MISPR: An Open-Source Computational Framework for Electrolyte and Electrode-Electrolyte Interfaces

IPAM Workshop 1: Embracing Stochastically in Electrochemical Modeling

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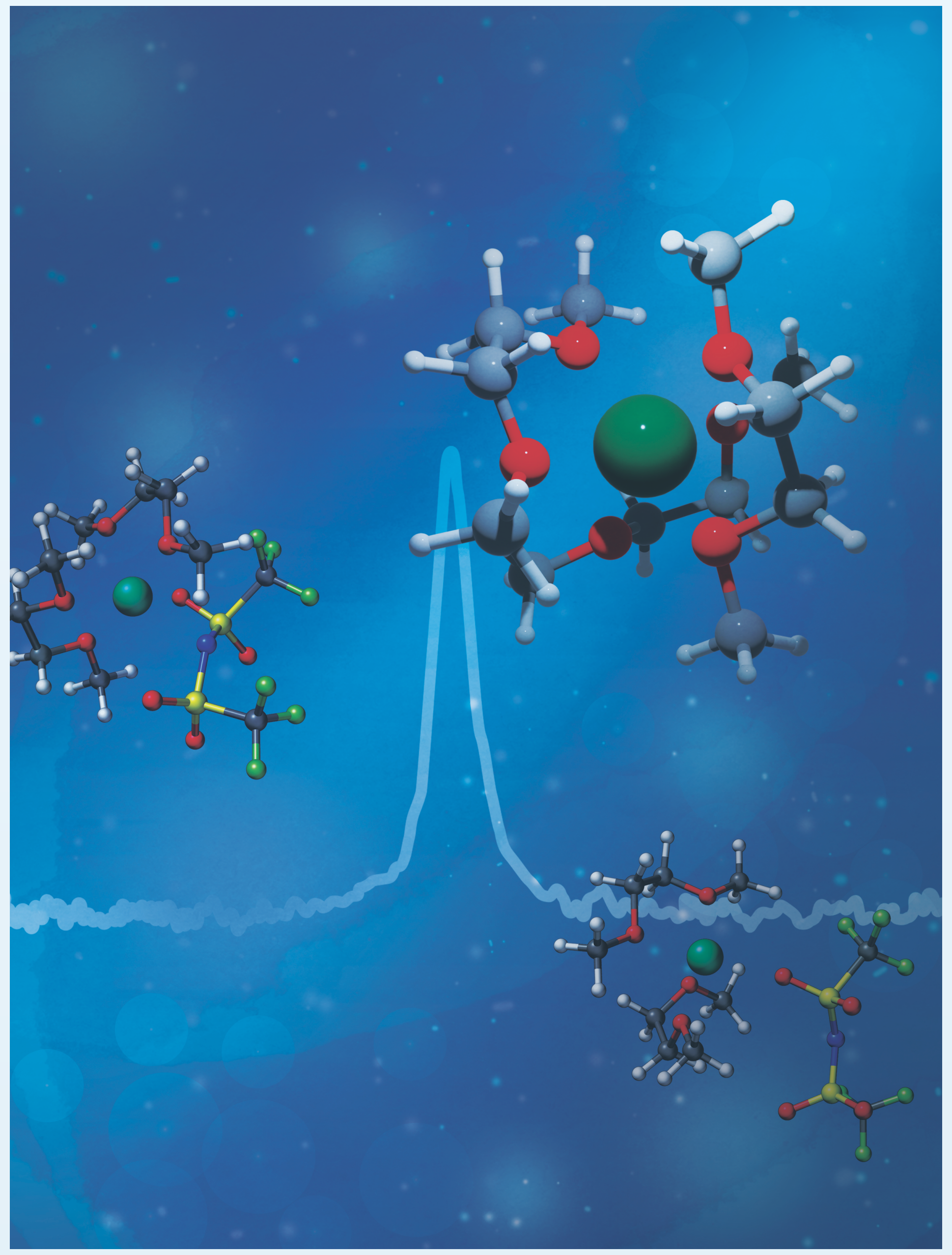
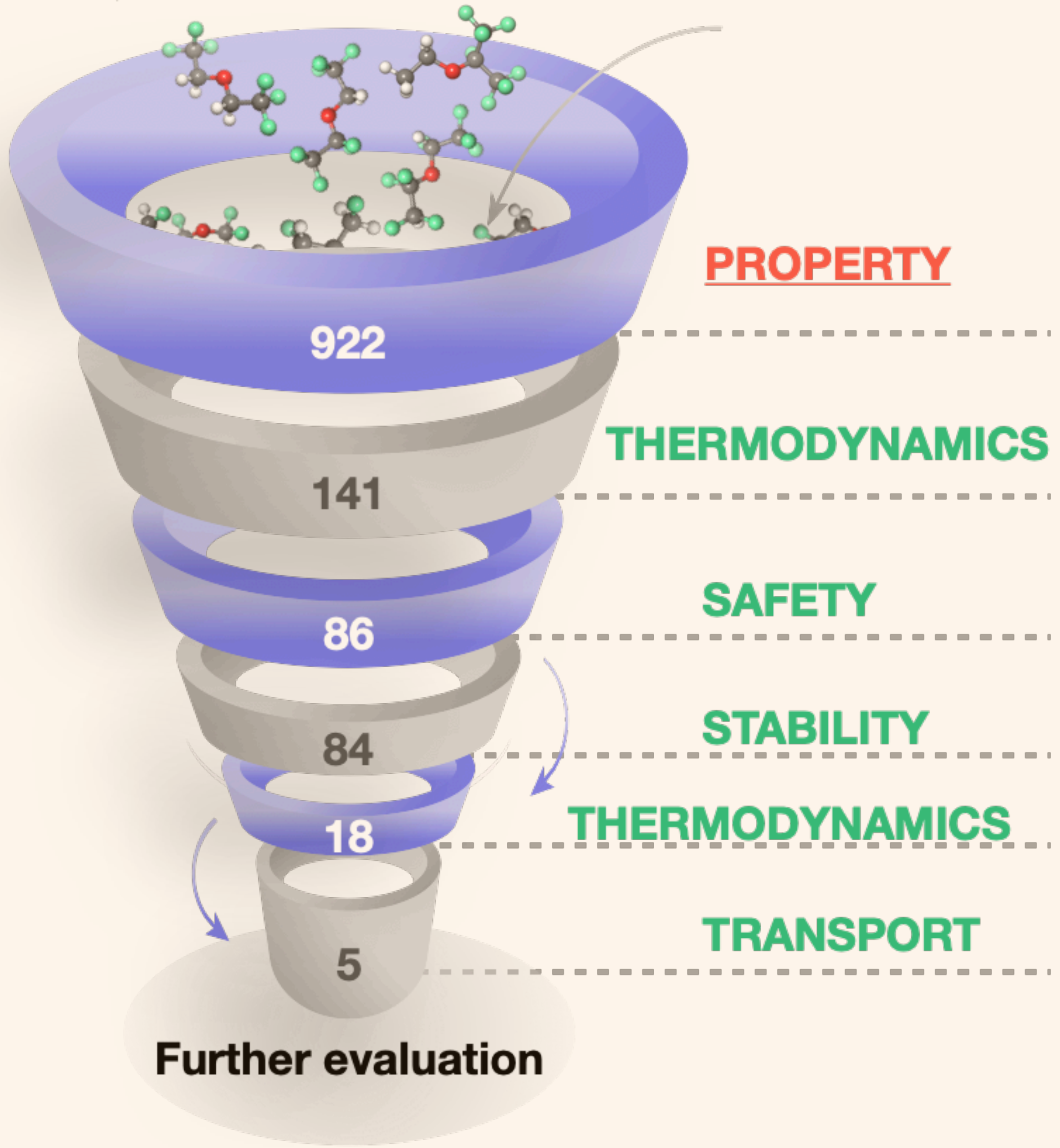
Outline

- Overview of MISPR

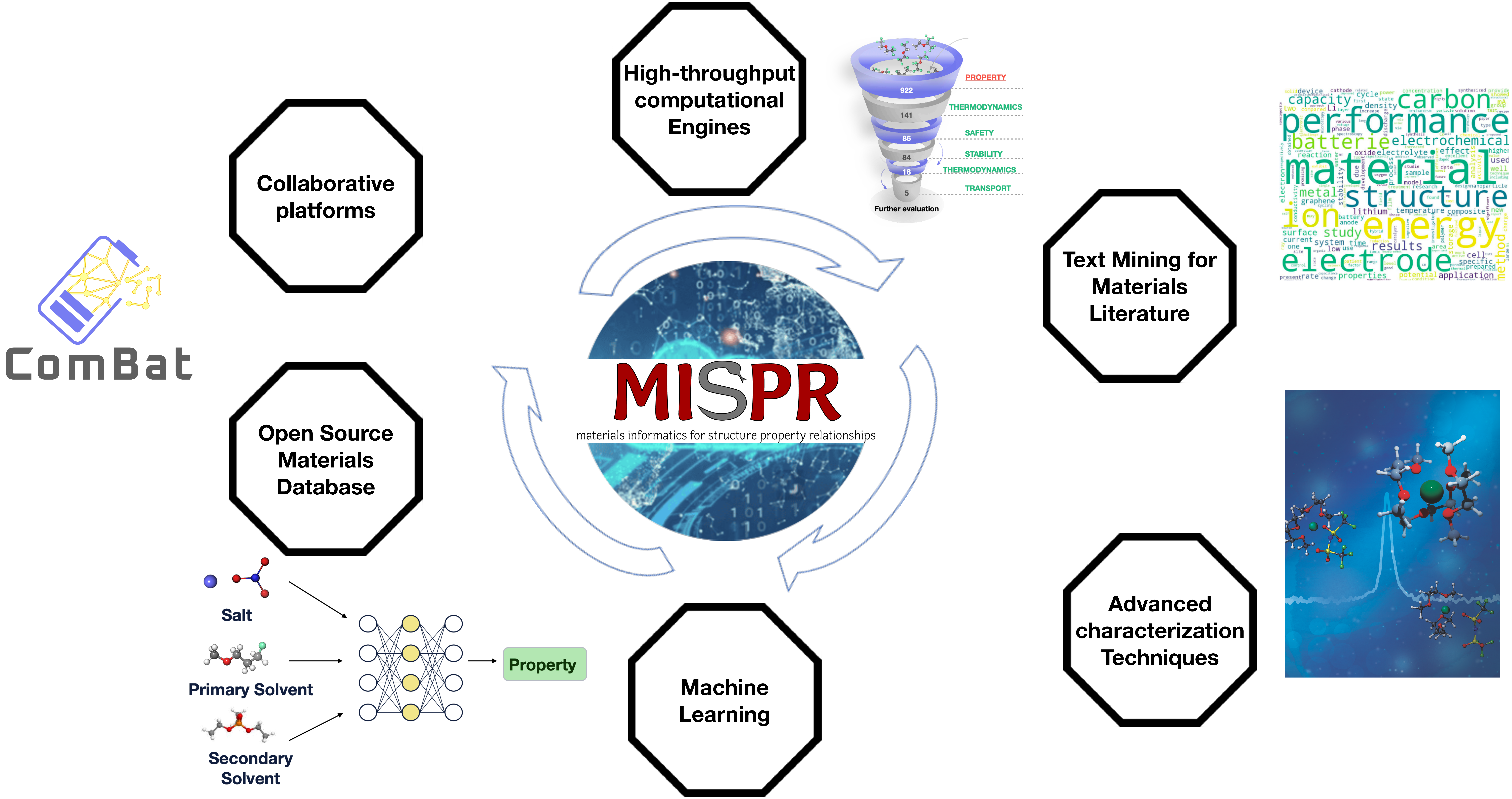
Computational Spectroscopic Analysis Tools (SAT) in MISPR



Designing optimal electrolytes for energy storage devices



Data-driven Discovery of Electrolytes



Open-Source Software for Materials Applications: What is Missing?

Persson, K.A. et al. (2013). *APL materials 1(1).*

Scheffler, M. et al. (2019). *Journal of Physics: Materials* 2(3), *036001.*

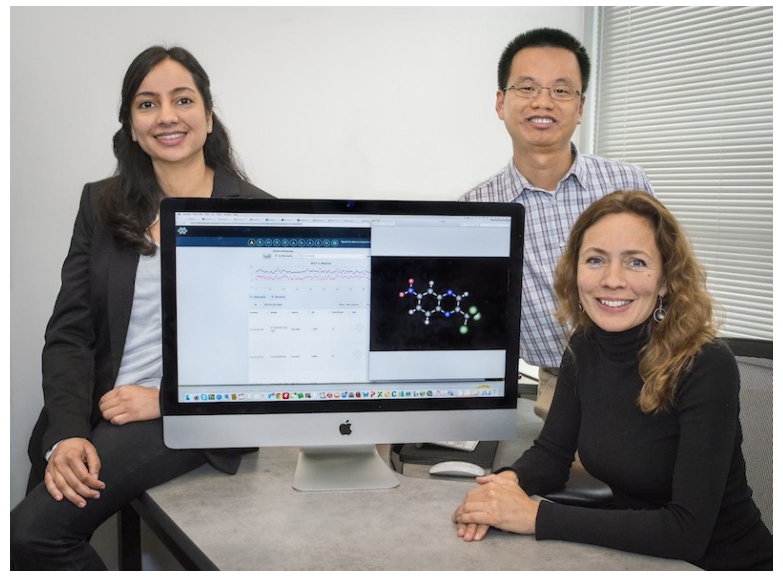
Morgan, D. et al. (2012). *Computational Materials Science, 58, 218-226.*

Choudhary, K. (2020) *npj Computational Materials, 6,173*

Wolverton, C. et al. (2013). *Jom, 65, 1501-1509.*

Jain, A. et al. (2017). *Computational Materials Science, 139, 140-152.*

Rosen, A. (2024). GitHub.

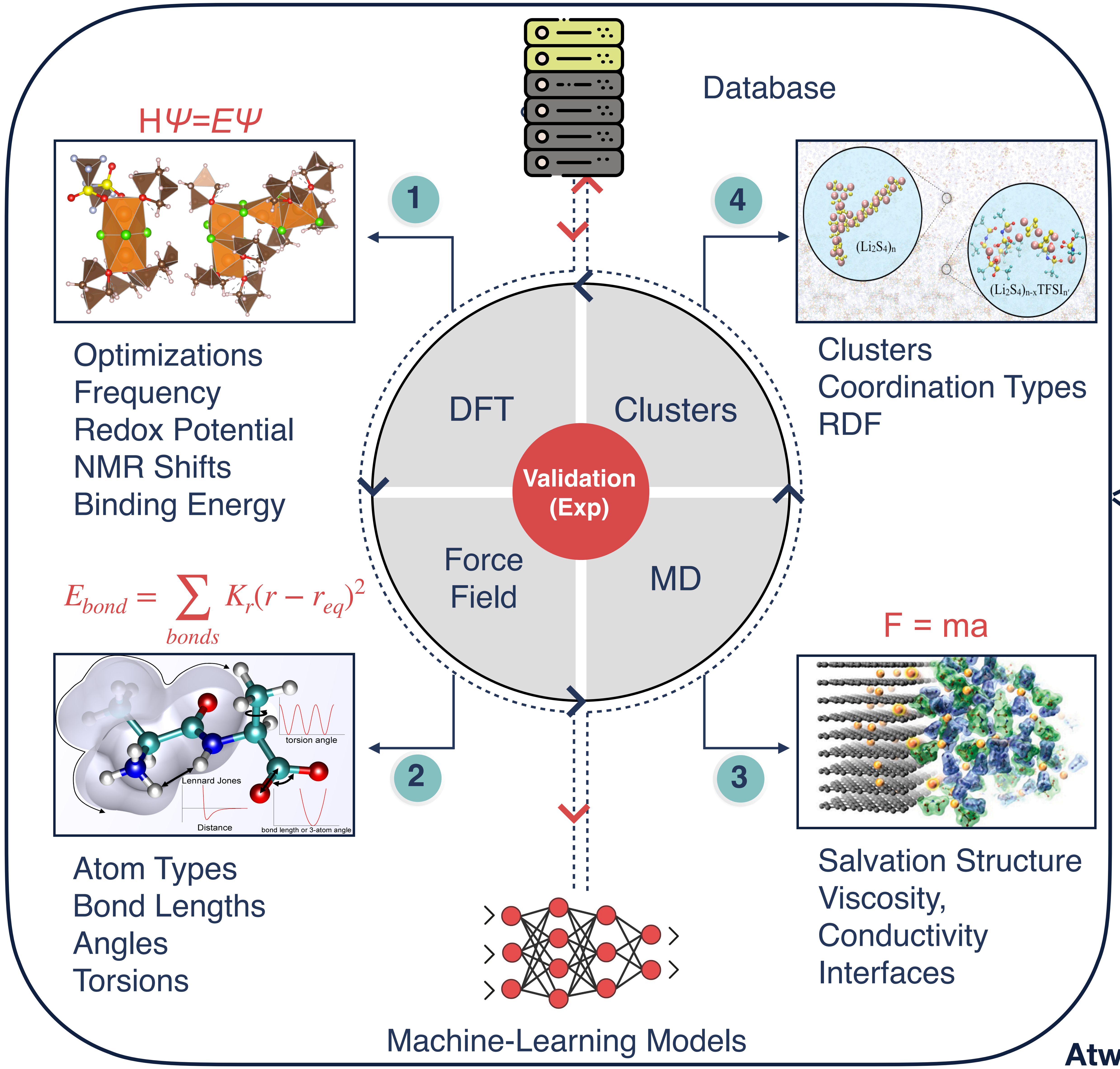


Qu, X. (2015) *Computational Materials Science, 103, 56-67*

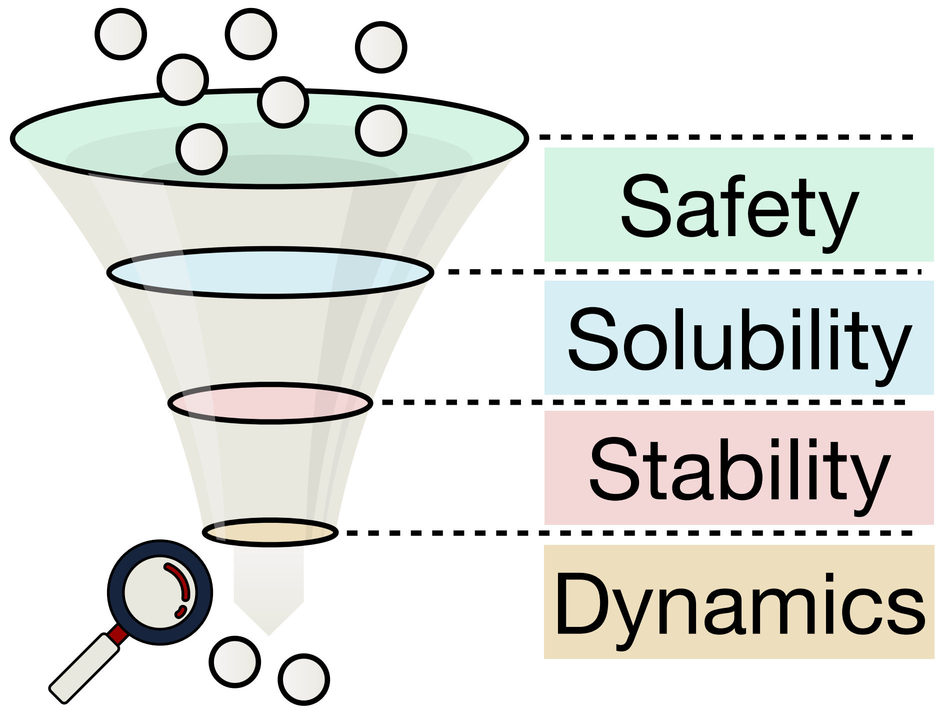
- Show maturity of the computational high-throughput approach in materials science
- Focus on crystal structures, nano-porous materials, band gaps, formation energies, piezoelectric coefficients, elastic tensors, magnetic moments
- Gaps in similar approaches at both quantum and classical levels for predicting molecular and ensemble properties in liquids and at solid-liquid interfaces.

MISPR Materials Informatics for Structure-Property-Relationship

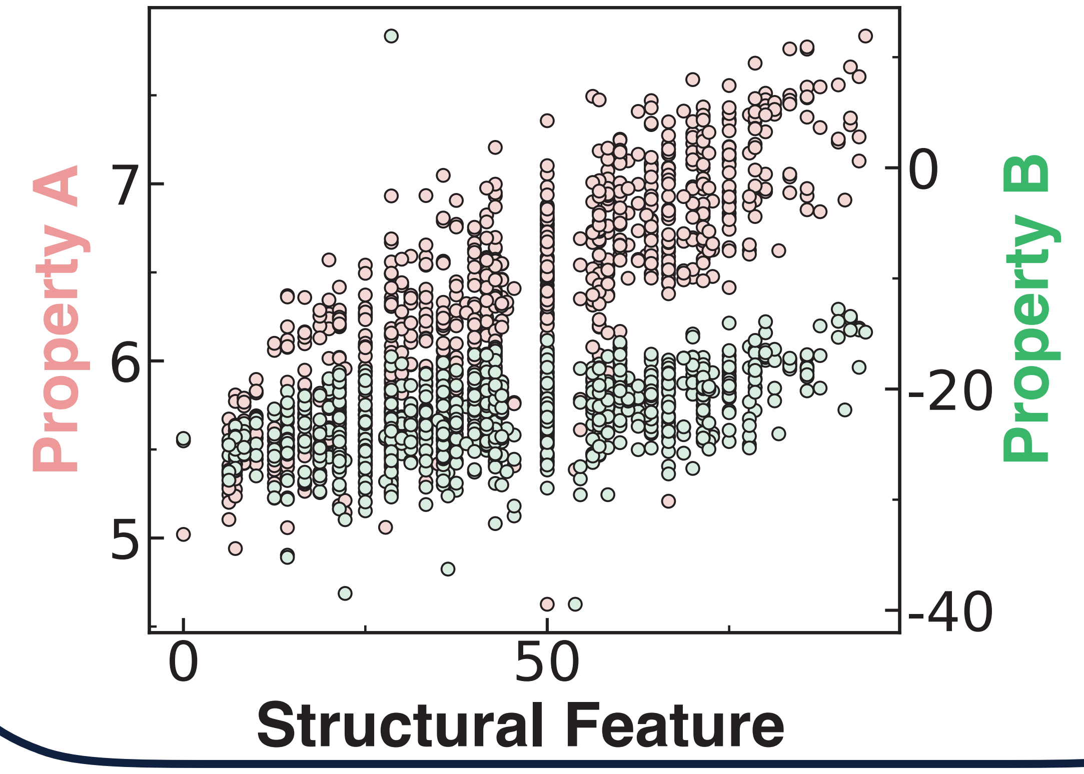
An Open-Source High-Throughput Multi-Scale Infrastructure for Materials Design



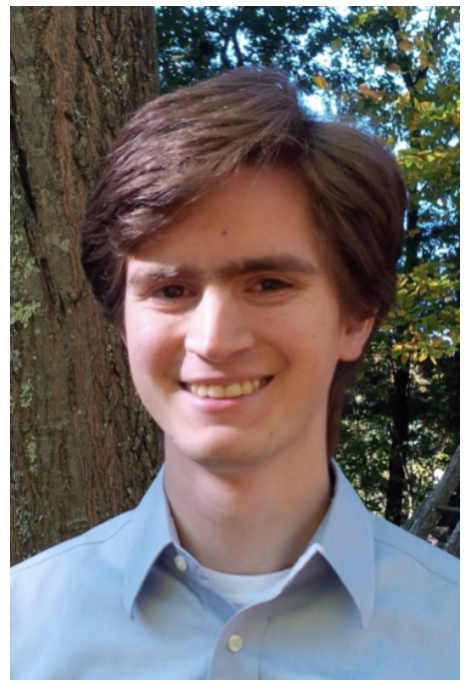
Screening potential candidates with optimal properties



