Microscopic Behavior of Battery Electrolytes through Molecular Dynamics Simulations

Shehan Parmar

DOE Computational Science Graduate Fellow
McDaniel Research Group

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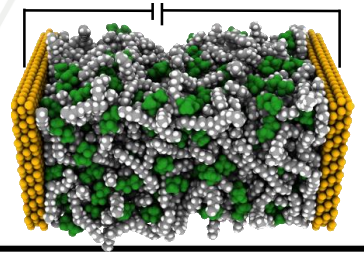
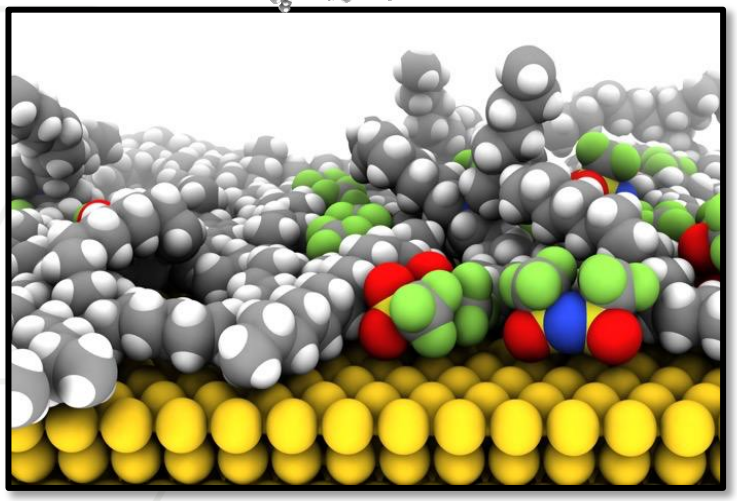
Fort Worth, Texas
March 4th, 2025

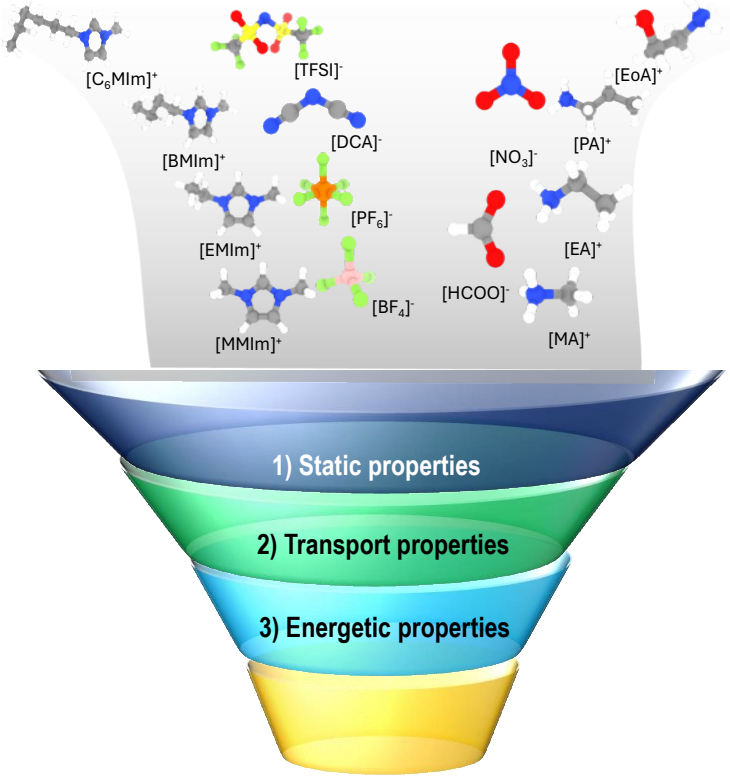
Battery Electrolytes





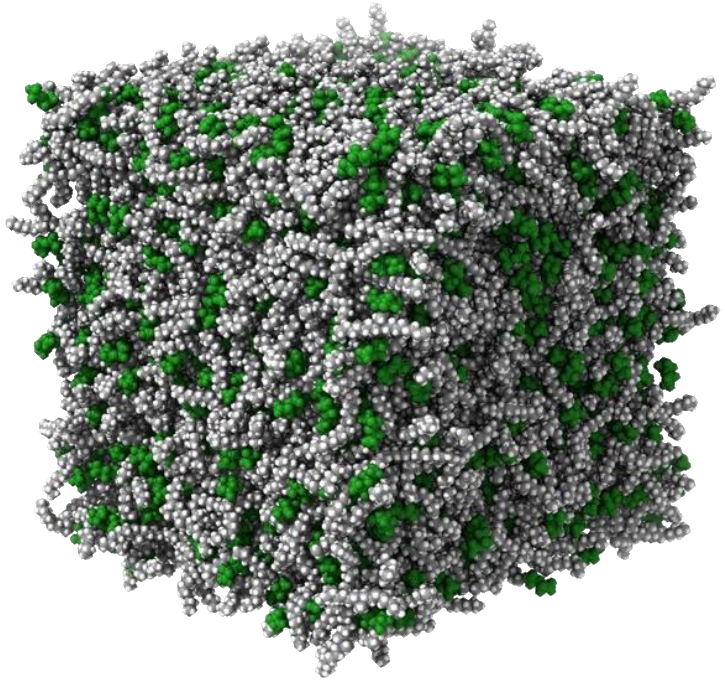
SMP et al. *J. Phys. Chem. B* 2025, In Prep.

High-throughput



SMP et al. *J Electr Propuls* 2025, *In Review.*

Molecular Dynamics

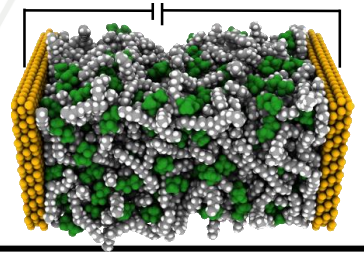


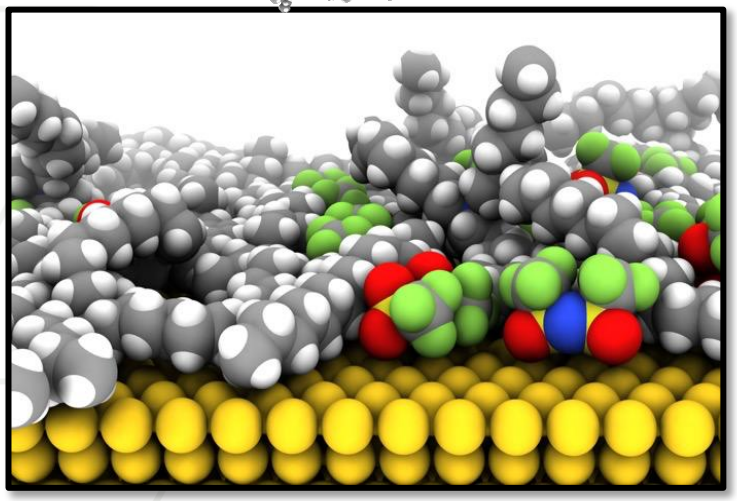
SMP et al. *J. Phys. Chem. B* 2023, 127, 40, 8616–8633
SMP et al. *J. Phys. Chem. B* 2024, 128, 45, 11313–11327

Material Discovery

HTMD

Battery Electrolytes





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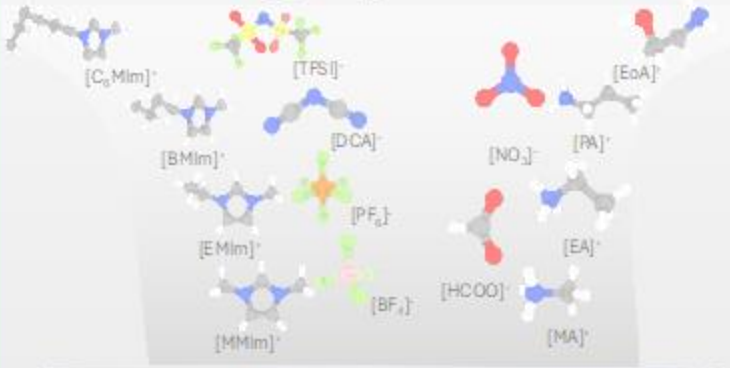

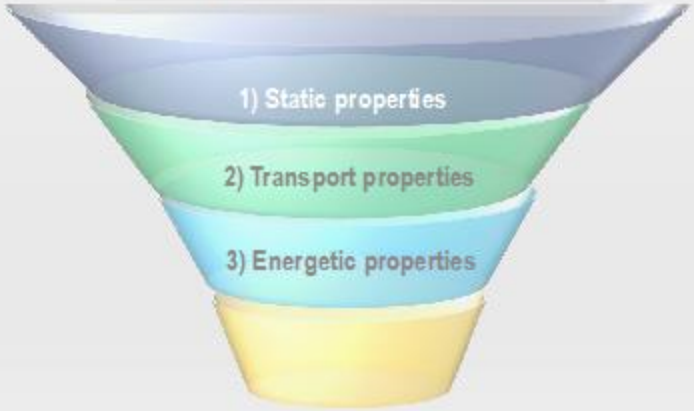

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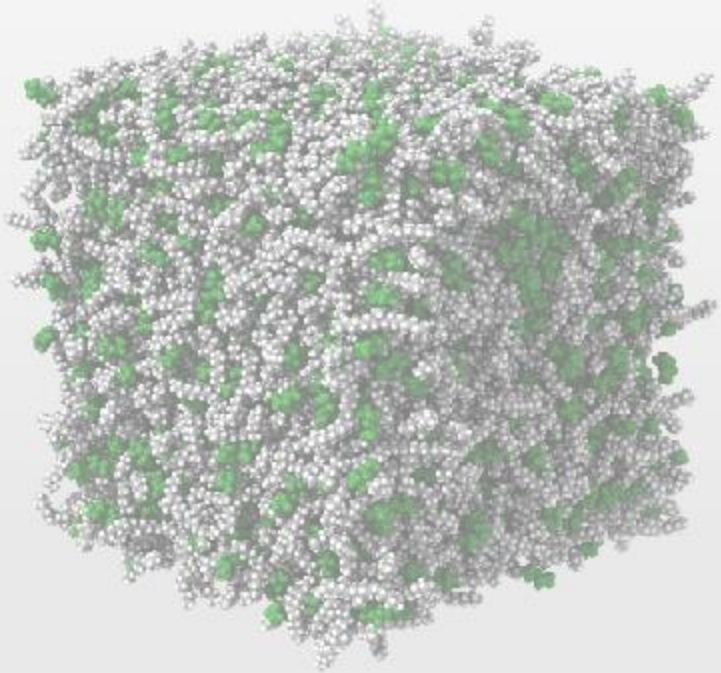
Molecular Dynamics



SMP et al. *J. Phys. Chem. B* 2023, 127, 40, 8616–8633
SMP et al. *J. Phys. Chem. B* 2024, 128, 45, 11313–11327

