Molecular Dynamics Study of Tetraglyme Solutions of Two Lithium Salts with Isomeric Anions: LiTFSI and LiFPFSI

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Motivation

- Rechargeable lithium-ion batteries have become very successful devices (Nobel Prize in chemistry 2019!)
- A significant effort is invested in research on metal-ion batteries

- Ion conducting electrolyte is an important component of the device
- Search for new, safer and environment-friendly electrolytes continues

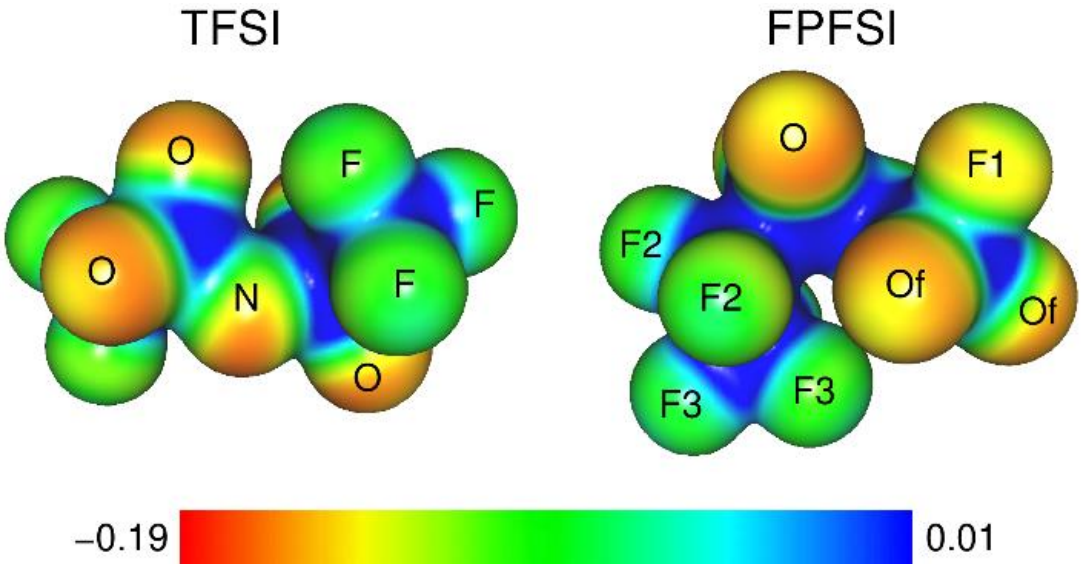
Weakly coordinating anions

- In commercial Li-ion batteries, $LiPF_6$ in organic carbonates is commonly used as an electrolyte
- Several promising salts are investigated experimentally, e.g. salts with weakly coordinating anions, such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)
- Some asymmetric perfluorinated sulfonimide anions were used in experiments, including the TFSI isomer, (fluorosulfonyl)(pentafluoroethanesulfonyl)imide (FPFSI)
- Recently, we performed quantum-chemical calculations and ab initio molecular dynamics simulations of LiTFSI and LiFPFSI.*

* P. Kubisiak, D. Narkevičius, C. Nicotri, A. Eilmes, Comparative Study of Isomeric TFSI and FPFSI Anions in Li-Ion Electrolytes Using Quantum Chemistry and Ab Initio Molecular Dynamics, *J. Phys. Chem. B* **2025**, *129*, 2560.

Weakly coordinating anions

- Recently, we performed quantum-chemical calculations and ab initio molecular dynamics simulations of LiTFSI and LiFPFSI.*
- Results indicated somewhat weaker Li^+ binding to FPFSI anion
- Nevertheless, long classical MD simulations are needed to study transport properties: diffusion coefficients, conductivity, ion transference numbers