Large Datasets for Quantifying Structure-Property Relations



Rasha Atwi



Matthew Bliss

Atwi et al Scientific Reports, 2022

Example of Implemented DFT-Based Workflows: Binding Energy

Critical for understanding stability of bonds between species …

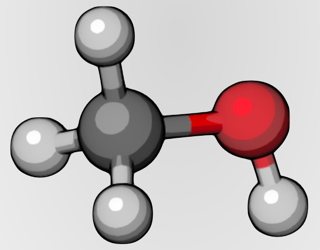
Inputs

Required: two structures, linking sites index

Optional: …

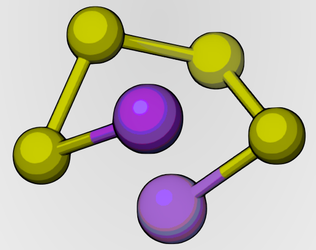
Structure 1 Fireworks

Optimization
Frequency



Structure 2 Fireworks

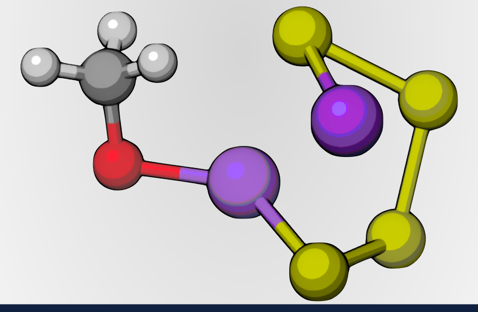
Optimization
Frequency



Join at indexes

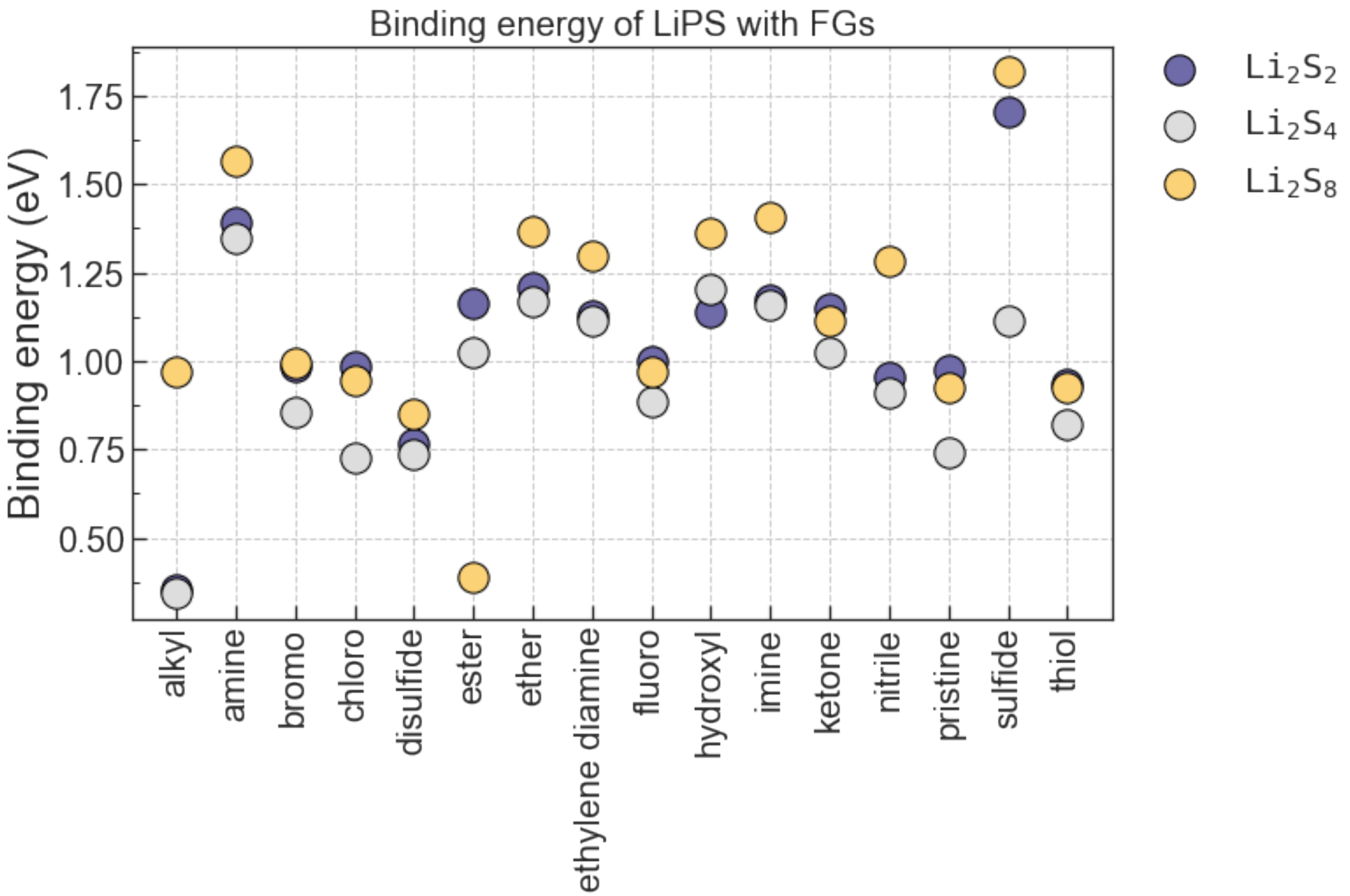
Complex Structure Fireworks

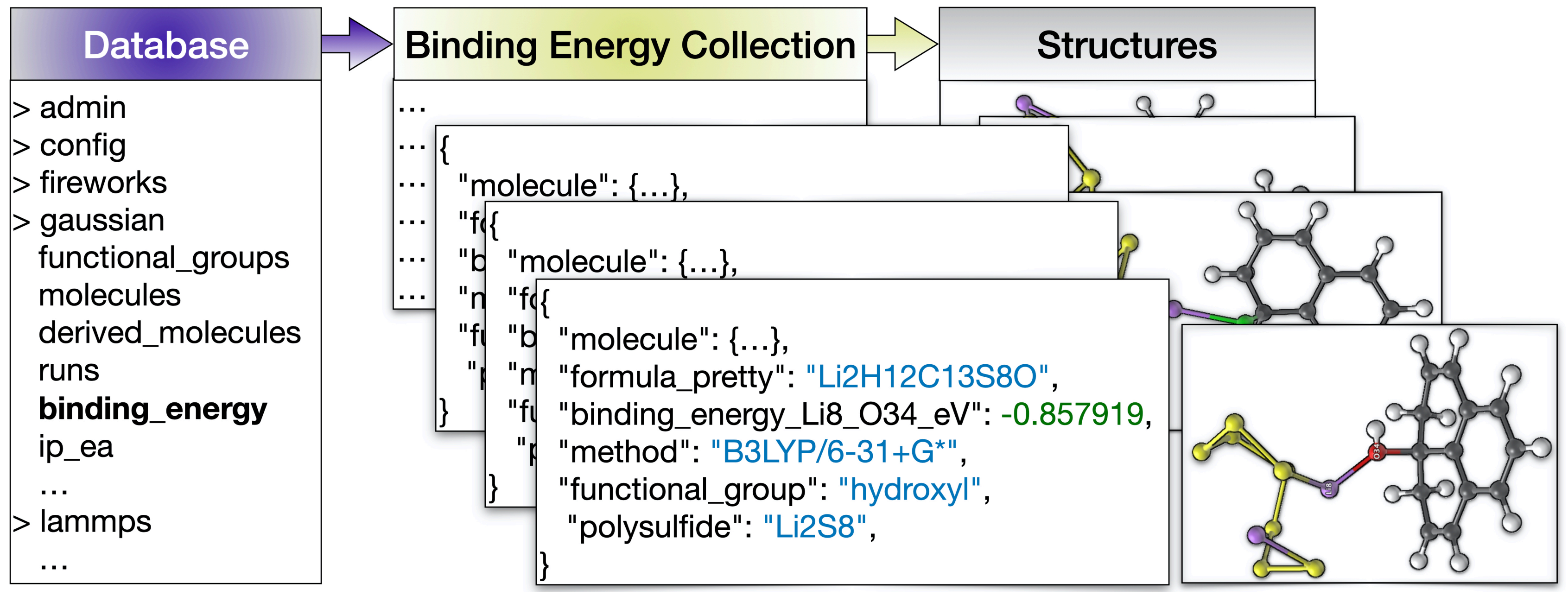
Optimization
Frequency



Data parsing & optional save to DB

$$BE = E_{Complex} - (E_1 + E_2)$$



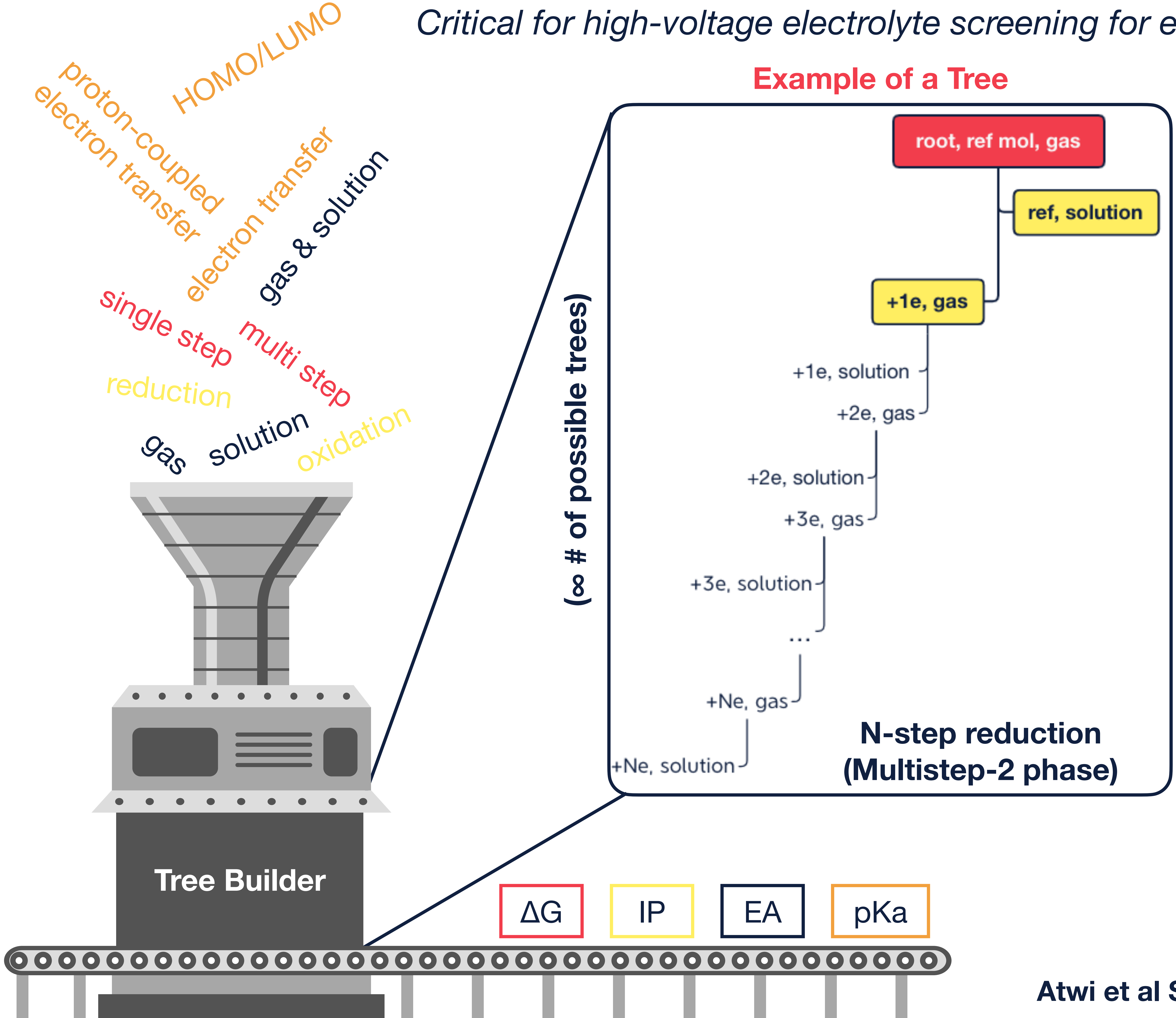


Atwi et al Scientific Reports, 2022

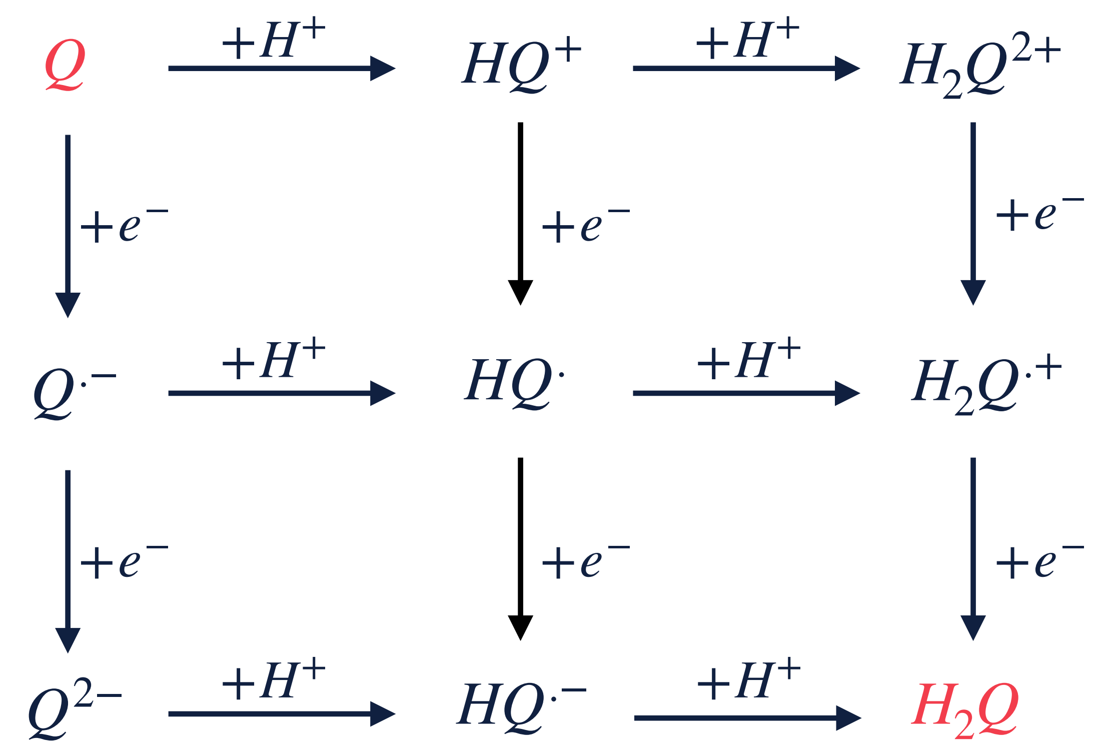
Example of Implemented DFT-Based Workflows: Redox Potentials

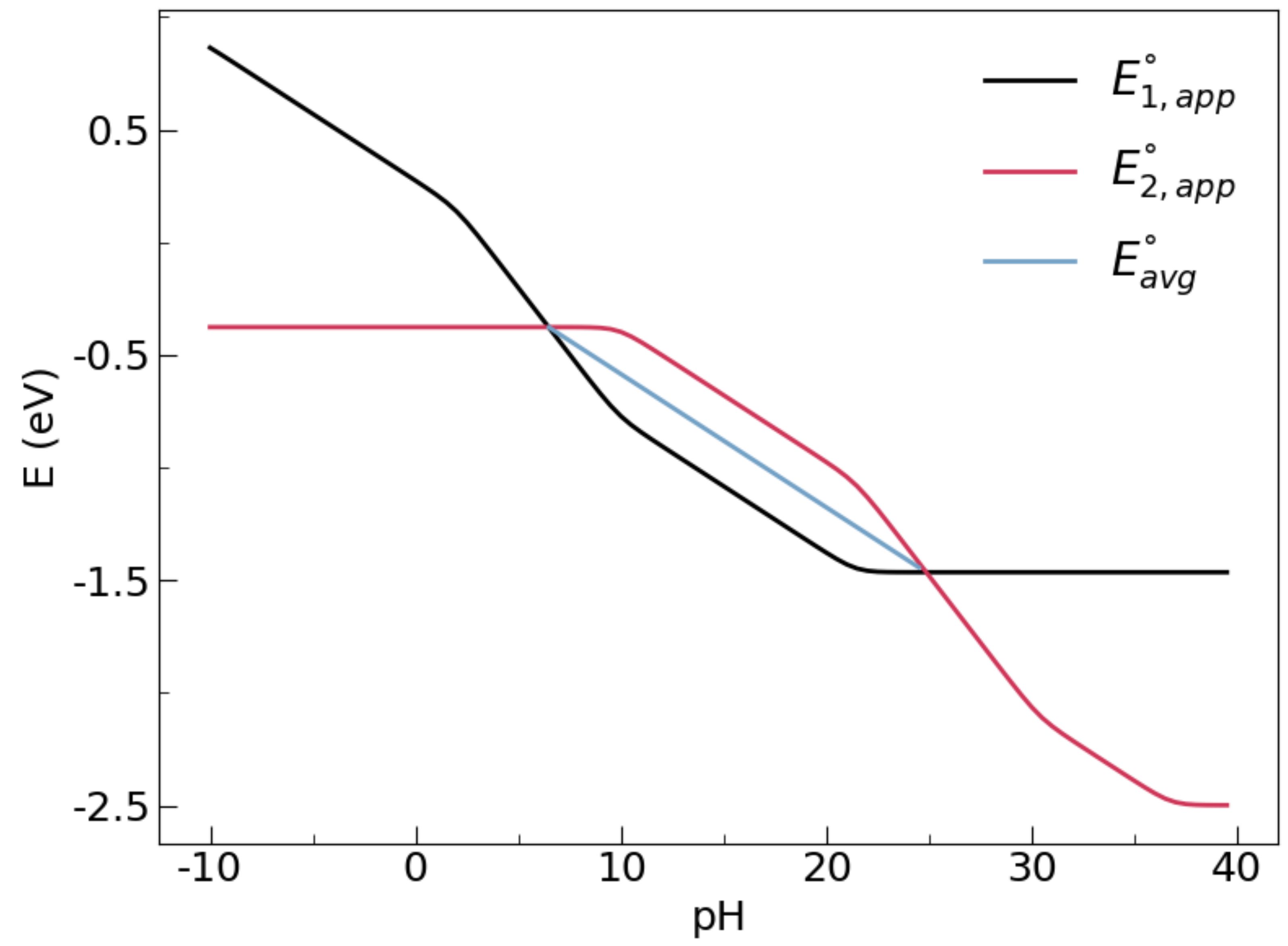
Critical for high-voltage electrolyte screening for energy storage applications …

Example of a Tree



Q Proton-Coupled Electron Transfer Process

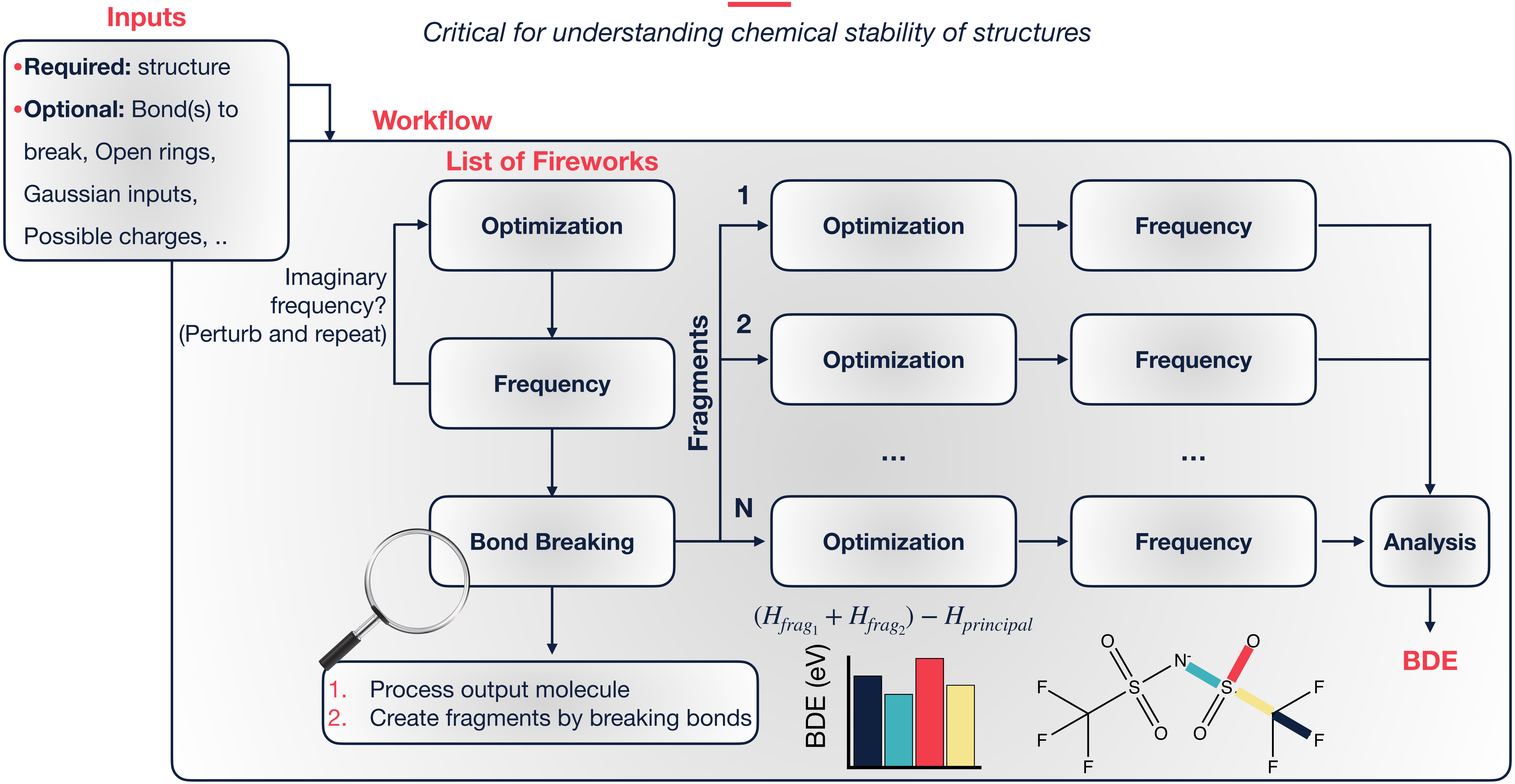




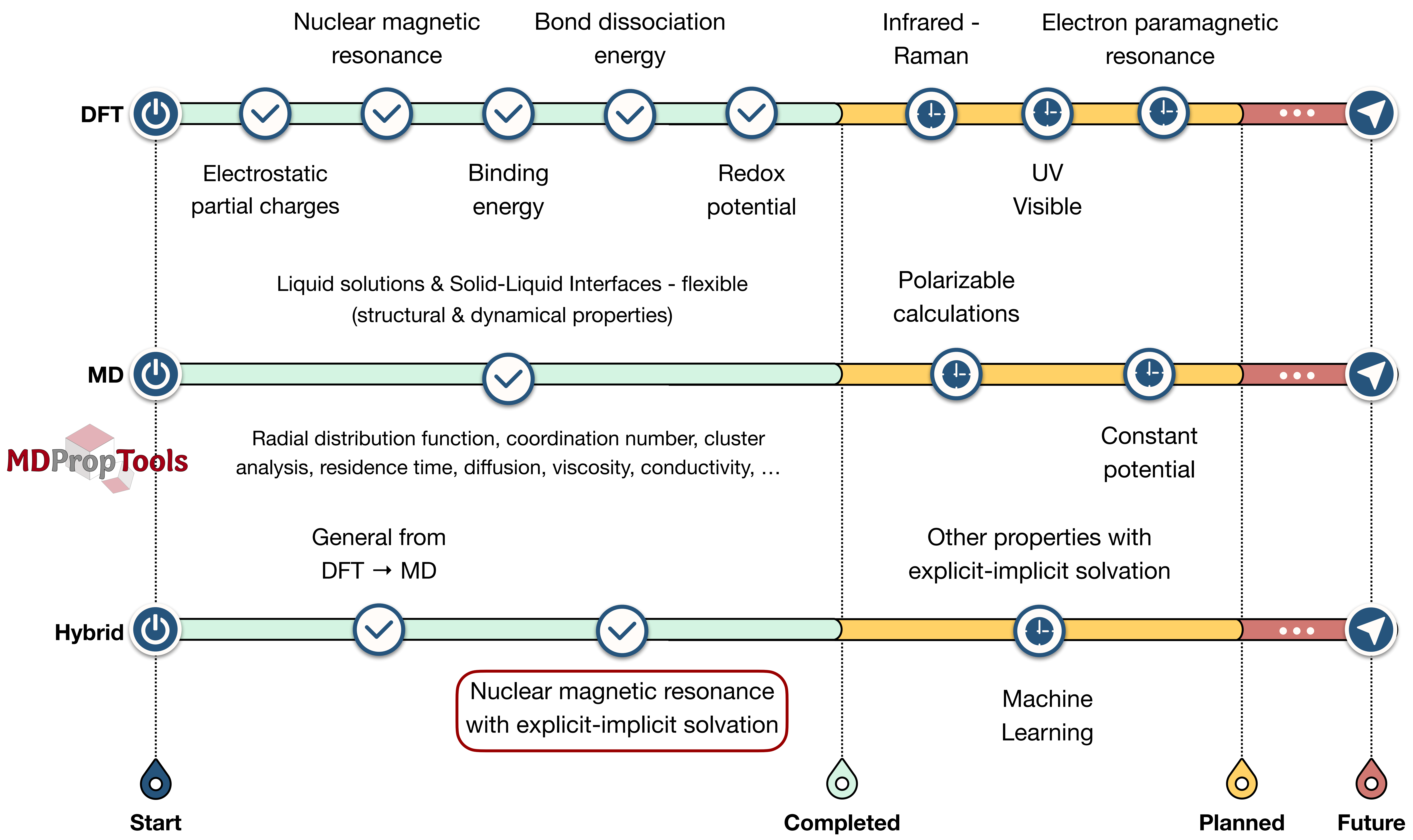
Atwi et al Scientific Reports, 2022

Example of Implemented Gaussian-Based Workflows: BDE

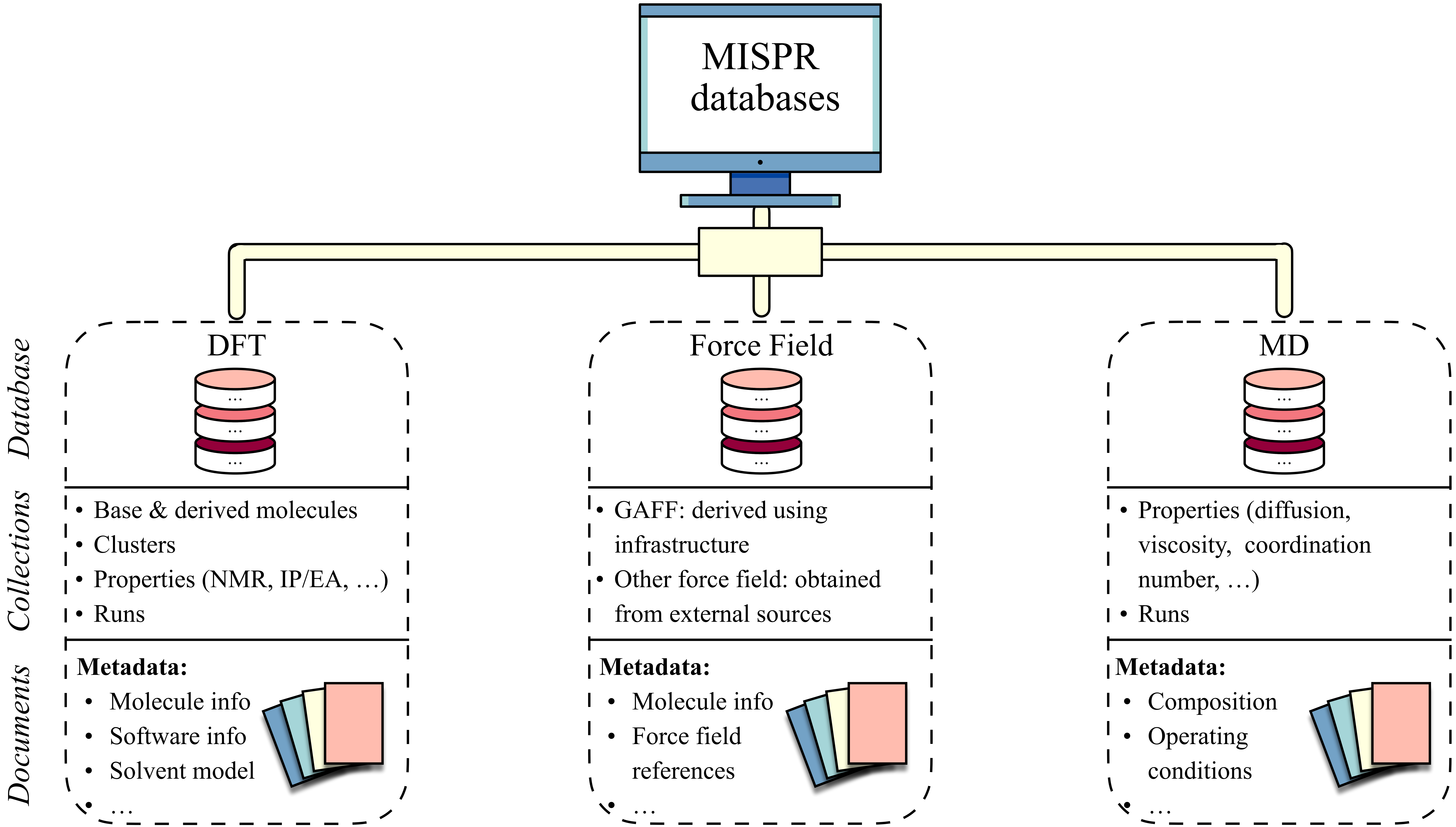
Critical for understanding chemical stability of structures



Roadmap of Workflows



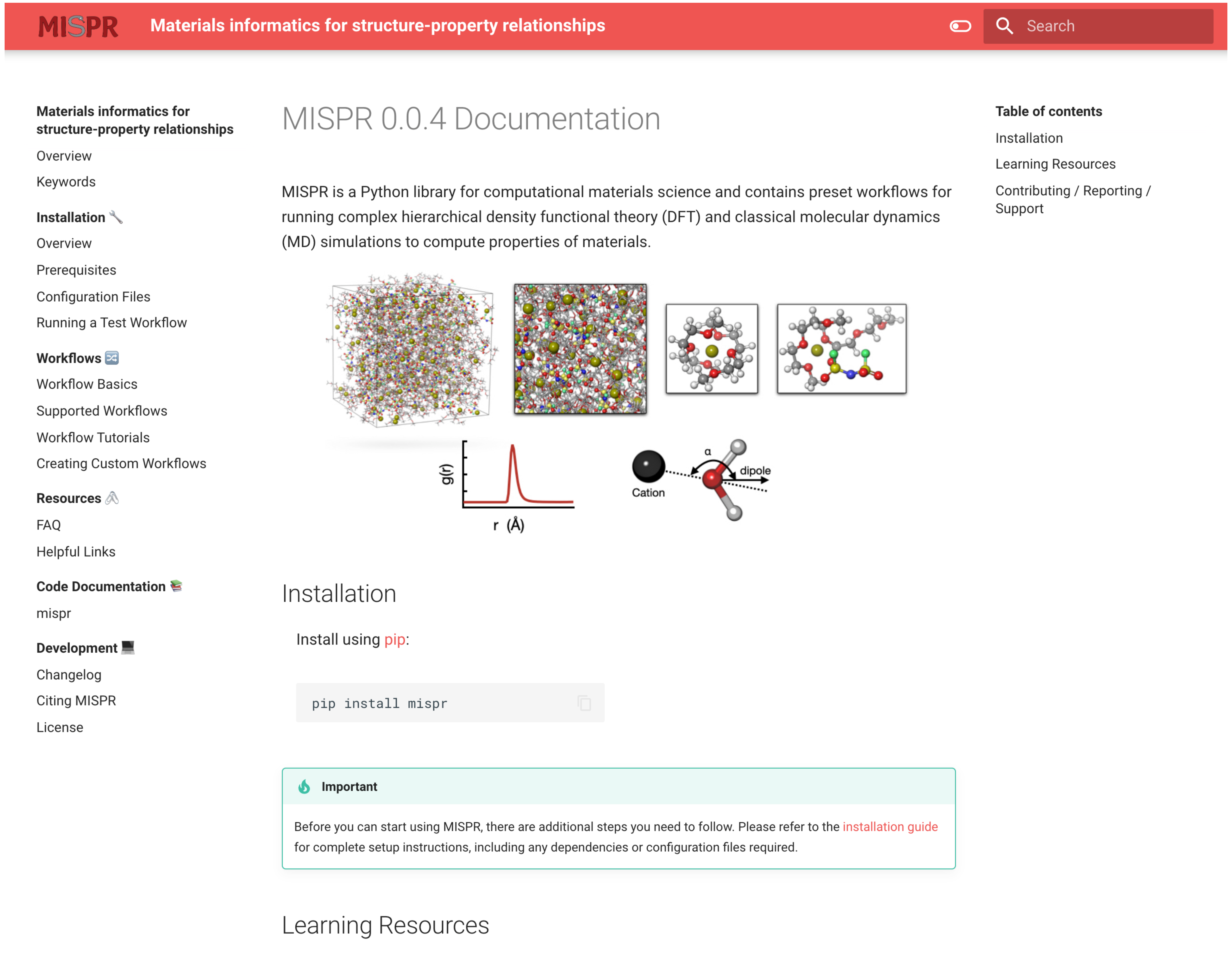
Atwi, R. et al. (2022). Scientific Reports, 12(1), 15760.

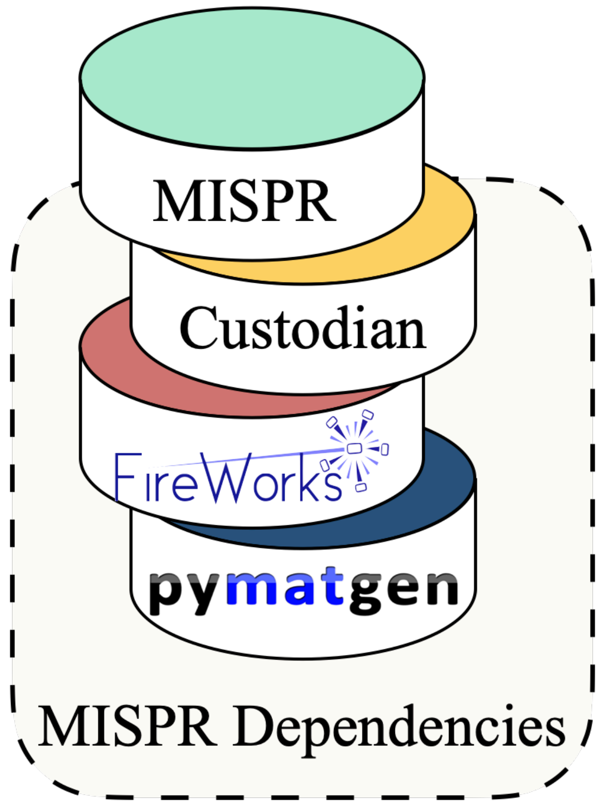

MISPR databases
Database
Collections
Documents
DFT
Base & derived molecules
Clusters
Properties (NMR, IP/EA, …)
Runs
Metadata:
Molecule info
Software info
Solvent model
…
Force Field
GAFF: derived using infrastructure
Other force field: obtained from external sources
Metadata:
Molecule info
Force field references
…
MD
Properties (diffusion, viscosity, coordination number, …)
Runs
Metadata:
Composition
Operating conditions
…

MISPR Materials Informatics For Structure-Property Relationships

MISPR features include:

- Computational database building - MongoDB
- Inherit support for multiple queuing systems - SLURM, PBS, SGE, etc.
- Automatic error handling
- Template workflows for various materials properties
- Seamless integration of DFT and MD simulations
- Utilities for post-processing and analyzing results





Source code: https://github.com/molmd/mispr

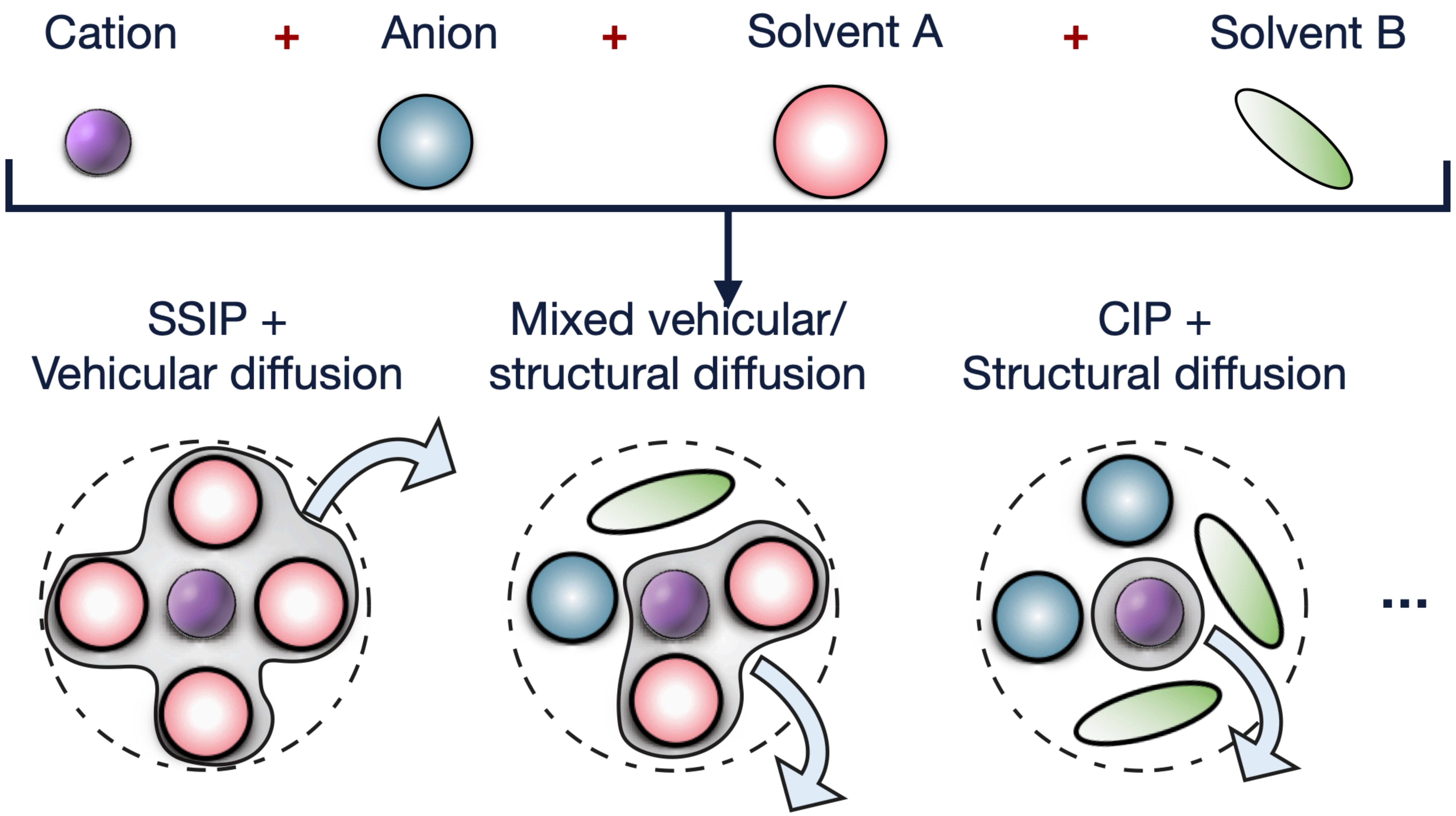
Website: https://molmd.github.io/mispr/

Atwi, R. et al. (2022). Scientific Reports, 12(1), 15760.