Material Discovery

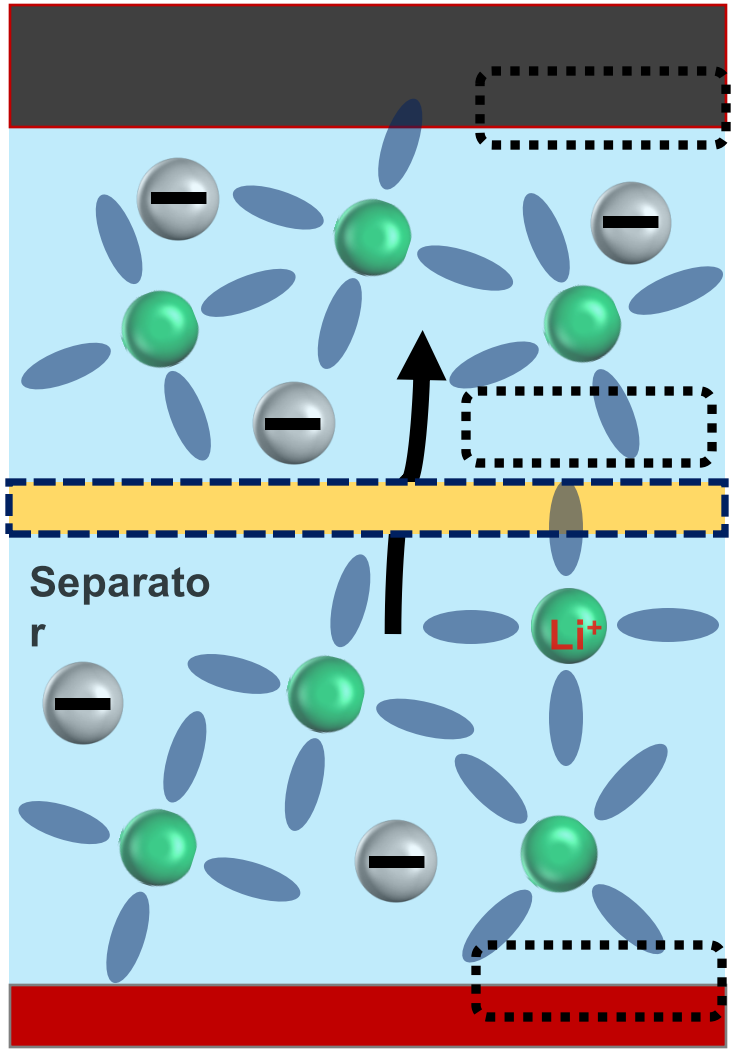
HTMD

Motivation: Li-ion Batteries (LiB)

Anode
(e.g., graphite)

Electrolyte

Cathode
(e.g., $LiCoO_2$)



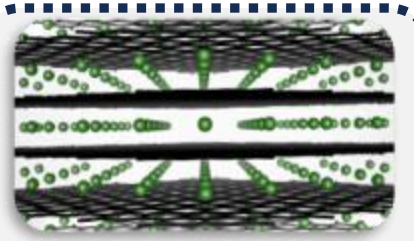
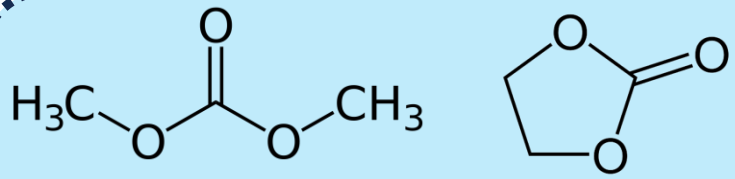
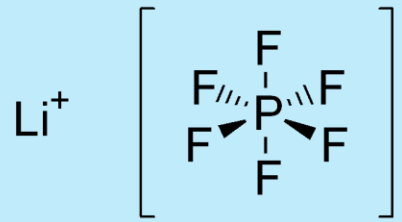


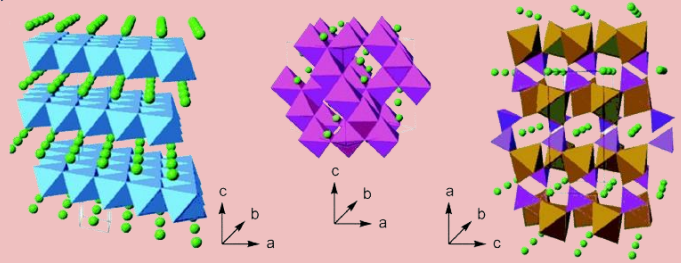
Image: Argonne National Laboratory



Dimethyl/ethylene carbonate

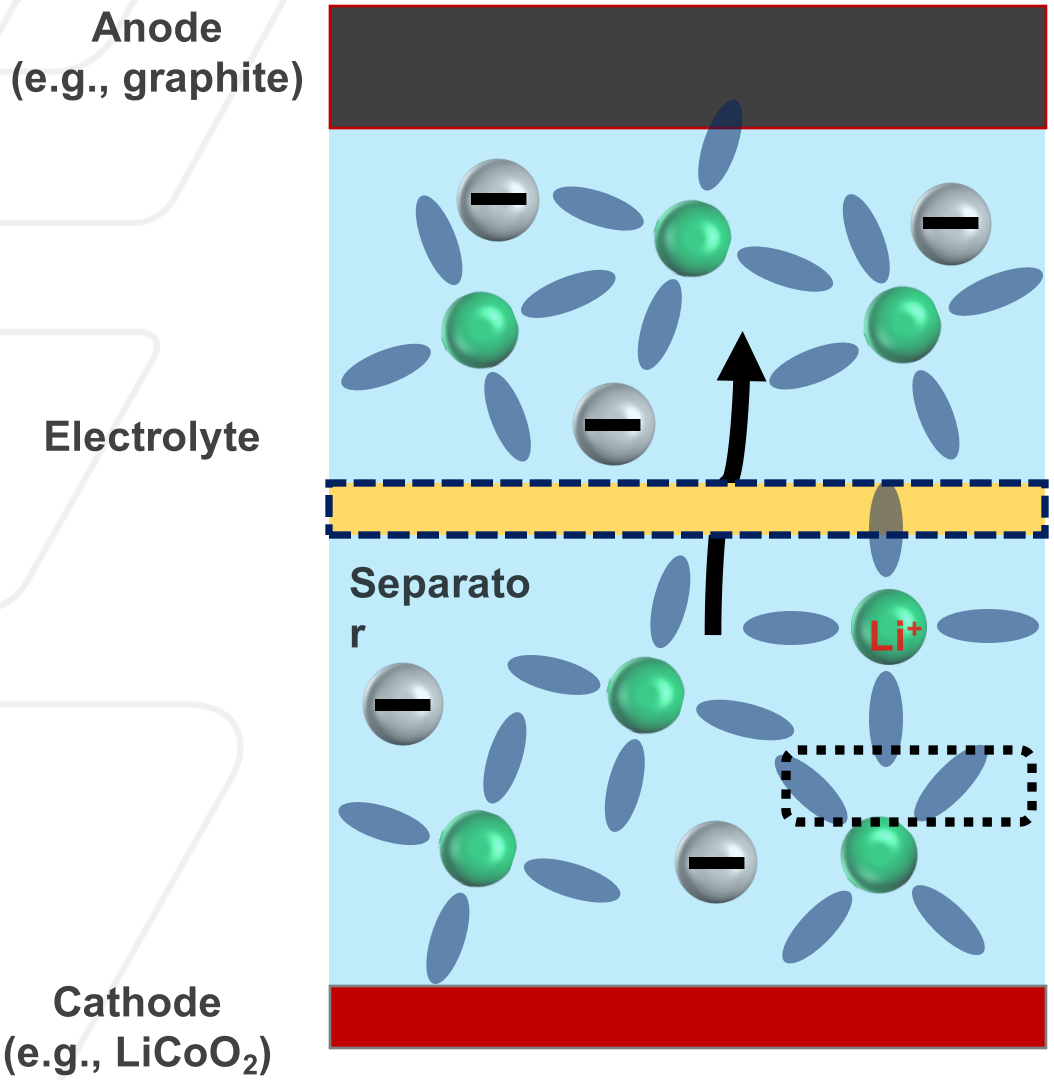
Li salt

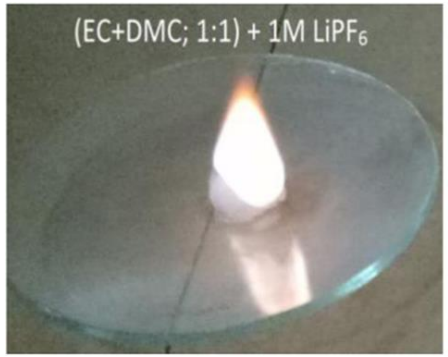


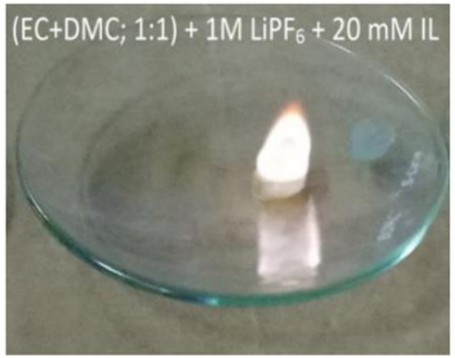


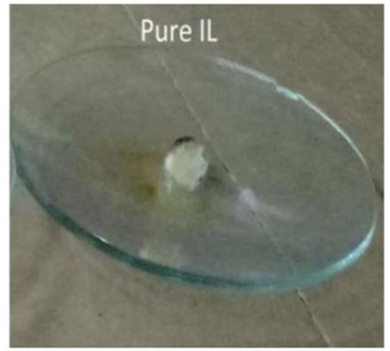
Somo, T.R et al. *Coatings* **2021**, *11*, 744.

Motivation: Li-ion Batteries (LiB)

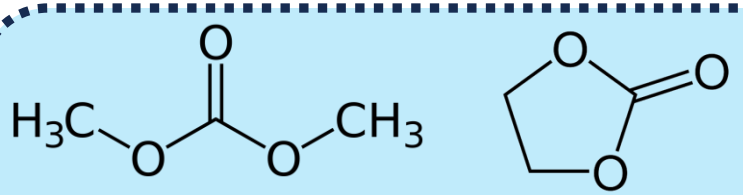






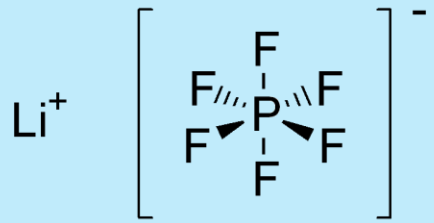


Chatterjee, K., Pathak, A.D., Lakma, A. *et al.* Synthesis, characterization and application of a non-flammable dicationic ionic liquid in lithium-ion battery as electrolyte additive. *Sci Rep* **10**, 9606 (2020).

