Supporting Information

Computational Investigation of Perfluorcarbonates as Multi-Functional Diluents in Localized High Concentration Electrolytes for Lithium Metal Batteries: Insights from MD and DFT Simulations

Zhuijun Xu[1], Tianle Zheng[1], Ying Yu[2], Yaozong Gu[3], Yinghui Li[3, 4], Jie Gao[3], Siqi Shi[4], Yonggao Xia[3, 5*], Ya-Jun Cheng[2, 3*], Peter Müller-Buschbaum[1*]

1. Technical University of Munich, TUM School of Natural Sciences, Department of Physics, Chair for Functional Materials, Garching, 85748, Germany

2. College of Renewable Energy, Hohai University, 1915 Hohai Ave, Jintan District, Changzhou, Jiangsu, 213200, P. R. China

3. Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang, 315201, P. R. China

4. School of Materials Science and Engineering, Shanghai University, Shanghai, 200444, P. R. China

5. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Shijingshan District, Beijing 100049, P. R. China

Email address: xiayg@nimte.ac.cn, chengyajun@hhu.edu.cn, muellerb@ph.tum.de

Table S1. Type and quantity of non-solvating solvents, along with their corresponding dielectric constants, for seven types of LHCE systems in the final frame of the MD simulation.

No.	FEC	DFEC	DFEC1	DFEC2	tri-FEC	tetra-FEC	TTE	1,2-DME	Dielectric constant
1	152	0	0	0	0	0	0	14	72.93
2	0	136	0	0	0	0	0	12	26.51
3	0	0	154	0	0	0	0	16	31.24
4	0	0	0	157	0	0	0	4	10.12
5	0	0	0	0	158	0	0	10	8.76
6	0	0	0	0	0	142	0	10	2.62
7	0	0	0	0		0	100	11	6.42

No.1-7 are LiFSI/1,2-DME/FEC, LiFSI/1,2-DME/DFEC, LiFSI/1,2-DME/DFEC1, LiFSI/1,2-DME/DFEC2, LiFSI/1,2-DME/Tri-FEC, LiFSI/1,2-DME/Tetra-FEC, LiFSI/1,2-DME/TTE, respectively.

In each LHCE system, the amount of 1,2-DME not involved in the solvation is relatively small compared to that of each diluent.
Therefore, for the calculation of HOMO/LUMO of Li^+ solvation structures, free anions, and solvent molecules in the seven types of LHCE systems (**Figure 6c-d**), an implicit solvation model was used, and the dielectric constant of the mixed solvent was determined via a linear combination of the dielectric constants presented in **Figure 1d**.[1]

Table S2. Distance of Ni-O bond (In FEC and its derivatives, the O refers to the carbonyl oxygen in FEC and its derivatives).

FEC	DFEC	DFEC1	DFEC2	tri-FEC	tetra-FEC	TTE
2.551 Å	2.730 Å	2.605 Å	2.795Å	2.859 Å	2.864 Å	3.466 Å

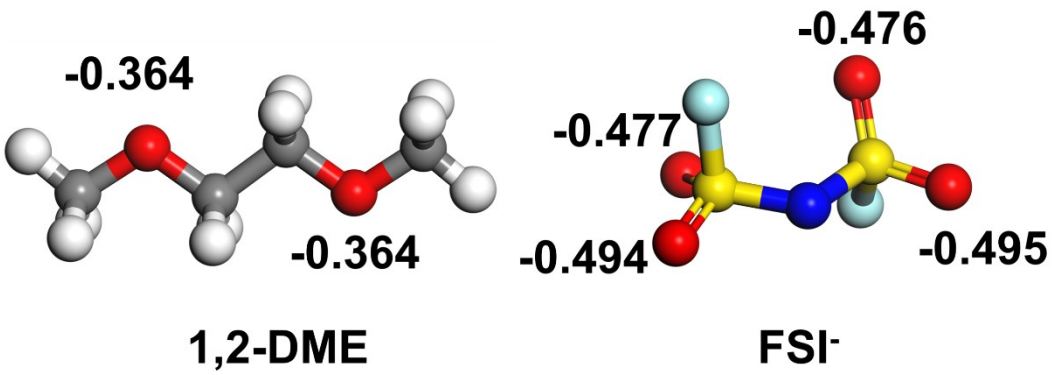

Figure S1 Charge distribution on oxygen atoms of 1,2-DME and FSI- anions without considering the solvation model.