Solvation Structures in Complex Multi-Component Liquid

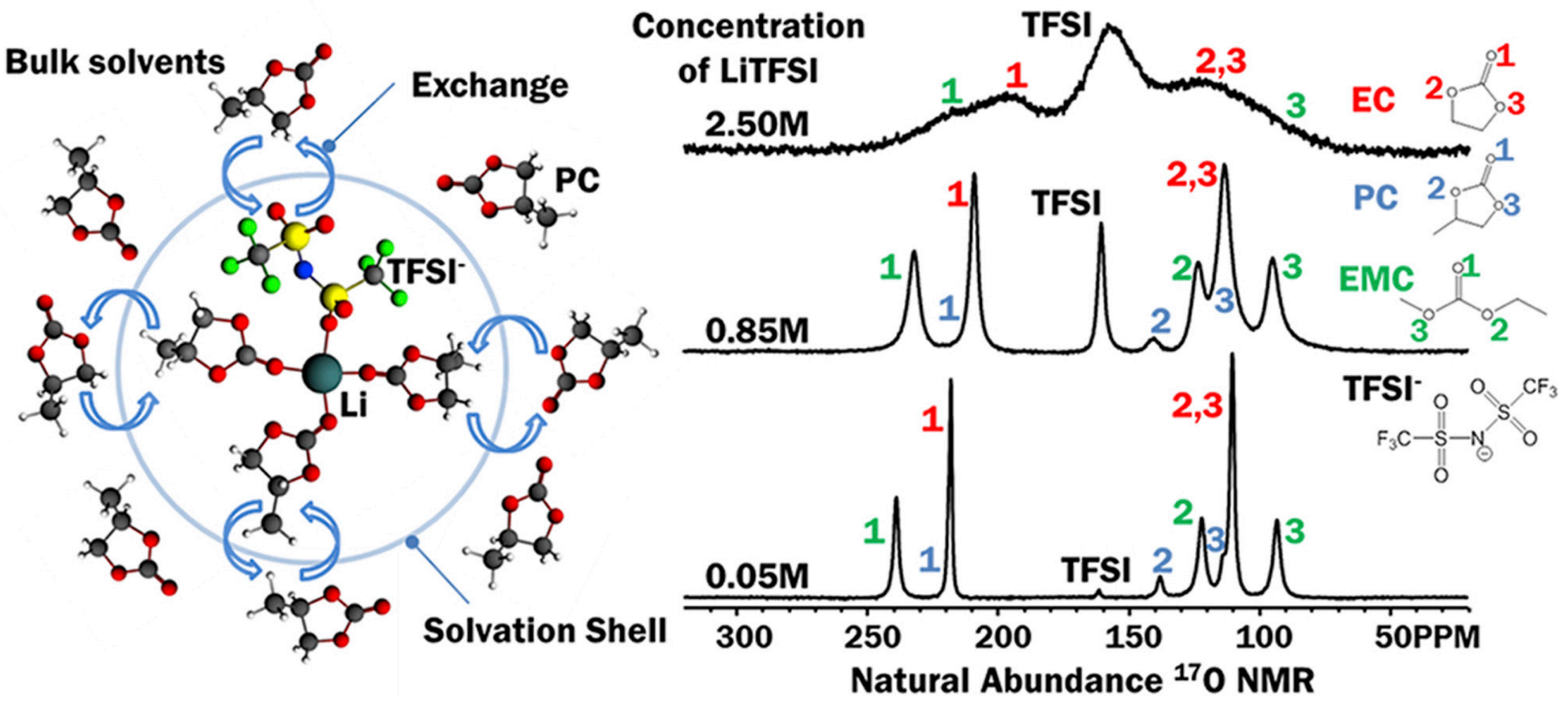
Understanding solvation, where the intimate dance of solvent molecules around solutes influences chemical reactivity and physical properties.

Most structure–property correlations in multicomponent liquids are usually build upon favorable static solvation structures, often overlooking solvent exchange dynamics and multiple stable species.



- Small change in molecular features results in radical change in mesoscopic properties
- Non-additive properties and complex interactions

Experimental & Computational Spectroscopy Analysis of Liquid Solutions

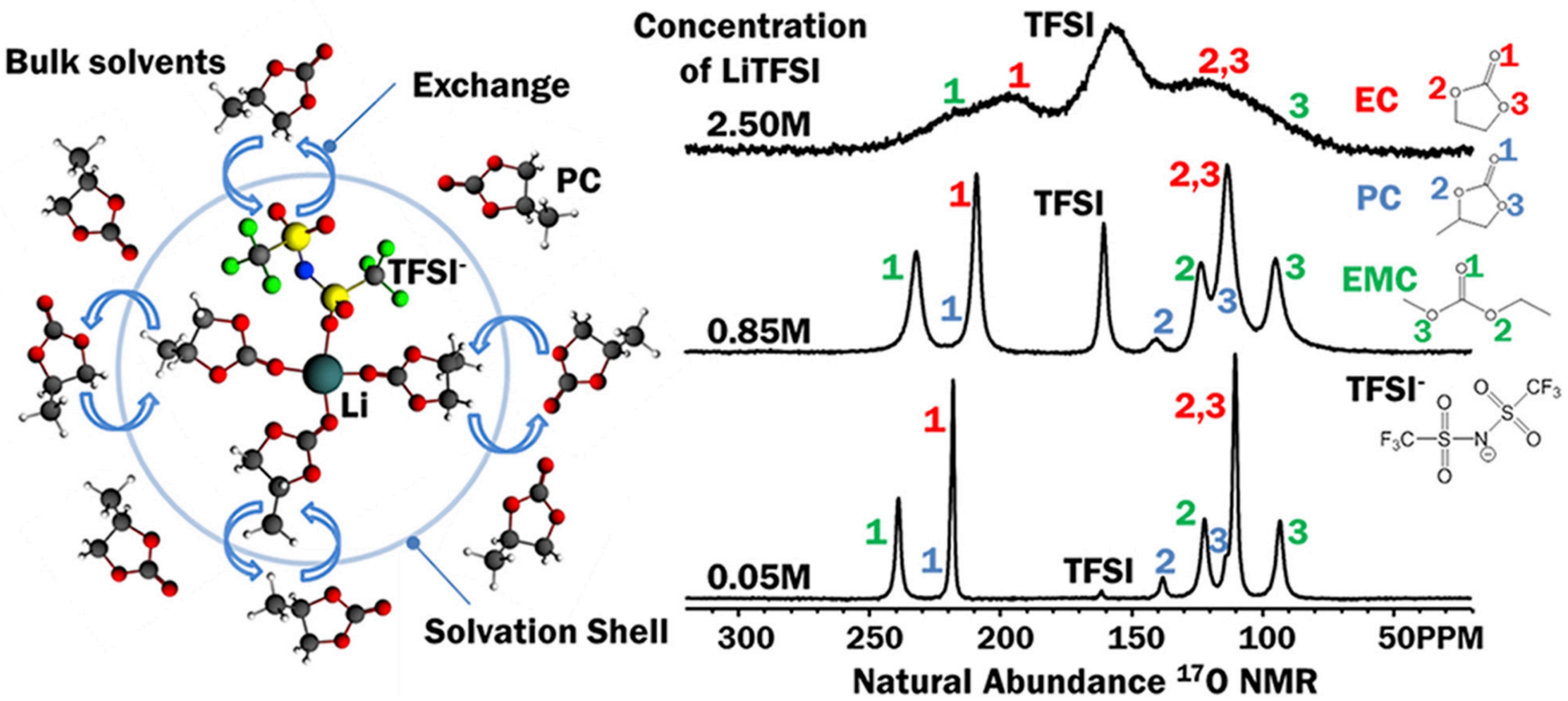


Deng, X. et al. (2015). *Journal of Power Sources*, 285, 146-155.

Challenges with experimental approaches

- Nuclear magnetic resonance (NMR), Raman, and X-ray pair distribution function, SCXRD, are some of the most widely used techniques for characterizing liquid solutions
- Limited by the temporal scale and low sensitivity
- A time-averaged spectroscopic response such as an NMR chemical shift is more often referred to as a specific static solvation structure leads to oversimplification of the structural complexities

Experimental & Computational Spectroscopy Analysis of Liquid Solutions



Challenges with traditional computational approaches

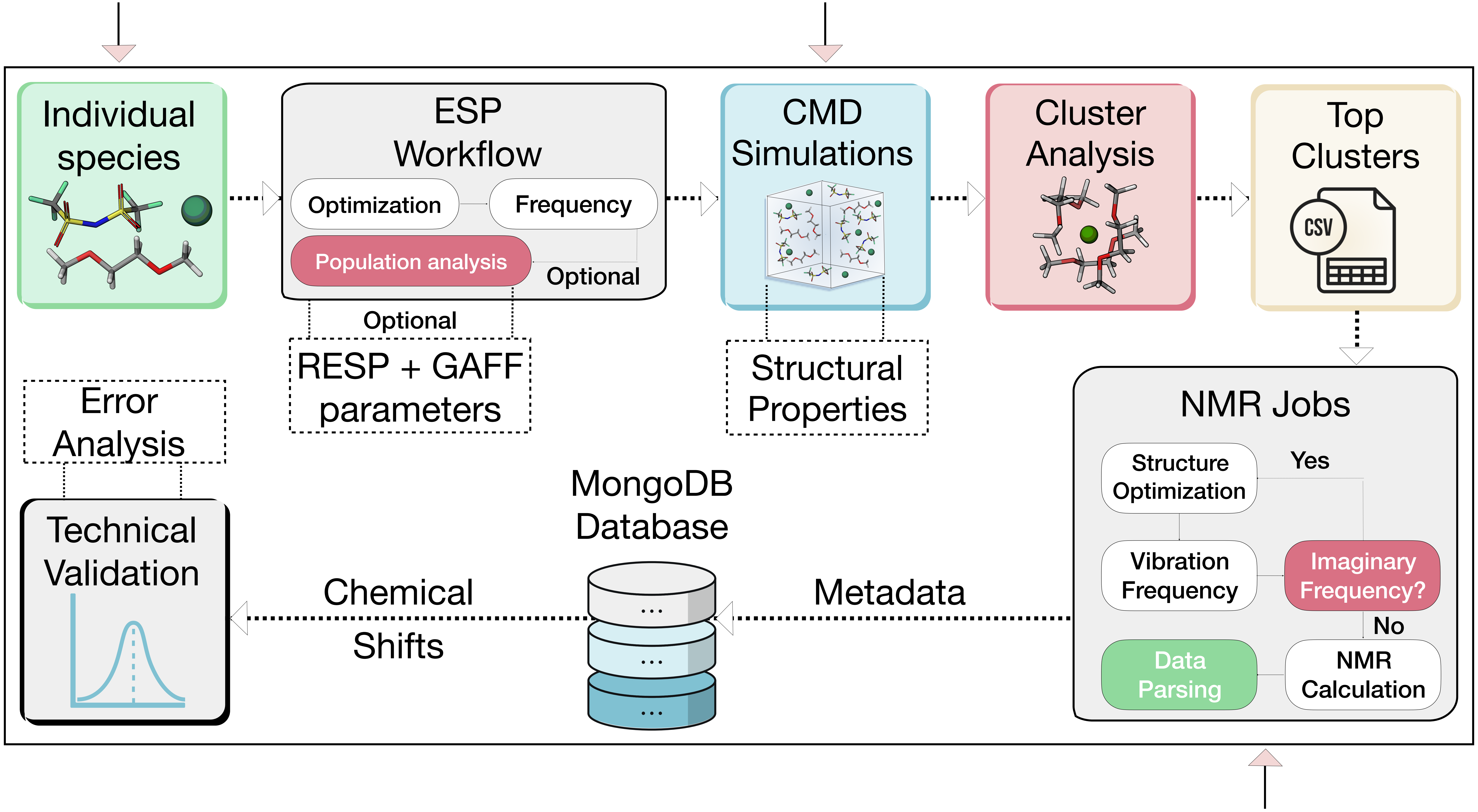
- High computational cost for large systems (>100 atoms) and time scales (~10 ps)
- Inaccurate account of solvation effects
- Fail to fingerprint the temporal evolution of solvation structure under exogenous and endogenous conditions
- Focus on singular clusters

- Manual operations
- Trial and error
- Chemical intuition

Computational Spectroscopy Analysis Tools (SAT) in MISPR

Inputs: structures

Inputs: C, T, force field parameters (optional), etc.



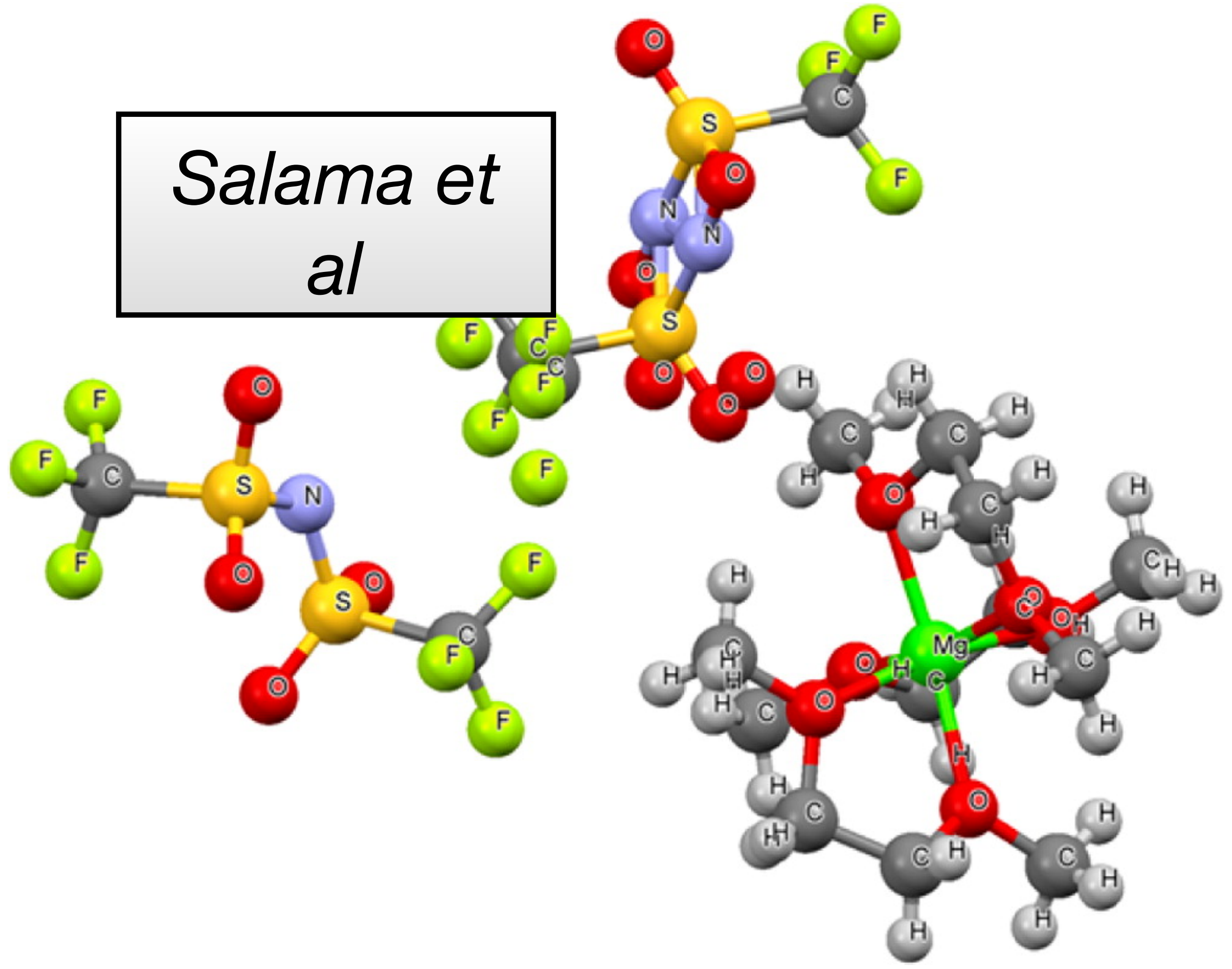
Optional inputs: method, basis set, implicit solvation model, etc.

Atwi et al Nature Computational Science, 2022

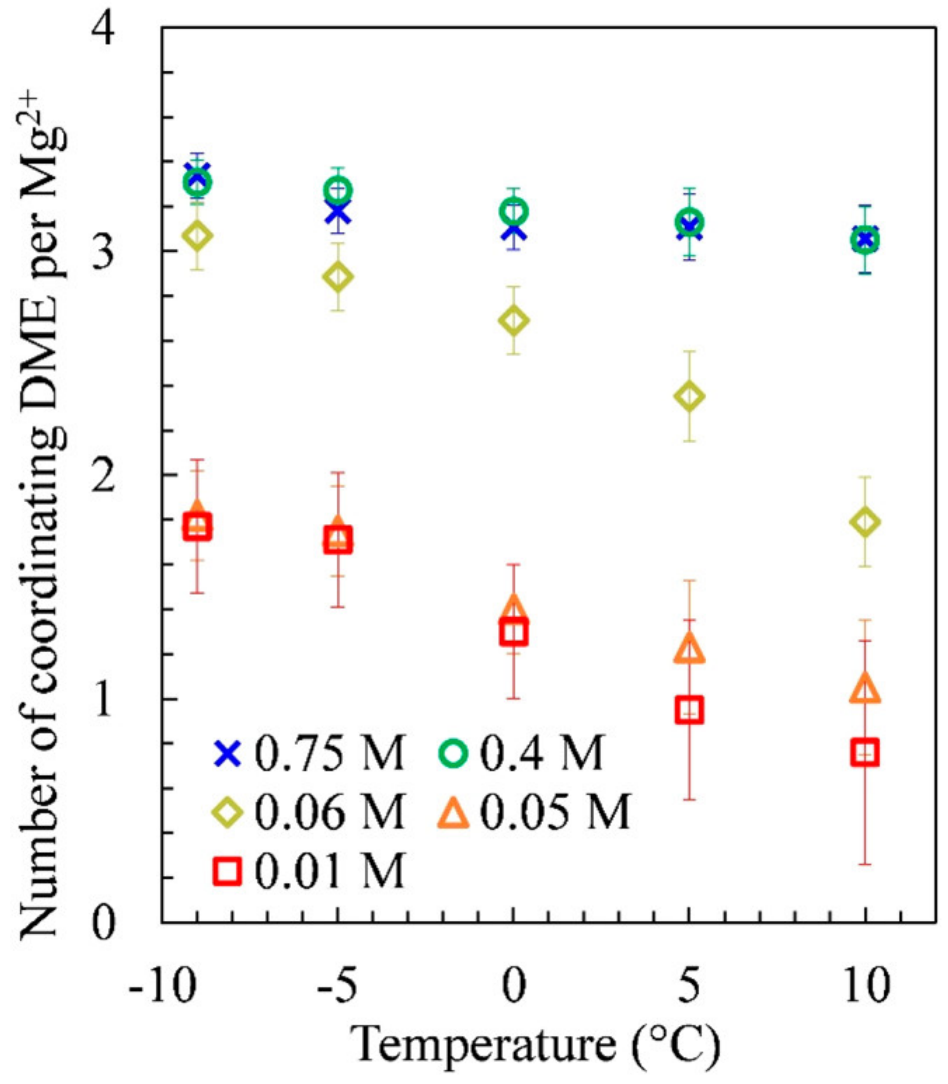
Discrepancies in literature regarding solvation structure of $Mg(TFSI)_2$ in DME

SCXRD: Structure for $MgTFSI_2$ single crystal, recrystallized from solution

Salama et al



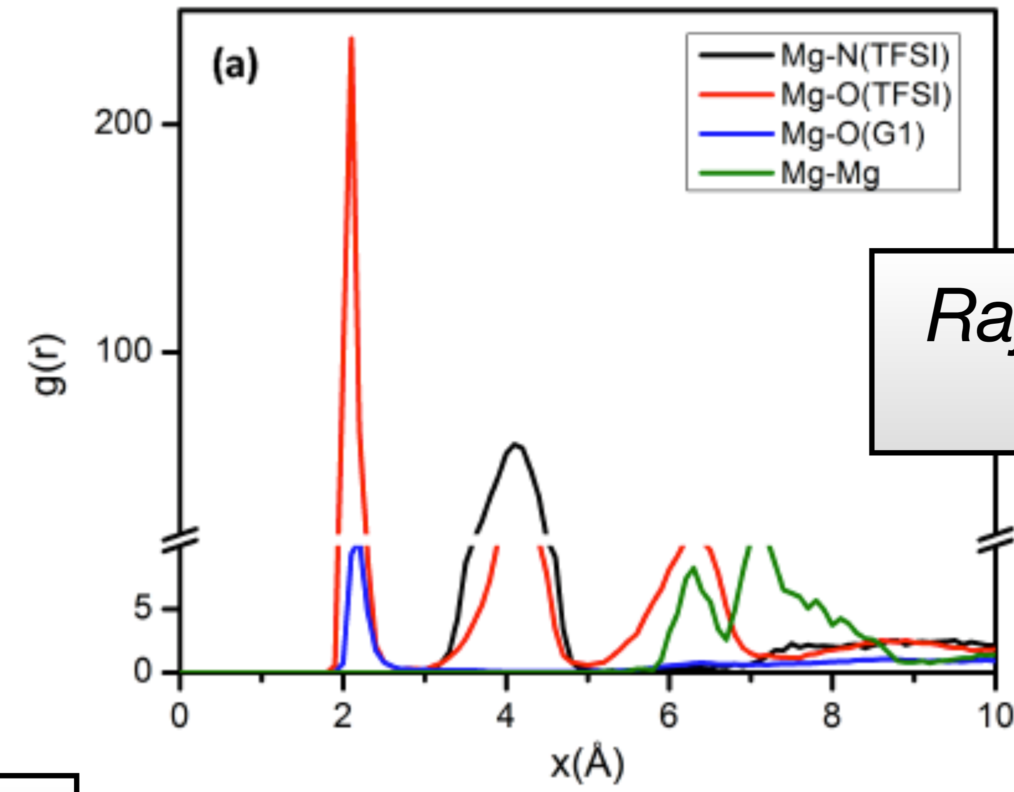
NMR: Number of bound DME per Mg^{2+} at varying temperatures and concentrations



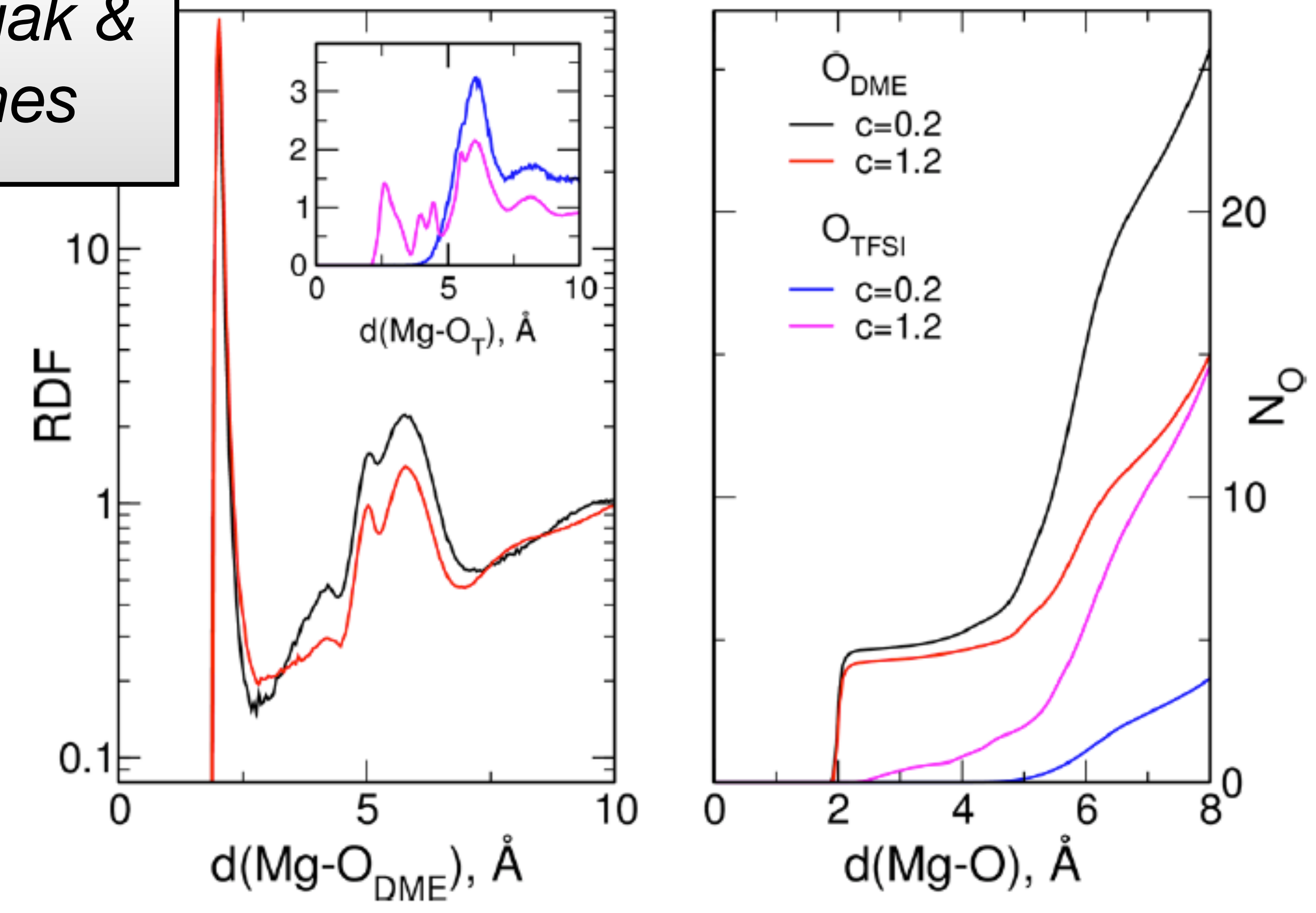
Ying et al 2020

MD Simulations: Coordination between Mg^{2+} and other electrolyte components

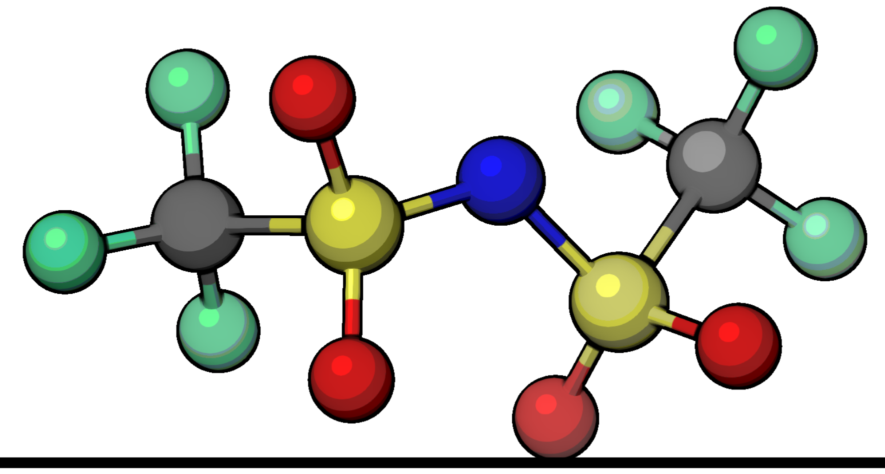
Rajput et al



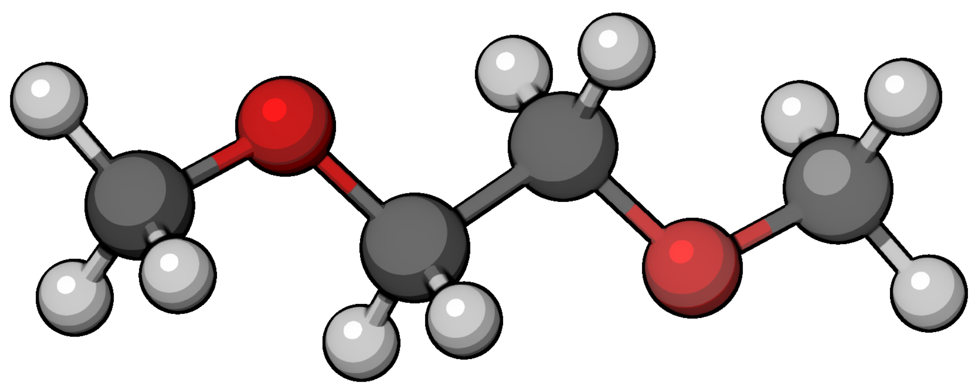
Kubisiak & Eilmes



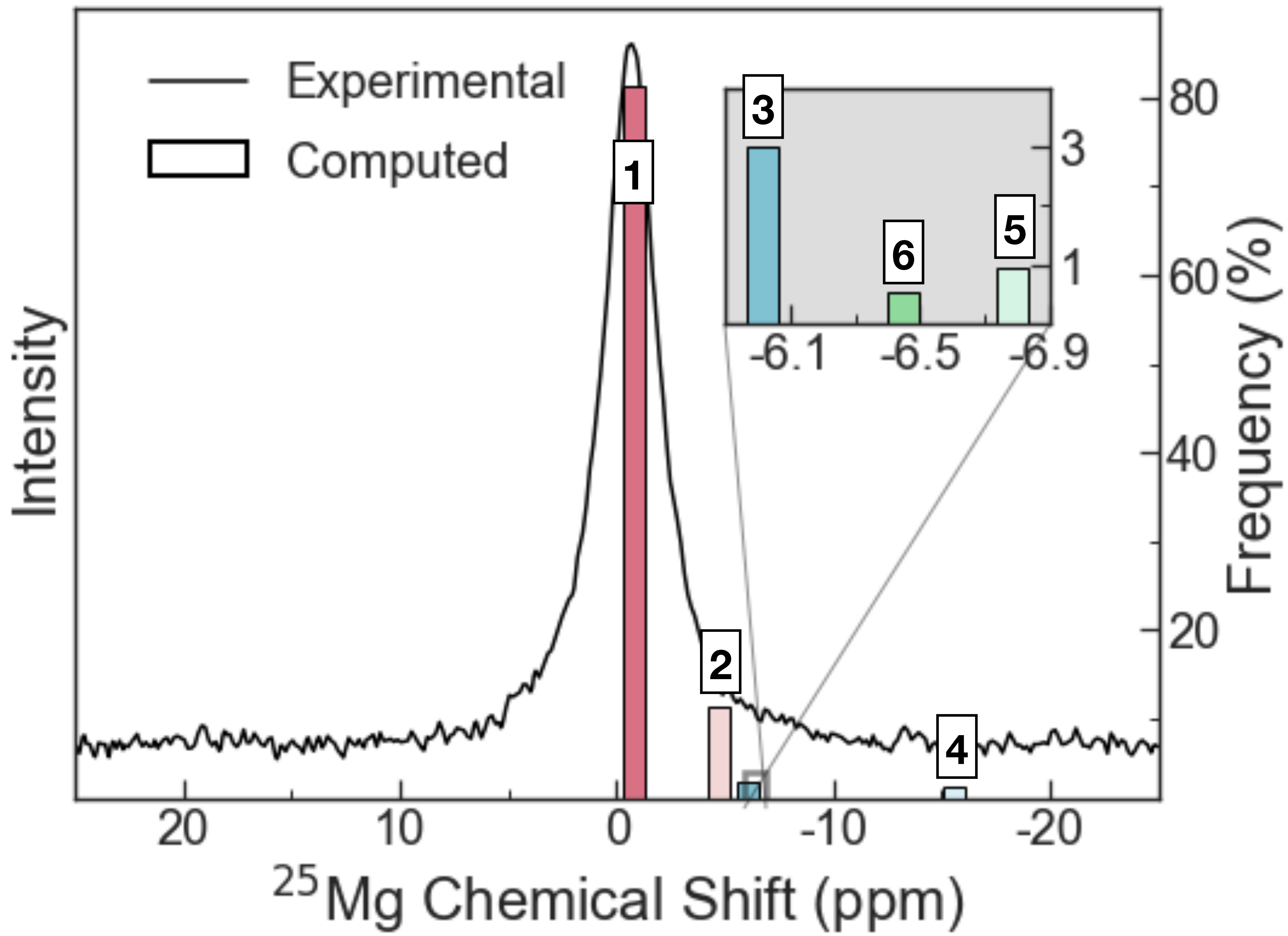
TFSI

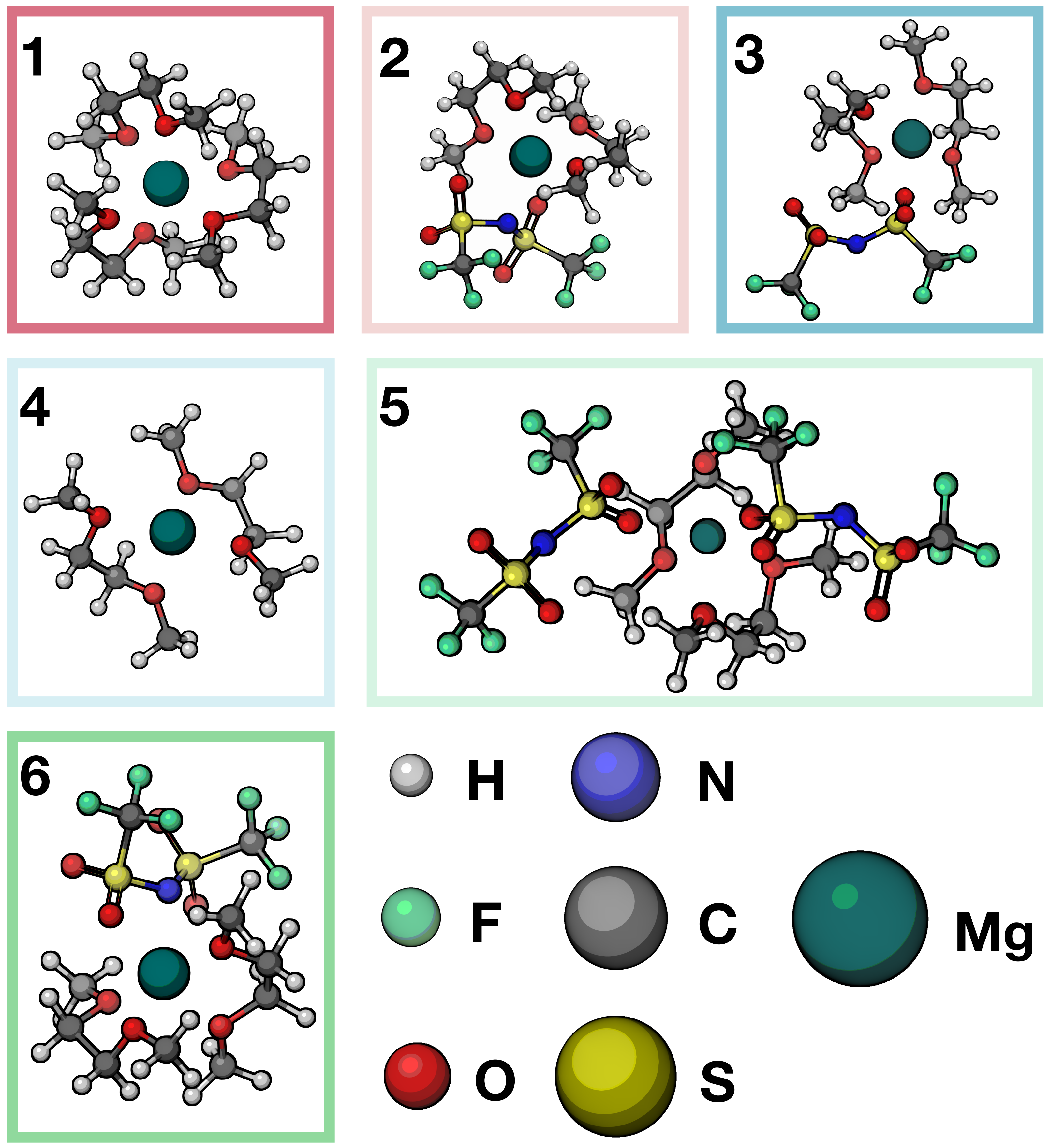


DME



“Spectra of Ion Solvation”: Do we have just one stable structure in the Solution?