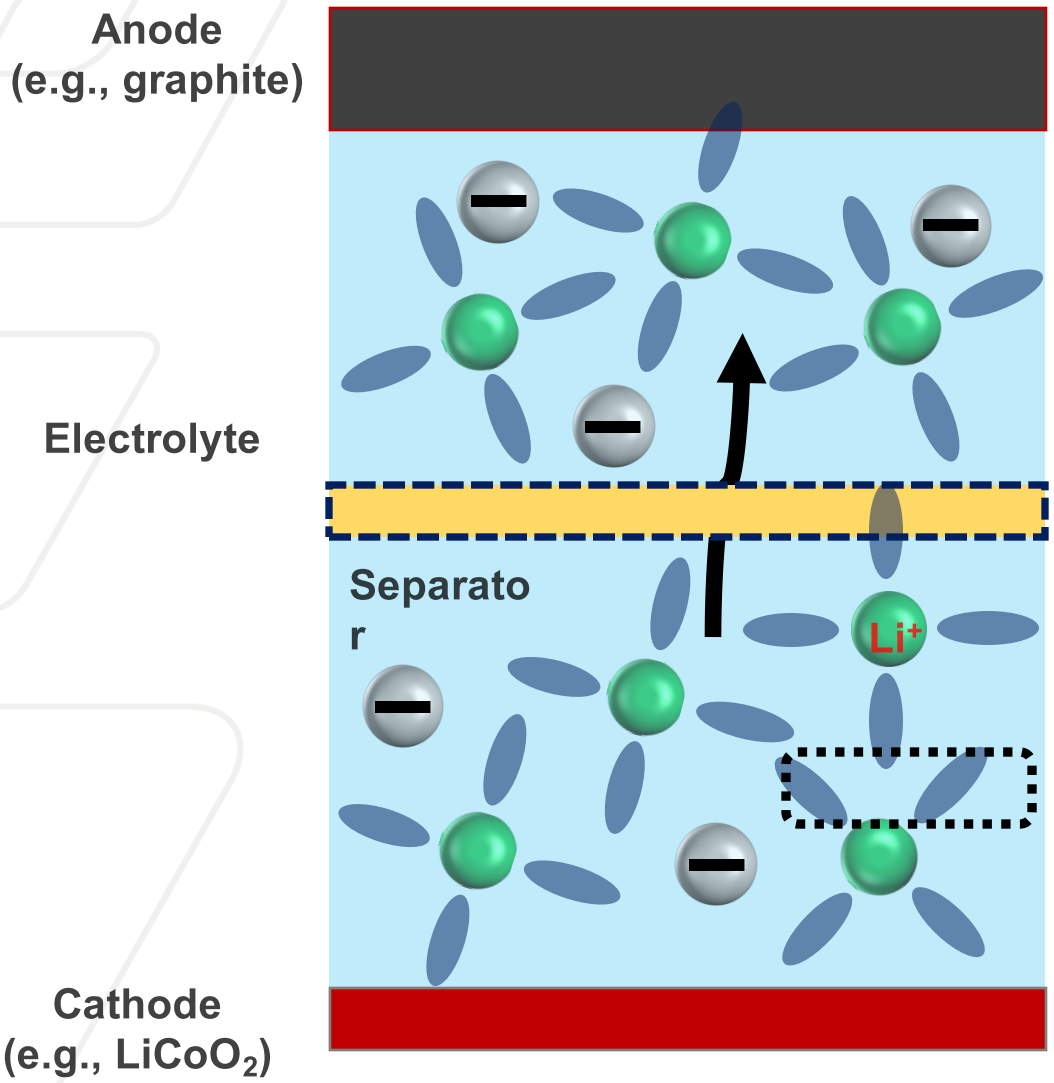


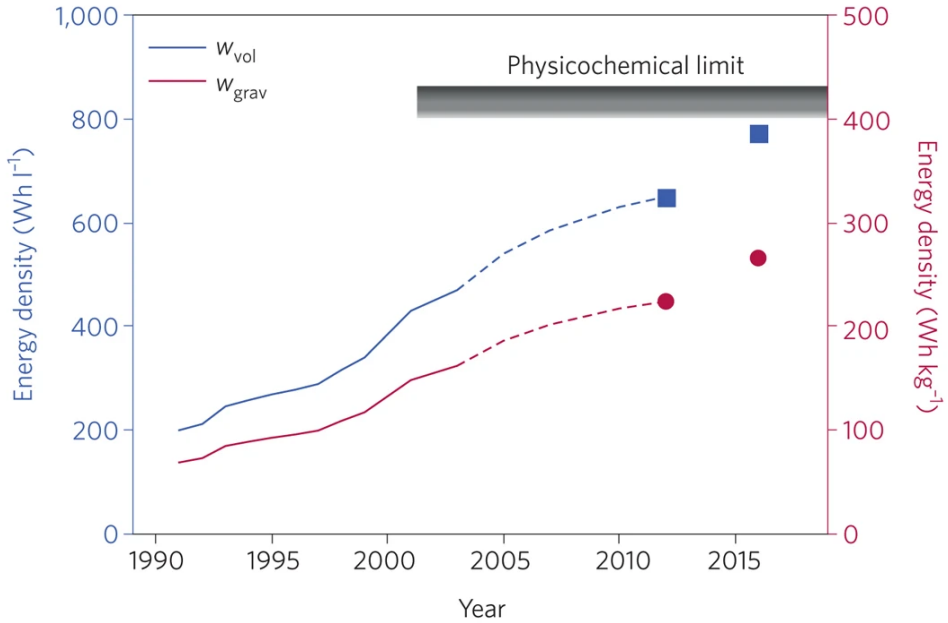
Dimethyl/ethylene carbonate

Li salt

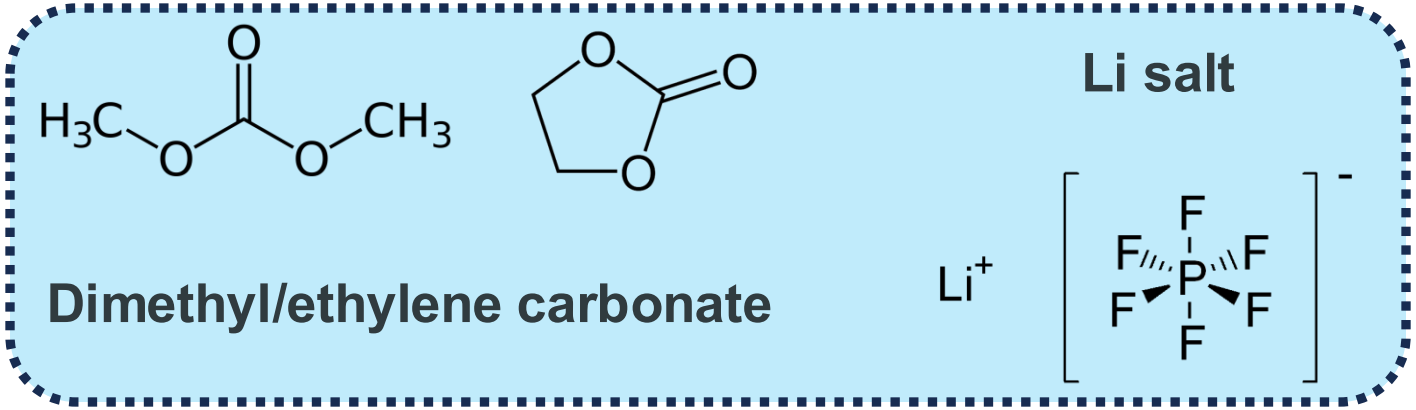


Motivation: Li-ion Batteries (LiB)

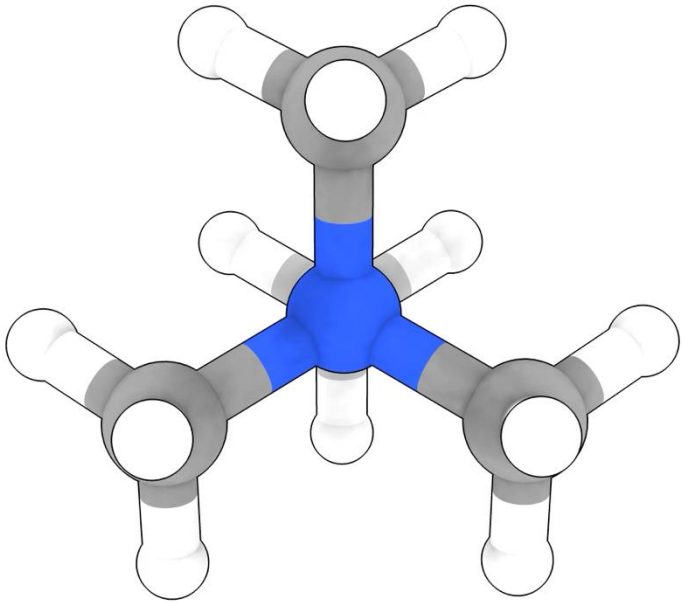


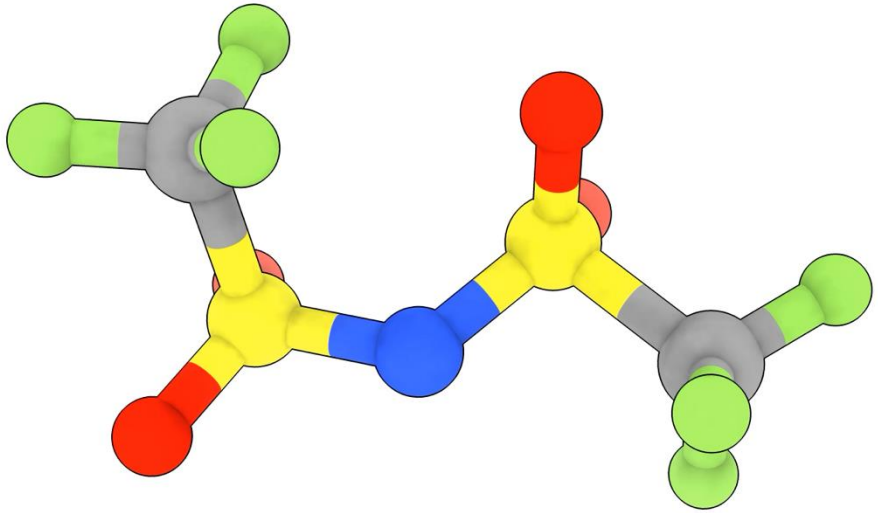


Janek, J., Zeier, W. A solid future for battery development. *Nat Energy* **1**, 16141 (2016).



Ionic liquids are candidate alternatives.



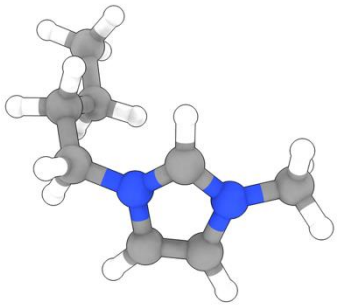


$[N_{1111}]^+$

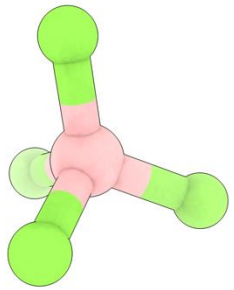
$[TFSI]^-$

Room-temperature, “molten” salts composed of cation-anion pairs.

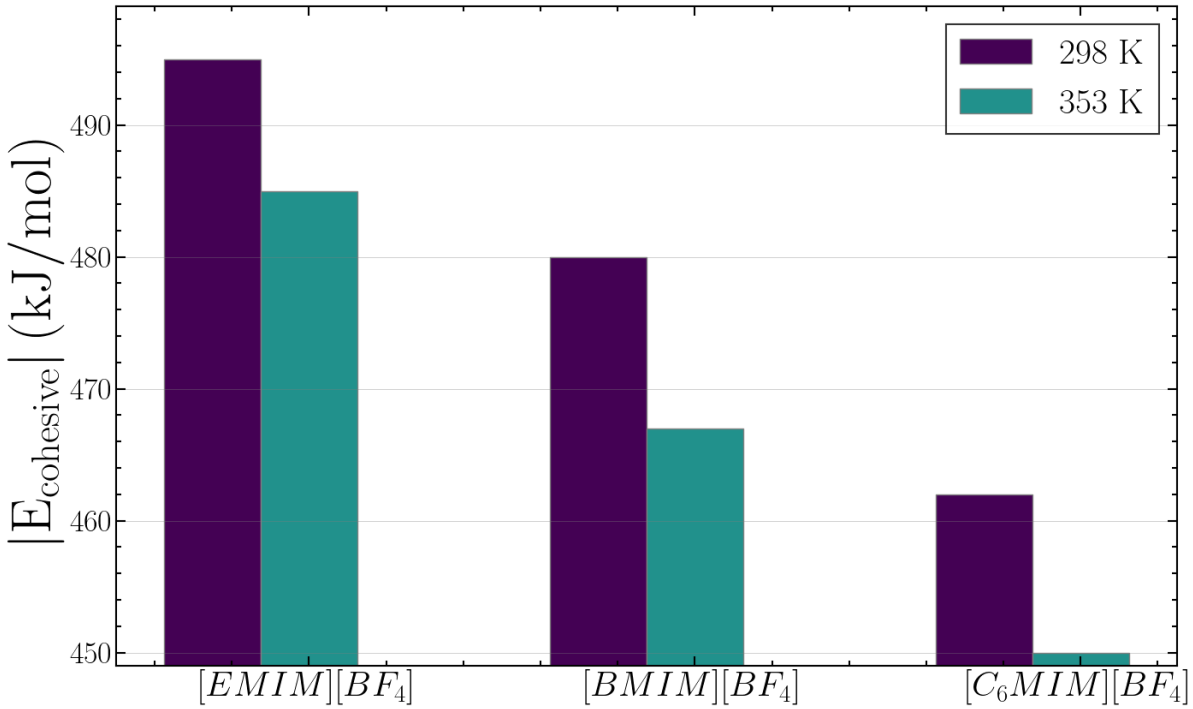
What are Ionic Liquids?