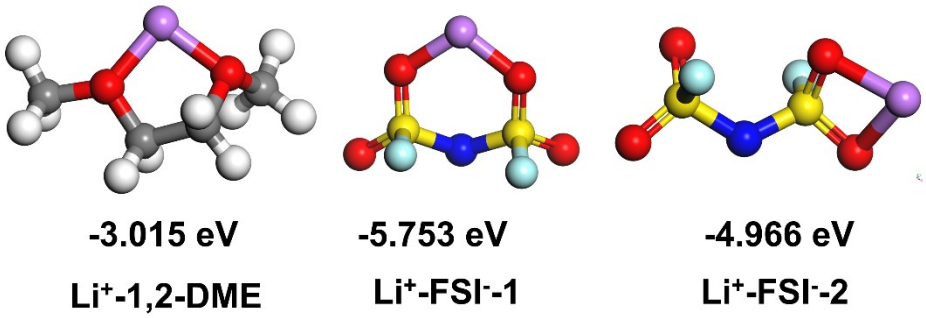

Figure S2 Binding energies between solvent/anion (1,2-DME, FSI^-) and Li^+.

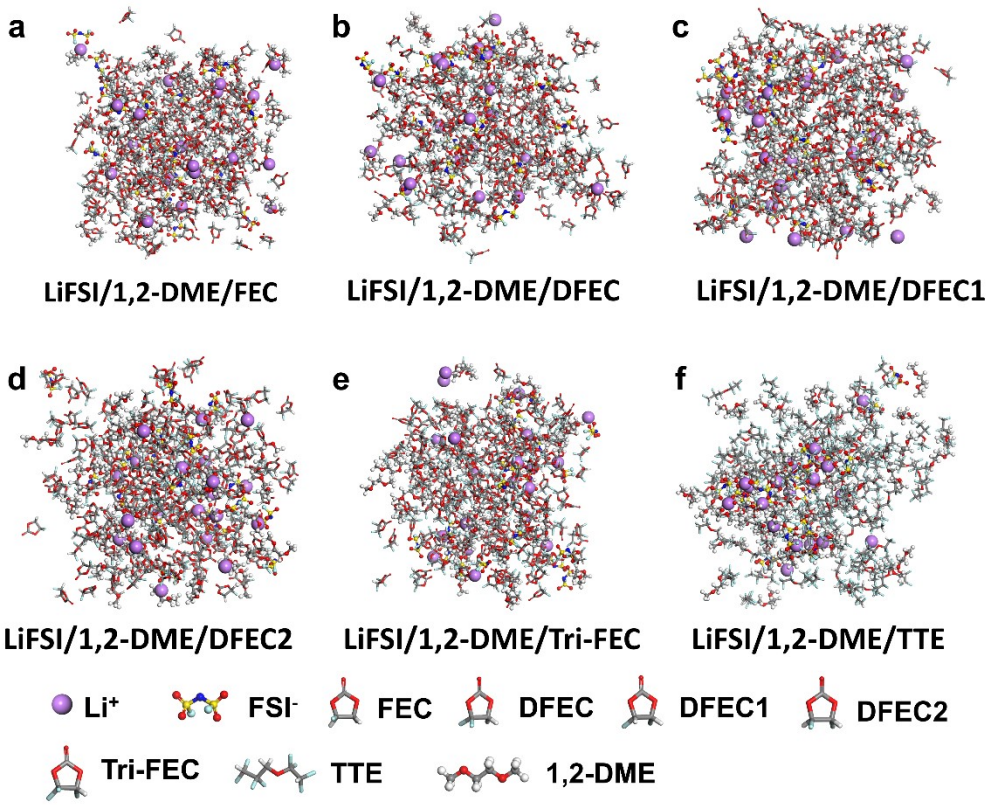

Figure S3 a-b) Snapshots of different LHCE systems of LiFSI/1,2-DME/FEC, LiFSI/1,2-DME/DFEC, LiFSI/1,2-DME/DFEC1, LiFSI/1,2-DME/DFEC2, LiFSI/1,2-DME/Tri-FEC, LiFSI/1,2-DME/Tetra-FEC, LiFSI/1,2-DME/TTE.

