-ETFEC with electric fields.(a,d: 0.1V  $\text{\AA}^{-1}$ ; b,e: 0.2V  $\text{\AA}^{-1}$ ; c,f: 0.3V  $\text{\AA}^{-1}$ )



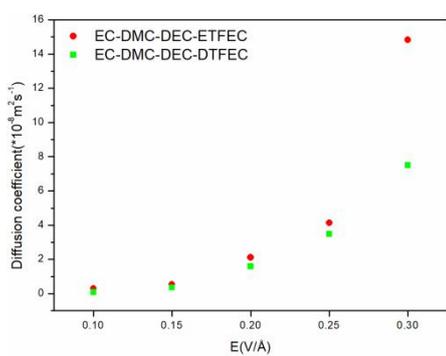
**Figure S10.** The plots of radial distribution functions between  $\text{Li}^+$  and different species(top), and of the mean coordination numbers of  $\text{Li}^+$  for EC-DMC-DEC-DTFEC with electric fields.(a,d: 0.1V  $\text{\AA}^{-1}$ ; b,e: 0.2V  $\text{\AA}^{-1}$ ; c,f: 0.3V  $\text{\AA}^{-1}$ )



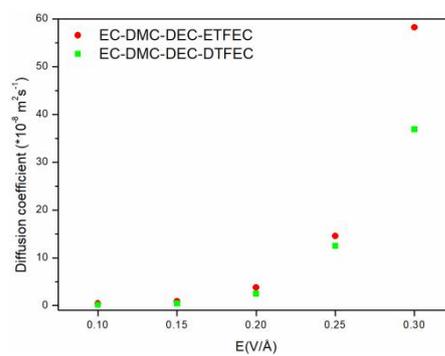
(a)



(b)