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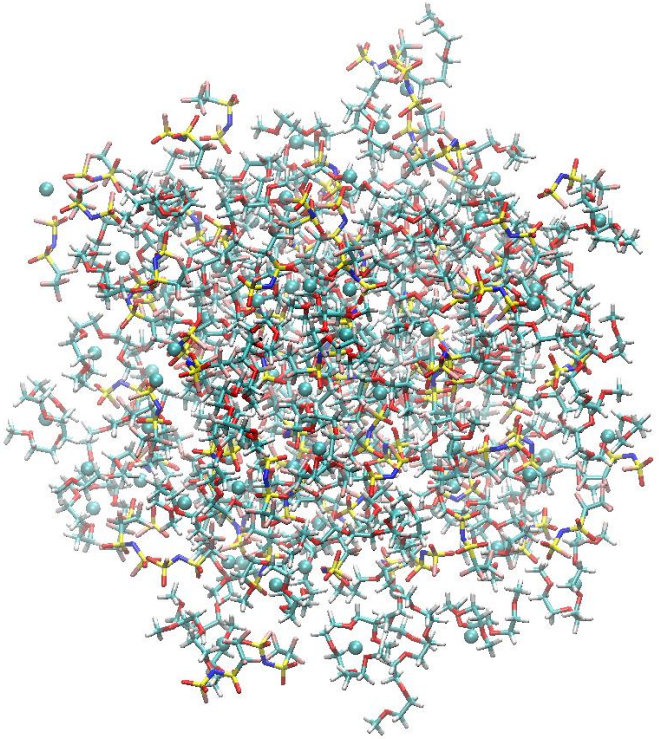
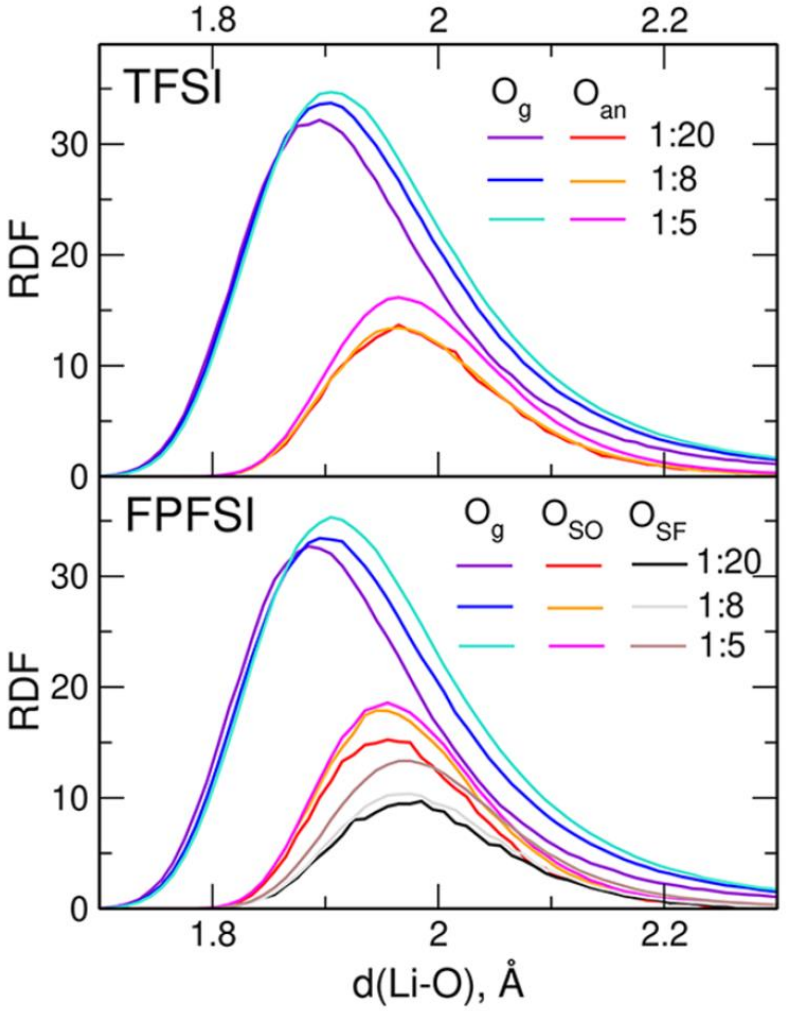
MD simulations