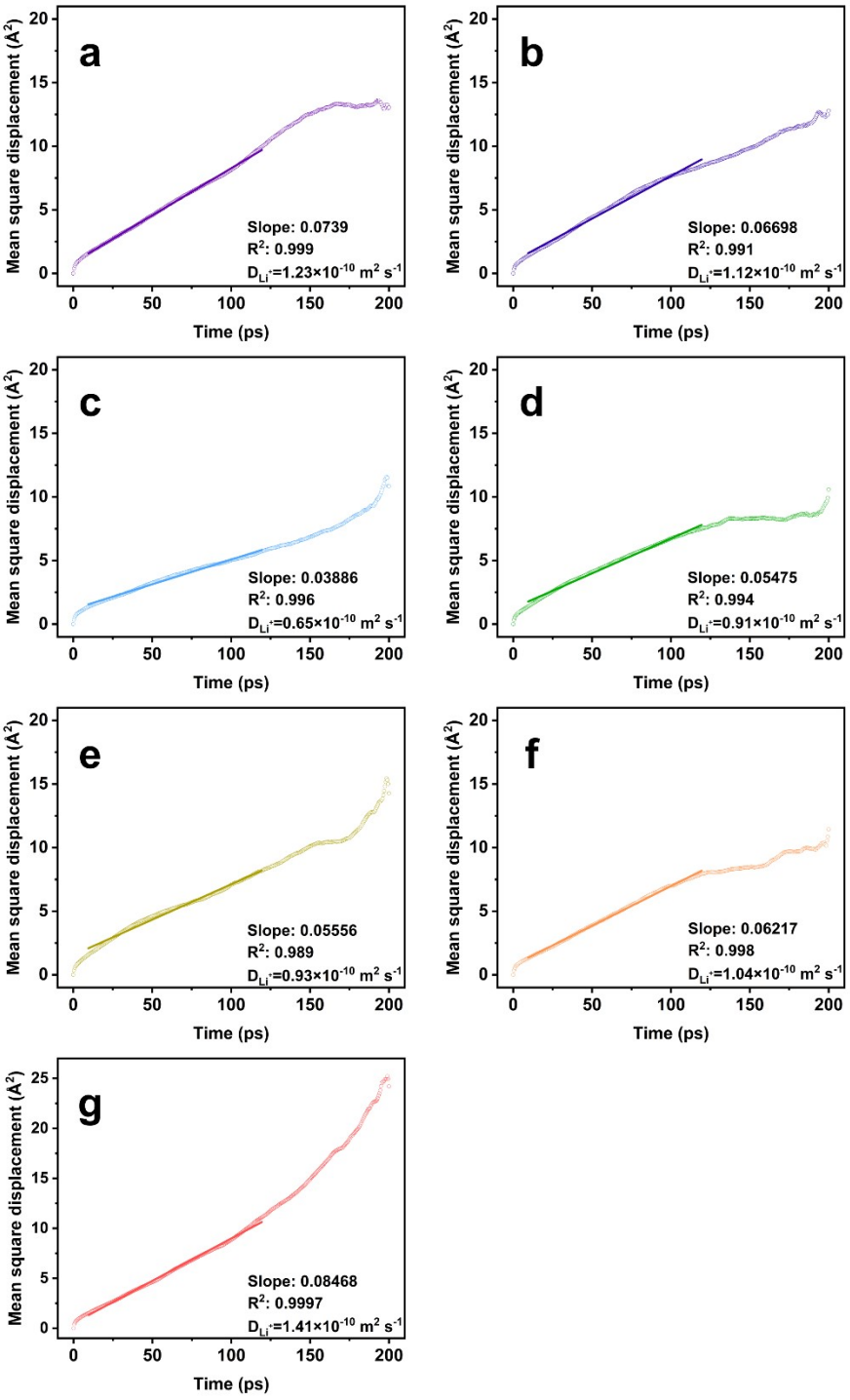

Figure S4 a-b) Li^+ mean square displacement curves and corresponding fits of LiFSI/1,2-DME/ FEC, LiFSI/1,2-DME/ DEFC, LiFSI/1,2-DME/ DEFC1, LiFSI/1,2-DME/DEFC2, LiFSI/1,2-DME/Tri-FEC, LiFSI/1,2-DME/Tetra-FEC, LiFSI/1,2-DME/TTE at 298 K.