$[BMIM]^+$

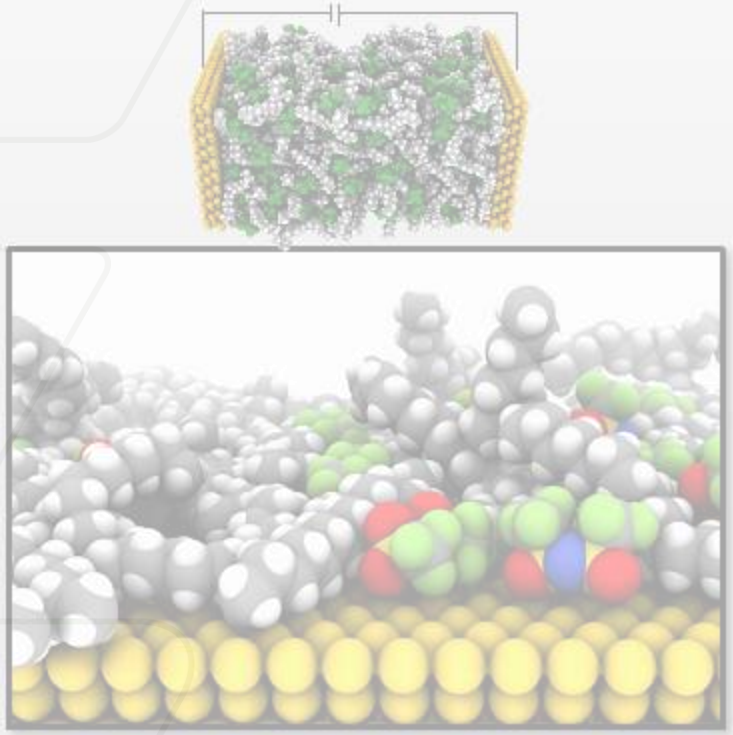


$[BF_4]^-$



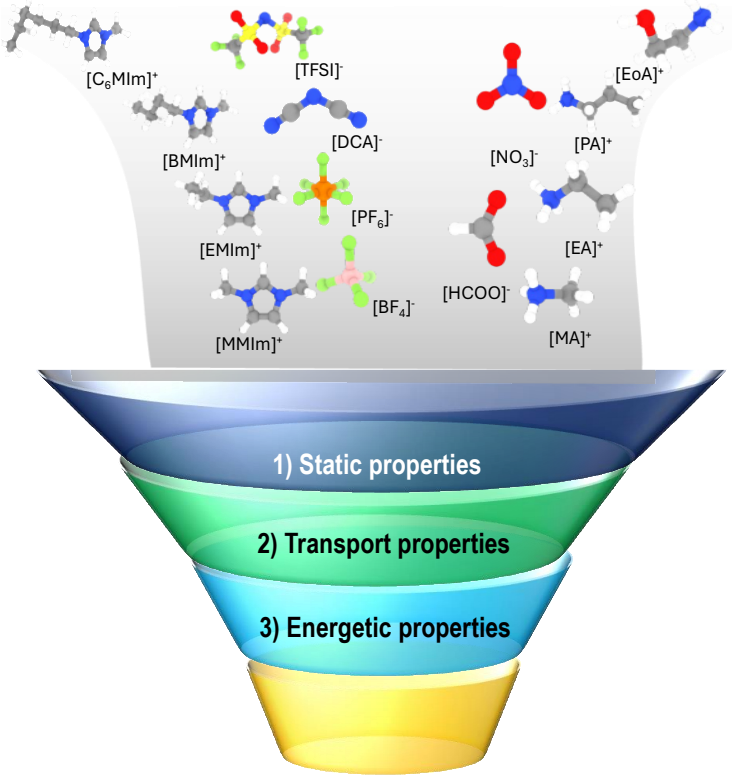
- Room temperature molten salts
- Strong Coulombic attraction → **large cohesive energies**
- Favorable properties like…
  - **Low vapor pressures**
  - High electrical conductivities
  - Wide electrochemical windows
  - Tunability
  - …and many more!

Battery Electrolytes



SMP et al. *J. Phys. Chem. B* 2025, In Prep.

High-throughput



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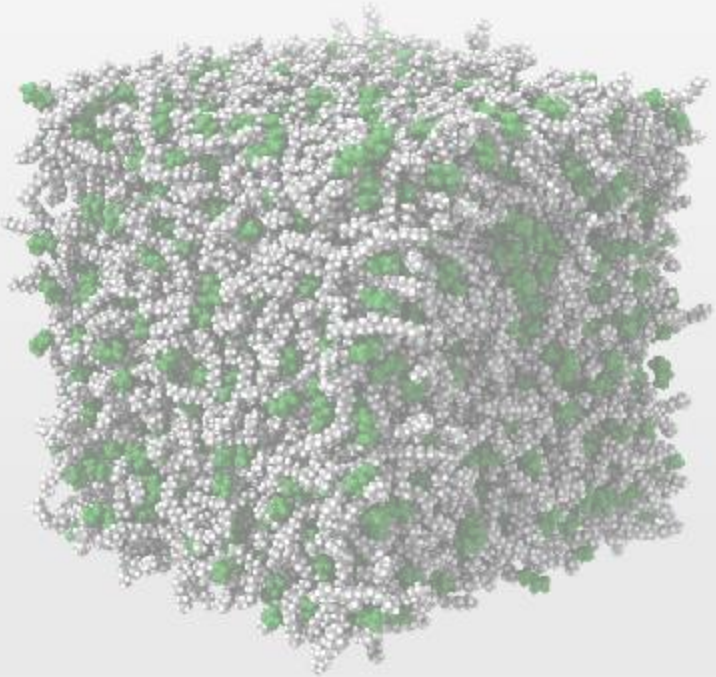
Molecular Dynamics



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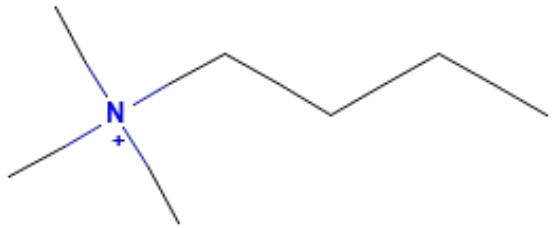
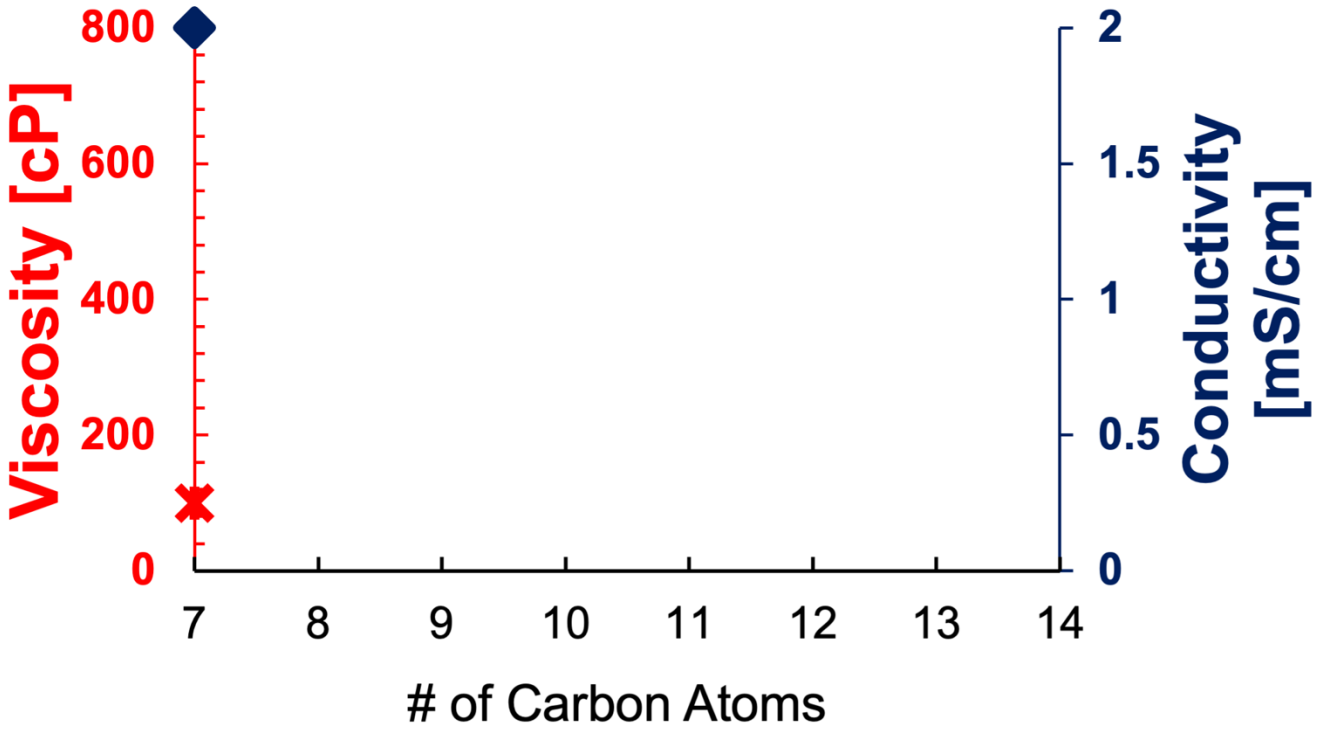
Material Discovery