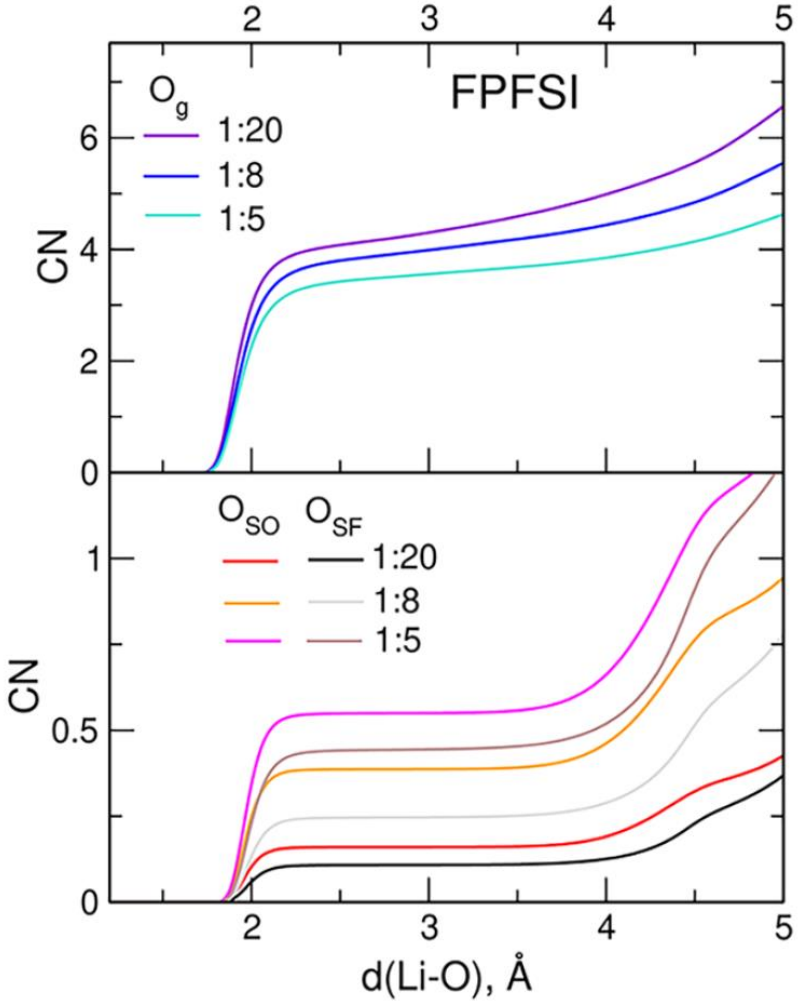
- classical molecular dynamics for LiTFSI/LiFPFSI in tetraglyme (G4)
- Li:O_g ratios 1:20, 1:8 and 1:5
- NAMD v 2.14 used
- polarizable force field



- 400 or 450 ns of trajectories collected in the NVT ensemble at T = 303 K (5 or 10 replicas)
- calculations consumed about 600 k CPU hours on Ares

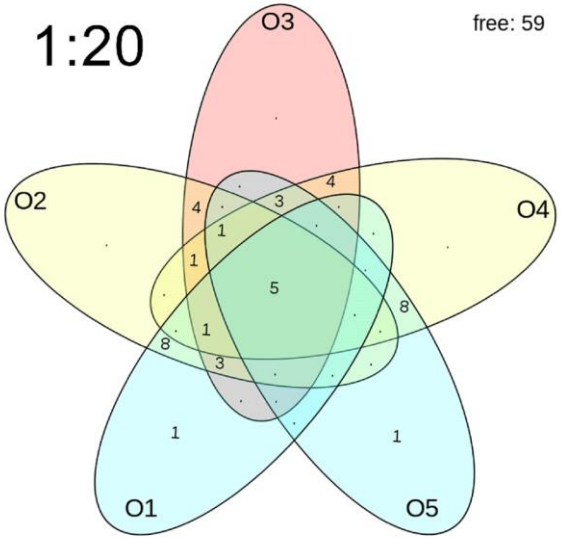
Radial Distribution Functions and coordination