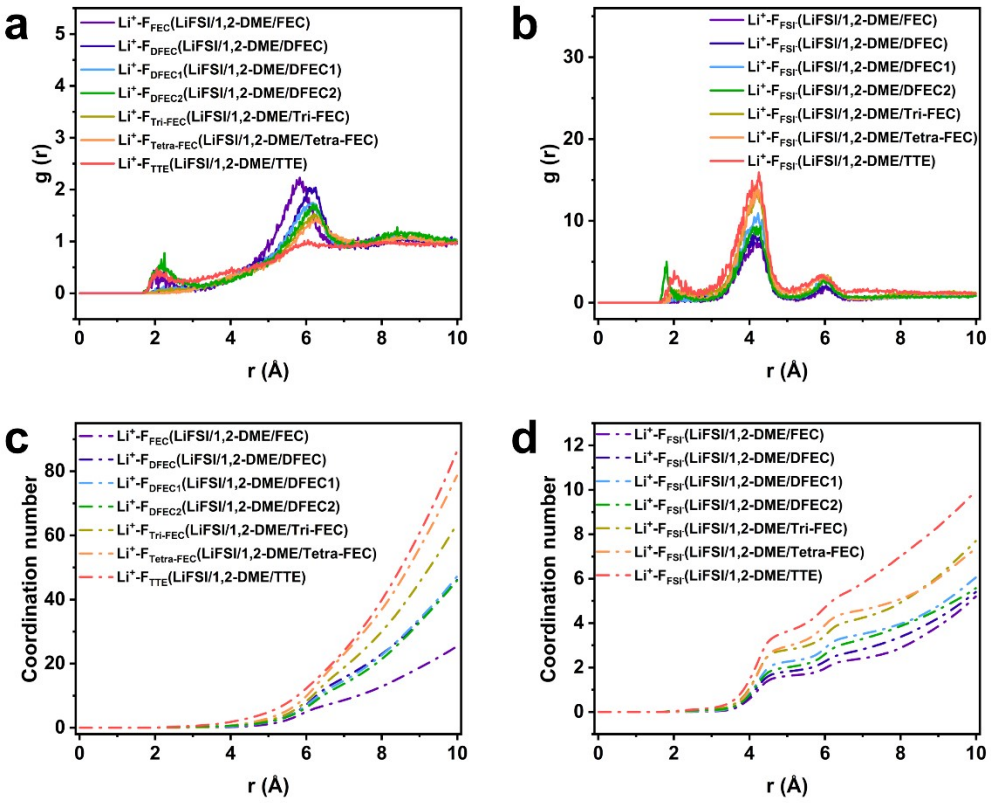

Figure S5 a-b) Radial distribution function of Li^+-$F_{diluents,}$ Li^+-F_{FSI}^- of LiFSI/1,2-DME/FEC, LiFSI/1,2-DME/ DEFC, LiFSI/1,2-DME/ DEFC1, LiFSI/1,2-DME/DEFC2, LiFSI/1,2-DME/Tri-FEC, LiFSI/1,2-DME/Tetra-FEC, LiFSI/1,2-DME/TTE at 298 K; d-f) corresponding coordination number around Li^+ in all the LHCE systems.