HTMD

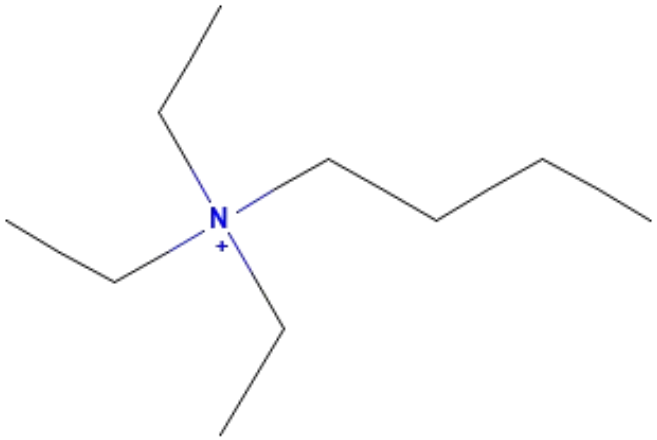
Ionic Liquid Tunability



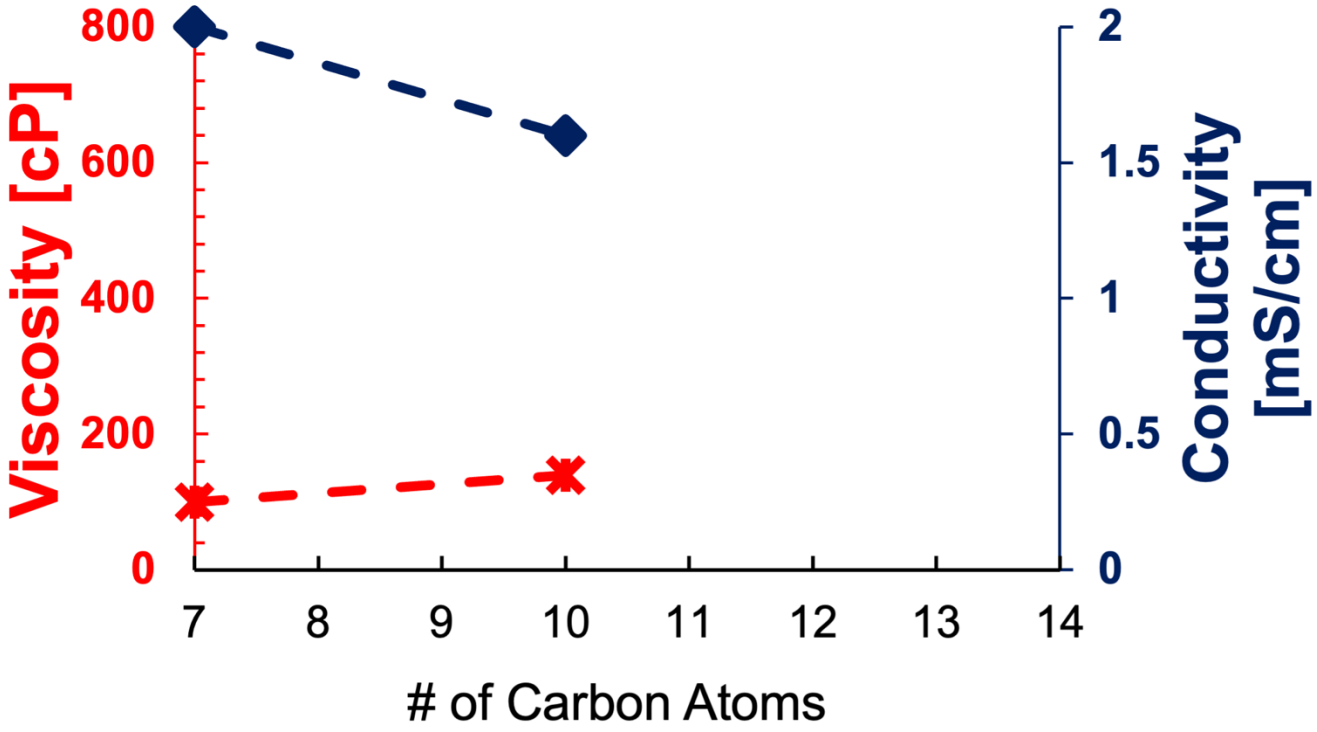
$[N_{1114}]^+$



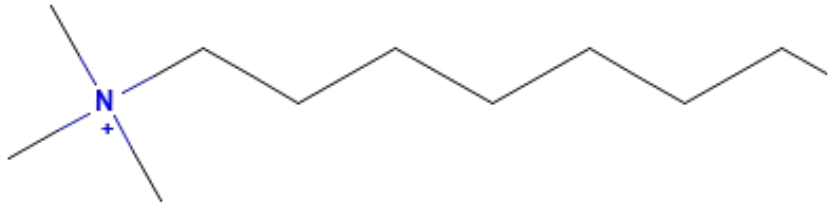
Ionic Liquid Tunability

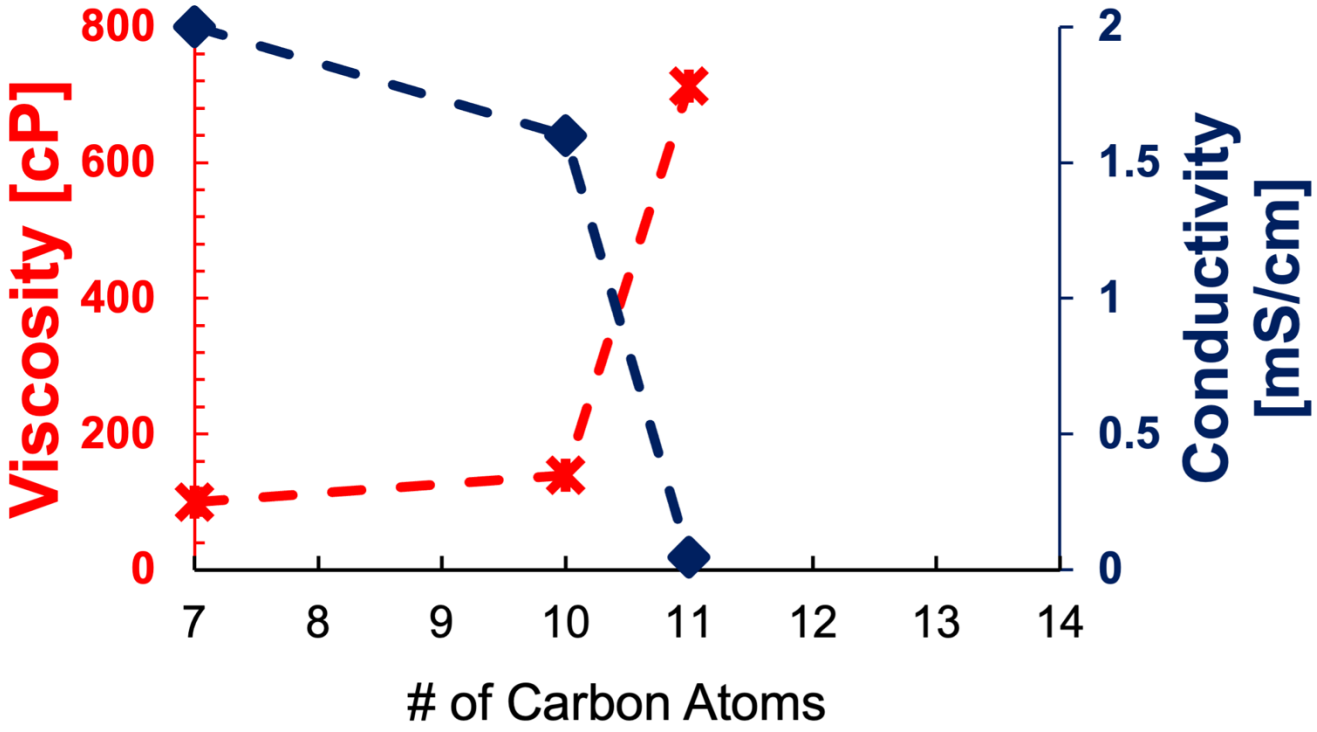


$[N_{2224}]^+$



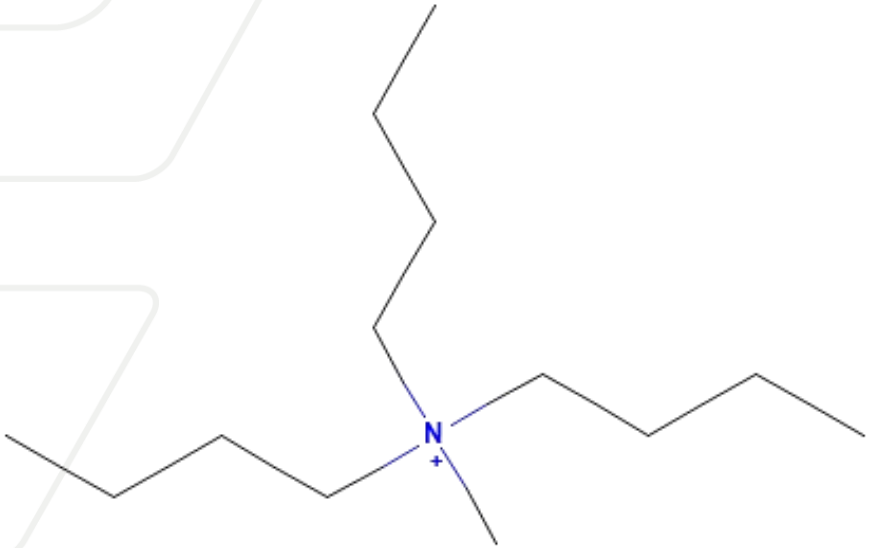
Ionic Liquid Tunability



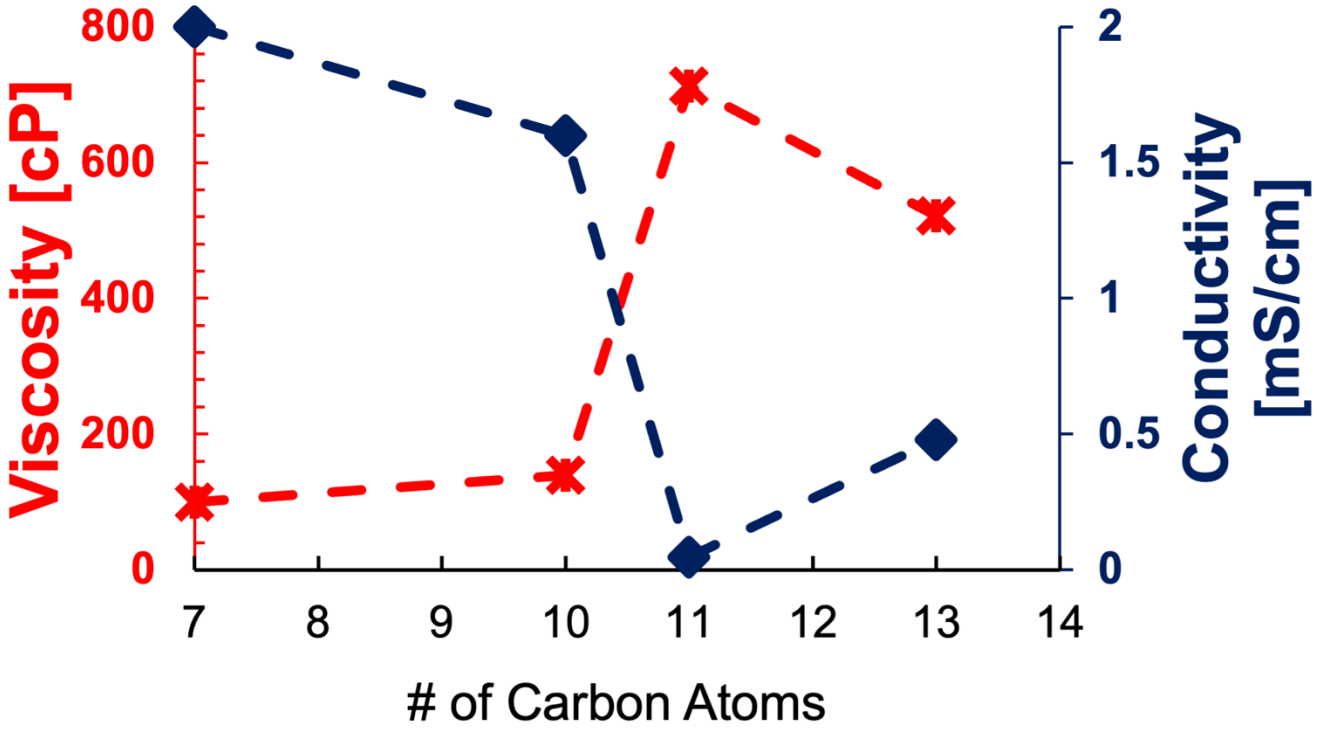


$[N_{1118}]^+$

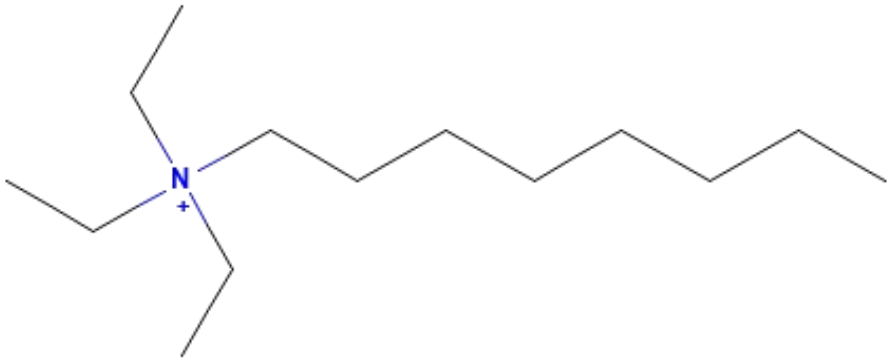
Ionic Liquid Tunability

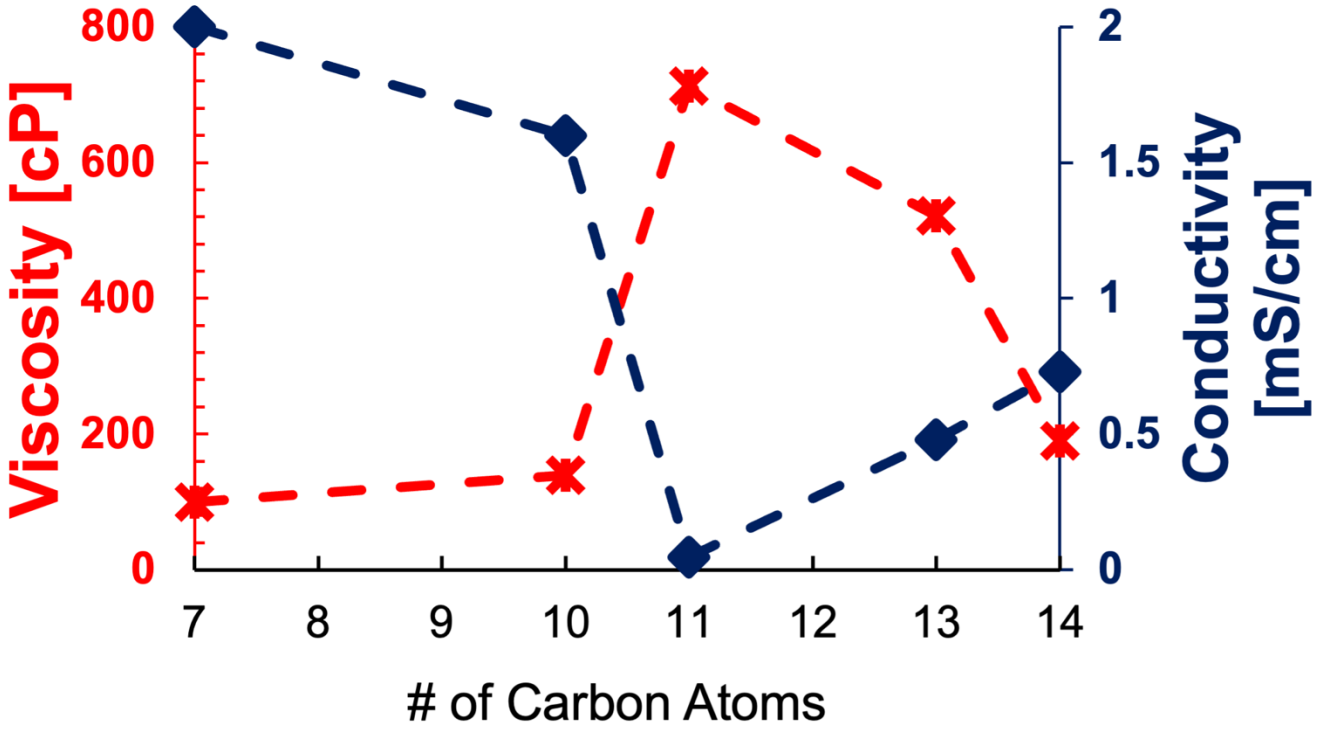


$[N_{1444}]^+$



Ionic Liquid Tunability





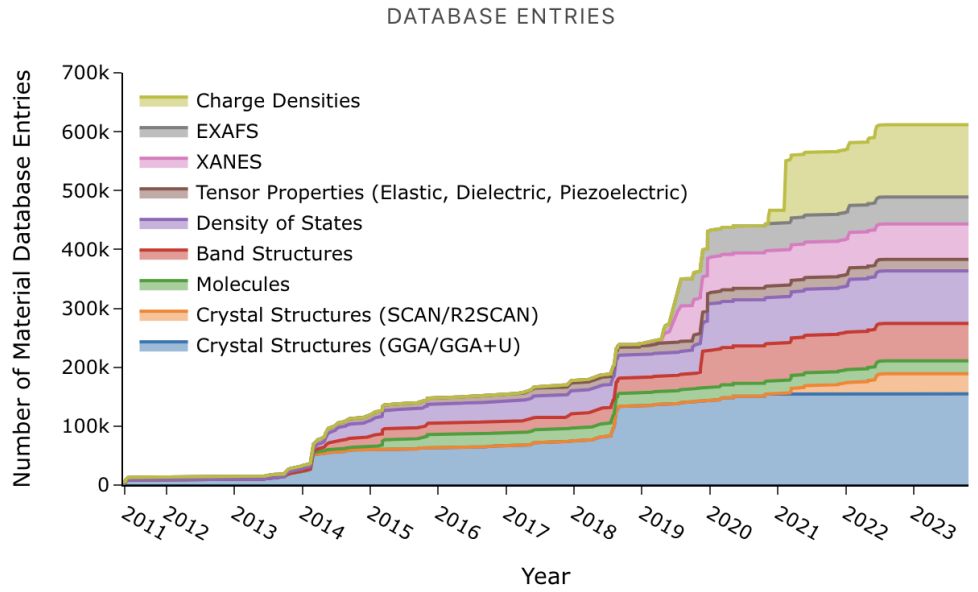
$[N_{2228}]^+$

The Materials Project

Prof. Kristin A. Persson

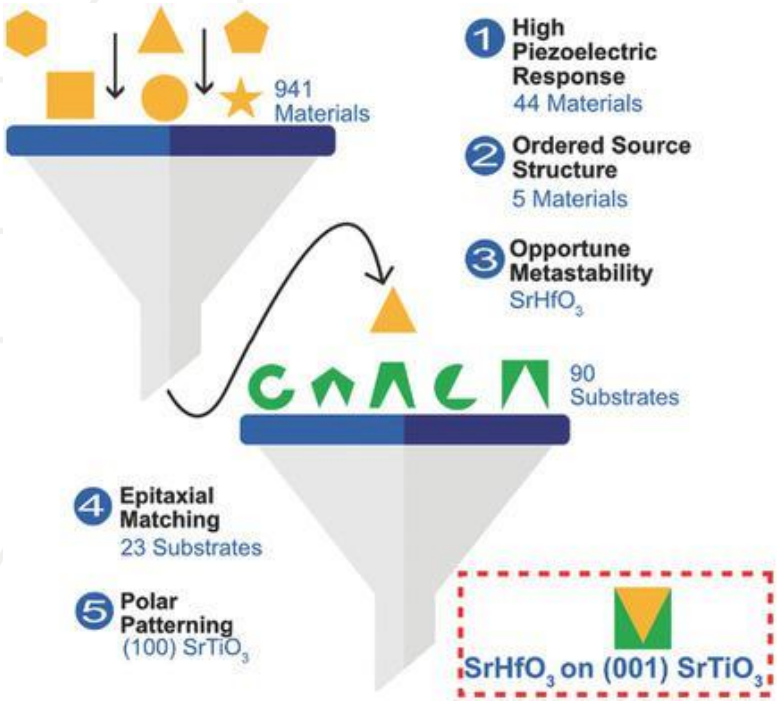
The Materials Project by the numbers

MATERIALS 154,718	REGISTERED USERS 460,000+
INTERCALATION ELECTRODES 4,351	CITATIONS 42,000+
MOLECULES 172,874	CPU HOURS/YEAR 100 million