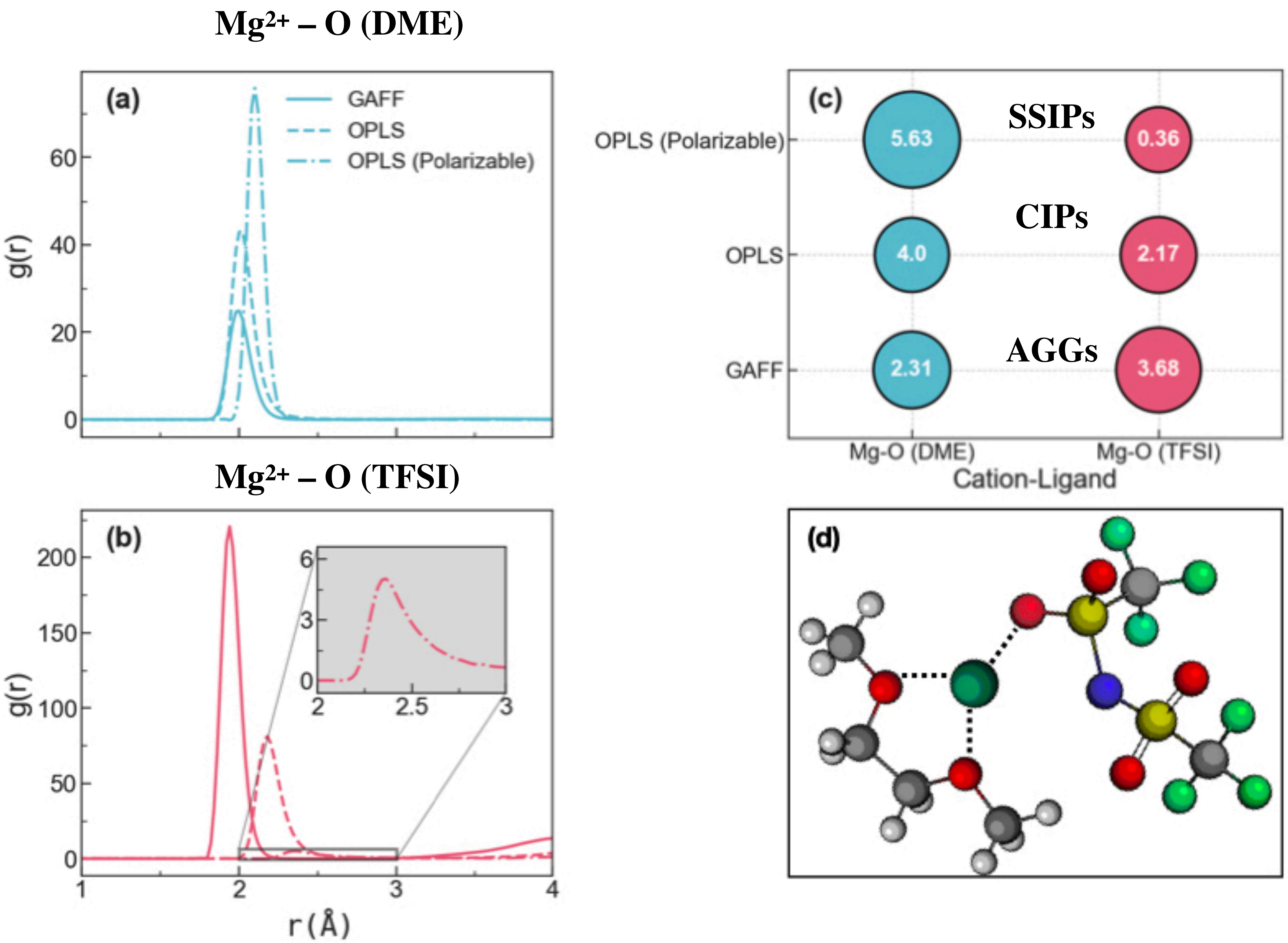


Atwi et al Nature Computational Science, 2022

How to Accurately Predict the NMR Chemical Shift Computationally?

1. **Role of force field parameters used in MD simulations**
2. **Role of DFT level of theory**
3. **Role of implicit solvation model**
4. **Role of conformer**
5. **Effect of geometry optimization**
6. **Choice of chemical reference**

Role of Force Field Parameters on Properties of $Mg(TFSI)_2$ in DME



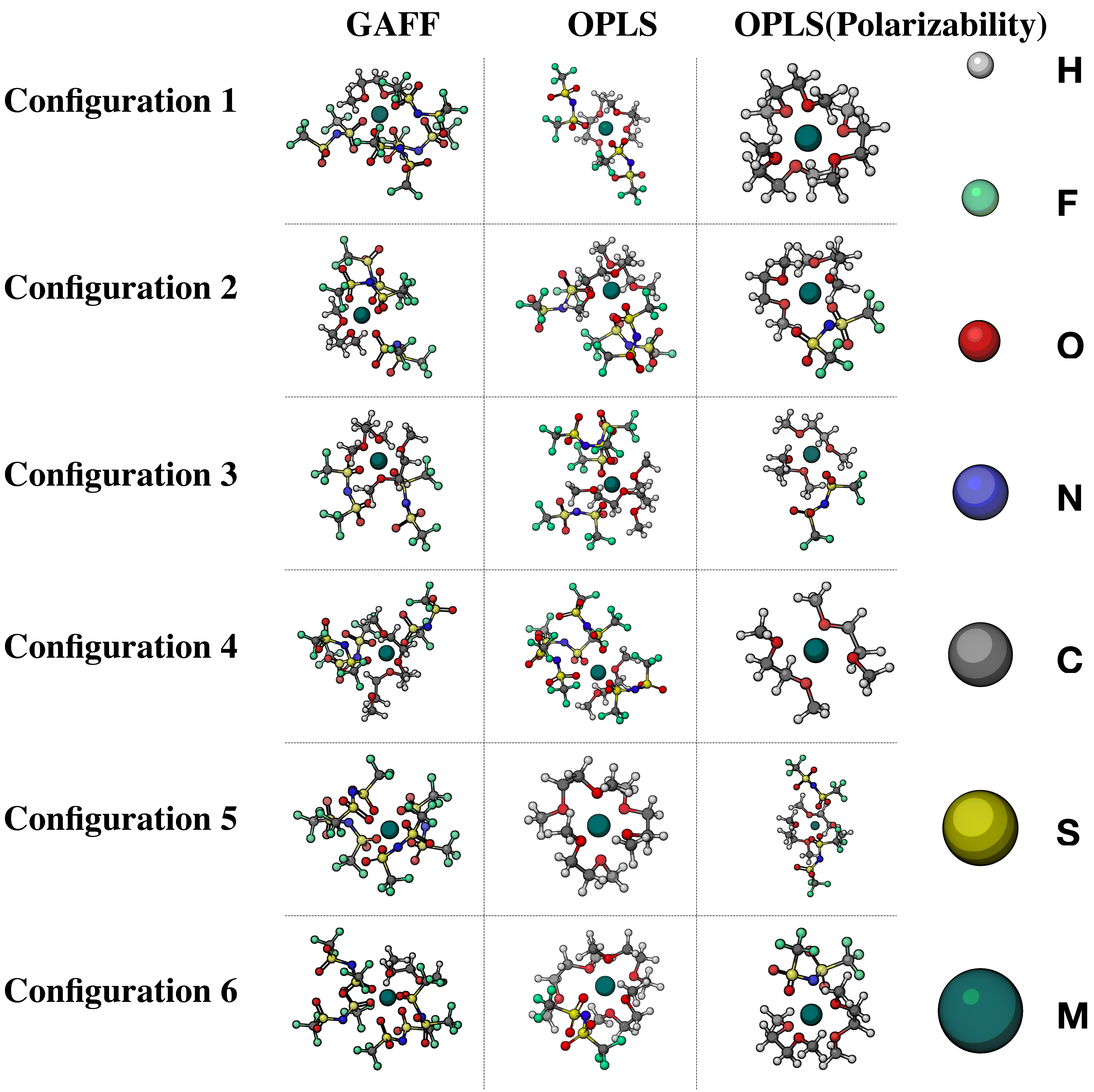
GAFF results in the weakest interaction of Mg^{2+} with DME and the strongest interaction with $TFSI^-$

OPLS with polarizability, shows negligible coordination with the anion

Polarizable OPLS FF shows formation of solvent separated ion pairs (SSIPs), OPLS shows formation of contact ion pairs (CIPs) and GAFF shows formation of aggregates (AGGs) in the solution.

Atwi et al Nature Computational Science, 2022

Role of Force Field Parameters on Properties of $Mg(TFSI)_2$ in DME

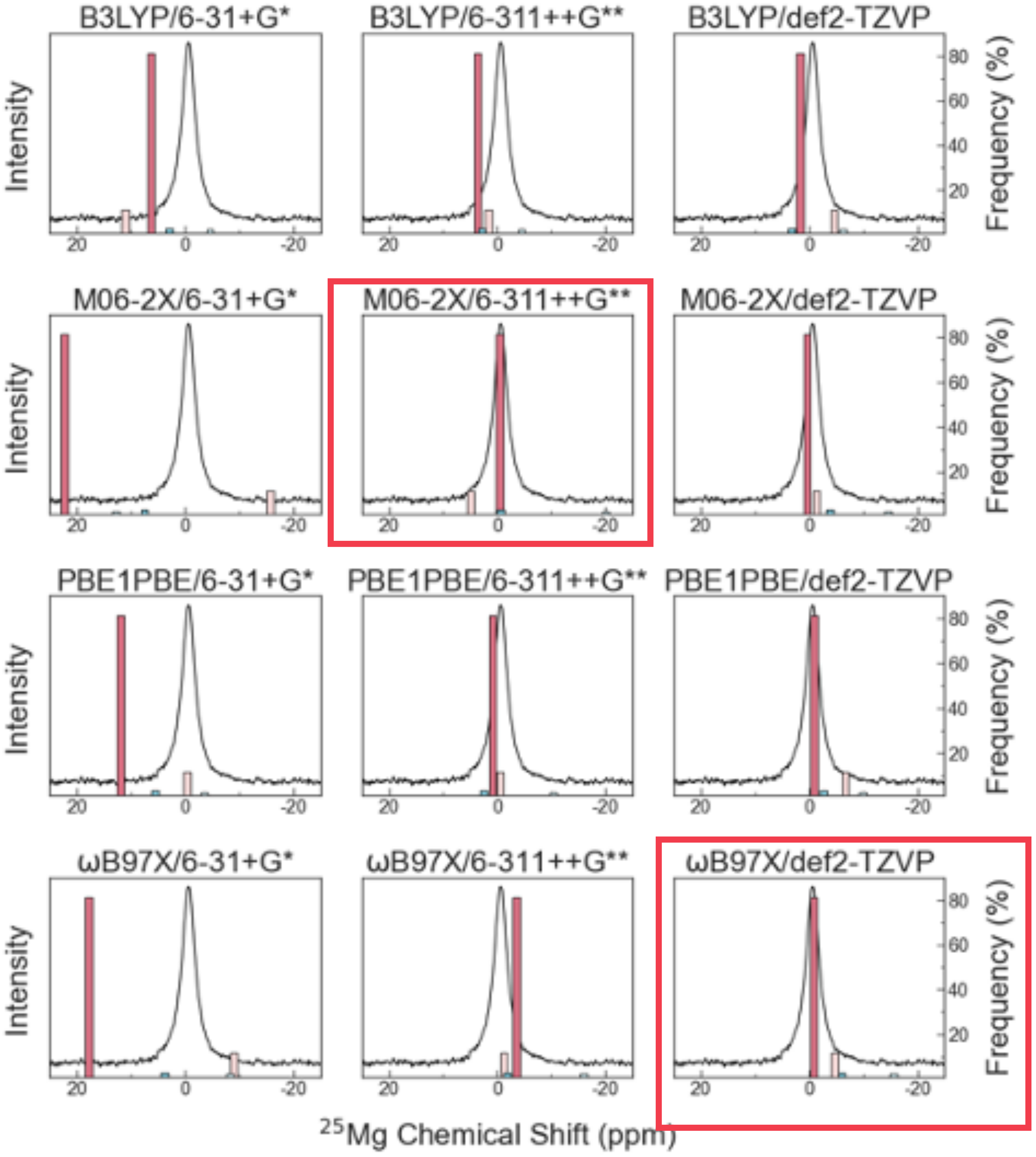


- Configurations fromGAFF and OPLS show more cation-anion interactions
- Configurations from polarizable OPLS FF show more cation-solvent interaction
- Polarizable force fields are three times more expensive than non-polarizable force fields (GAFF & OPLS)

Polarizable force field results in more accurate prediction of structural properties for $Mg(TFSI)_2$/DME electrolyte

Atwi et al Nature Computational Science, 2022

Role of Level of Theory on the NMR Chemical Shift



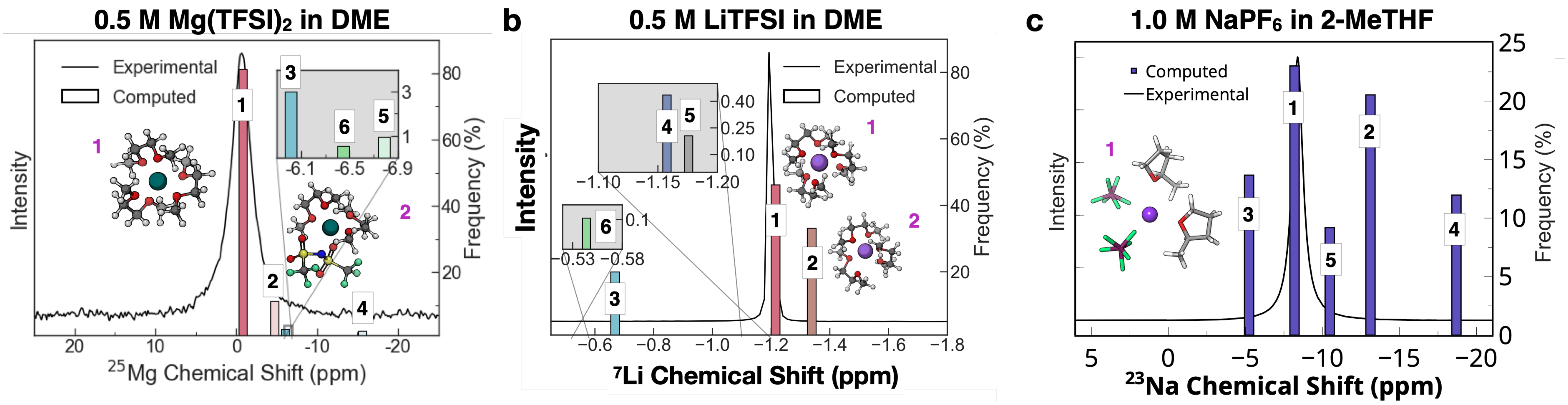
- Performance of selected DFT functionals and basis sets in predicting chemical shifts of ^{25}Mg,. Similar benchmarking is performed for ^{13}C, and ^{1}H

- M06-2X/6-311++G** and ωB97X/def2-TZVP are the best performing methods.

The choice of the level of theory can lead to contradictory conclusions regarding the dominant species in solution

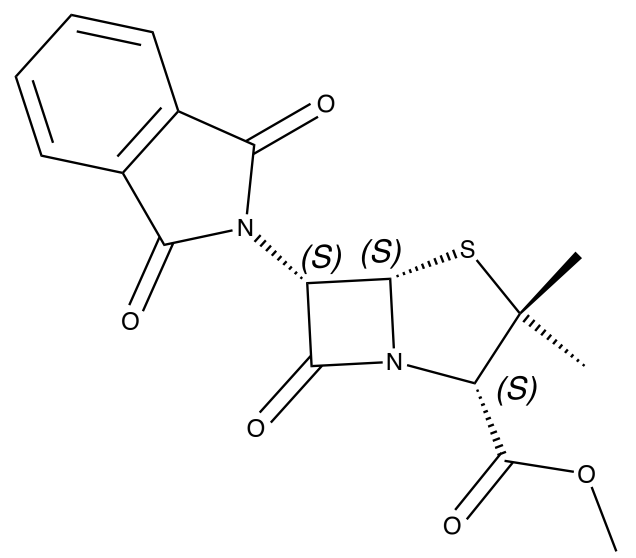
Atwi et al Nature Computational Science, 2022

Generalizability of MISPR-SAT

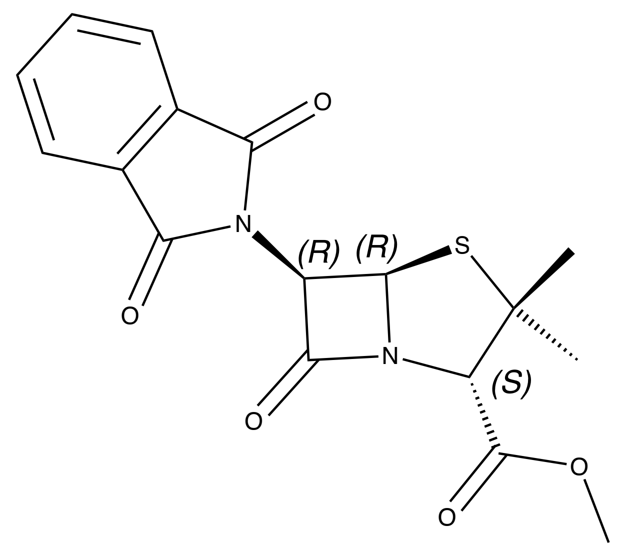


Penam β-lactams 1-4 in chloroform

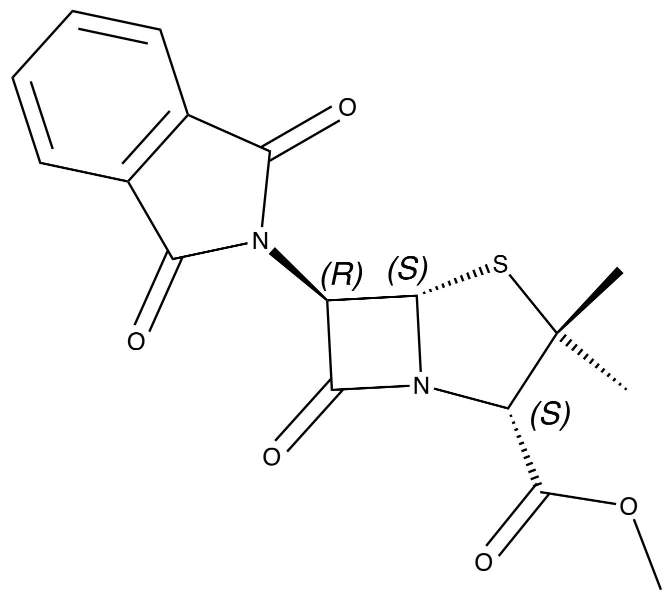
Structure 1



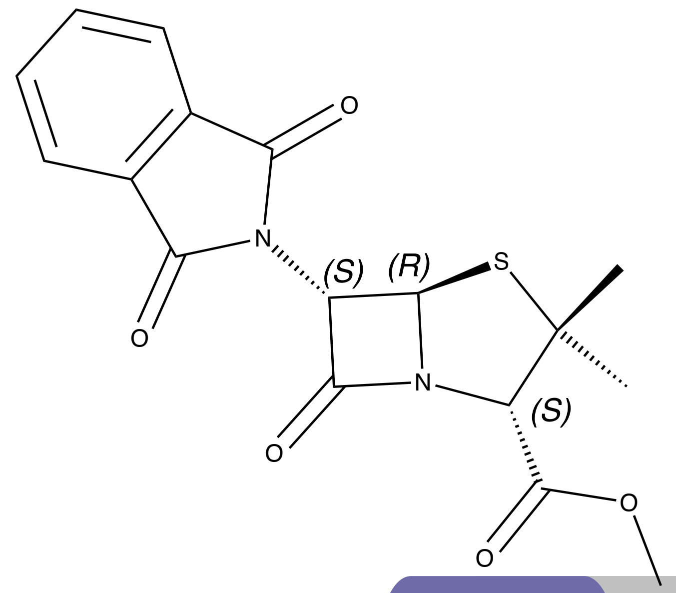
Structure 2



Structure 3



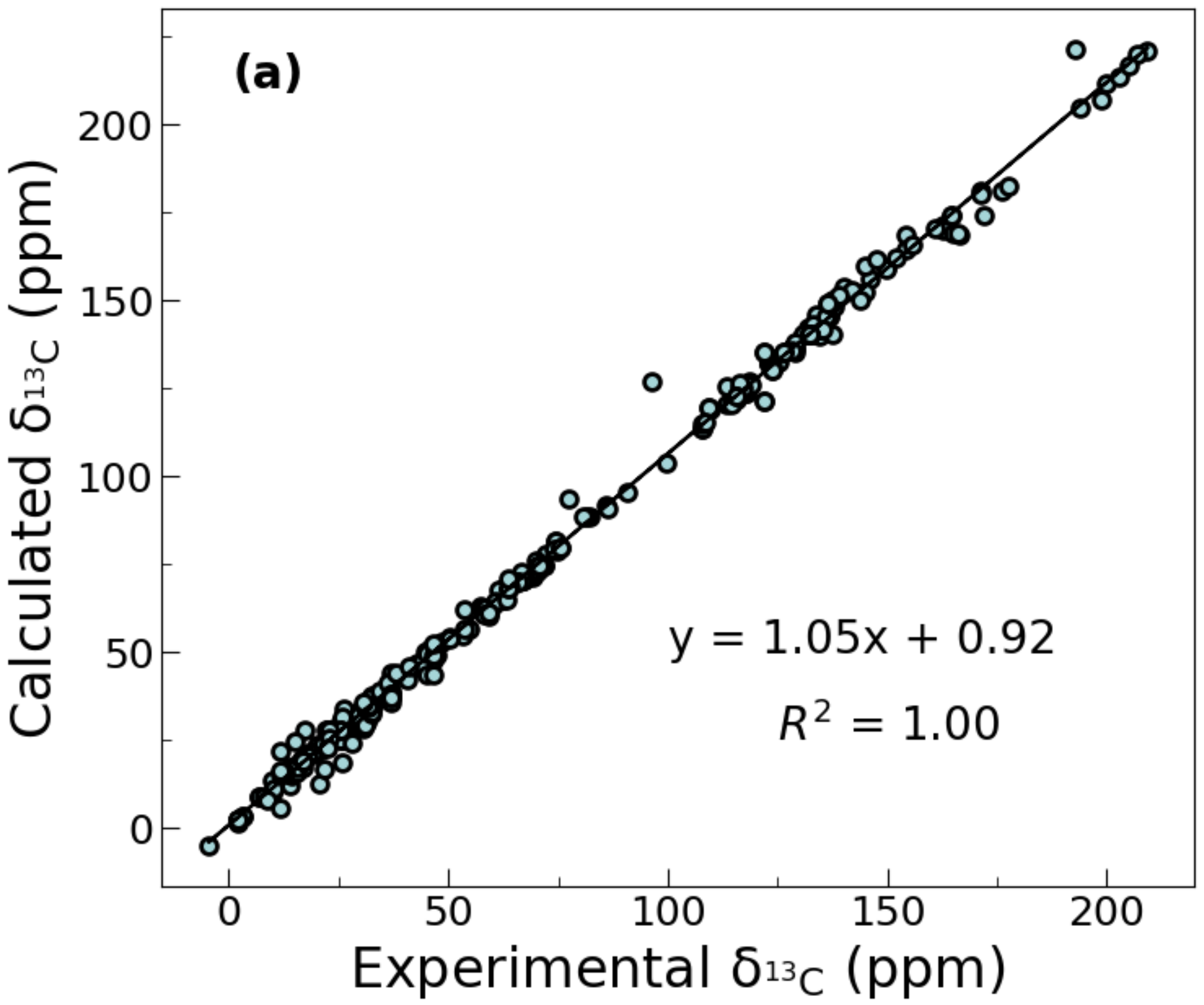
Structure 4

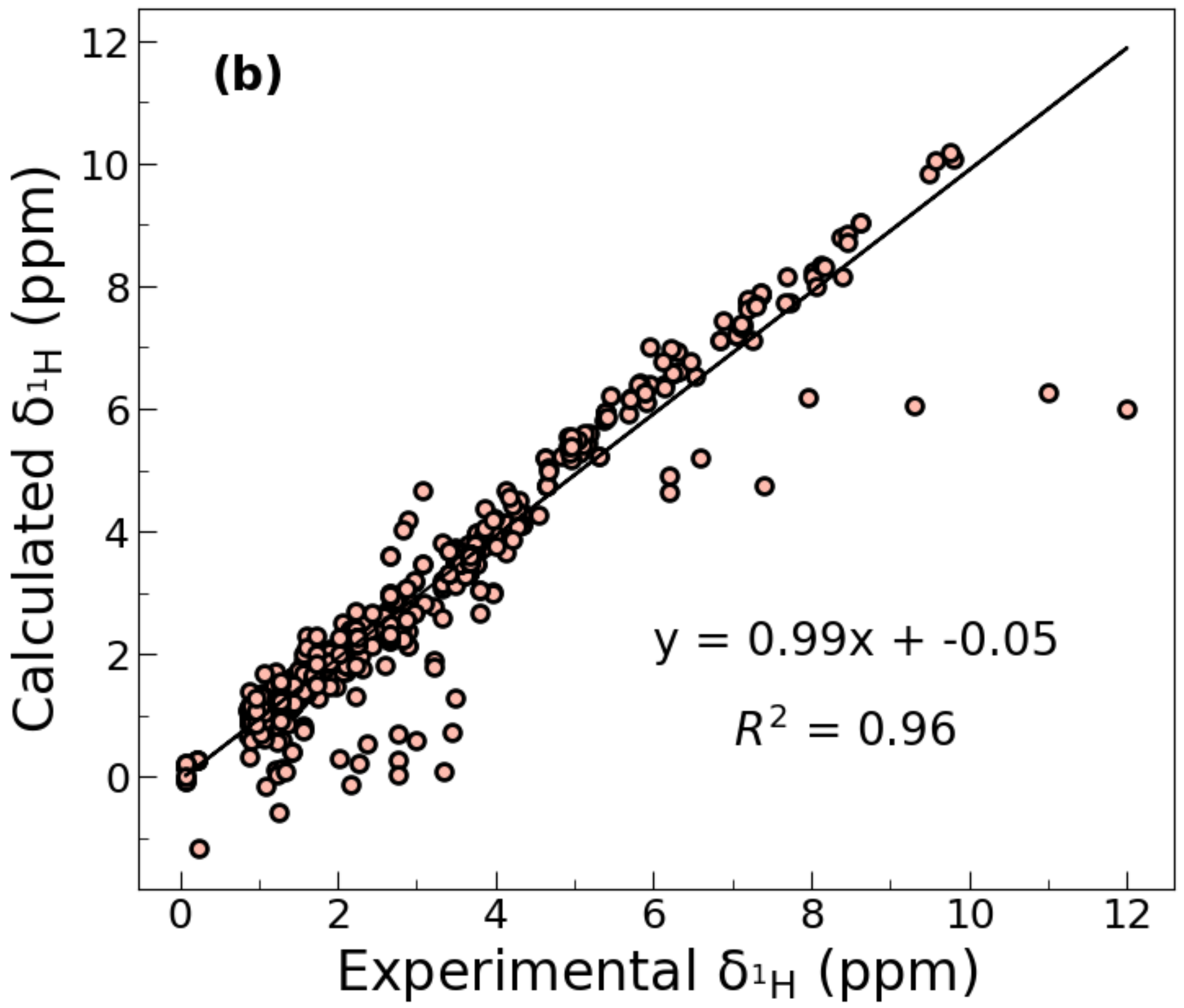


Atwi et al Nature Computational Science, 2022

Shelke & Atwi et al Joule (under review)

High-throughput Capability of the Workflow: ^{13}C and ^{1}H NMR chemical shift of 100 molecules





- **DFT details:**
  - Solvent: chloroform
  - Solvation model: PCM
  - Level of theory: ωB97X/def2-TZVP

- Computed ^{13}C and ^{1}H chemical shifts deviate from unity (desired slope = 1) by 0.05 and 0.01 ppm, respectively
- High correlation coefficients are obtained

Sample NMR Document as Saved in the Computational Database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                  “eigenvalues”: […, …, …],
           …},
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Molecule/cluster geometry

Metadata for easy retrieval

Calculation results

DFT parameters

Software version

mongoDB

Li-S Battery Technology

Why Li-S batteries?