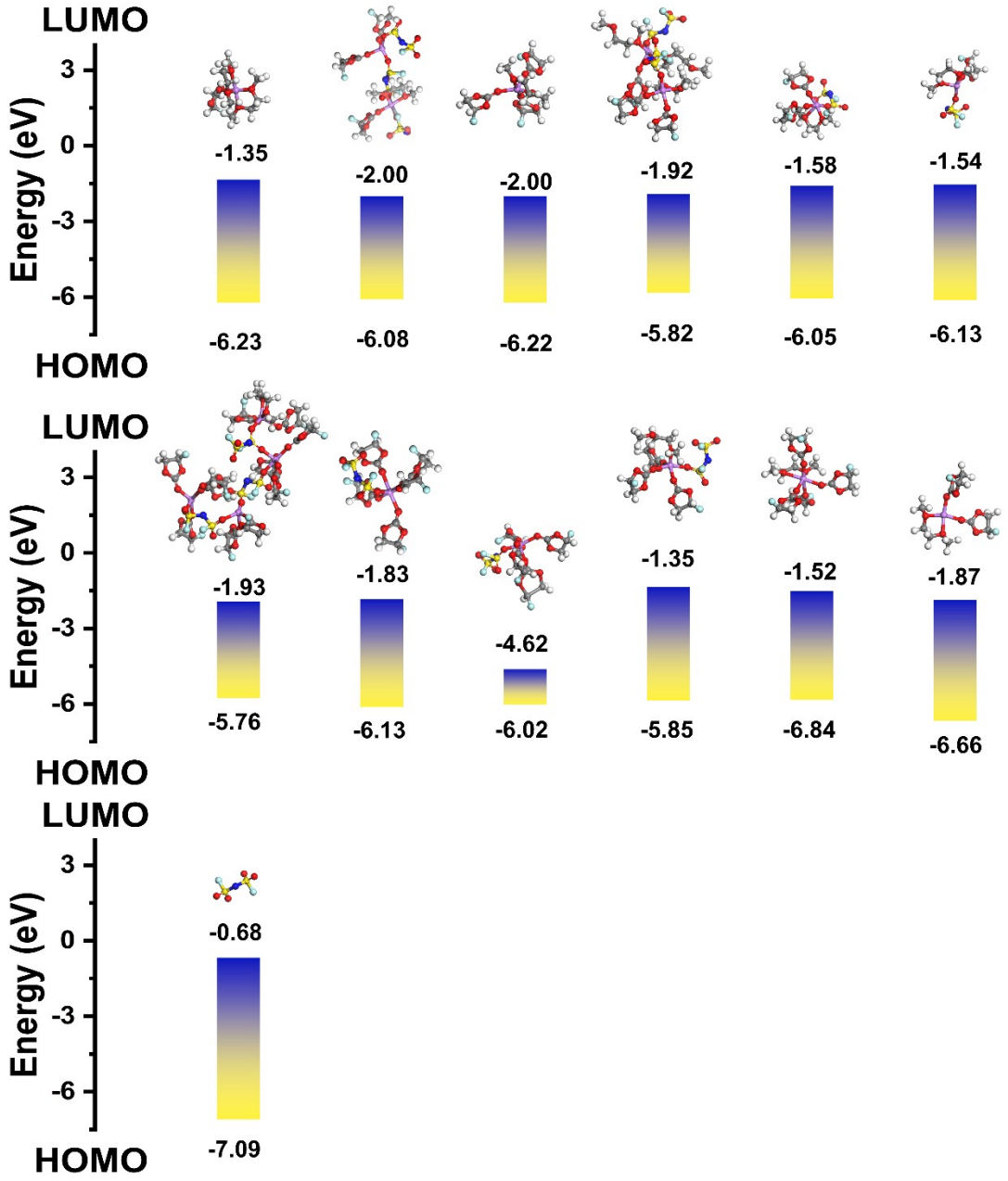

Figure S6 LUMO and HOMO levels of the Li clusters in the last frame in the LiFSI/1,2-DME/ FEC LHCE system.