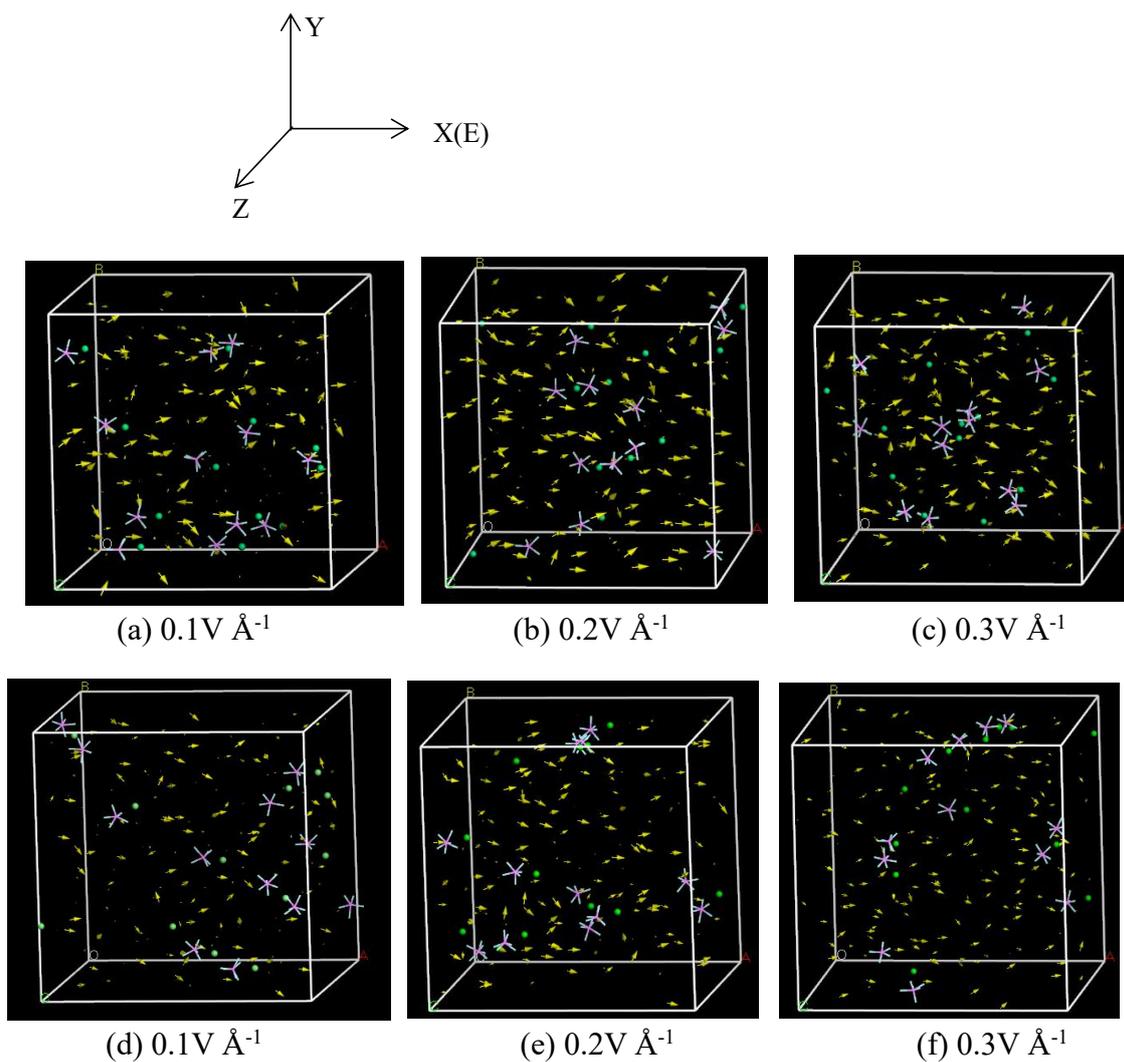


(c)



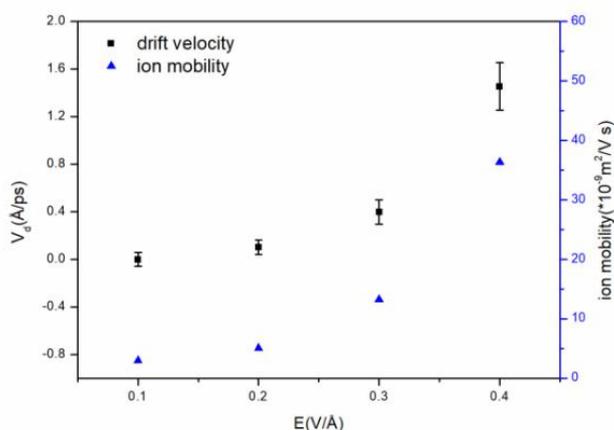
(d)

**Figure S11.** The plots of mean-square displacement as a function of time and diffusion coefficient at different electric fields for  $\text{Li}^+$  (a) (c) and  $\text{PF}_6^-$  (b) (d). (The full line is EC-DMC-DEC-ETFEC, dashed line is EC-DMC-DEC-DTFEC)

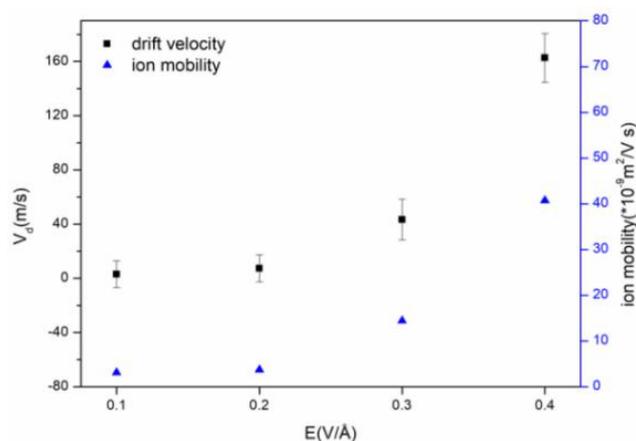


**Figure S12.** Size and direction of the dipole moments of all the solvent molecules displayed with electric fields. (a)~(c) for the containing ETFEC electrolytic solution; (d)~(f) for the containing DTFEC electrolytic solution. a,d:  $0.1V \text{ \AA}^{-1}$ . The yellow arrows represent dipole moments of the solvent molecules. The green ball is  $\text{Li}^+$  ion, and the blue-pink lines are  $\text{PF}_6^-$  anion);

In order to validate our calculations effectiveness, the  $v_{\text{drift}}$  of the 1.0 M  $\text{LiPF}_6$  in pure EC at 318 K was first selected for test with a linear voltage of 0.1~0.4  $\text{V}/\text{\AA}$ . We observe that drift velocity slowly increases within 0.2  $\text{V}/\text{\AA}$  and then increases dramatically from 0.2 ~ 0.4  $\text{V}/\text{\AA}$  field strengths. Both the observed curve change and  $v_{\text{drift}}$  values are in good agreement with the previous reports, as showed in Figure S11. Using the same method, we could calculate the drift velocities of 0.7 M  $\text{LiPF}_6$  in EC-DMC-DEC-ETFEC and EC-DMC-DEC-DTFEC with the line voltages from 0.1 ~ 0.3  $\text{V}/\text{\AA}$ . The results show that the similar changes of the drift velocities are also observed. The  $v_{\text{drift}}$  values were very small at 0.1  $\text{V}/\text{\AA}$  and close to the corresponding value in pure EC system, as seen in Figure S12.