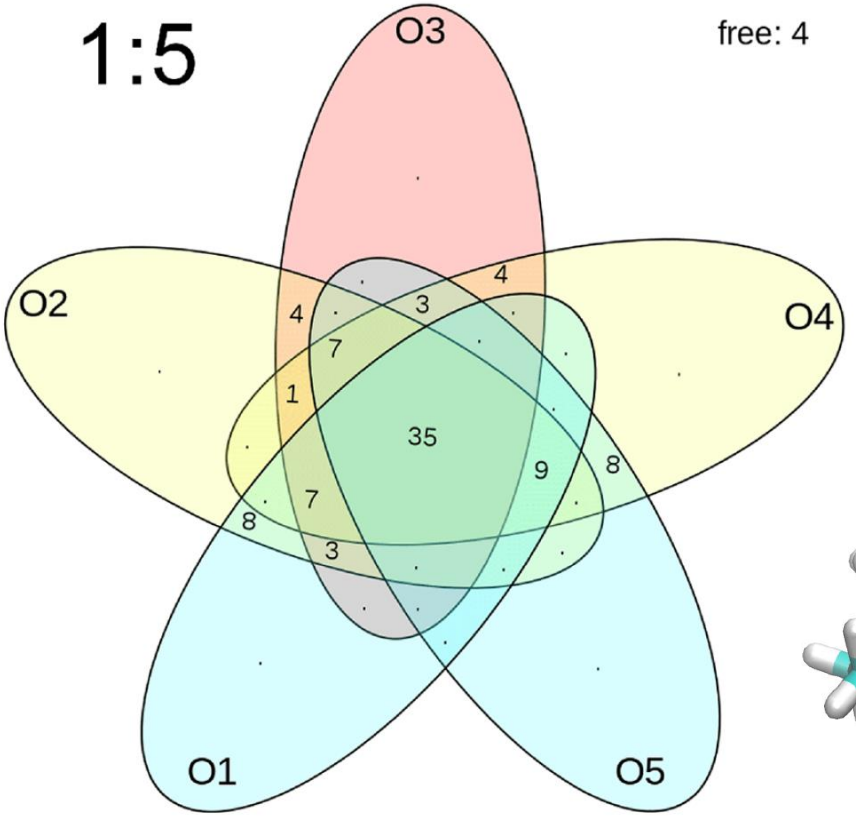


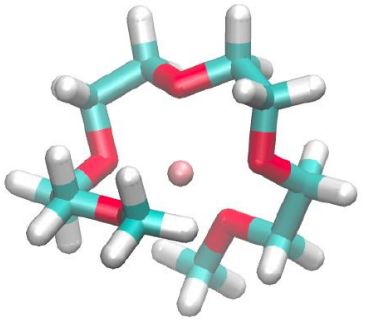


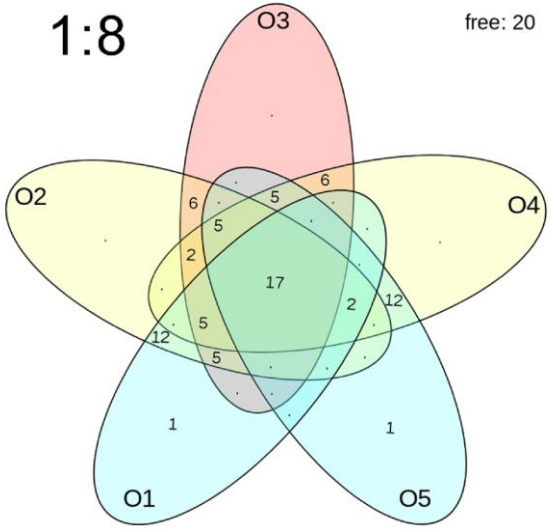
No significant differences between anions. Li^+ cations are predominantly coordinated to solvent molecules