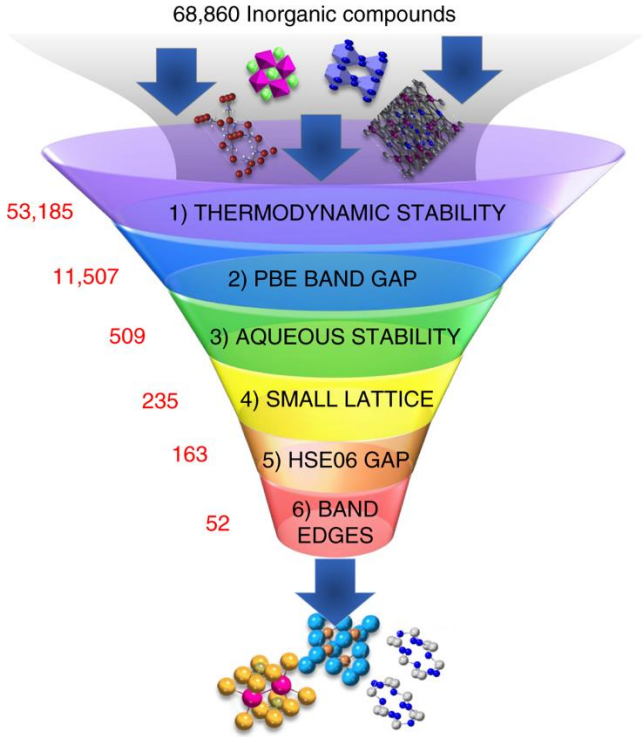
"Harnessing the power of **supercomputing** and state-of-the-art methods, the Materials Project provides open web-based access to computed information on known and predicted materials as well as powerful analysis tools **to inspire and design novel materials**."

The Materials Project has led to the discovery of…



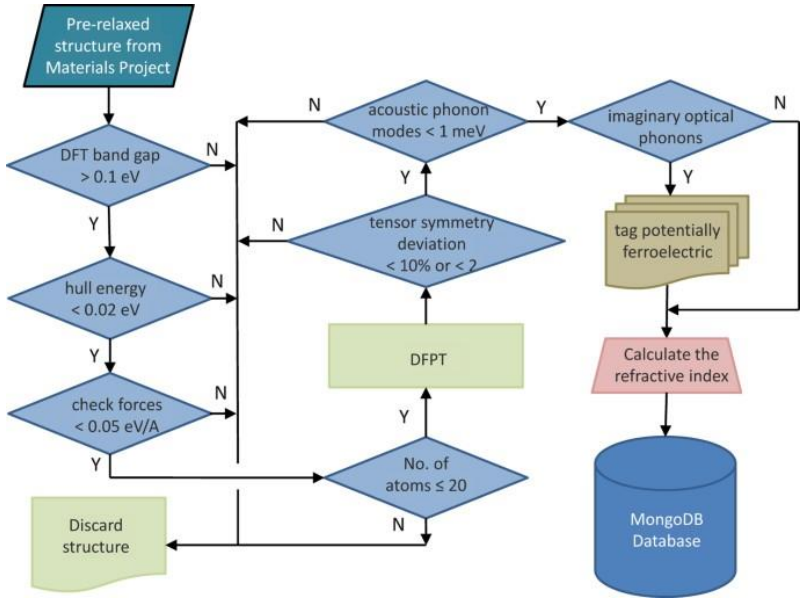
L. M. Garten, S. Dwaraknath, J. Walker, J. S. Mangum, P. F. Ndione, Y. Park, D. A. Beaton, V. Gopalan, B. P. Gorman, L. T. Schelhas, M. F. Toney, S. Trolier-McKinstry, K. A. Persson, D. S. Ginley, *Adv. Mater.* 2018, 30, 1800559.

piezoelectric materials



Singh, A.K., Montoya, J.H., Gregoire, J.M. *et al.* Robust and synthesizable photocatalysts for CO_2 reduction: a data-driven materials discovery. *Nat Commun* **10**, 443 (2019).