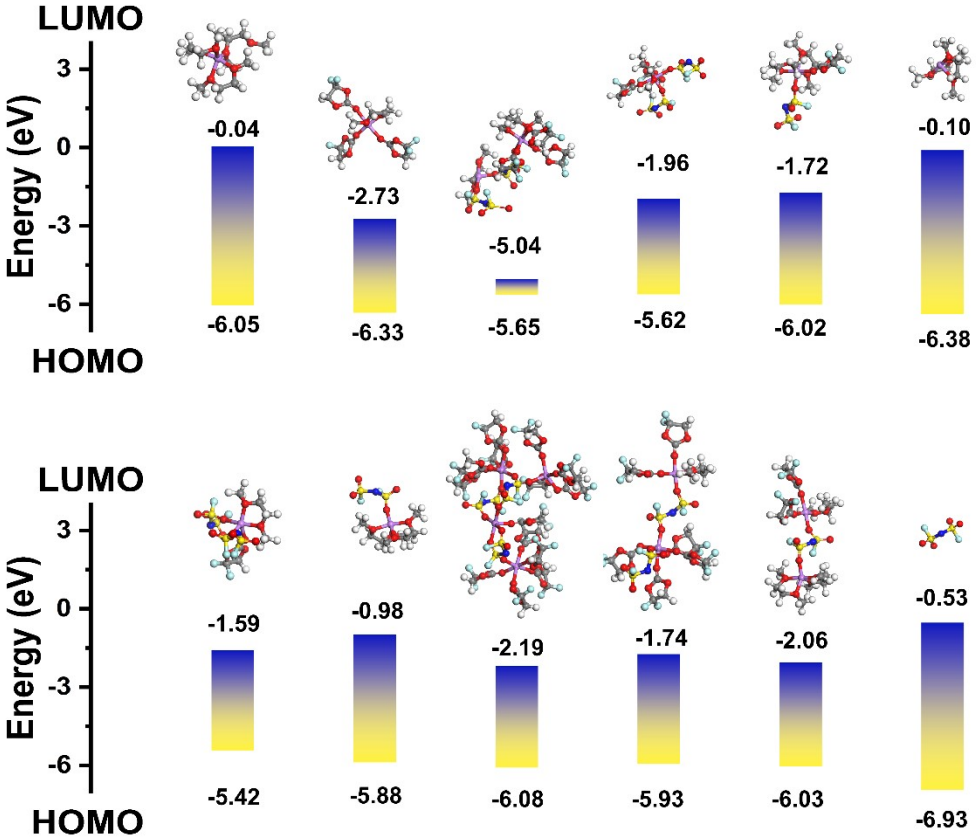

Figure S7 LUMO and HOMO levels of the Li clusters in the last frame in the LiFSI/1,2-DME/ DFEC LHCE system.