Li^+ - tetraglyme coordination patterns







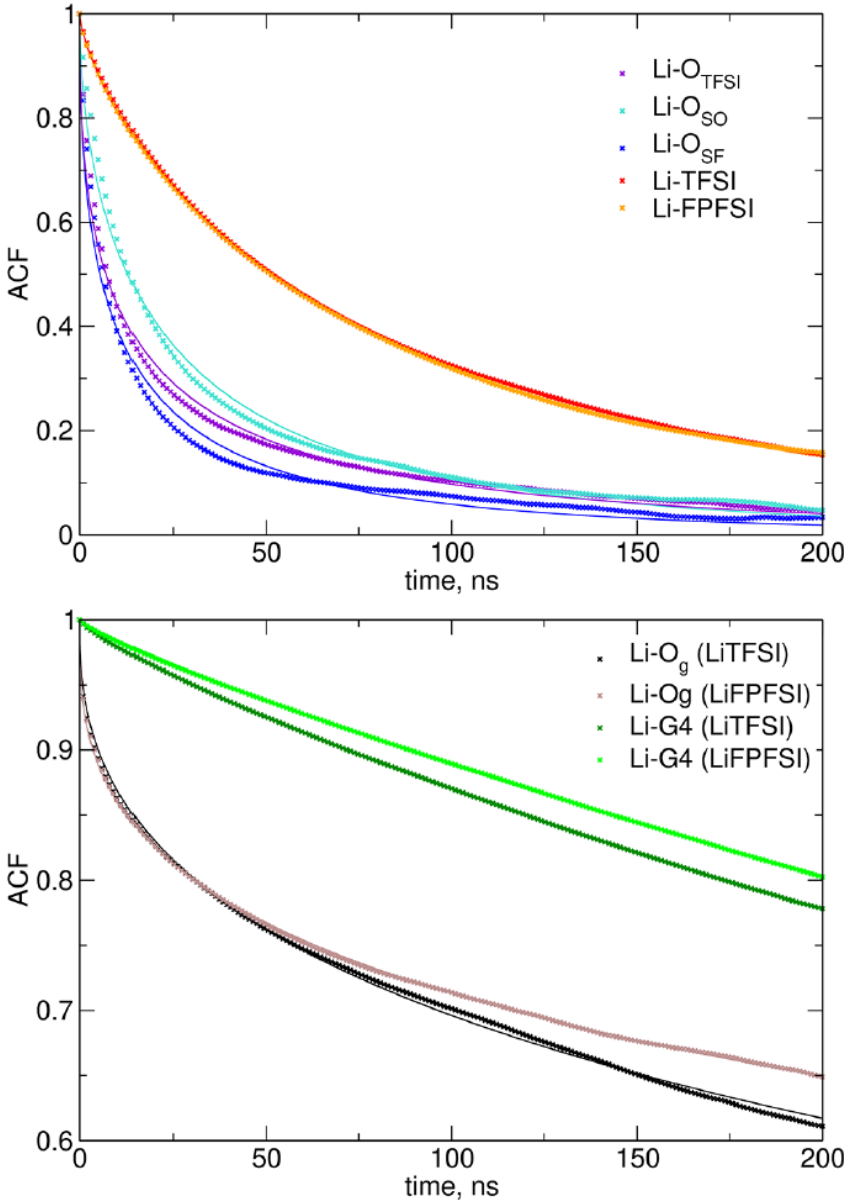


LiTFSI

At the equimolar electrolyte composition there are no free solvent molecules.

$[Li(G4)]^+$ solvates are formed.