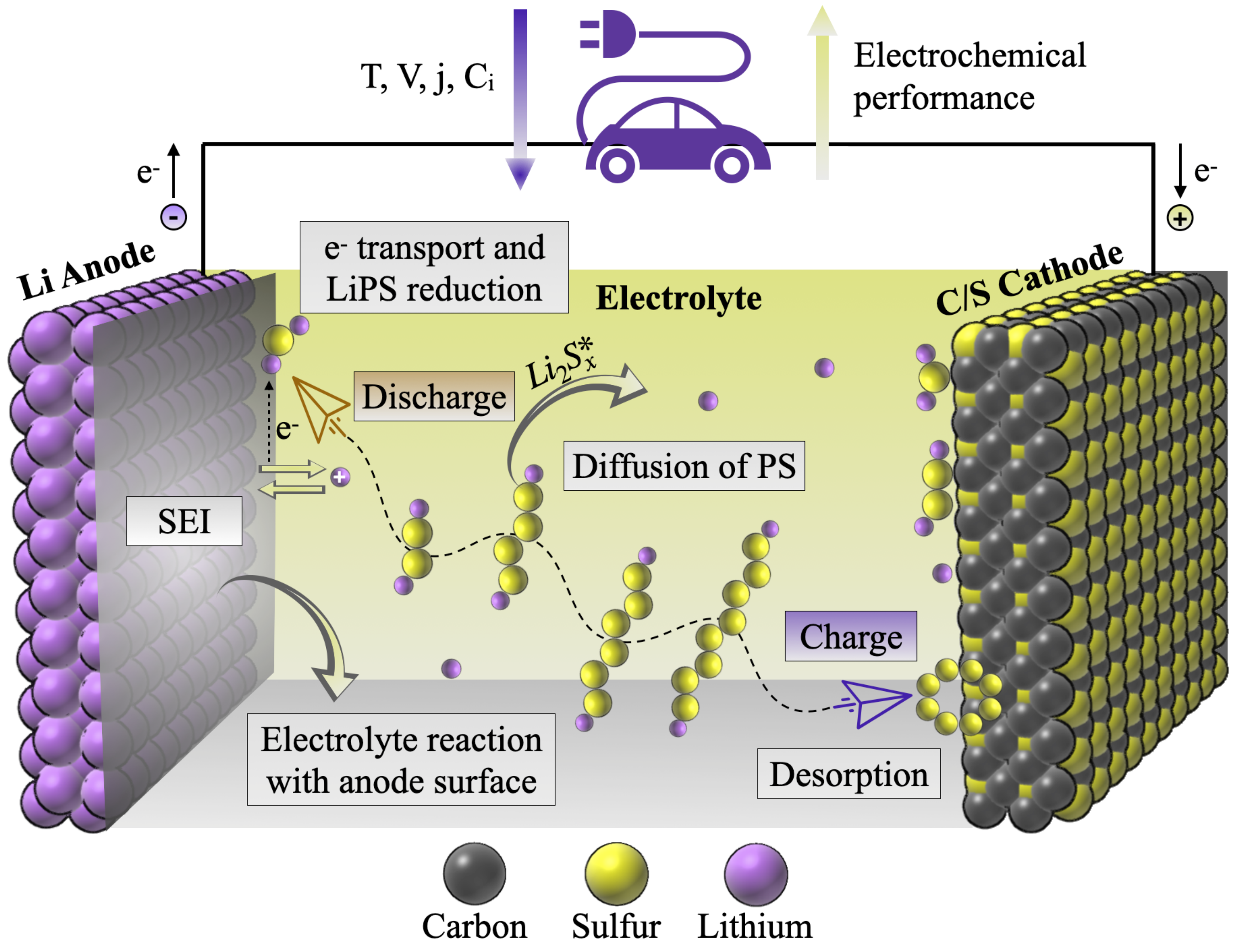
- Five times higher energy density compared to Li-ion battery (2600 Wh/kg)
- Low cost(S is 17th richest element in earth crust)
- Smaller and lighter than Li-ion

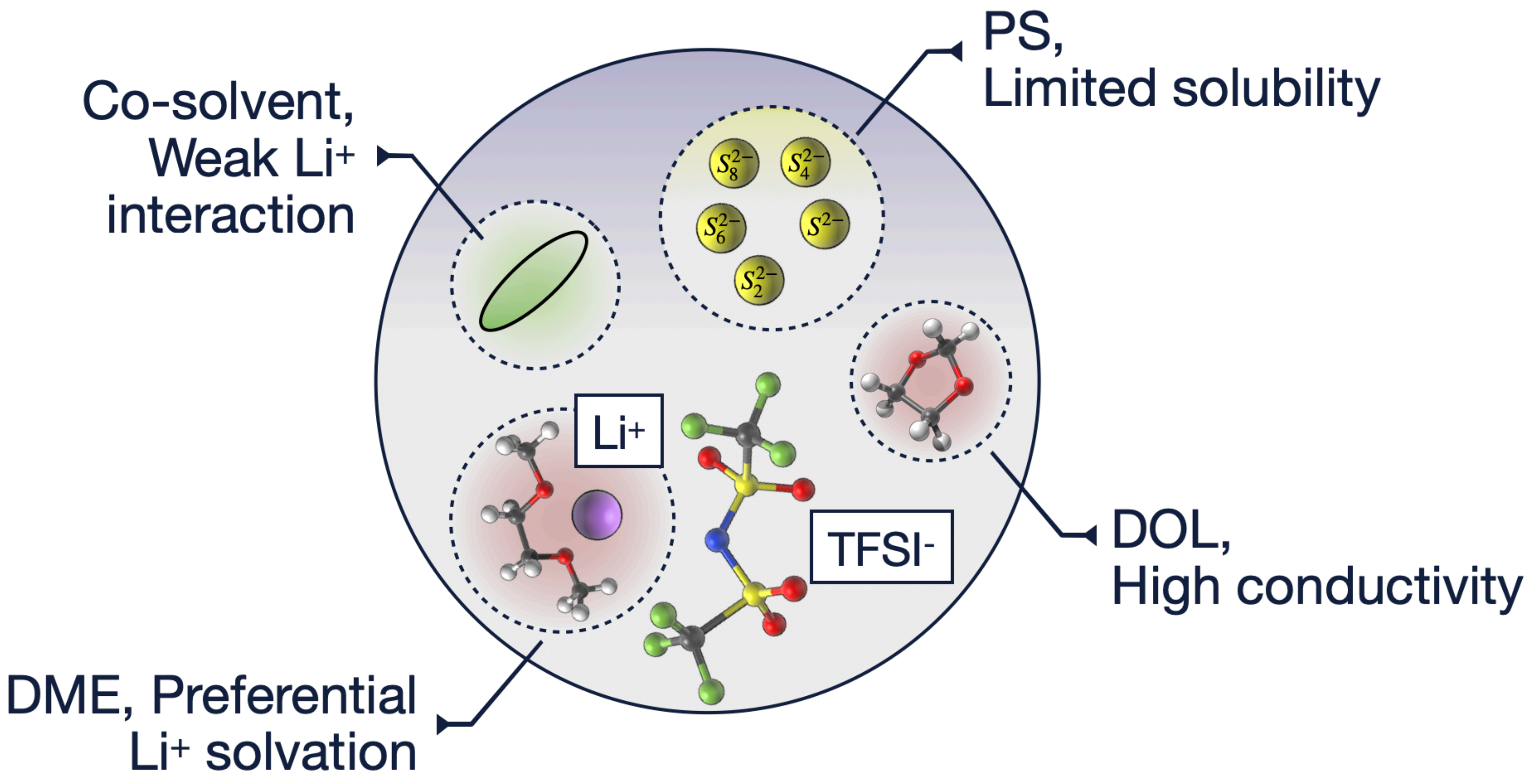
Major problems associated with Li-S batteries

- Short cycle life, low charging efficiency, poor safety
- **Major issues** include polysulfide (PS) dissolution and parasitic reactions at Li metal anode

Possible Solution

- **Design** optimal electrolytes with
  - Low solubility of PSs
  - High solubility of salt
  - High ionic conductivity
  - Low viscosity





Classes of Explored Solvents for Li-S Liquid Electrolytes

16 chemical classes (56 solvents)

Acetamide	**2**
Acetate	**1**
Azole	**2**
Ether	**14**
Fluorinated	**17**
Formamide	**1**
Nitrile	**2**
Nonpolar	**2**
Phosphate	**2**
Phosphite	**1**
Silane	**1**
Sulfide	**1**
Sulfite	**2**
Sulfonamide	**2**
Sulfone	**5**
Sulfoxide	**1**

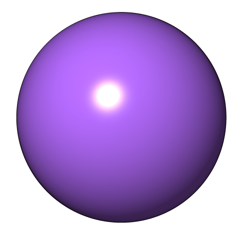
Some experimentally tested solvent mixtures

Combination	Class
DOL + DME	Ethers
DOL + TTE	Ether + Fluorinated
DOL + TEGDME	Ethers
DOL + PEGDME	Ethers
TEDGME + Toluene	Ether + Nonpolar
TEGDME + ETFE	Ether + Fluorinated
DOL + ETFE	Ether + Fluorinated
SL + DMS	Sulfone + Sulfite
SL + DES	Sulfone + Sulfite
DOL + TFEE	Ether + Fluorinated
SL + TTE	Sulfone + Fluorinated
TEGDME + TTE	Ether + Fluorinated

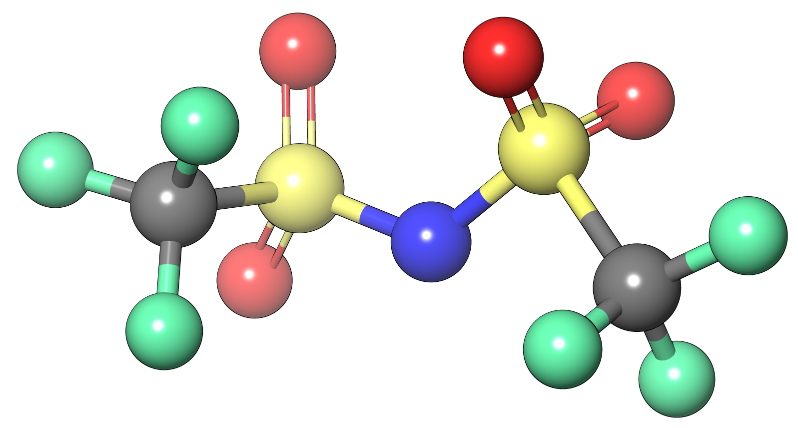
Electrolyte compositions to model

1 M LiTFSI, 0.25 M Li_2S_n,

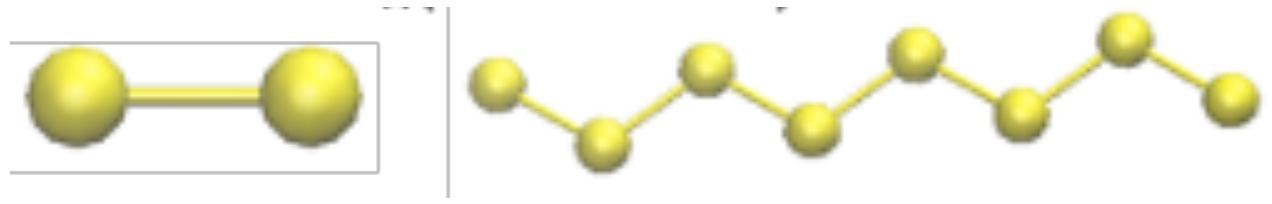
Li^+



$TFSI^-$

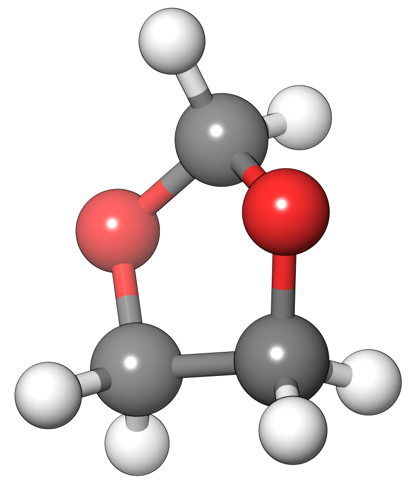


S_n (n = 2 to 8)

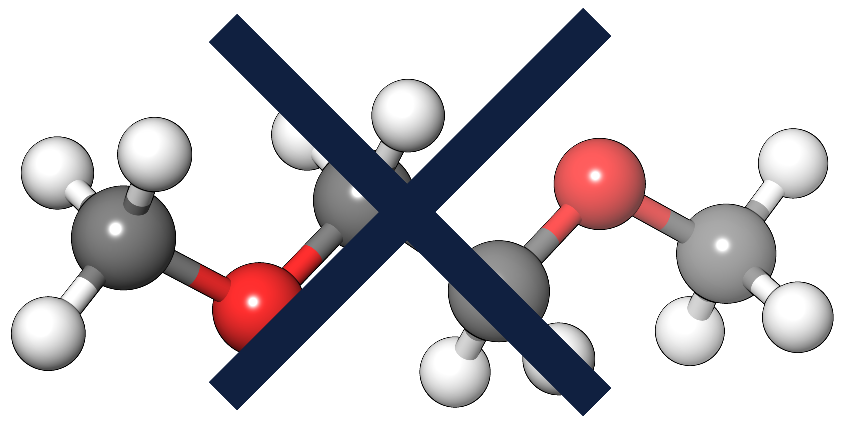


in a mixture of:

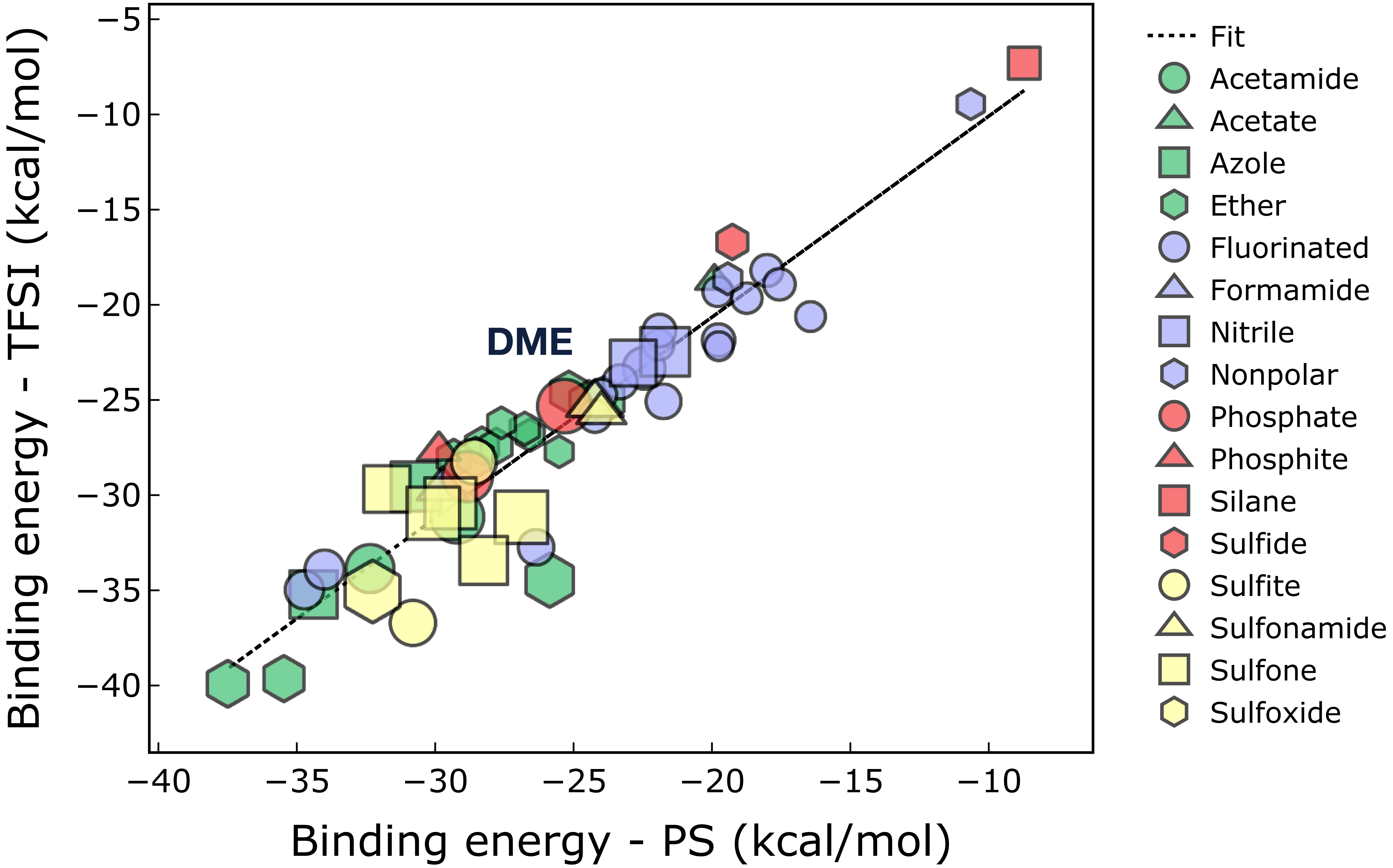
DOL



DME



Binding Energy as a Descriptor for Solvent Coordinating Power



- Binding energy (BE) is computed between the solvents with each of the salt and the polysulfide
- High absolute BE is indicative of strong binding affinity with the electrolyte component
- Solvents of the same chemical class exhibit similar orders of BE and degree of Li^+ dissociation
- Ethers such as TEGDME and G3 exhibit highest binding affinity while silane shows the weakest interaction strength

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Impact of the Solvent on the Clustering Tendency of LiPSs

		Bridging	BE (PS)	P (s = 1.0)	P (s = 2.0)	P (s = 3.0)	P (s = 4.0)
Acetamide	NMA	0.02	-29.2	0.87	0.13	0	0
	DMA	0.02	-32.35	0.94	0.06	0	0
Acetate	MA	0.04	-19.91	0.8	0.19	0.01	0
Azole	DMI	0.01	-34.39	0.87	0.13	0	0
	MEIM	0.01	-30.7	0.89	0.11	0	0
Ether	MTBE	0.06	-26.57	0.62	0.27	0.09	0.01
	DIPE	0.04	-27.78	0.65	0.31	0.04	0
	DBE	0.06	-25.52	0.68	0.31	0.02	0
	EPE	0.04	-26.76	0.69	0.27	0.04	0
	TEGDME	0.05	-37.49	0.71	0.26	0.03	0
	HME	0.05	-27.6	0.73	0.27	0.01	0
	THF	0.03	-28.31	0.78	0.21	0.02	0
	PEGDME	0.02	-25.86	0.79	0.21	0	0
	DME	0.03	-25.17	0.86	0.13	0.01	0
	DEGDBE	0.02	-28.54	0.87	0.13	0	0
	DEGDME	0.02	-23.91	0.88	0.12	0.01	0
	EEE	0.01	-24.45	0.88	0.12	0	0
	G3	0.01	-35.46	0.9	0.1	0	0
	METHF	0.01	-29.33	0.91	0.08	0	0
Fluorinated	FDE	0.1	-21.75	0.35	0.5	0.15	0
	TFEE	0.07	-21.93	0.51	0.41	0.08	0
	TFEPE	0.06	-21.9	0.51	0.38	0.11	0
	TFEP	0.06	-23.31	0.53	0.35	0.12	0
	TPE	0.06	-17.56	0.58	0.41	0.01	0
	TFEIBE	0.05	-16.44	0.61	0.33	0.06	0
	HFME	0.05	-19.76	0.64	0.32	0.04	0
	TFETFE	0.07	-18.02	0.66	0.2	0.07	0.07
	TTE	0.05	-19.79	0.67	0.28	0.03	0.02
	DFEP	0.04	-24.01	0.67	0.27	0.05	0
	ETFE	0.05	-19.75	0.69	0.29	0.02	0
	OFE	0.06	-18.74	0.71	0.26	0.03	0
	ETTFPE	0.05	-24.23	0.74	0.21	0.04	0
	BTFE	0.02	-22.45	0.76	0.24	0	0
	DTFEG	0.04	-26.35	0.8	0.2	0	0
	TFPG	0.03	-33.99	0.81	0.19	0	0
	TFEG	0.01	-34.72	0.89	0.11	0	0

		Bridging	BE (PS)	P (s = 1.0)	P (s = 2.0)	P (s = 3.0)	P (s = 4.0)
Formamide	DMF	0.02	-29.73	0.88	0.11	0.01	0
Nitrile	PRN	0.02	-22.84	0.81	0.16	0.02	0
	ACN	0.02	-21.69	0.92	0.08	0	0
Nonpolar	TOLUENE	0.06	-19.43	0.59	0.38	0.03	0
	CYCLOHEXANE	0.05	-10.65	0.63	0.3	0.08	0
Phosphate	TMP	0.01	-25.33	0.83	0.16	0.01	0
	TEP	0.01	-28.83	0.94	0.06	0	0
Phosphite	TTFP	0.07	-29.86	0.66	0.3	0.03	0
Silane	TFMTMS	0.08	-8.72	0.59	0.37	0.05	0
Sulfide	DMDS	0.04	-19.26	0.72	0.26	0.02	0
Sulfite	DMS	0.01	-28.6	0.88	0.09	0.02	0
	DES	0.02	-30.8	0.96	0.04	0	0
Sulfonamide	DPT	0.02	-23.99	0.78	0.21	0	0
	DMT	0.01	-24.23	0.9	0.1	0	0
Sulfone	DPS	0.02	-31.74	0.82	0.17	0.01	0
	EMS	0	-26.88	0.91	0.09	0	0
	EIPS	0.01	-28.25	0.91	0.09	0	0
	IPMS	0.01	-30.07	0.97	0.03	0	0
	SL	0	-29.45	0.97	0.03	0	0
Sulfoxide	DMSO	0	-32.26	0.97	0.03	0	0

0 0.05 0.1

−40 −30 −20 −10

0 0.5 1

- Fluorinated, non polar, silane, and sulfide solvents result in the formation of nanometric aggregate domains in the solution
- Highest PS solubility occurs in sulfite, sulfonamide, sulfone, and sulfoxide containing electrolytes

- Bridging: probability of more than one polysulfide in the cation first solvation shell
- P (s): probability of forming a PS of cluster size s (1-4)

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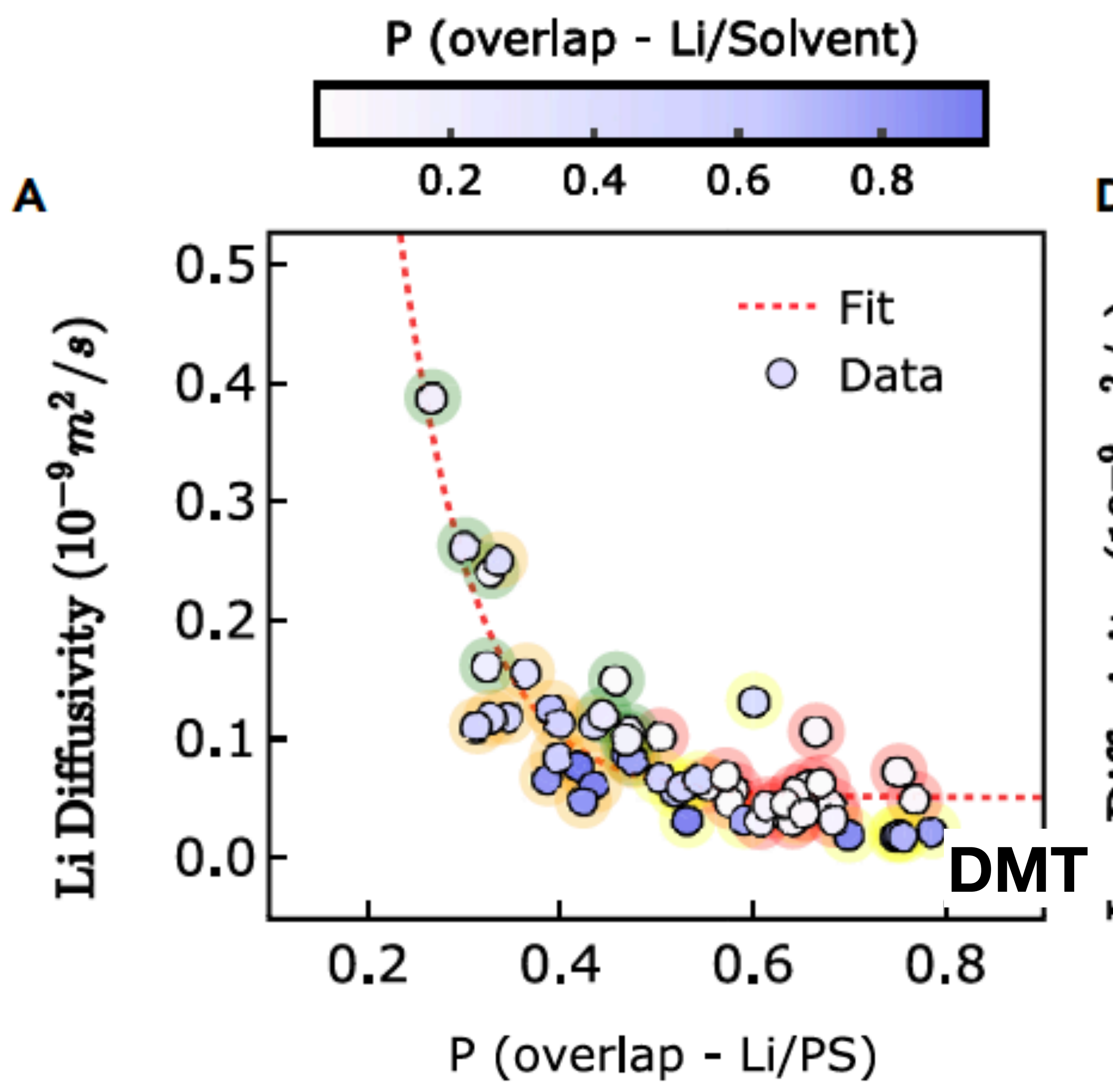
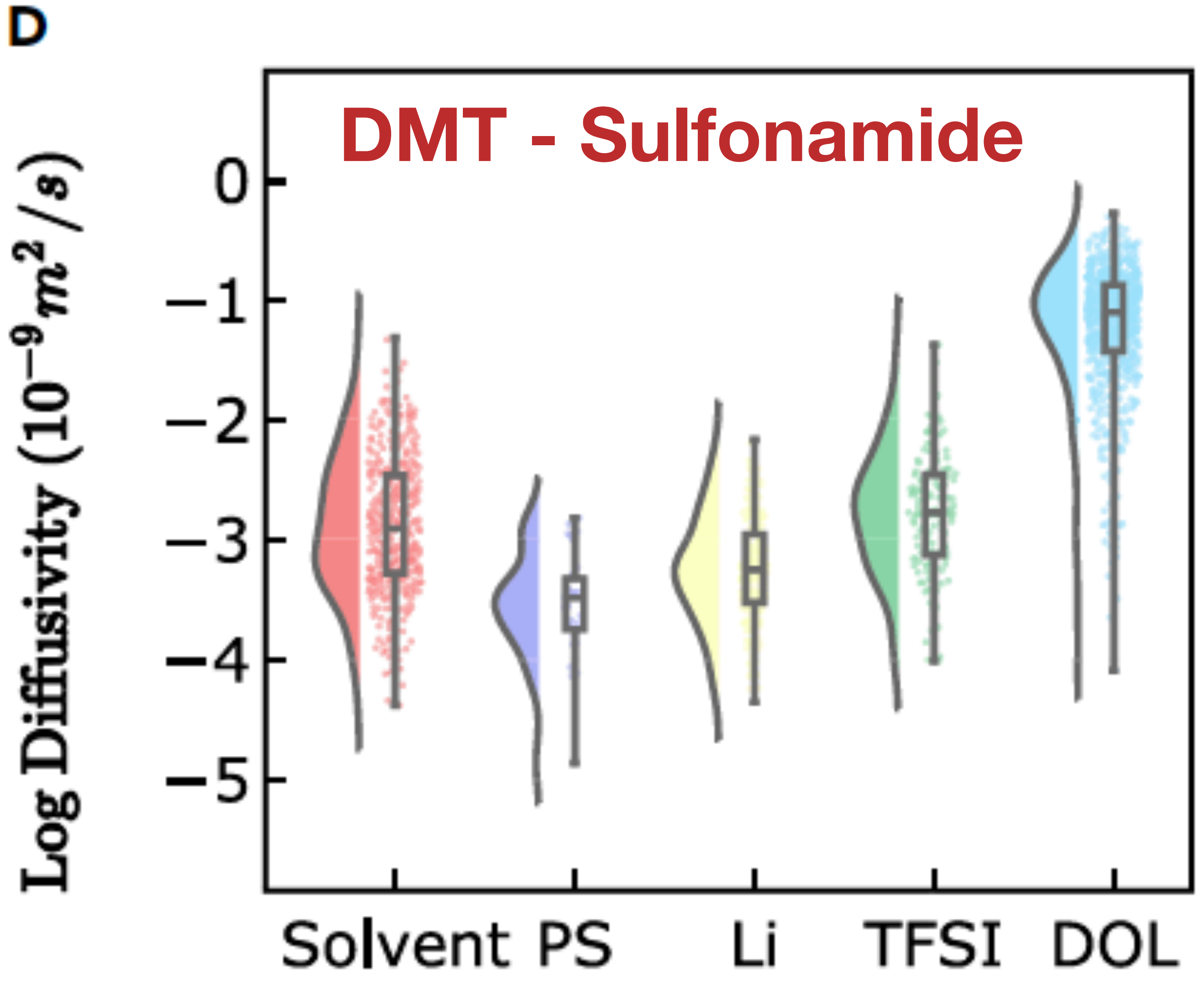
Dynamical Behavior As a Function of the Solvent Type





$$D = \frac{1}{6N}\lim_{t\to\infty}\frac{d}{dt}\sum_{i=1}^{N}\langle[r_i(t)-r_i(t_0)]^2\rangle$$

$$P_{overlap} = 1 - \frac{\int_{D_{min}}^{D_{max}}|d_{Li^+} - d_i|}{2}$$

- The diffusion of ionic species decays exponentially as the P (overlap) of the diffusion of the cation with that of the PS increases indicating much slower dynamics
- Group A: High $P_{overlap}$ and slow ionic dynamics (phosphate-, phosphite-, sulfonamide-,sulfone-, and sulfoxide-containing electrolytes)
- Origins of the observed dynamical behavior include viscosity of the pure solvent, PS aggregation in solution, nature of the cation solvation structure (e.g. tight solvation versus rapidly exchanging environment)

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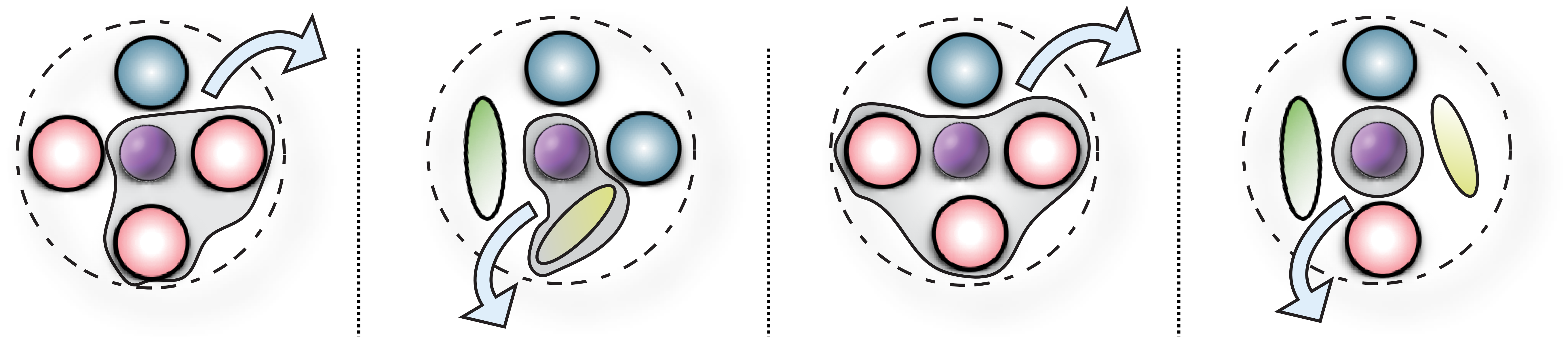
Categorization of solvents based on structural and dynamical analysis