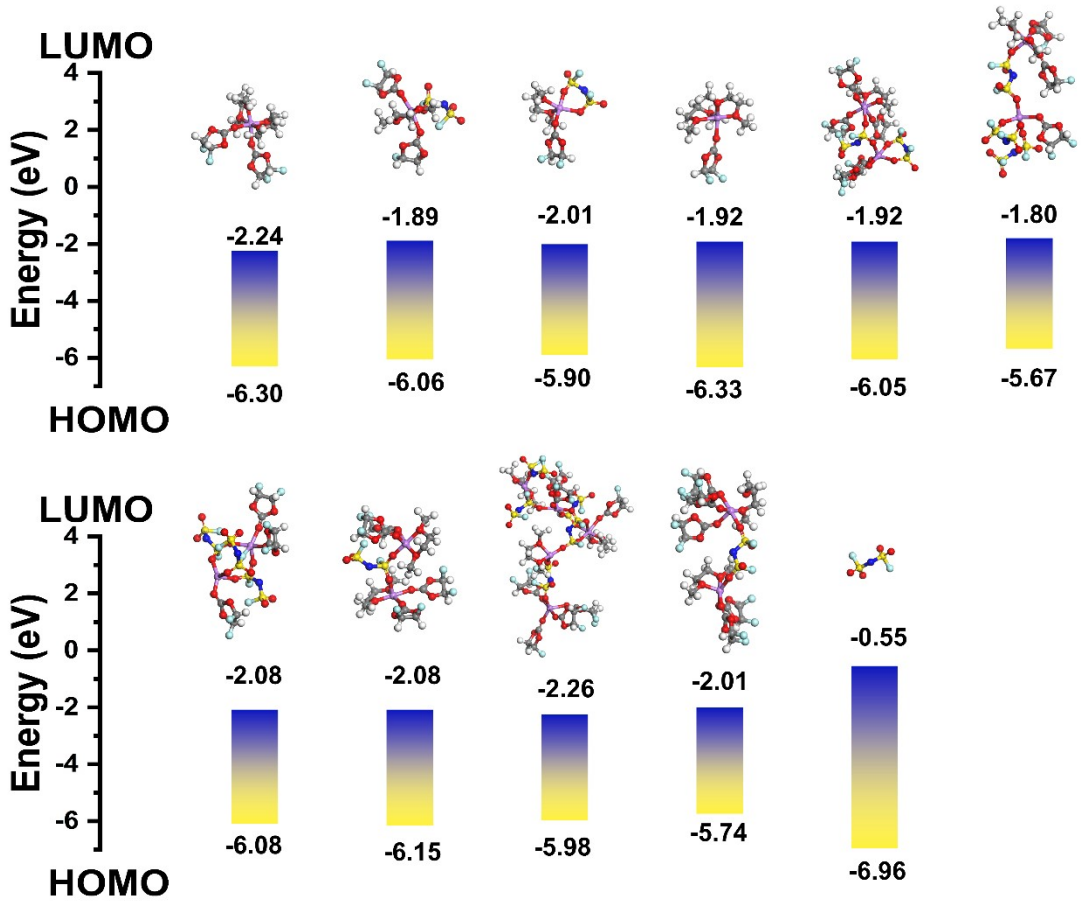

Figure S8 LUMO and HOMO of the Li clusters in the last frame in the LiFSI/1,2-DME/ DFEC1 LHCE system.

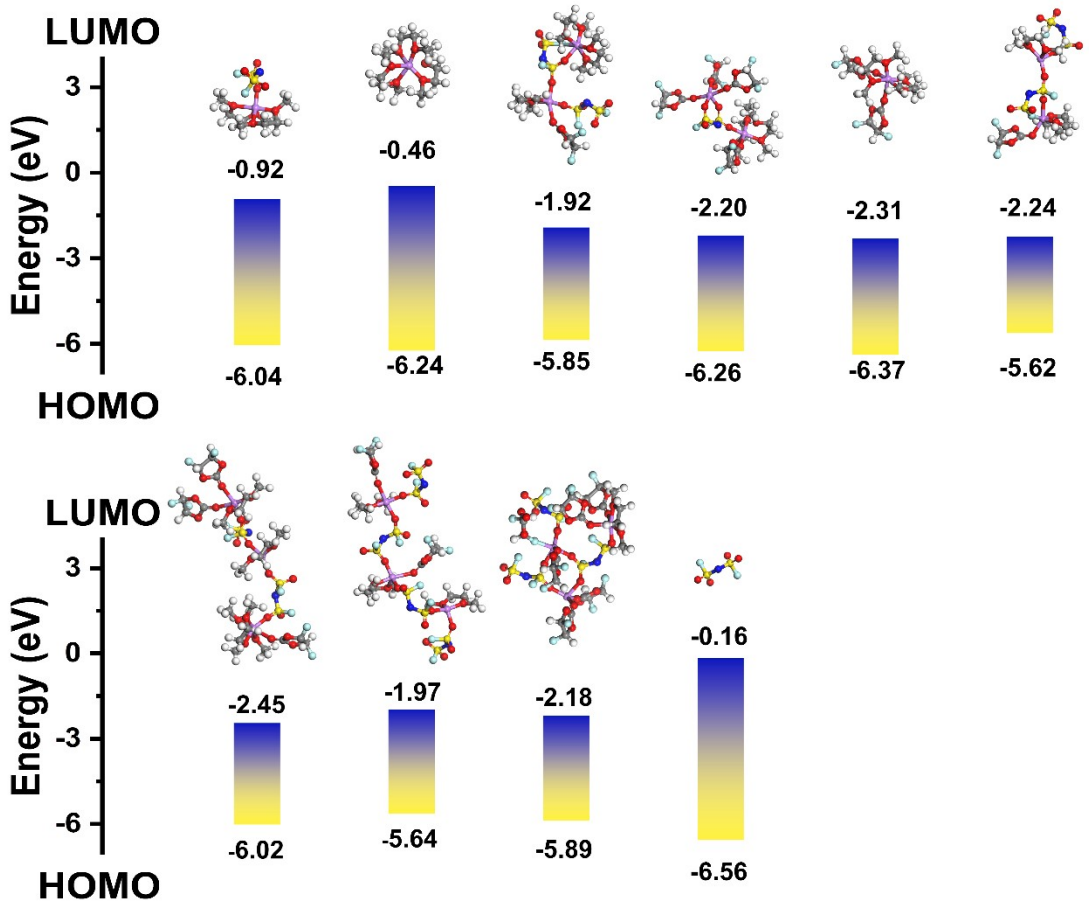

Figure S9 LUMO and HOMO levels of the Li clusters in the last frame in the LiFSI/1,2-DME/ DFEC2 LHCE system.