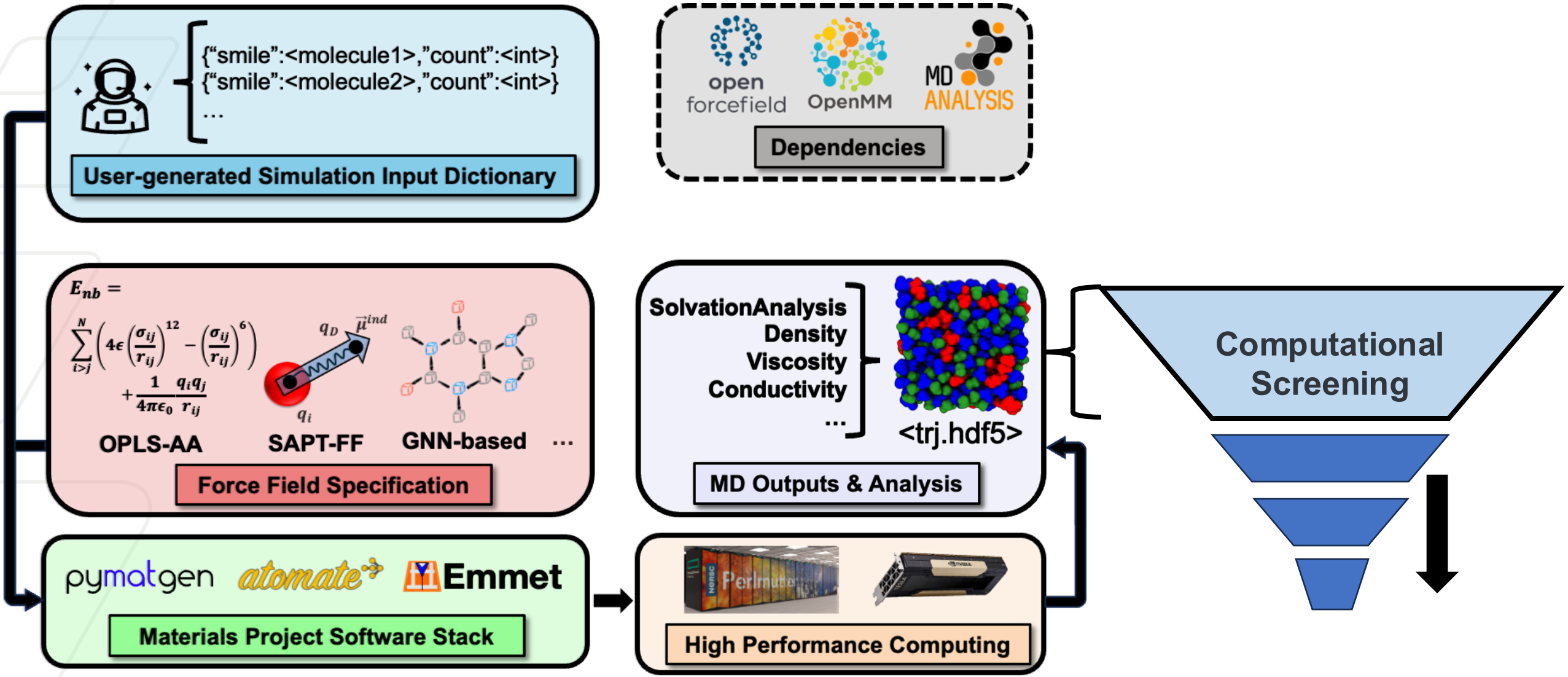
photocatalysts



Petousis, I., Mrdjenovich, D., Ballouz, E. *et al.* High-throughput screening of inorganic compounds for the discovery of novel dielectric and optical materials. *Sci Data* **4**, 160134 (2017).

dielectrics

Computational High-throughput Screening for Ionic Liquids



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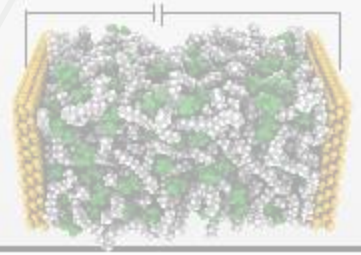

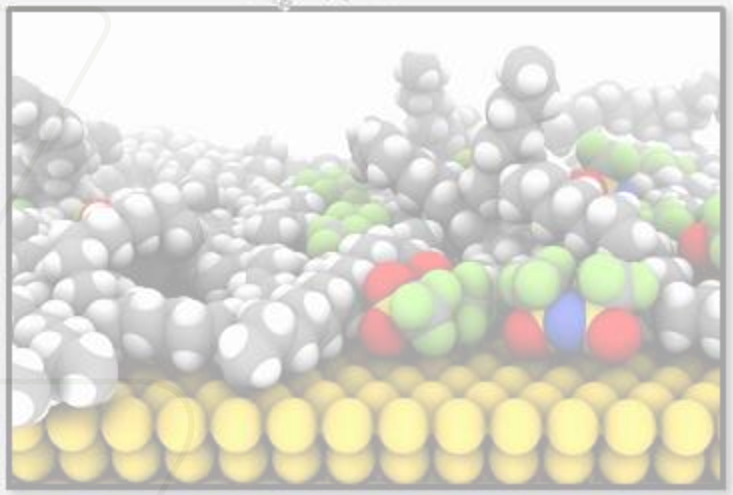

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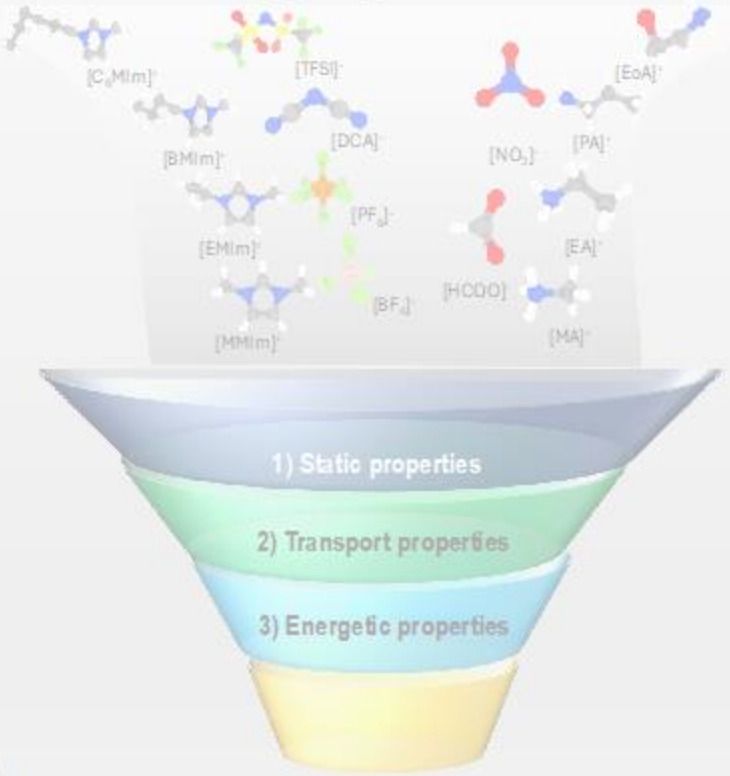

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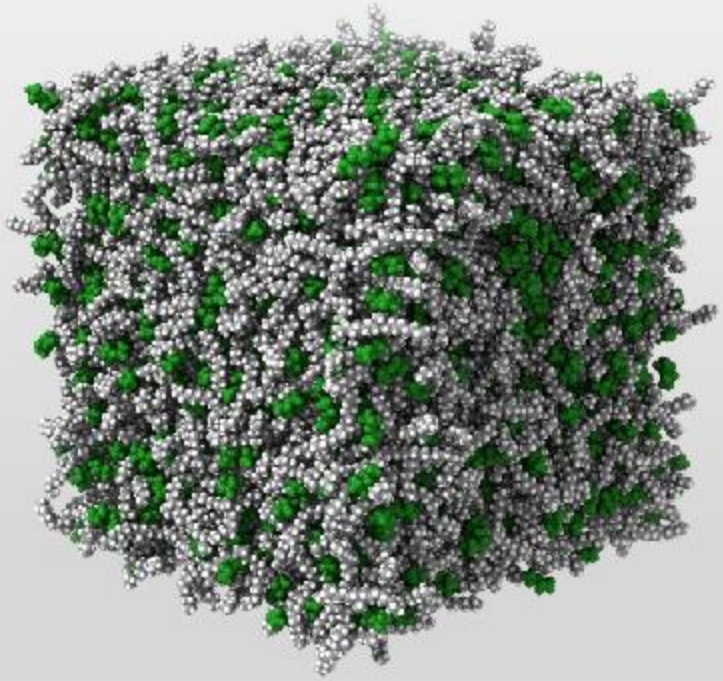

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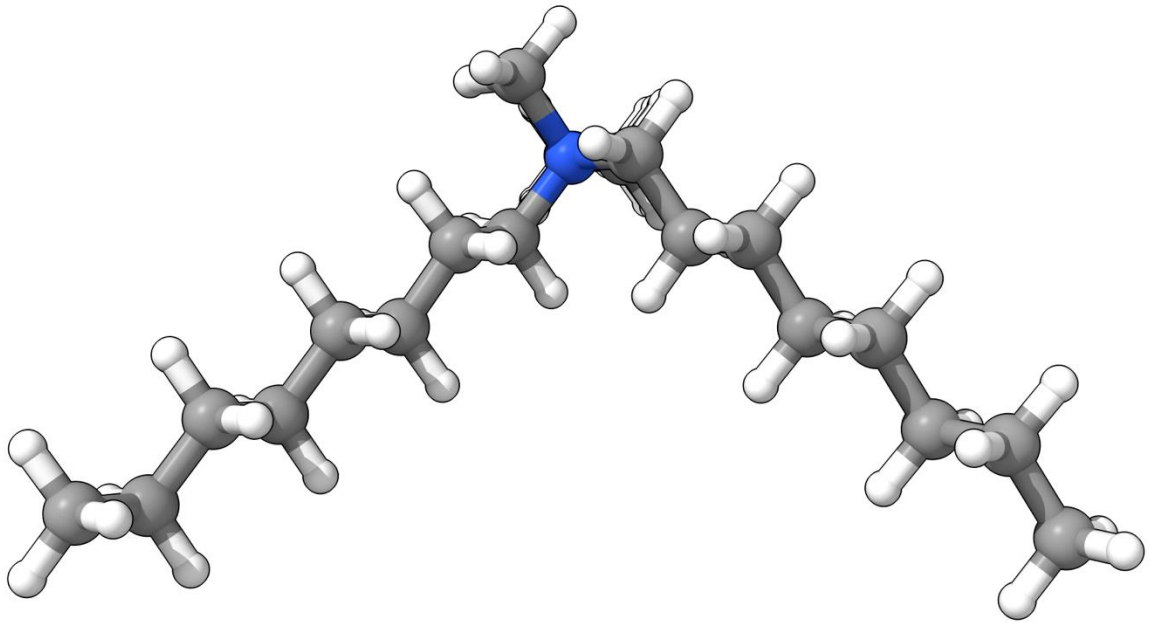
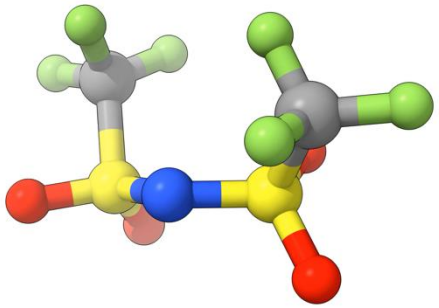
Material Discovery

HTMD

$[N_{1888}][TFSI]$

	ρ (kg/m^3)	η (cP)	σ (S/m)
$[N_{1888}][TFSI]$	**1108**	**~650**	**~0.07**
$[BMIM][BF^-_4]$	1181	~90	~0.4
H_2O	1000	~0.9	0.005-0.05