	Group 1	Group 2	Group 3	Group 4
Structure	SSIP	CIP	SSIP	CIP
Polysulfide solubility	High	Lowest	High	High
Diffusion	Slowest	Slow	Intermediate	Fast
Viscosity	High	Intermediate	Low	Lowest
Conductivity	Low	Low	Intermediate	High
Classes	Phosphates, Sulfones, Sulfonamides	Fluorinated, Nonpolar, Silane	Acetamide, Ether, Sulfite	Acetate, Nitrile, Few ethers

Legend

- Li^+
- $TFSI^-$
- Polysulfide
- DOL
- Cosolvent

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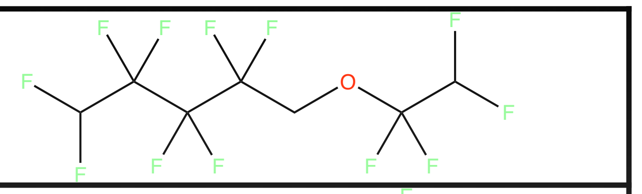
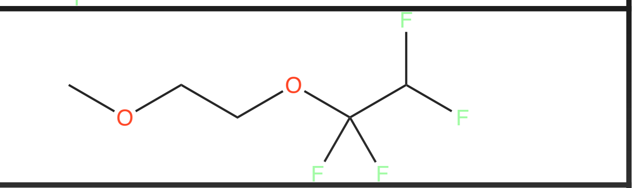
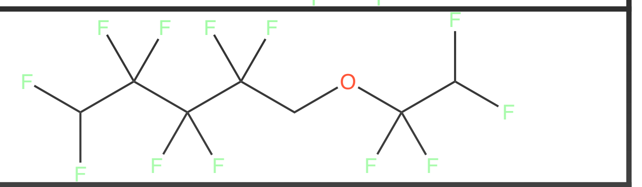
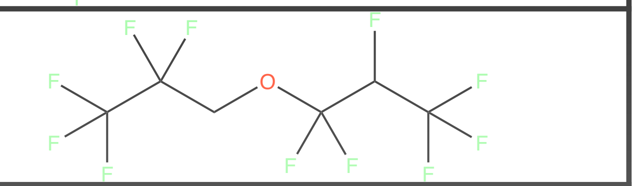
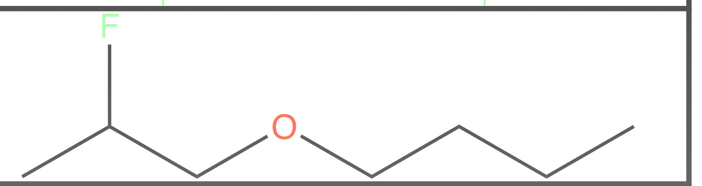
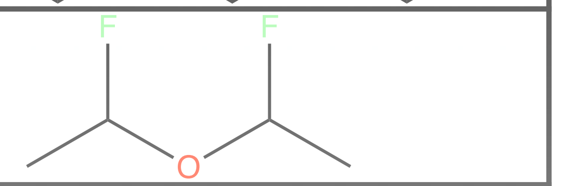
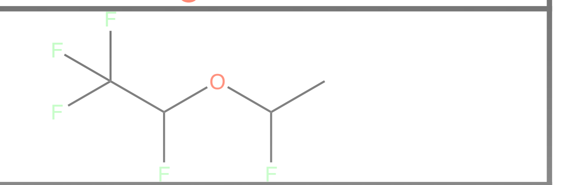
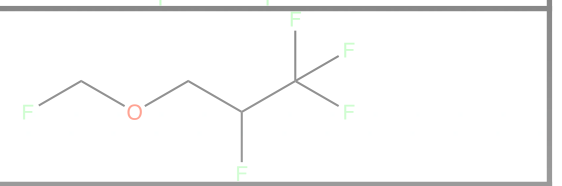
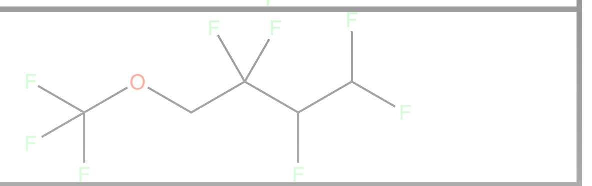
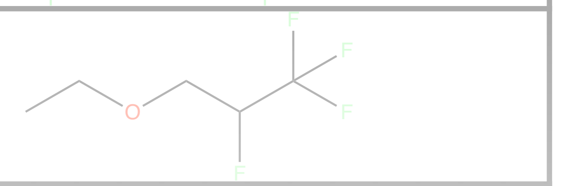
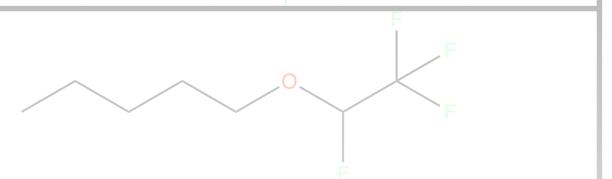
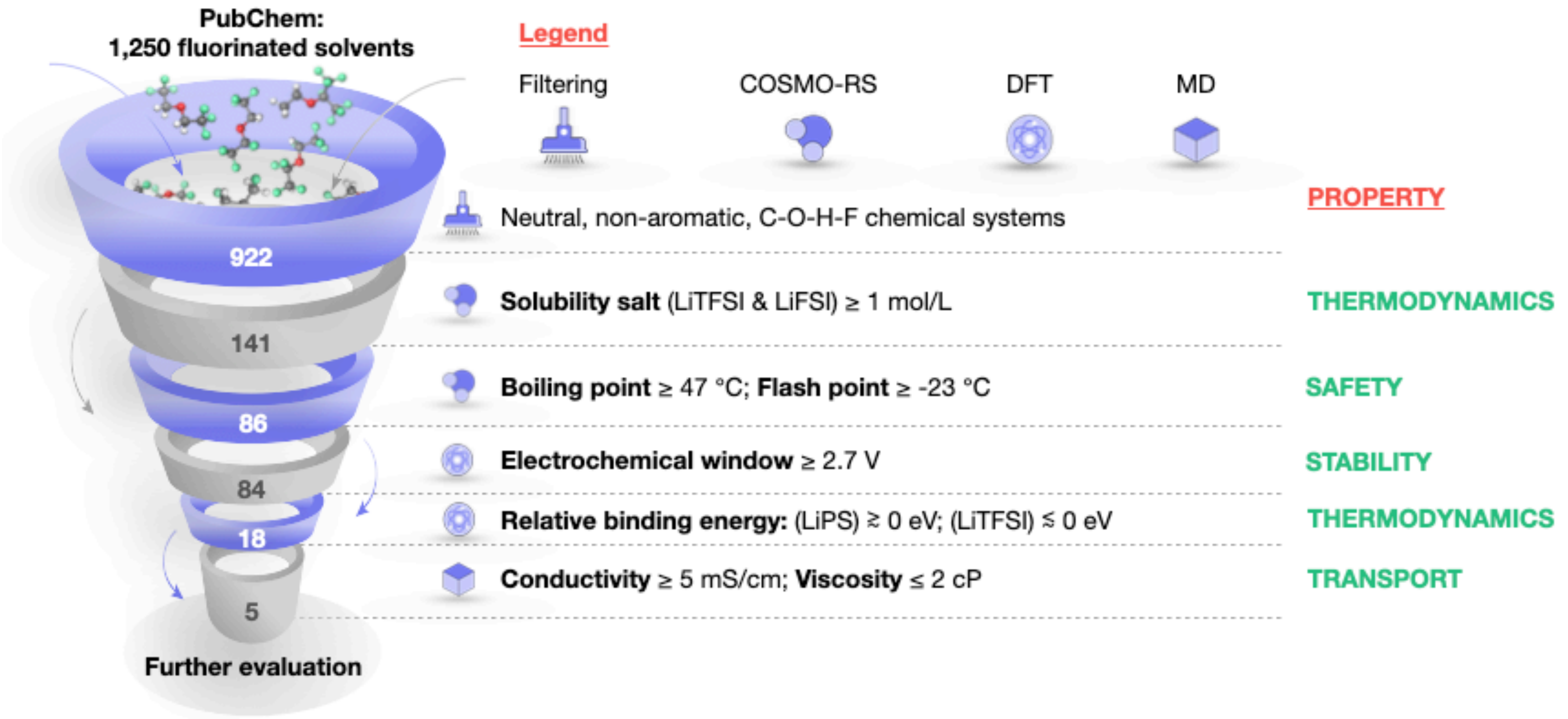
An overview of the high-throughput screening approach

We built a library of ~1,250 FLS molecules, only ~1.3% of which has been reported in Li-S literature.

FLS1	
FLS2	
FLS3	
FLS4	
FLS5	
FLS6	
FLS7	
FLS8	
FLS9	
FLS10	
FLS11	
FLS12	
FLS13	



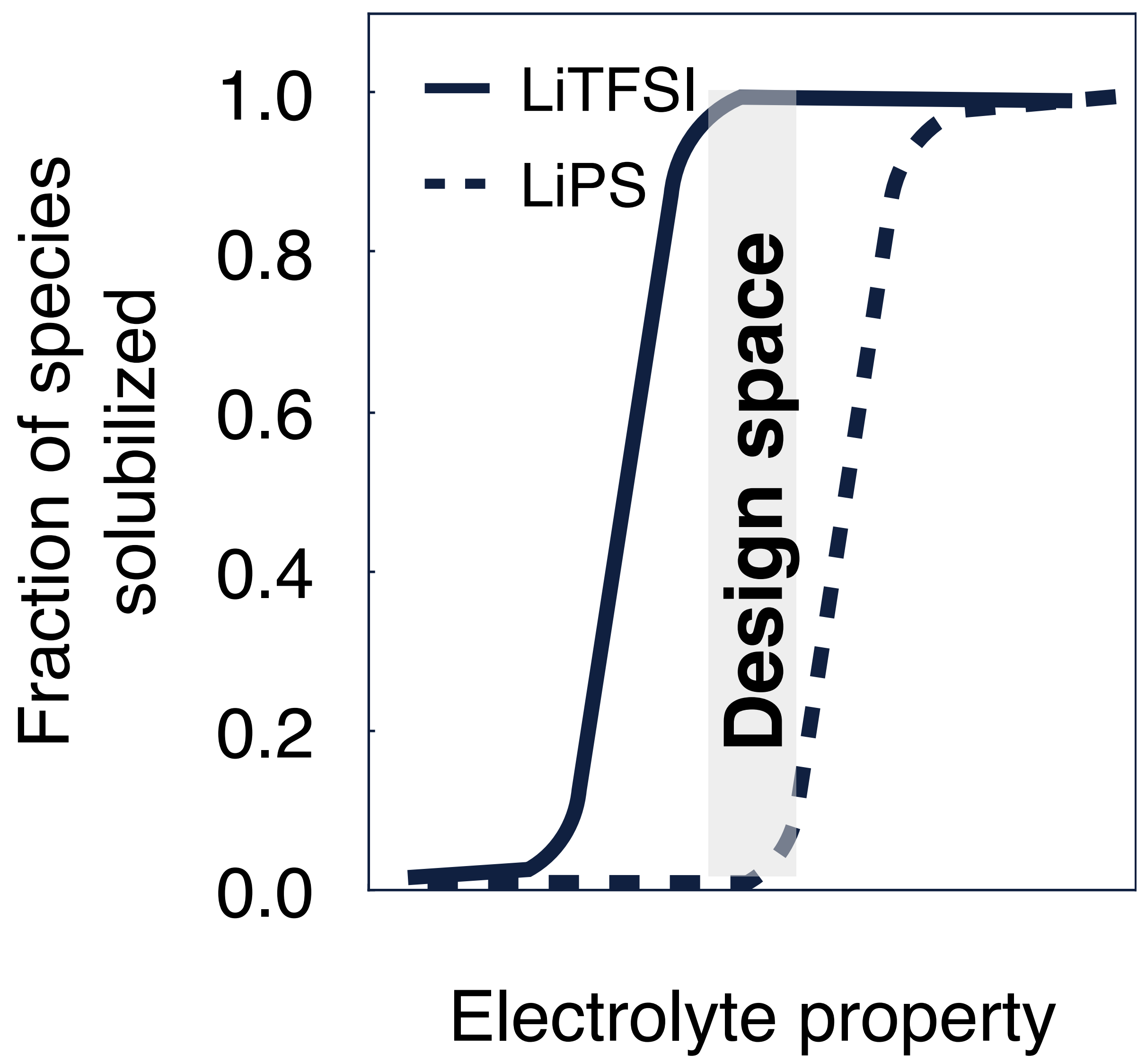
The optimal electrolyte composition will be identified as the one that meets LG-Energy's target.

Metric	Values
Cell cycle	> 200th
Viscosity	< 2 cP
Ionic conductivity	> 5 mS/cm
Li efficiency	> 99%

High-throughput Screening of Fluorinated Solvents

List of computed structural and DFT-based properties

Derived	COSMO	DFT	CMD
Molecular weight	Boiling point	Binding energy with LiTFSI	RDF
Complexity	Flash point	Binding energy with Li2S4	Coordination number
Radius	Solubility of LiTFSI	Electrochemical window	Conductivity
Gyration radius	Solubility of LiFSI	Polarizability	Viscosity
van der Waals volume		Dipole moment	
Proximity of F to O			
Fluorination degree			
Shape index			
Electro count			



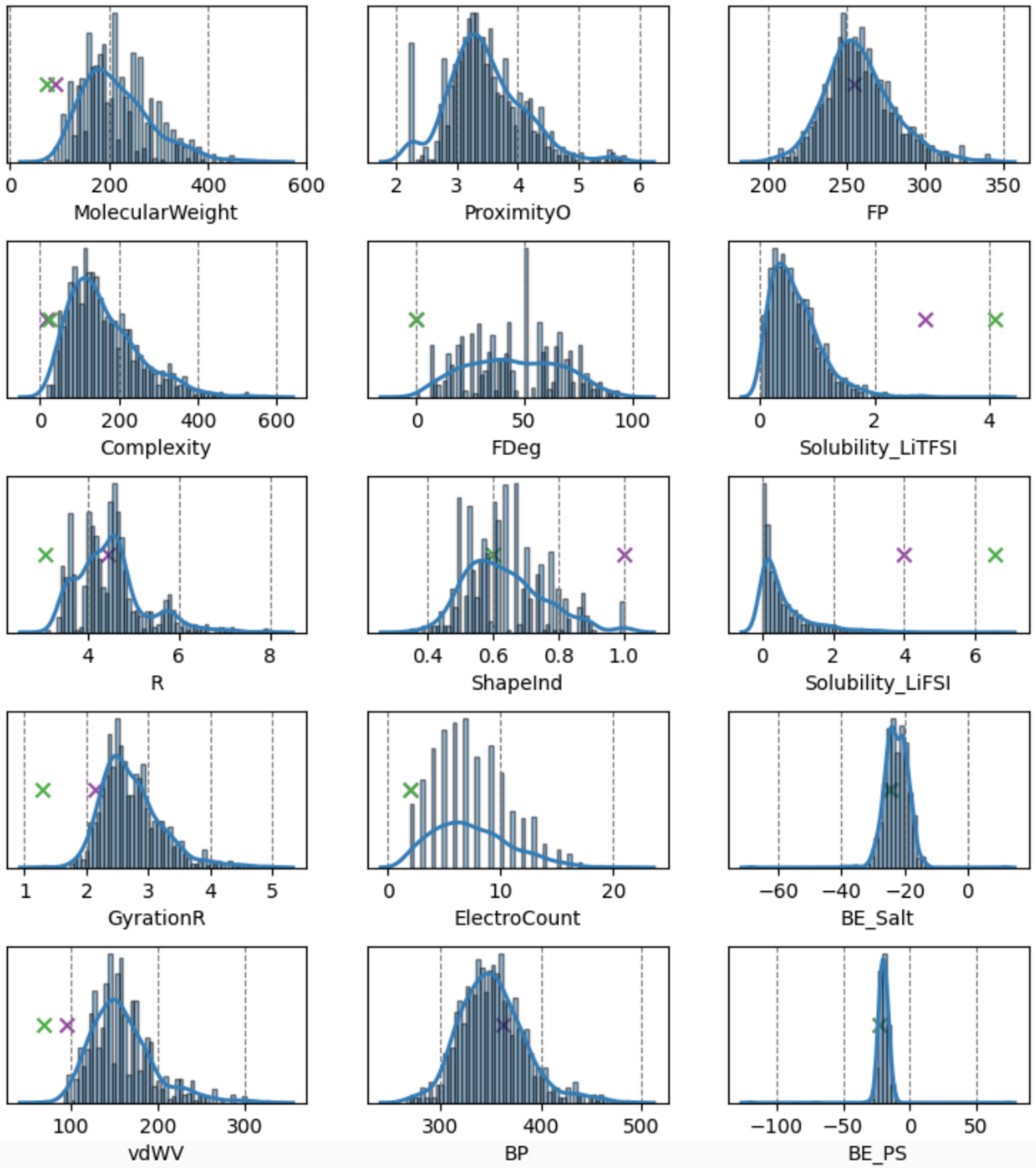
Legend

Low

Intermediate

High

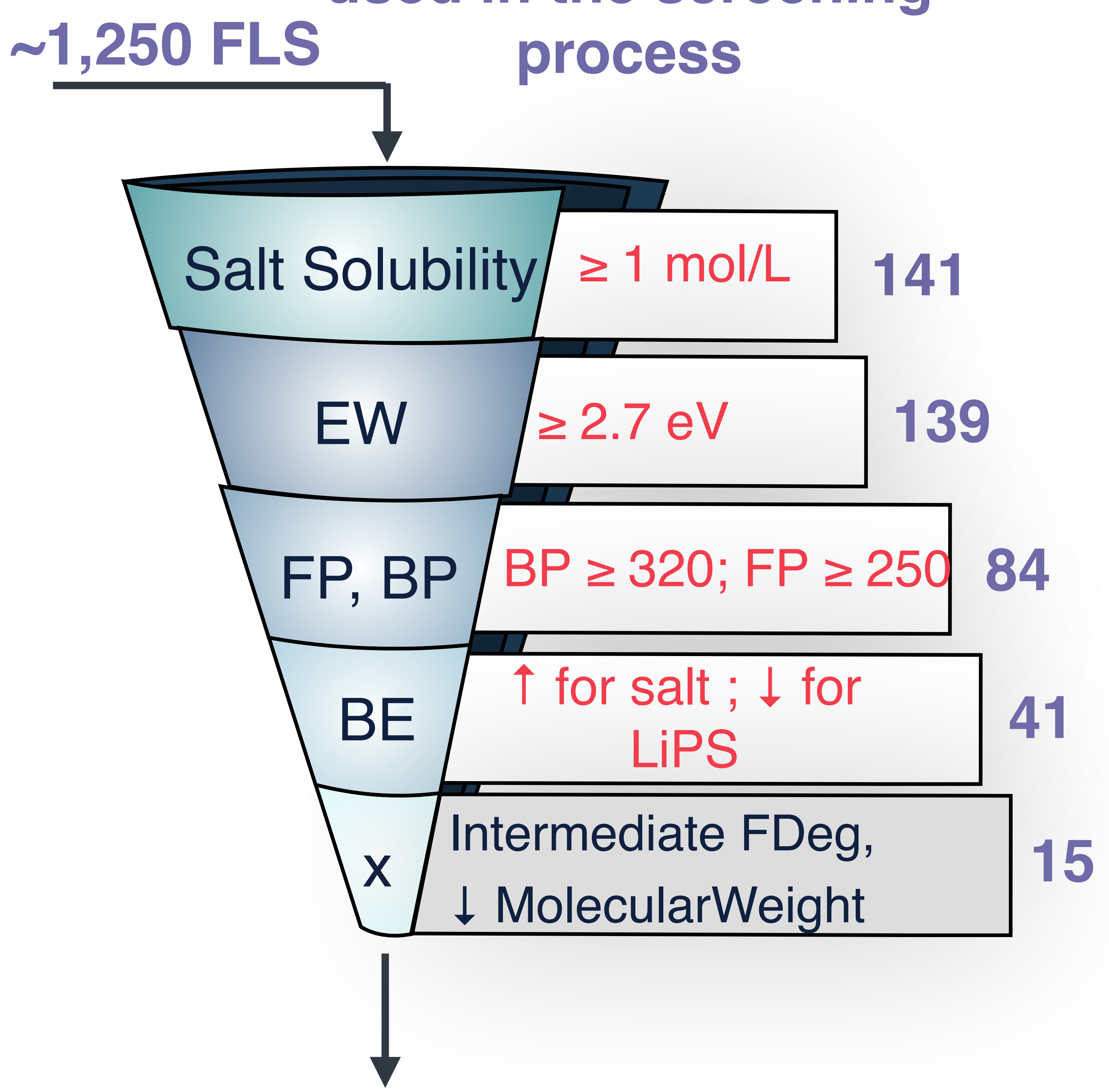
Critical quantitative limits used in the screening process



× DOL
× DME

Computed Properties of ~1,000 solvents

Structural
COSMO
DFT



18 FLS screened for further evaluation

- The first screening step identified solvents that allow for <u>salt dissolution</u>, can result in <u>medium-high voltage cells</u>, meet the <u>safety</u> limitations, and can potentially lead to <u>optimal solubility</u>

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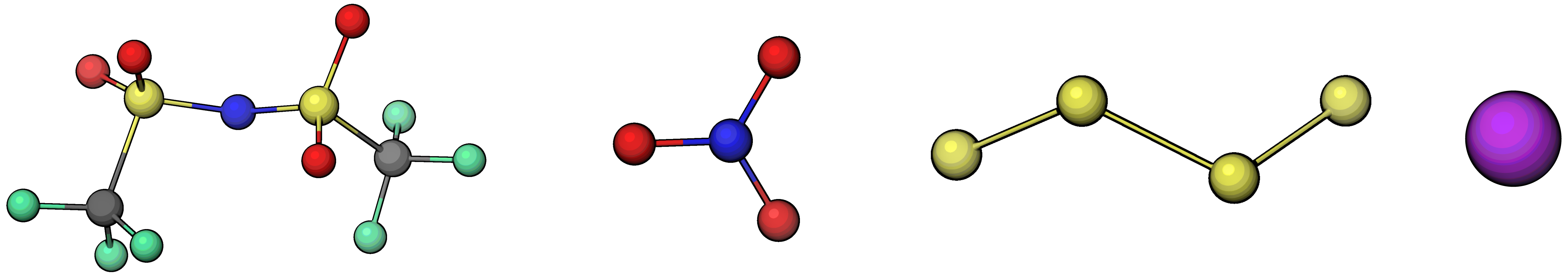
Electrolyte Compositions Selected for Further Evaluation