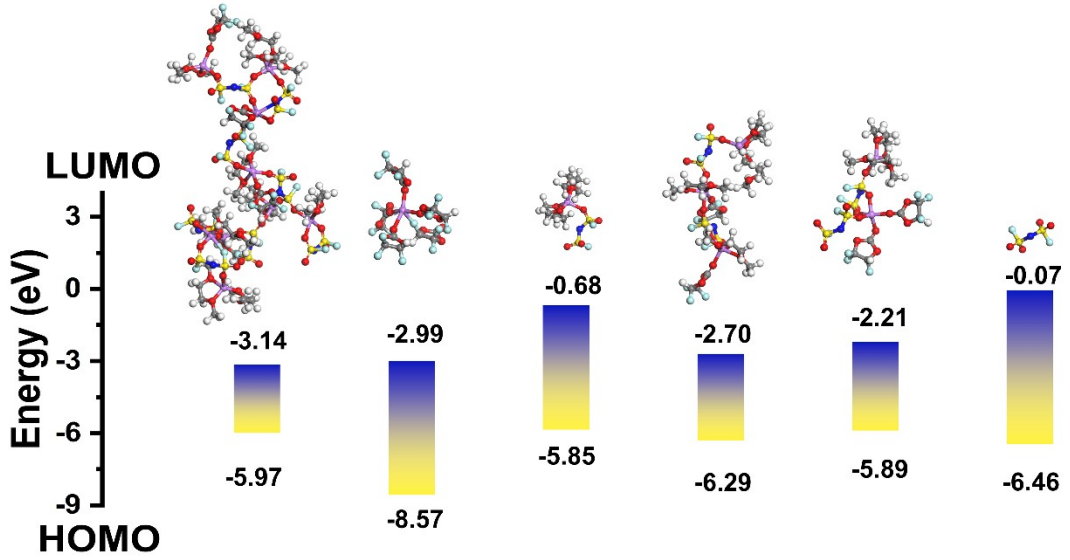

Figure S10 LUMO and HOMO levels of the Li clusters in the last frame in the LiFSI/1,2-DME/ Tri-FEC LHCE system.

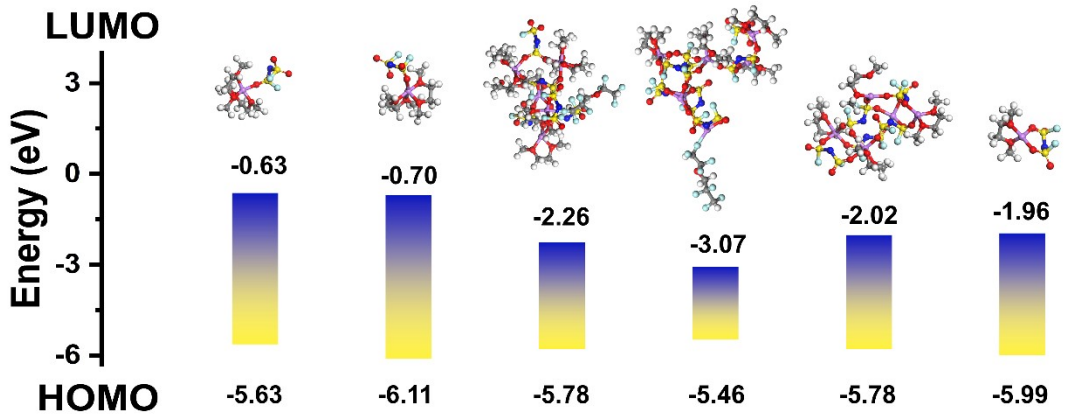

Figure S11 LUMO and HOMO levels of the Li clusters in the last frame in the LiFSI/1,2-DME/ TTE LHCE system.

1. N. Yao, X. Chen, X. Shen, R. Zhang, Z. H. Fu, X. X. Ma, X. Q. Zhang, B. Q. Li and Q. Zhang, *Angew. Chem. Int. Ed.*, 2021, **60**, 21473-21478.