Autocorrelation functions of Li-O interactions



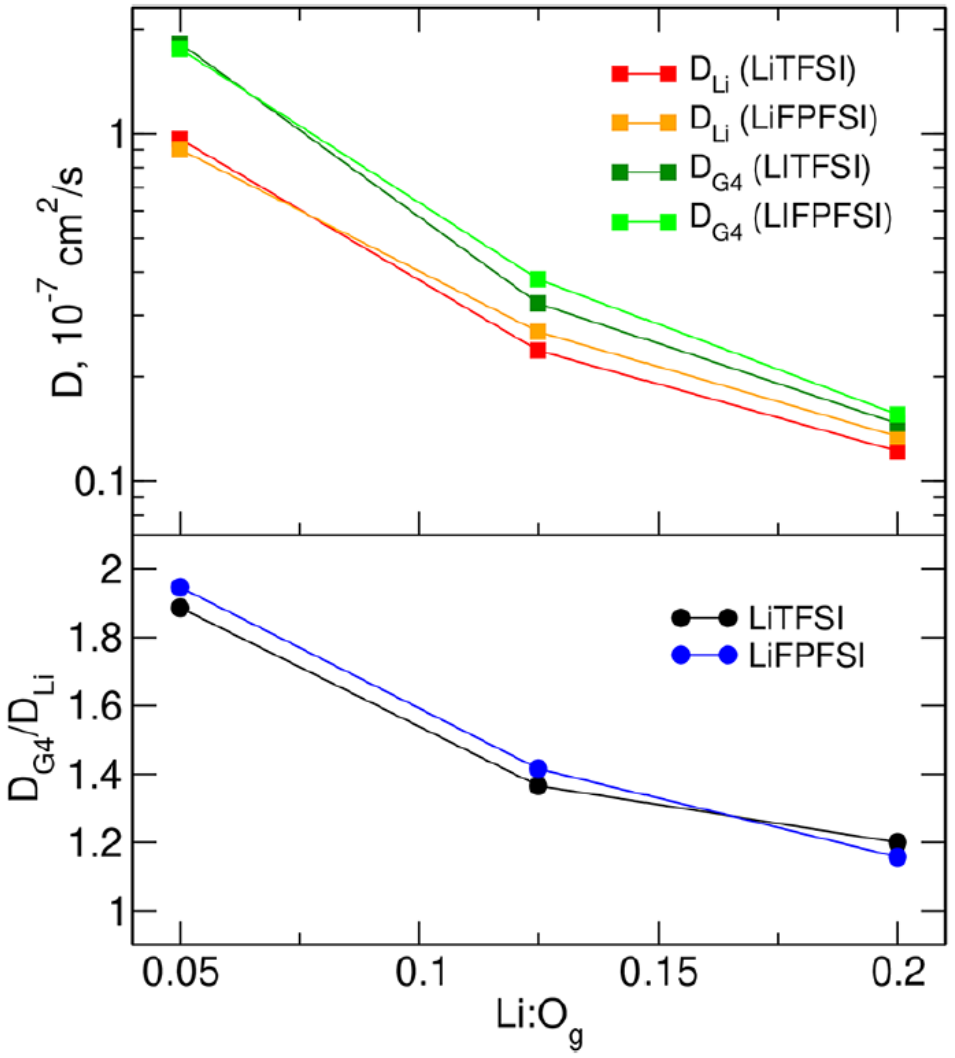
$$C_{\mathrm{Li-O}}(t) = \frac{\langle H_{ij}(t) H_{ij}(0) \rangle}{\langle H_{ij}(0) H_{ij}(0) \rangle}$$

Long-living $[Li(G4)]^+$ solvates (residence time of the order of μs).

At 1:5 Li:O_g ratio, the electrolyte becomes a solvate ionic liquid.

Solvates more stable in LiFPFSI solutions.

Diffusion coefficients



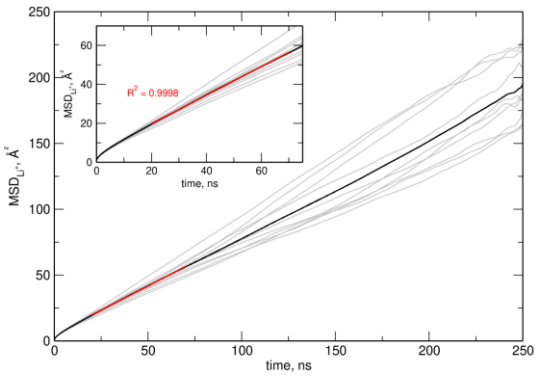
$$D_i = \lim_{t\to\infty} \frac{1}{6t}\langle[\mathbf{R}_i(t) - \mathbf{R}_i(0)]^2\rangle$$