$TFSI^-$ NO_3^- S_4^{2-} Li^+



<u>1 M LiTFSI, 0.25 M Li_2S_4, 1 wt% $LiNO_3$ **in:**</u>

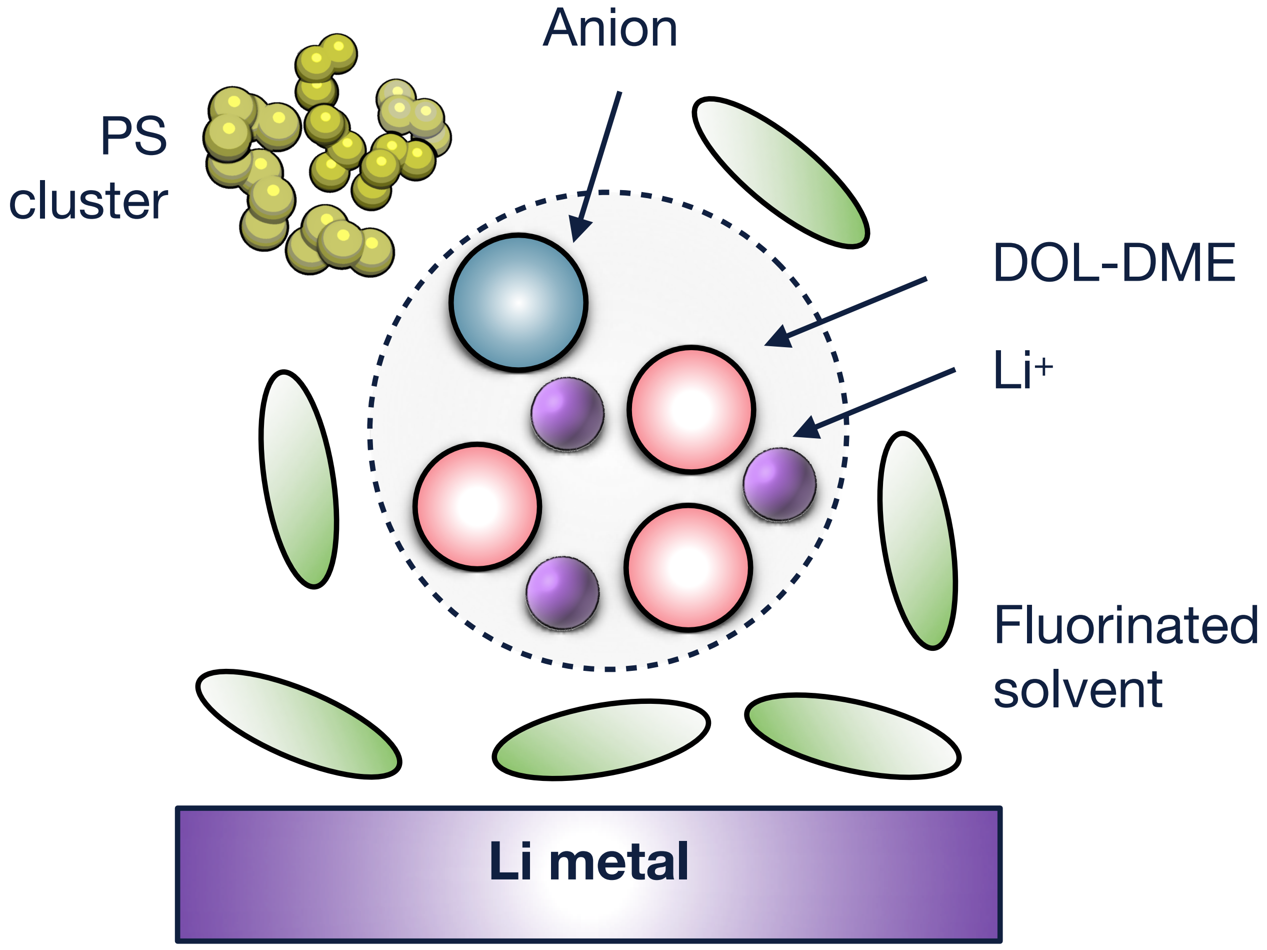
Reference Systems

1:1 DOL:DME

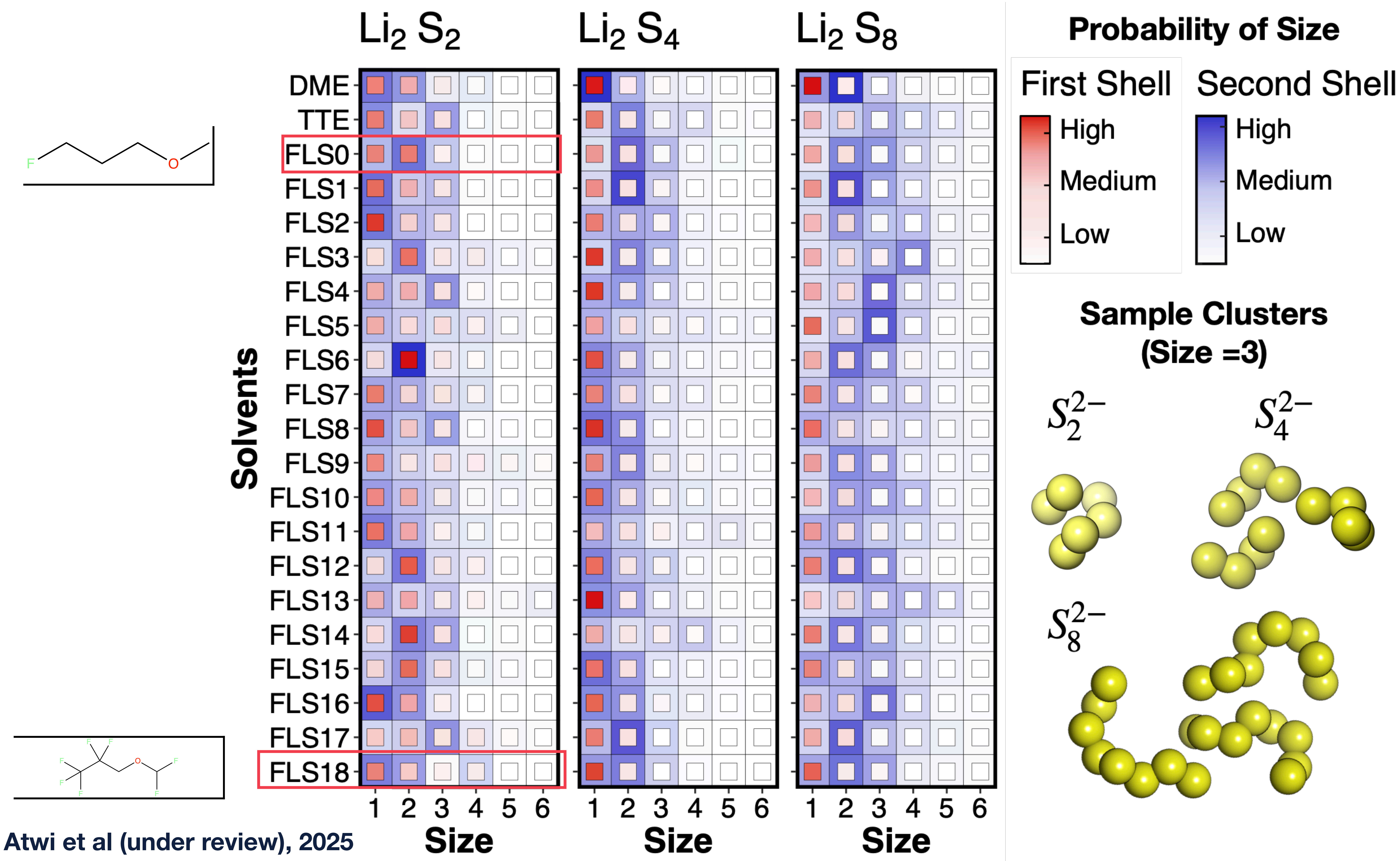
1:1 DOL:TTE

Proposed Systems

1:1 DOL:FLSn for n = 1-18



Cluster formation in Screened Electrolytes



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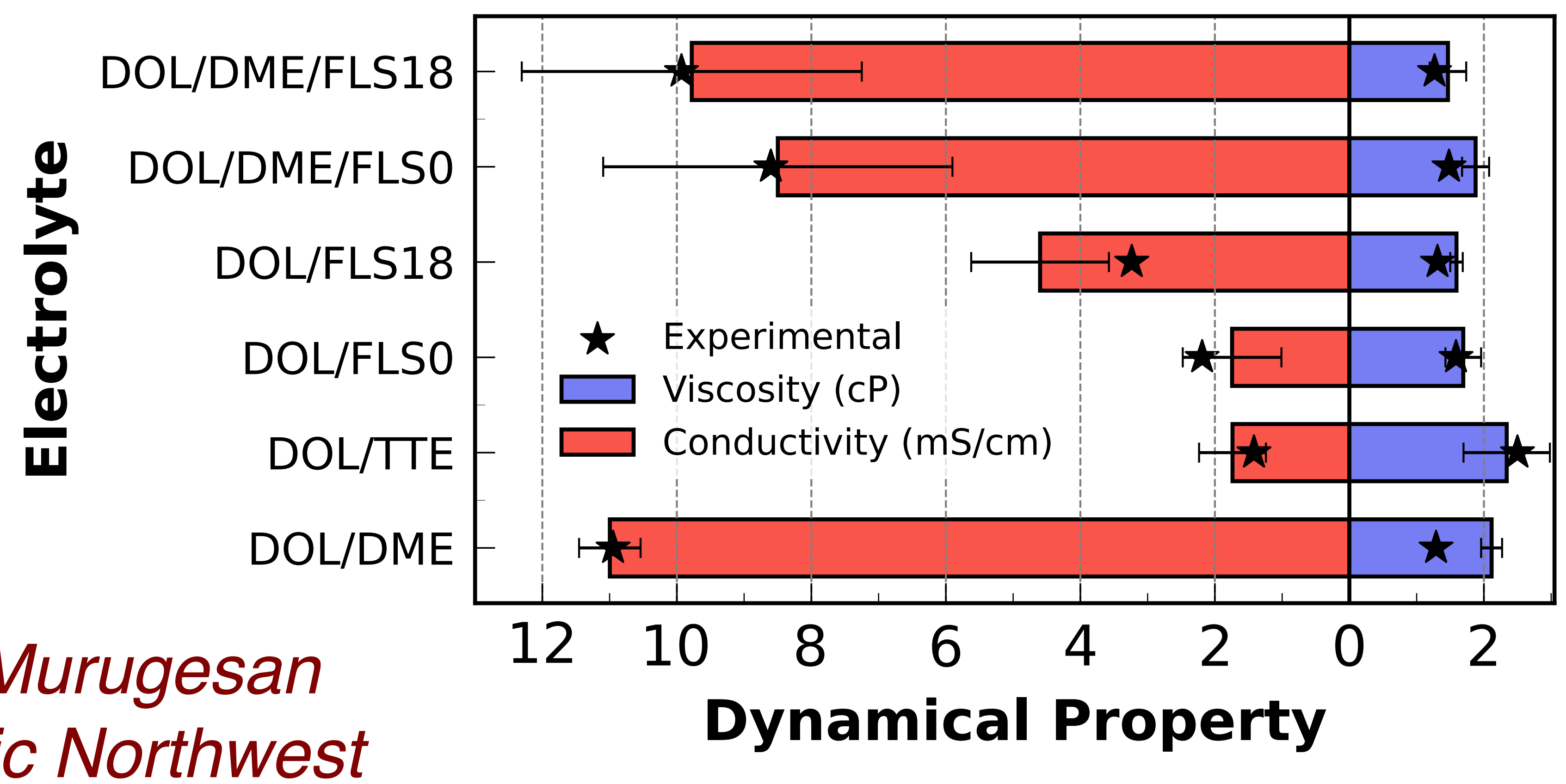
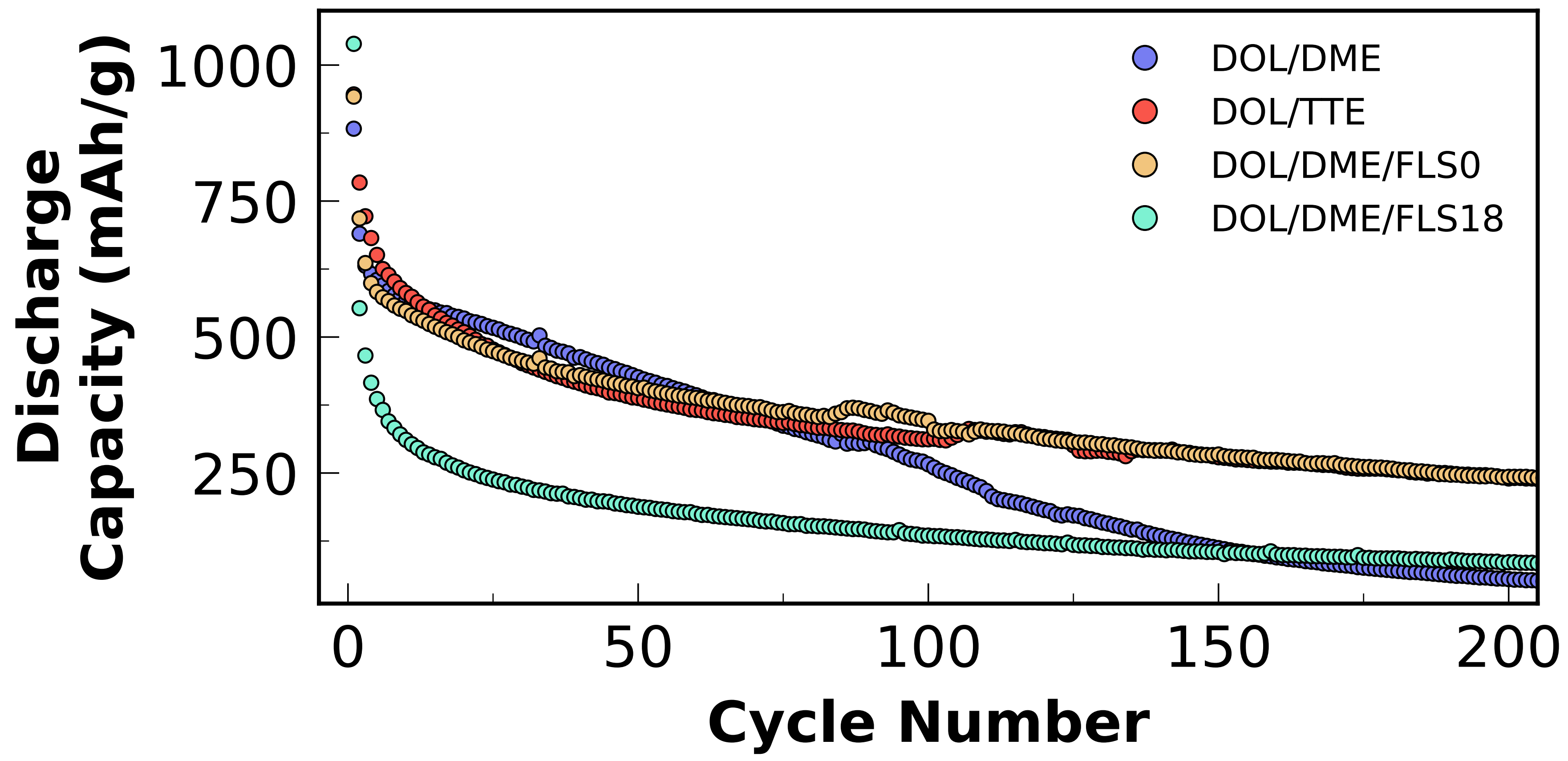
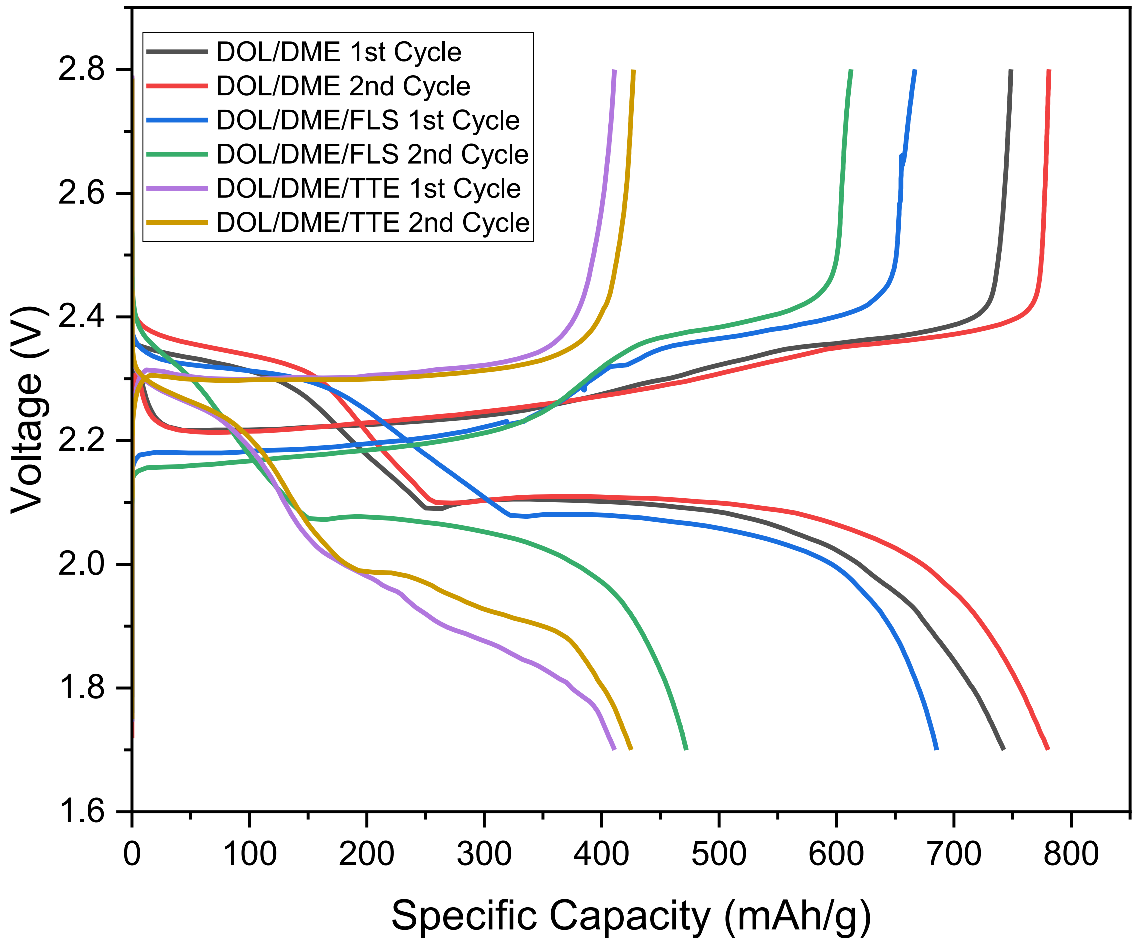
Dynamical and Electrochemical Properties of Screened Systems

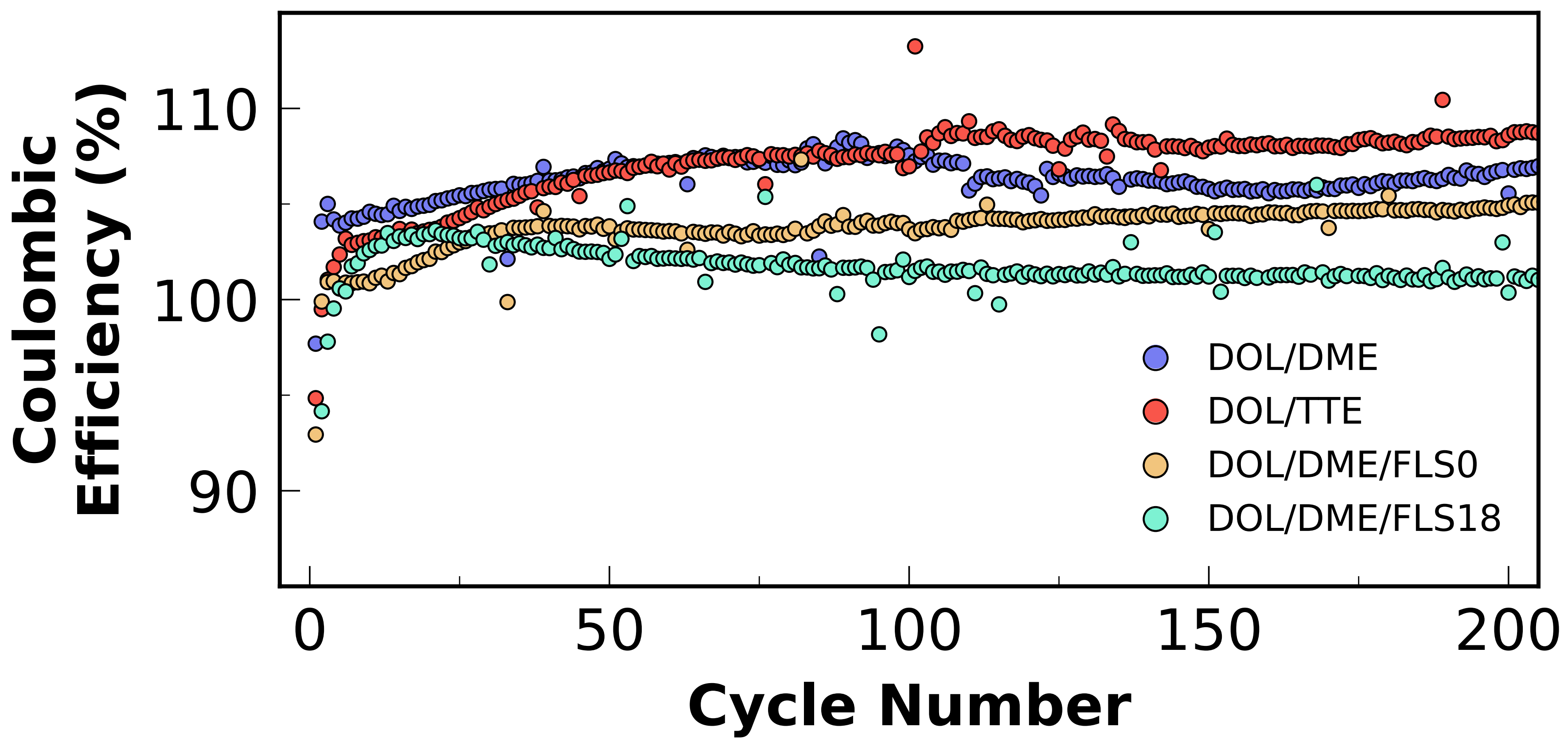


Vijay Murugesan (Pacific Northwest National Lab)



Vilas Pol (Purdue University)



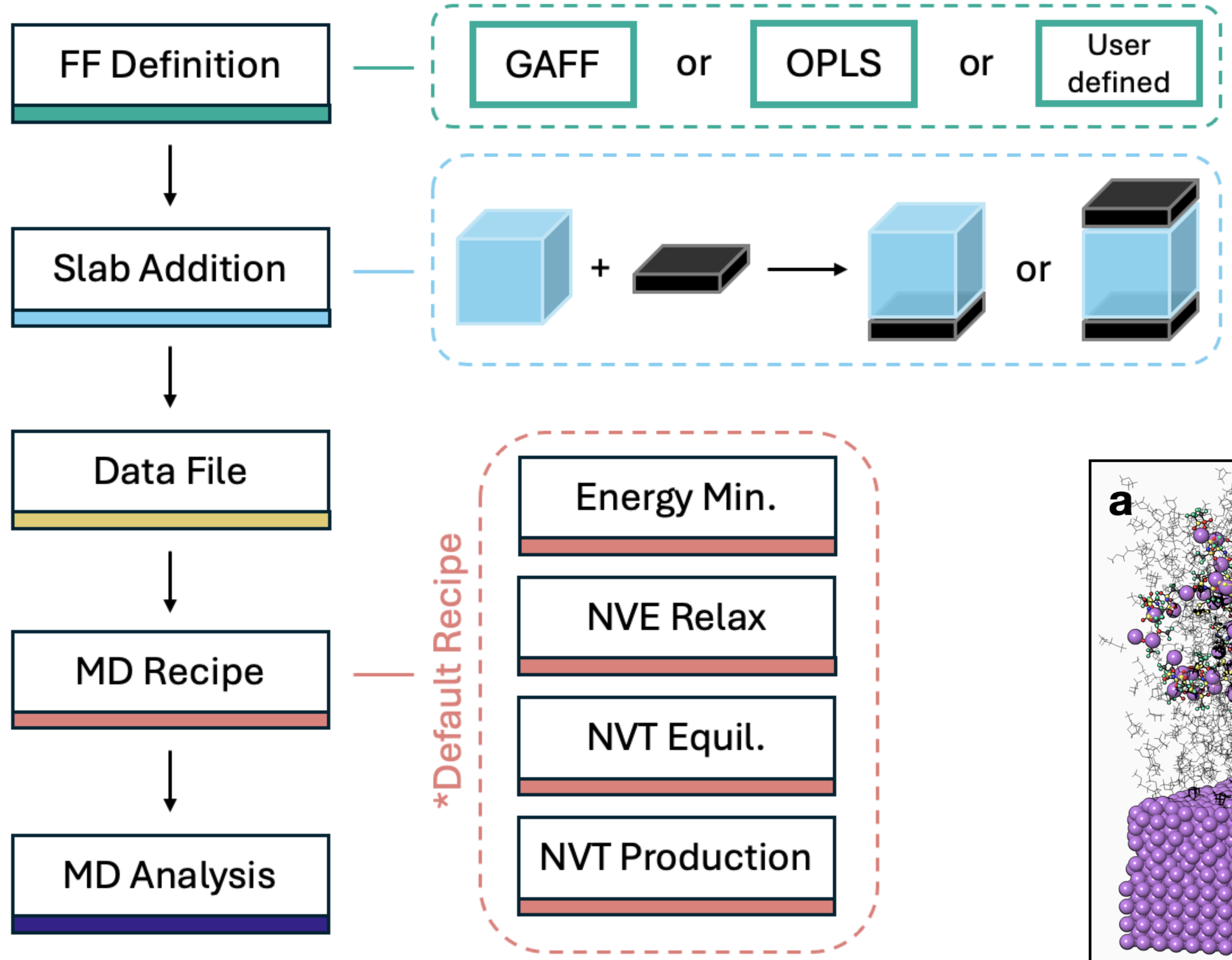


- Screened systems show better dynamical properties compared to the state-of-the-art fluorinated solvent (TTE)
- For FLS0, the capacity retention and Coulombic efficiency appear to be similar to the system containing TTE
- Reduced self-discharge occurs in FLS0, indicating less polysulfide shuttling
- FLS18 showed poor performance, indicating the need for further optimization

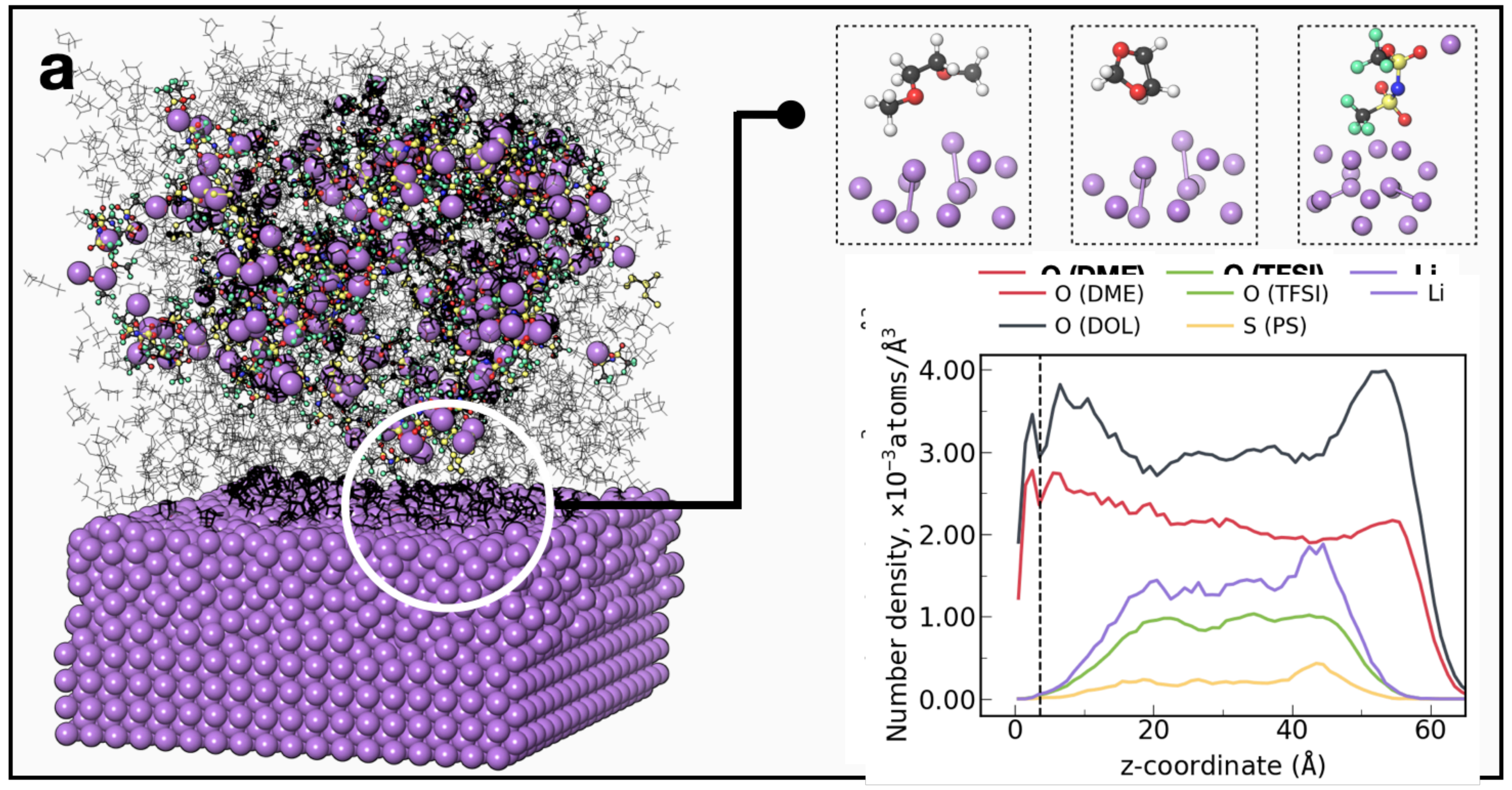
Electrode-Electrolyte Interface Workflow in MISPR

Required:
- Molecular species structure(s)
- Solid structure
- Composition
- Box data

Optional:
- Force field
- MD recipe
- Recipe settings (T, P, ...)
- Analysis steps
- Analysis settings (n(z) length, bin size, ...)

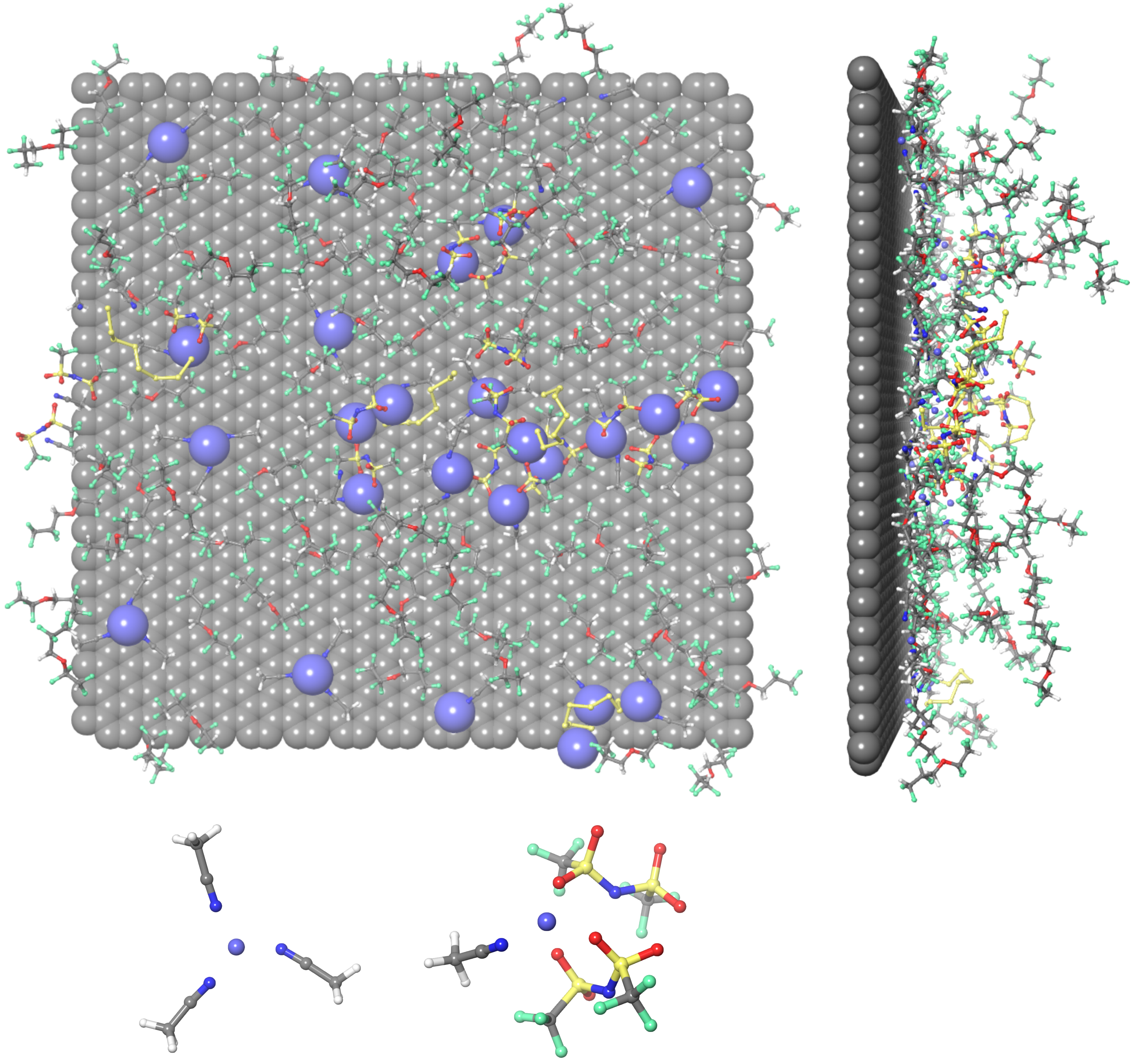


Anode - Electrolyte Interfacial Analysis

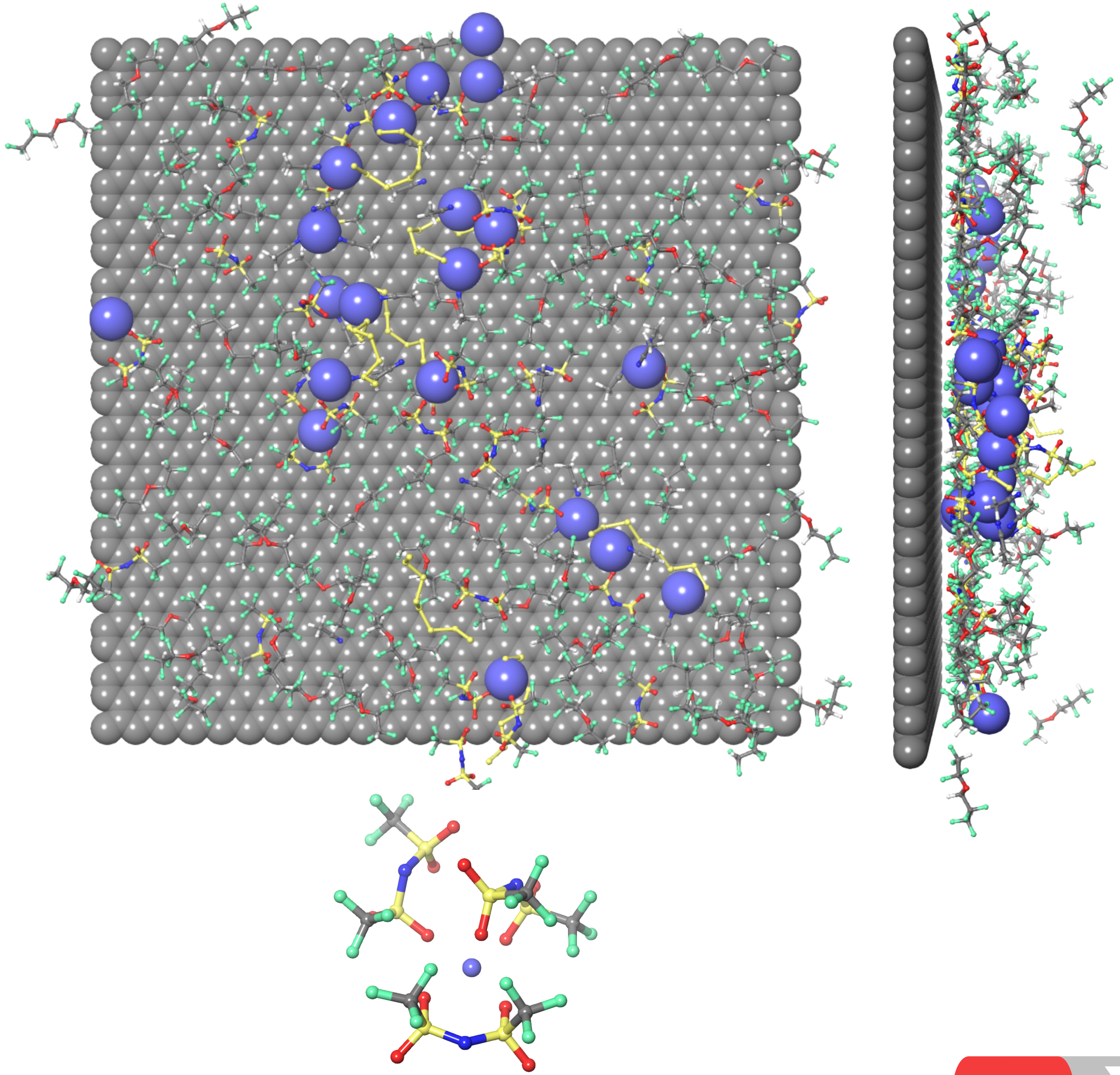


MD Snapshots at the Model Electrode Surface Showing Top and Side Views

ACN/TTE (-ve electrode)

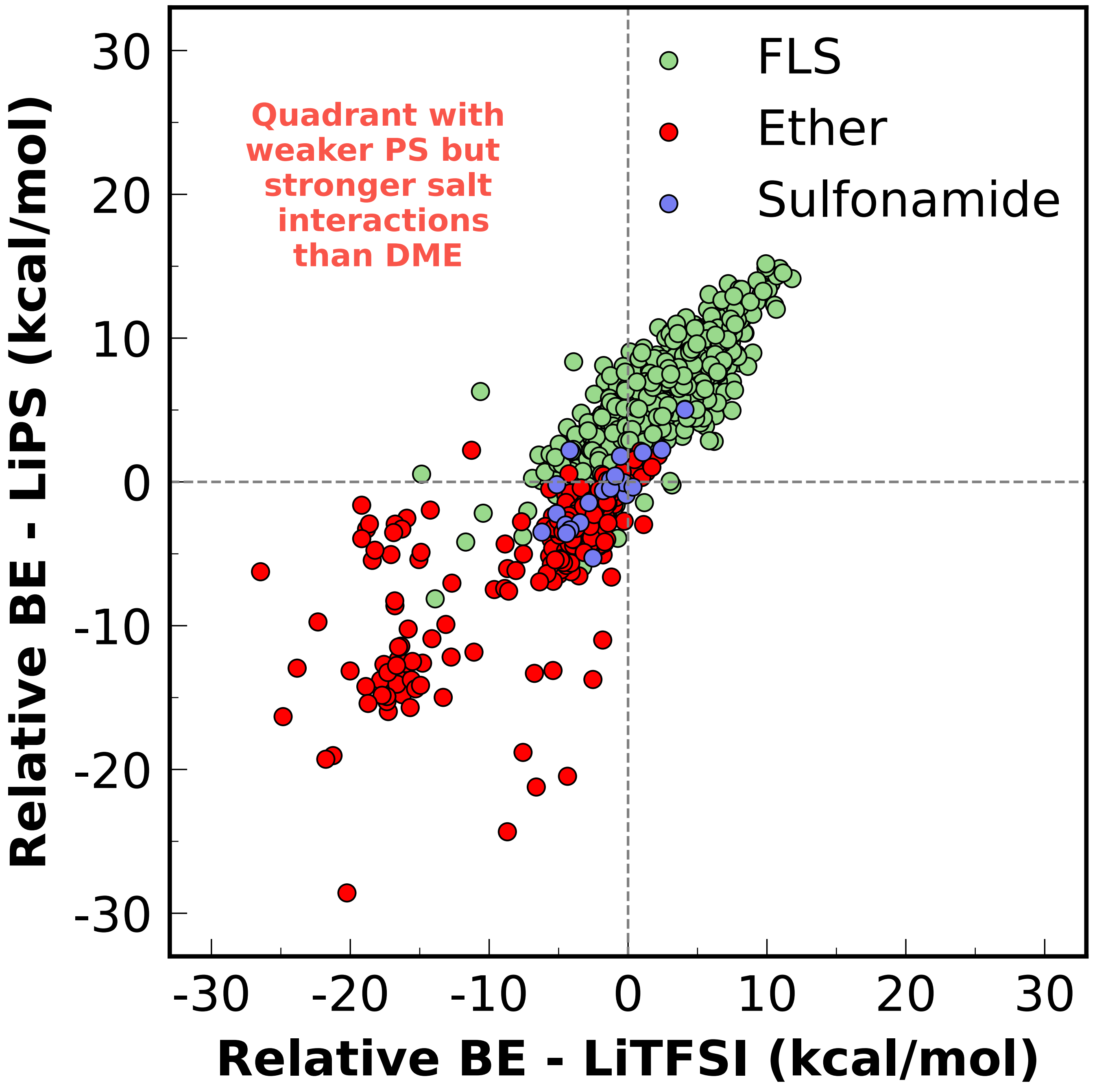


ACN/TTE (+ve electrode)