**Figure S13.** Drift velocity and ion mobility of 1.0 M  $\text{Li}^+$  ion in EC under an external electric field at 318K



**Figure S14.** Drift velocity and ion mobility of 0.7 M  $\text{Li}^+$  ion in EC under an external electric field at 318K

**Table S1.** The mean diffusion coefficient ( $\times 10^{-10}$  m<sup>2</sup>/s) of all the species in the solutions at different temperature.

T/K	EC-DMC-DEC	EC-DMC-DEC-ETFEC	EC-DMC-DEC-DTFEC
318	16.7	15.7	12.1
308	15.9	14.2	11.6
298	14.2	11.4	10.2
288	12.5	10.5	8.7
278	8.1	7.9	6.4
268	7.0	6.7	5.0
258	5.4	5.0	4.0

**Table S2.** Transference number for Li<sup>+</sup> at varying temperatures.

Temp./K	In EC-DMC-DEC-ETFEC	In EC-DMC-DEC-ETFEC
318	0.19	0.16
308	0.19	0.16
298	0.15	0.13
288	0.16	0.16
278	0.19	0.13
268	0.15	0.11

**Table S3.** Dipole moment of molecule ( $\mu_e$ ) under electric field; Values of  $\tilde{\beta}$  from booth model <sup>a</sup>.

species	$\mu_e(\text{D})$	$\tilde{\beta}(\text{nm/V})$	$\epsilon_r$	
EC	6.3	36.6	2.8	
DMC	0.8	4.4	1.4	
DEC	1.1	6.1	1.4	
ETEFC	2.8	16.3	1.2	
DTFEC	1.6	9.5	0.9	
	0.1 V Å <sup>-1</sup>	1.4	8.0	5.3
	0.15 V Å <sup>-1</sup>	1.9	10.8	3.3
EC-DMC-DEC-ETEFC	<b>0.2 V Å<sup>-1</sup></b>	<b>1.9</b>	<b>11.3</b>	<b>2.7(1.6<sup>b</sup>)</b>
	0.25 V Å <sup>-1</sup>	2.4	13.6	2.1
	0.3 V Å <sup>-1</sup>	2.5	14.8	1.9
	0.1 V Å <sup>-1</sup>	1.4	8.4	5.2
	0.15 V Å <sup>-1</sup>	1.9	11.0	3.3
EC-DMC-DEC-DTFEC	<b>0.2 V Å<sup>-1</sup></b>	<b>2.0</b>	<b>11.7</b>	<b>2.6(1.4<sup>b</sup>)</b>
	0.25 V Å <sup>-1</sup>	2.4	14.1	2.1
	0.3 V Å <sup>-1</sup>	2.7	15.6	1.8

<sup>a</sup> L. Yang, B.H. Fishbine, A. Migliori, L.R. Pratt, *J.Chem.Phys.*, **132**, 044701(2010).

<sup>b</sup> the values are based on DFT calculations

The detailed application of Booth model is showed as follows.

$$\tilde{\beta} = \frac{5\mu_e}{2k_B T} (n^2 + 2) \quad (1)$$

Herein,  $\mu_e$  is molecular mean dipole moment, which is calculated by molecular dynamic for pure or mixed solvents,  $T$  is the absolute temperature,  $k_B$  is Boltzmann's constant and  $\tilde{\beta}$  as a fitting parameter for our data in this work.

$$L(x) = \coth(x) - 1/x \quad (2)$$

$$\epsilon_r = n^2 + \frac{3}{\tilde{\beta} E} [\epsilon(0) - n^2] L(\tilde{\beta} E) \quad (3)$$

where  $E$  is the magnitude of the electric field,  $\epsilon(0)$  is the zero-field dielectric constant,  $n$  is the index of refraction.

In addition,  $\mu_e$  is also determined by DFT calculations and finite field method. Thus the dielectric constant of the individual solvent,  $\epsilon_i$  can be estimated according to Booth's model. Based on the approximation of the ideal solutions, the dielectric constant of the mixture,  $\epsilon$ , depends on each  $\epsilon_i$ .

$$\varepsilon = \frac{\sum_i^n \varepsilon_i x_i v_i}{\sum_i^n x_i v_i} \quad (4)$$

$v_i$  is the molar volumes and  $x_i$  is the molar fractions.