D_{Li} slightly larger in LiFPFSI solutions

When salt concentration increases, the D_{G4}/D_{Li} ratio approaches 1

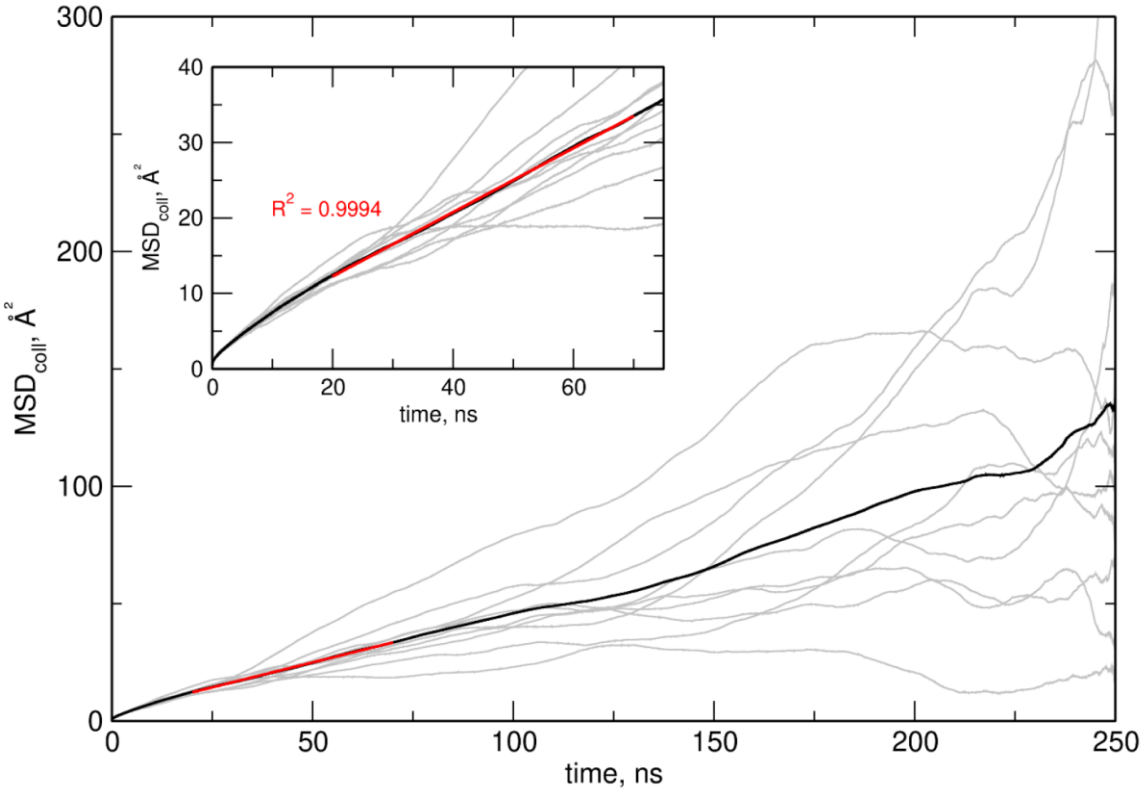
⇩

Another indication of solvate ionic liquid formation



Conductivity

$$\sigma = \lim_{t\to\infty} \frac{e^2}{6tVk_BT} \sum_{i,j} z_i z_j \langle [\mathbf{R}_i(t) - \mathbf{R}_i(0)][\mathbf{R}_j(t) - \mathbf{R}_j(0)] \rangle$$

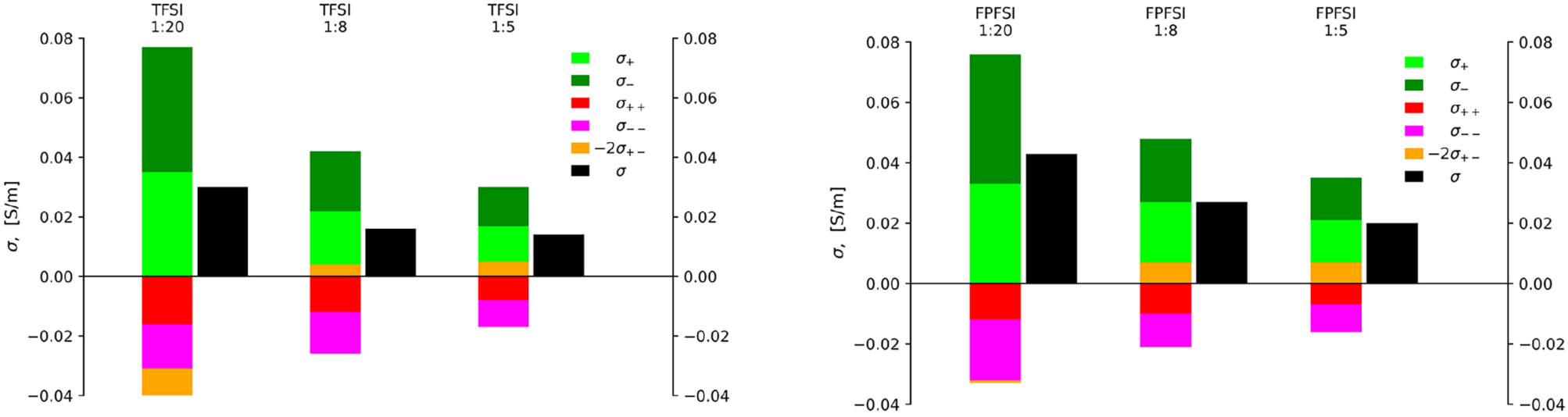


Averaging over several replicas is necessary to reliably estimate the conductivity from MD simulations