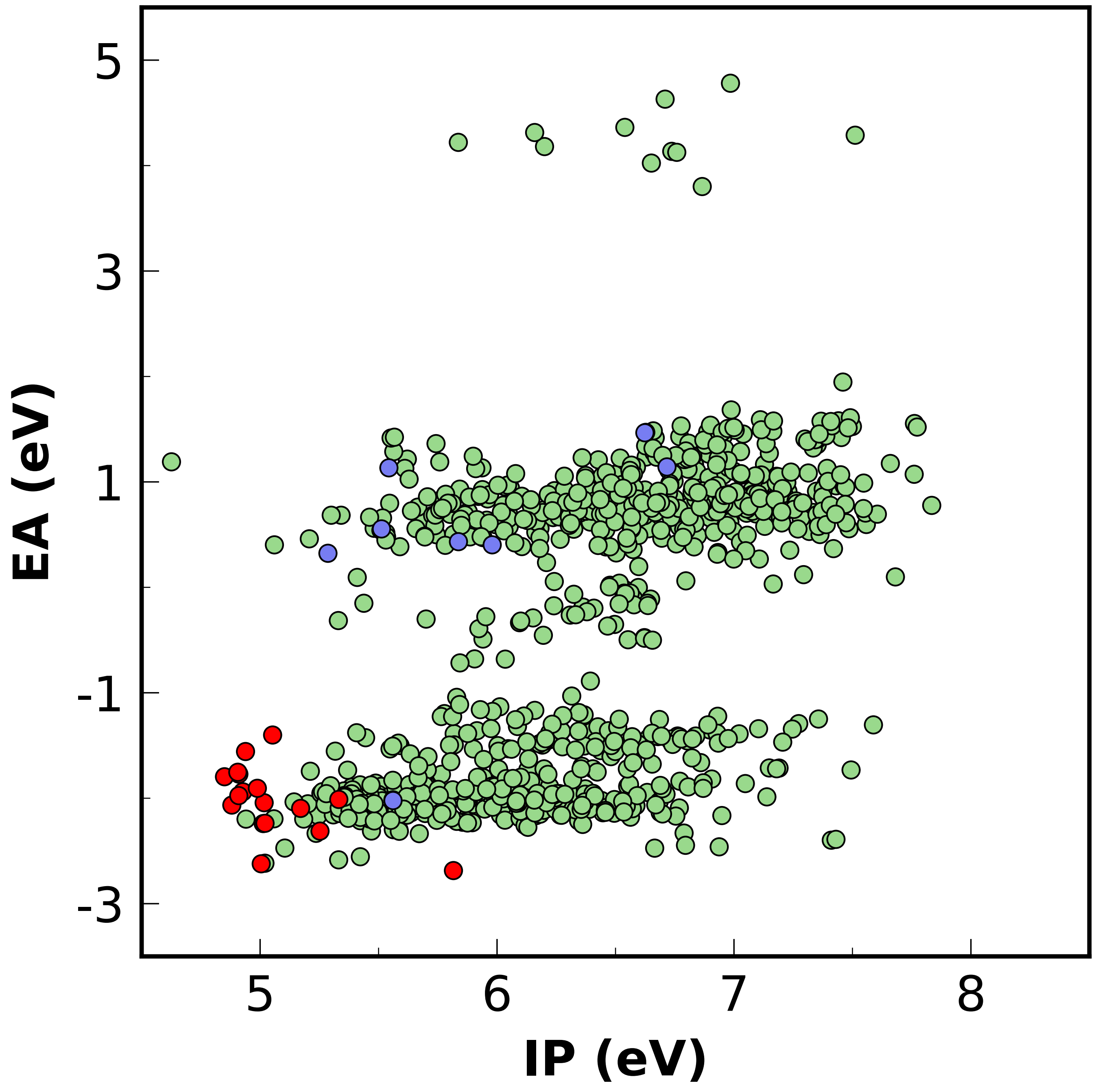


Properties of Fluorinated, Ether, and Sulfonamide Solvents

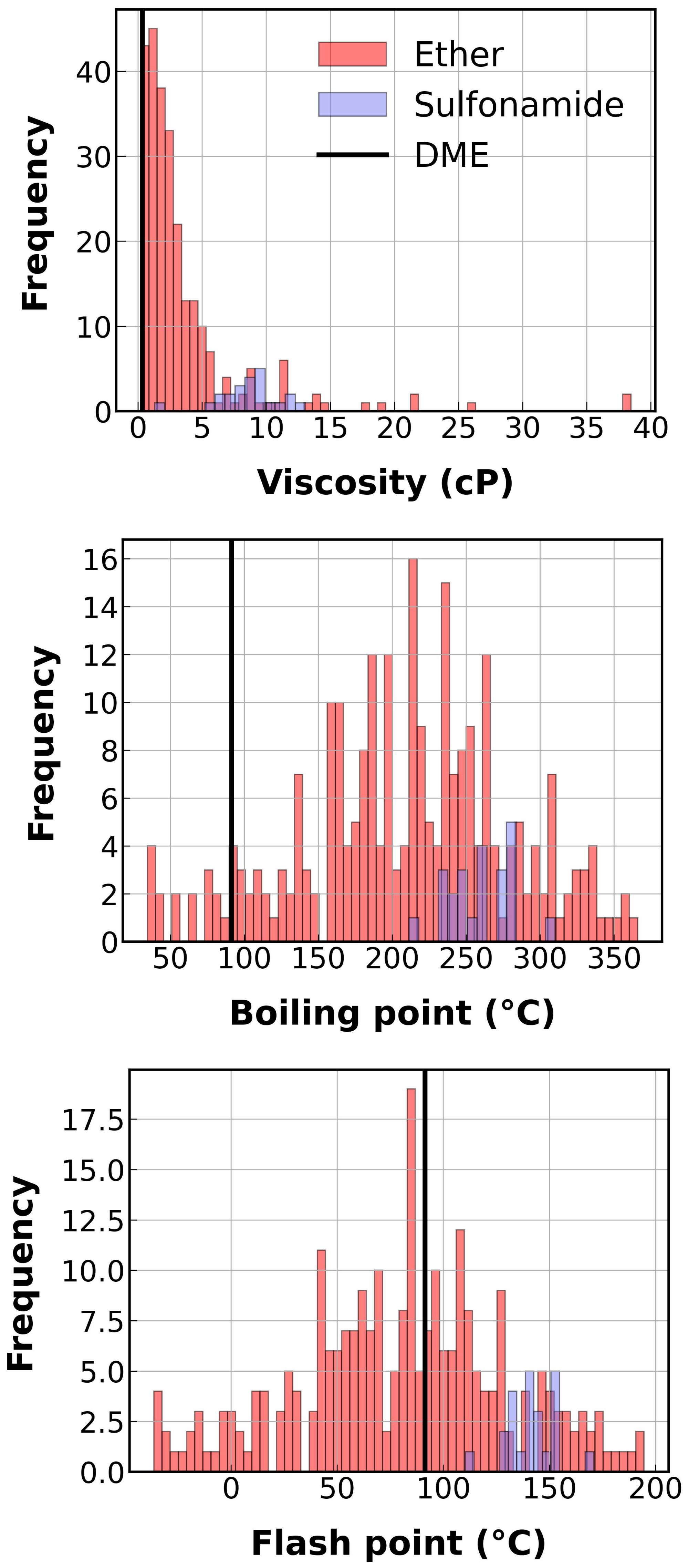
DFT



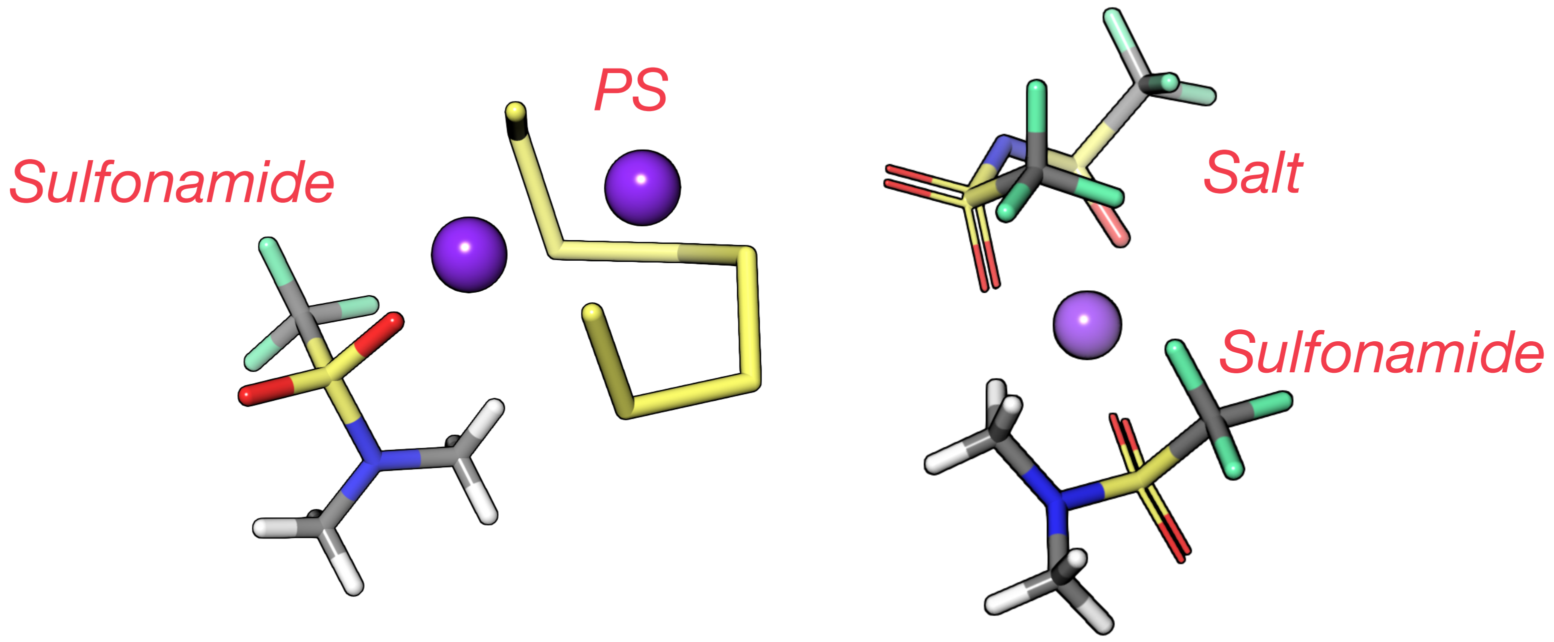
DFT



COSMO-RS



Binding between a sample sulfonamide in the database with LiPS and LiTFSI

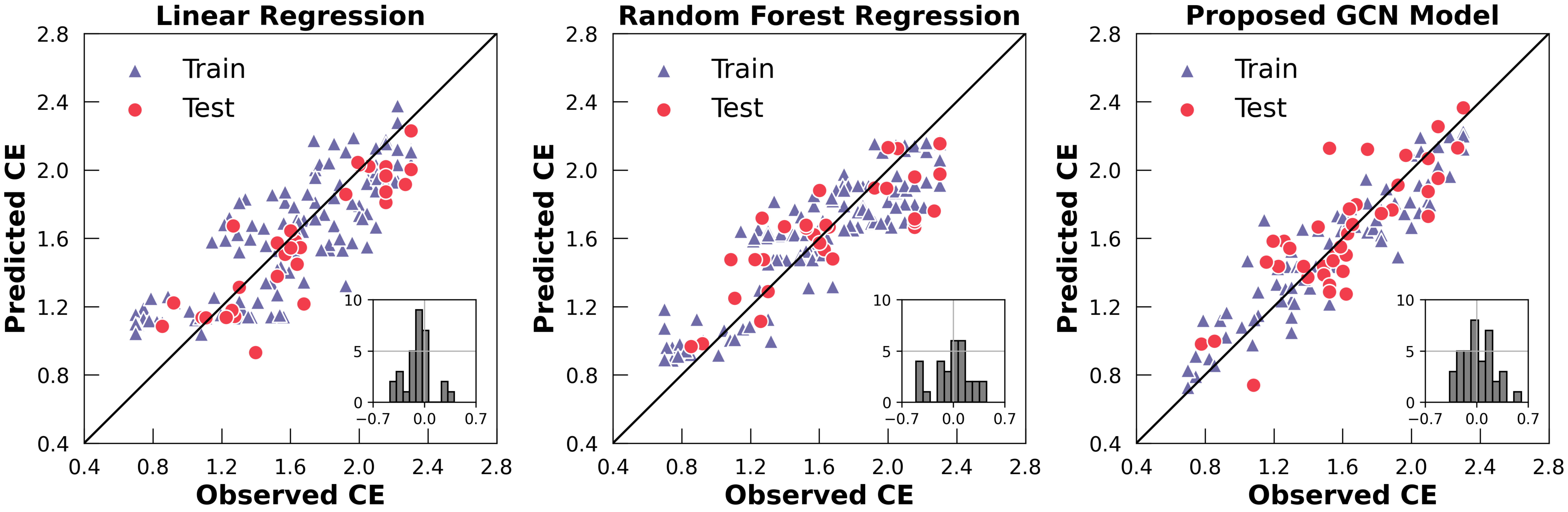


- IP/EA calculations were performed at the ωB97xD/def2-TZVPPD using the thermodynamics cycle and SMD solvent model with acetone as an implicit solvent

Architecture of the Graph Convolution Network Model for Li metal batteries

- Tested the performance of this model on an existing electrolyte dataset for Li metal batteries (https://www.pnas.org/doi/10.1073/pnas.2214357120).
- The dataset contains 150 electrolytes composed of 54 and 17 different solvents and salts, respectively.
- The dataset includes electrolyte formulations that might have the same salt and solvent types, but different concentrations.
- The experimental CE data are for Li | Cu cells.

Predicted CE vs. Observed CE



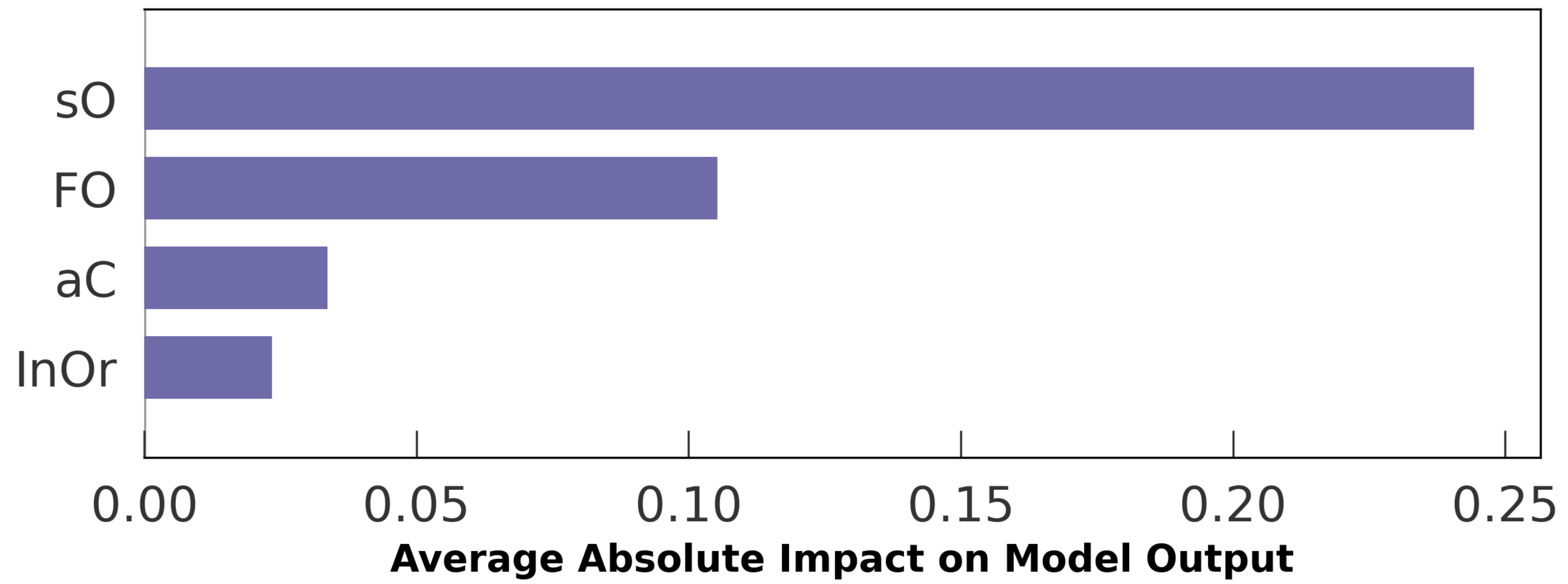
- 13 elemental composition features are used for training the different ML models. These include the solvent oxygen ratio, inorganic/organic ratio, anion carbon ratio, solvent fluorine ratio, etc.
- Data is split into 80% for training and 20% for testing using random sampling.
- Y-axis corresponds to **$-\log_{10}(1\text{-CE})$**, since this transformed data has better distribution than original CE % which naturally skewed towards high values and does not reflect the variation across the data points.

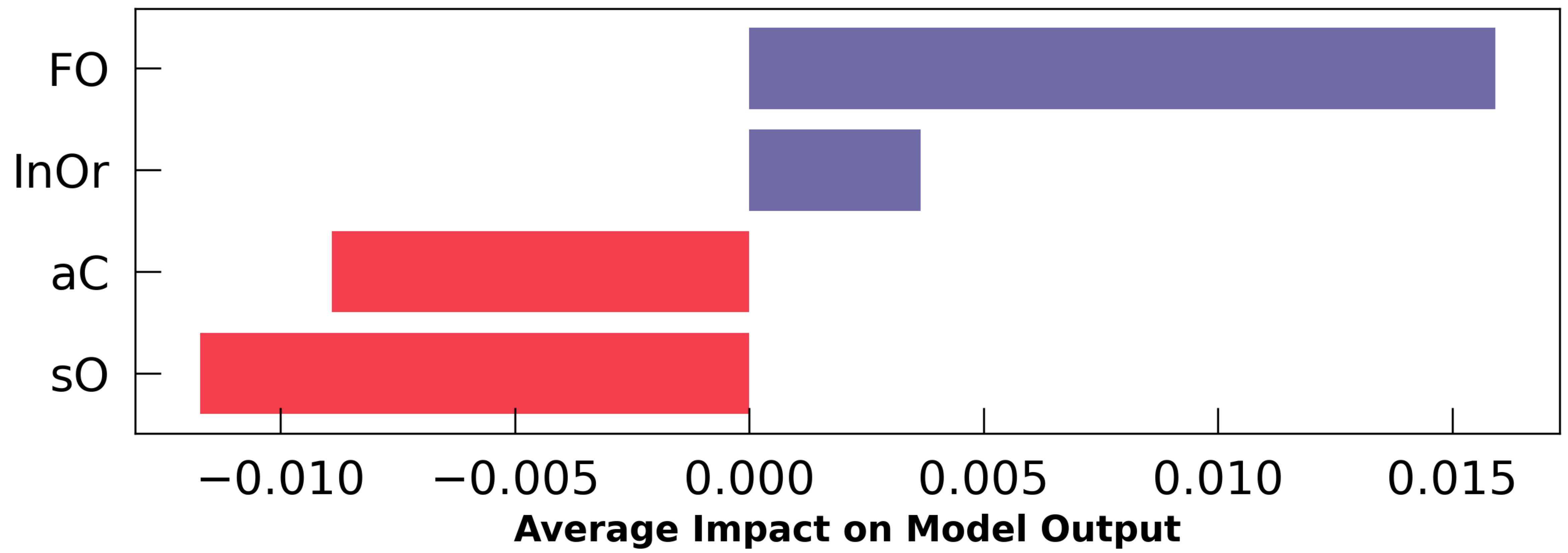
Model Performance and Interpretation

Comparison of the performance of the three tested models

Metric	Linear Regression	Random Forest Regression	Proposed GCN Model
Test R^2 value	0.75	0.65	0.65
Test Mean Squared Error	0.04	0.06	0.047

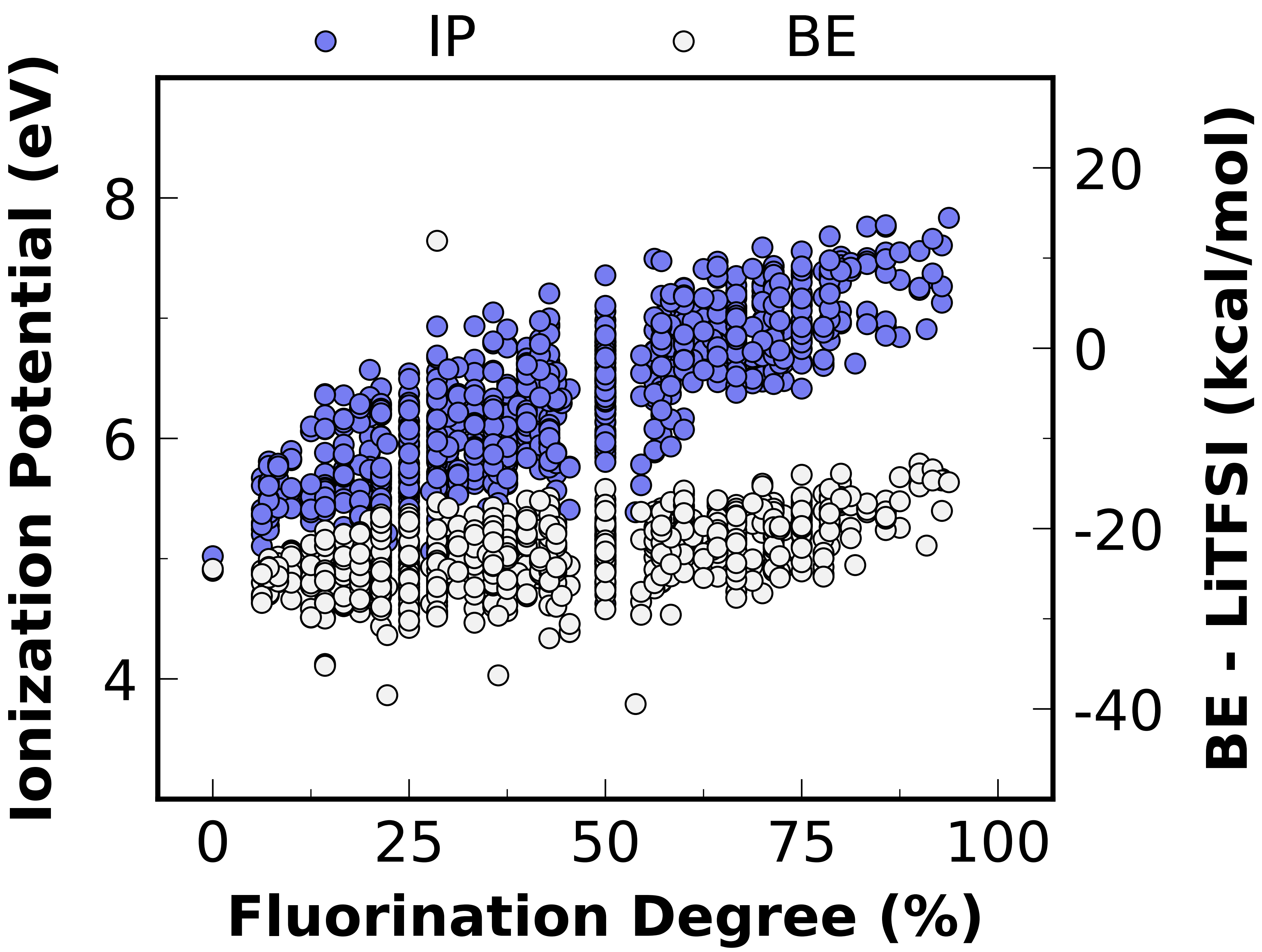
Model analysis and interpretation: what are the most important features affecting CE?

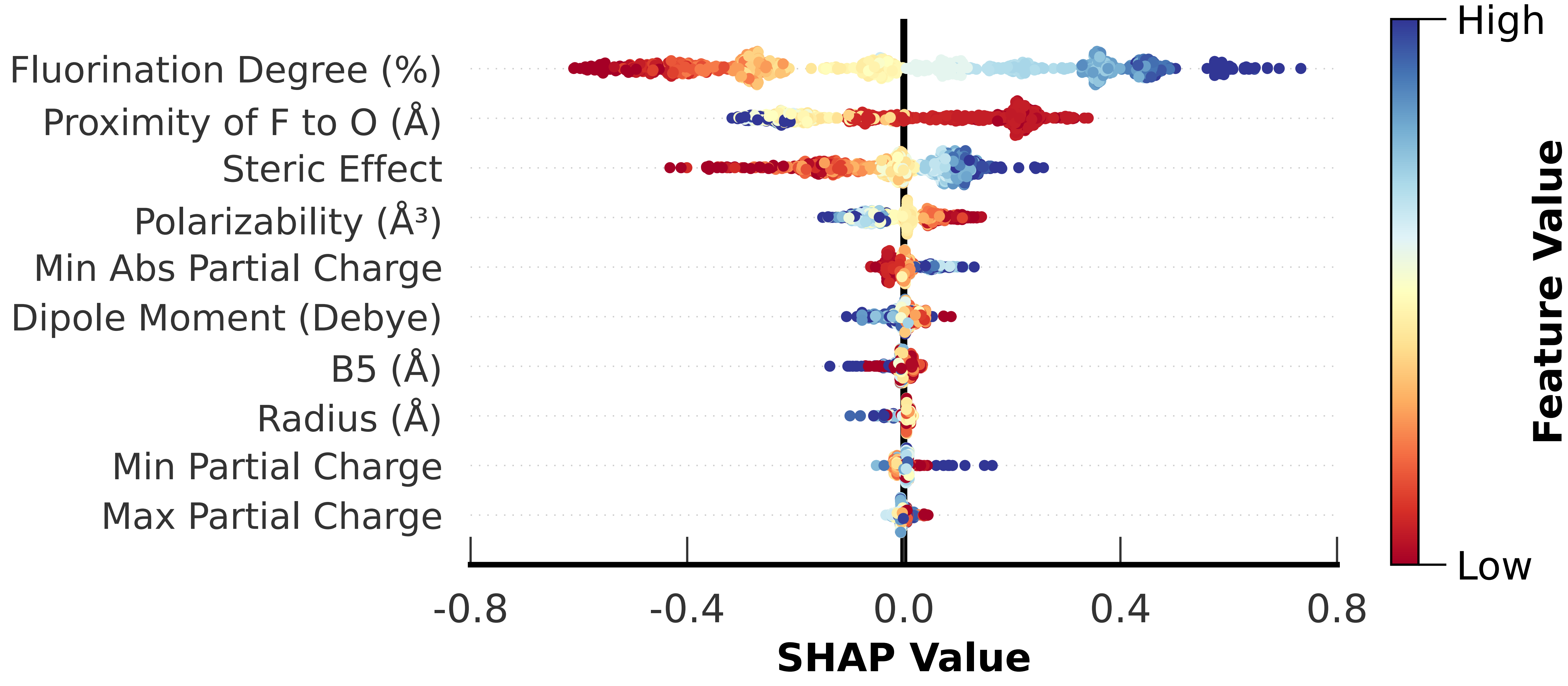




- sO (solvent oxygen ratio) appears to be the most important feature, negatively affecting the CE.
- fO (fluorine to oxygen ratio) is the second most important feature, with higher FO leading to superior CE.
- Based on these results, reducing sO and increasing FO in the electrolyte can lead to better performance.

Descriptors for fluorinated solvents





- Fluorination degree has more significant positive impact on the solvent IP than its BE with LiTFSI.

- XGBoost regression model to identify attributes of high impact

Computational Database of Electrolyte Properties

https://github.com/rashatwi/combat

56 electrolytes; > 2,000 properties

Paper ID: 3741952

MISPR

https://github.com/molmd/mispr

Package for HTP simulations

MDPropTools

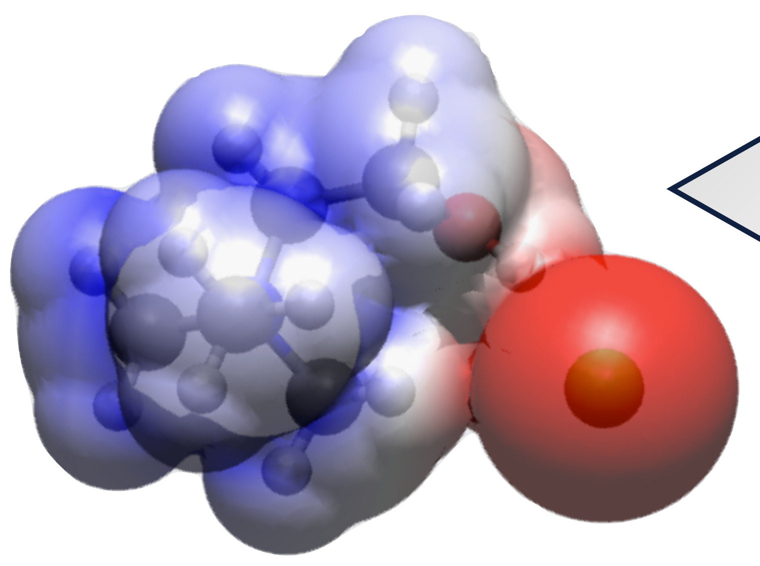
https://github.com/molmd/mdproptools

Package for MD analysis

Code powering the simulations

DFT Properties

Electronic & thermodynamic properties

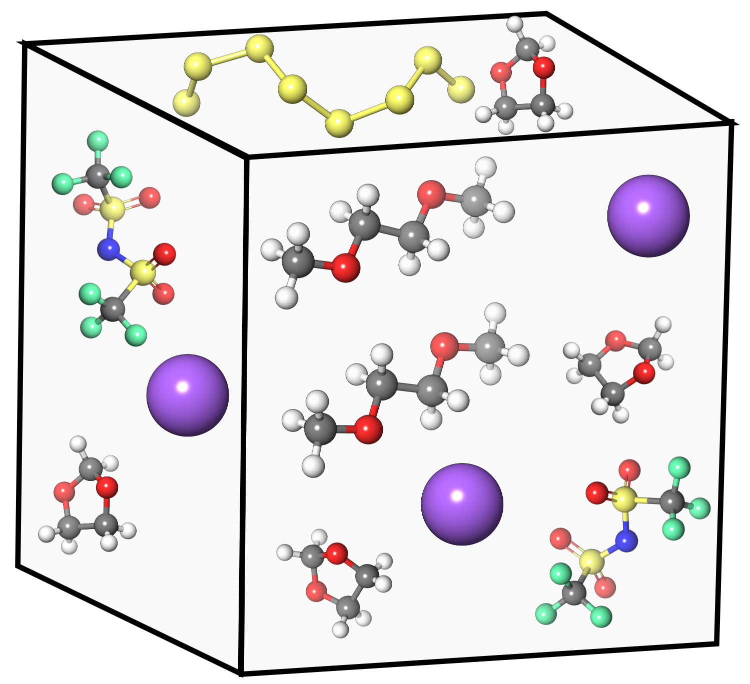


Li-S Database

ComBat

Ensemble Properties

Structural & dynamical properties



Guiding strategies for the development of effective solvents for Li-S liquid electrolytes

Electrolytes composition

1 M LiTFSI, 0.25 M Li_2S_8, **in:**

Base: DOL/DME (1/1, v/v)

Variable: DOL/**Co-solvent** (1/1, v/v)


https://molmd.github.io/mispr/

MolMD
MOLECULAR SIMULATIONS FOR MATERIALS DESIGN

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MISPR
materials informatics for structure property relationships

MDPropTools

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