Conductivity

$$\sigma = \lim_{t\to\infty} \frac{e^2}{6tVk_BT} \sum_{i,j} z_i z_j \langle [\mathbf{R}_i(t) - \mathbf{R}_i(0)][\mathbf{R}_j(t) - \mathbf{R}_j(0)] \rangle$$

$$\sigma = \sigma_+ + \sigma_- + \sigma_{++} + \sigma_{--} - 2\sigma_{+-}$$



LiFPFSI conductivities are larger than those of LiTFSI, although diffusion coefficients are similar in both systems – effect of positive cation-anion correlations.

A counterintuitive effect: *weaker* Li-anion interactions for LiFPFSI result in *stronger* Li-anion correlations – the system is closer to a solvate ionic liquid

Conductivity

Not only the total conductivity matters. We are interested in achieving high cation transference numbers t_+.

During stationary (dis)charging of a battery only cations are transported → anion blocking conditions.

Then the transference number t_+ reads:

$$t_+^{abc} = \frac{\sigma_+ + \sigma_{++} - \frac{(\sigma_{+-})^2}{\sigma_- + \sigma_{--}}}{\sigma}$$

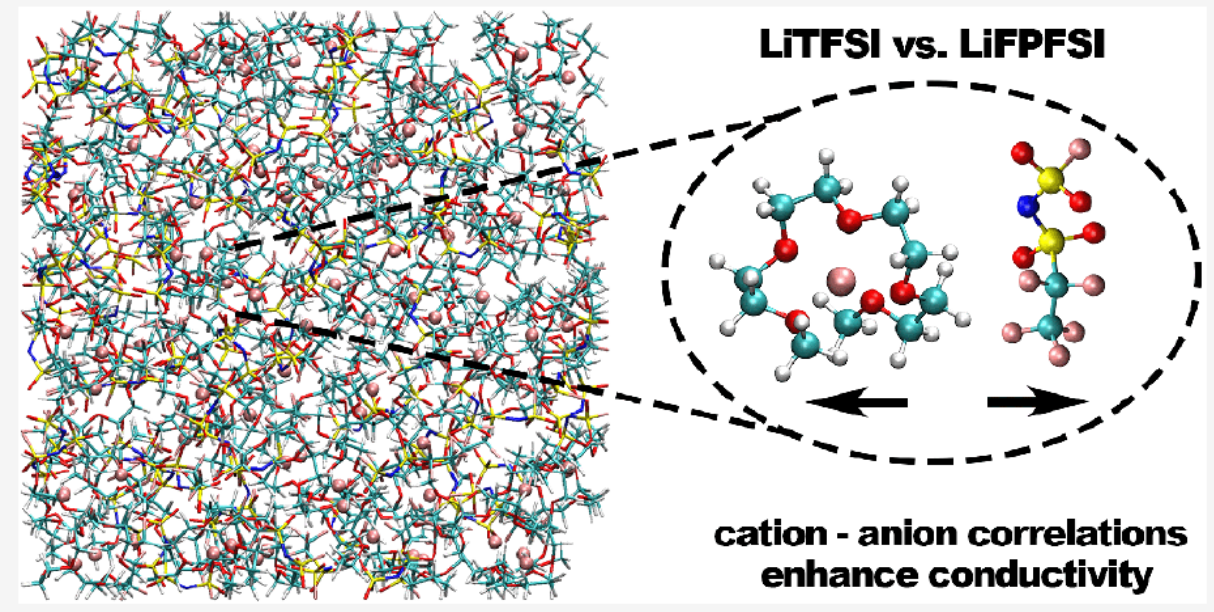
$$\sigma = \sigma_+ + \sigma_- + \sigma_{++} + \sigma_{--} - 2\sigma_{+-}$$

Cation-anion correlations in the solvate ionic liquid increase the conductivity, but also reduce the Li^+ transference number under anion blocking conditions.

With this respect LiFPFSI is not better than LiTFSI.

Conclusions

- Li-anion interactions are weaker for LiFPFSI
- Equimolar LiFPFSI solutions in tetraglyme are closer to an ionic liquid
- Ion-ion correlations largely affect conductivity and ion transport properties



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