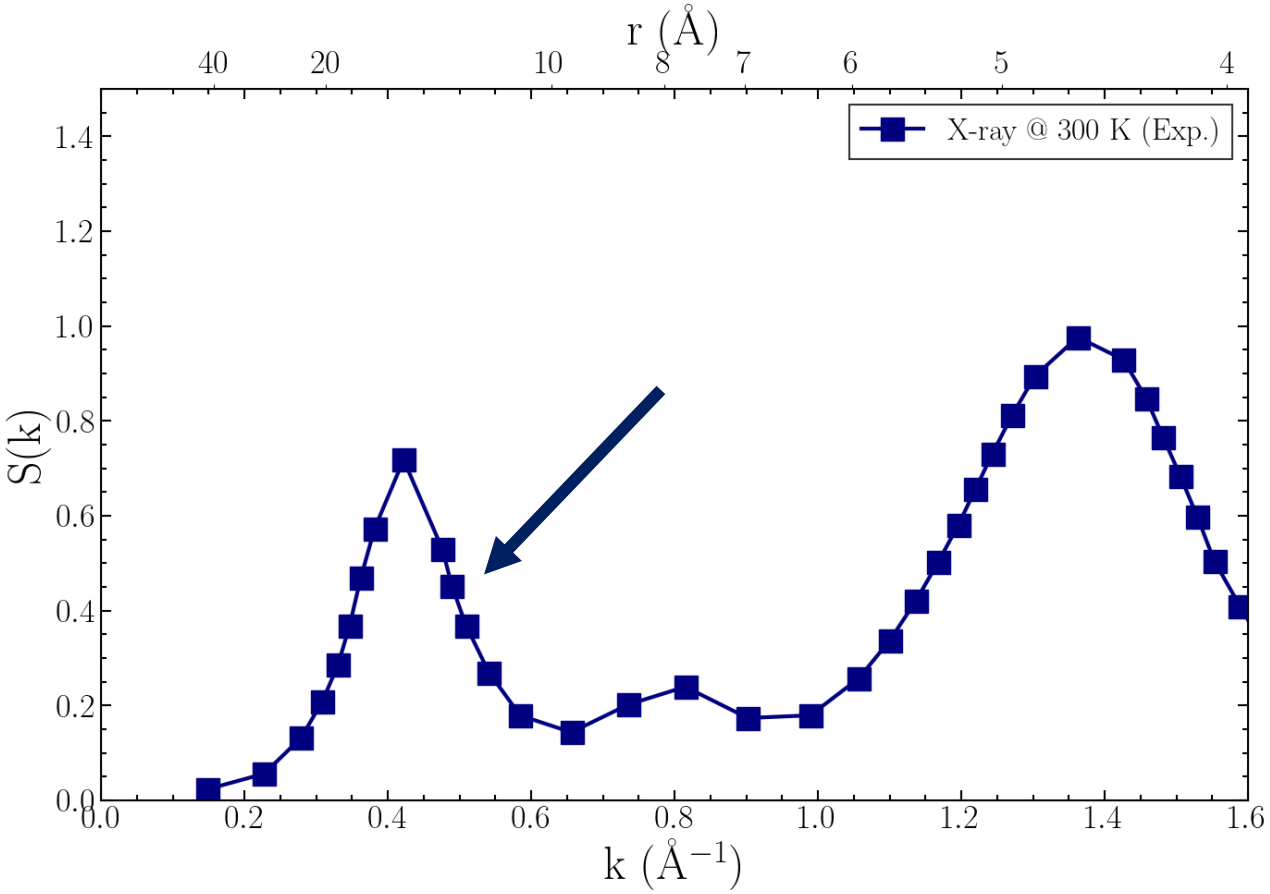




~20 Å

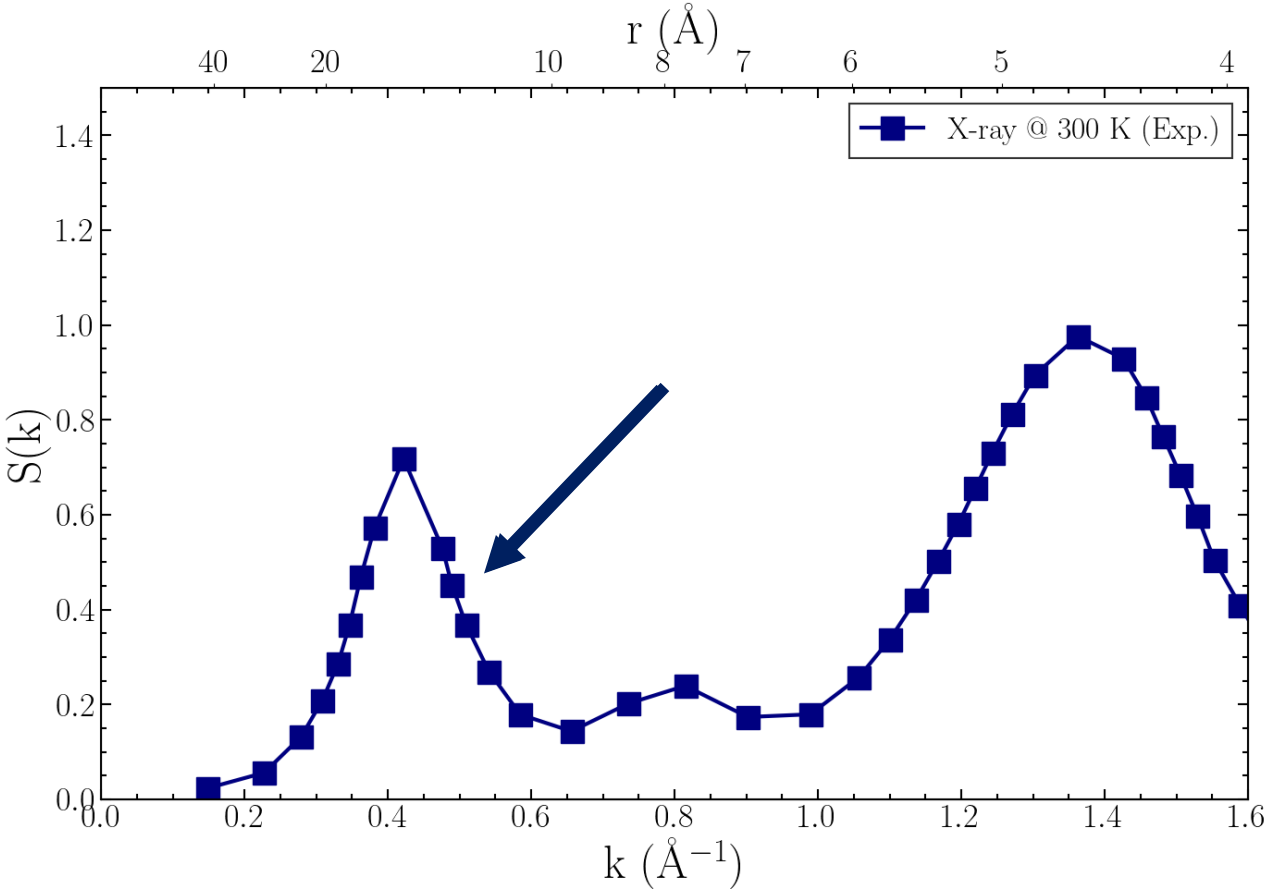
~6 Å

$[N_{1888}][TFSI]$: A Liquid Crystal?

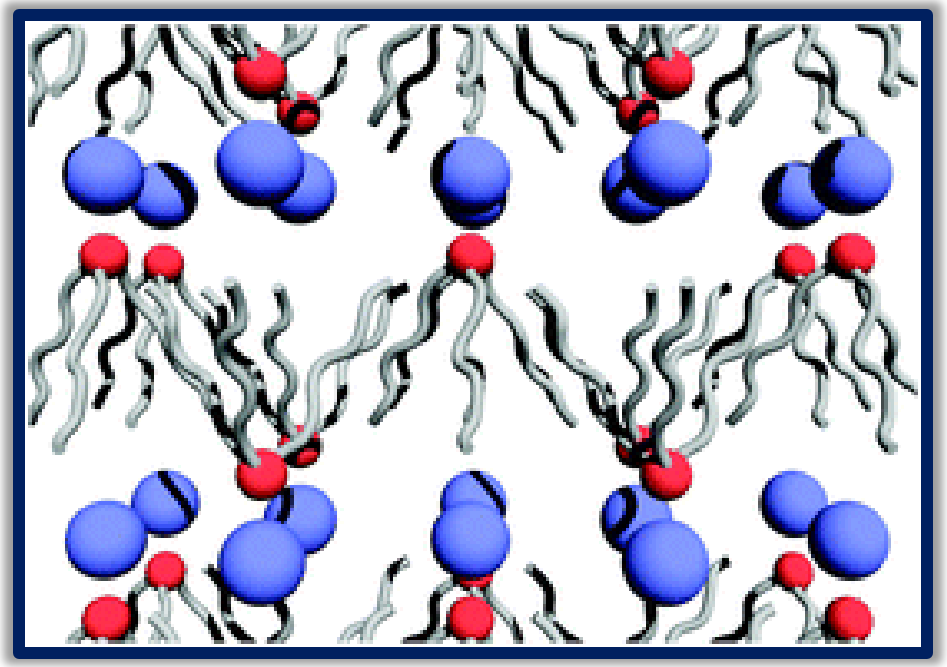


Phys. Chem. Chem. Phys., 2009,**11**, 5469-5475

$[N_{1888}][TFSI]$: A Liquid Crystal?

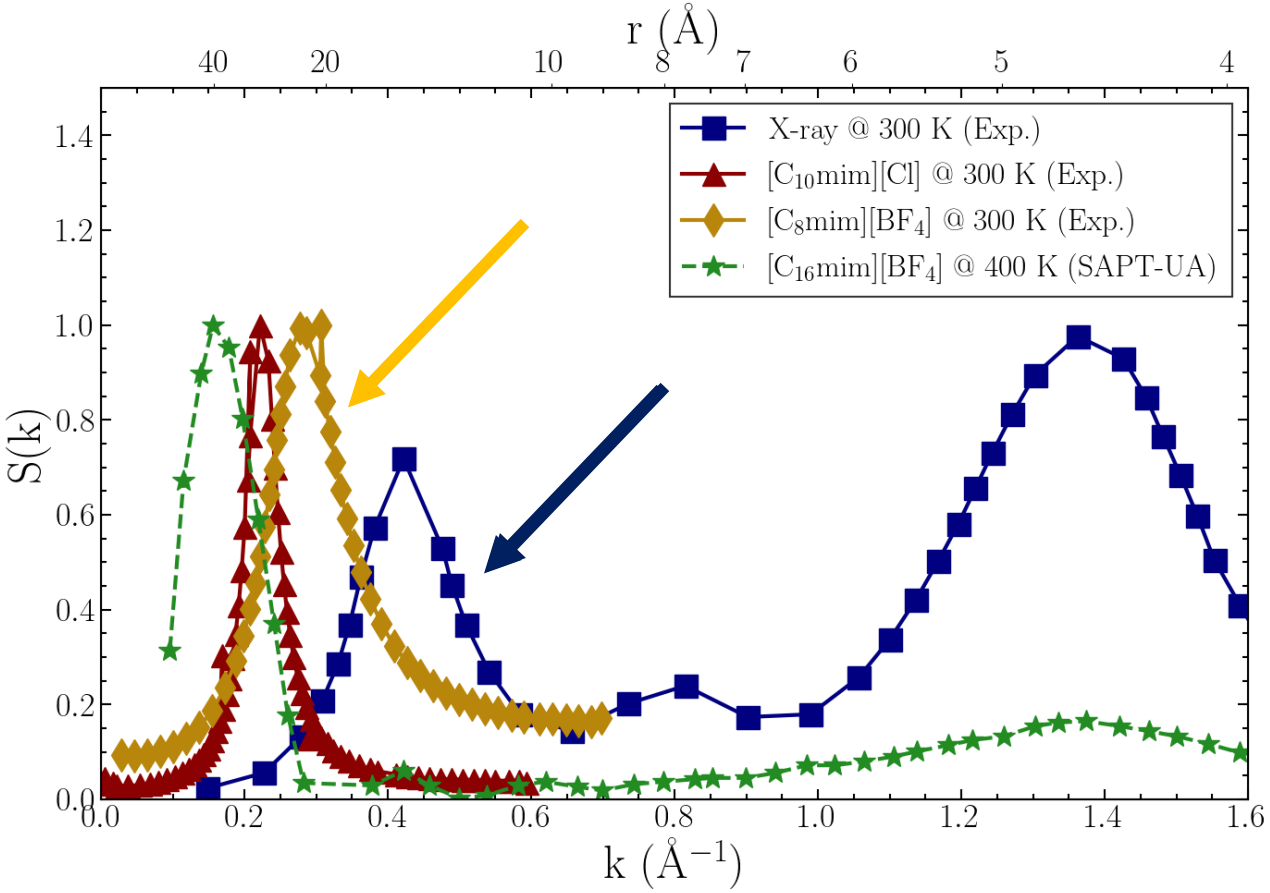


Phys. Chem. Chem. Phys., 2009,**11**, 5469-5475

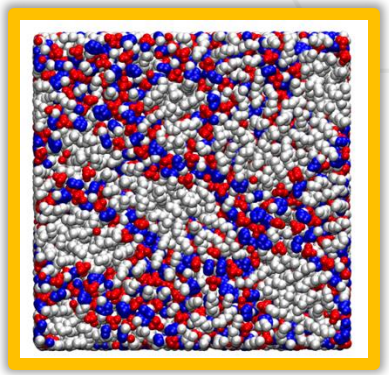


"disordered" smectic phase A?

$[N_{1888}][TFSI]$: A Liquid Crystal?

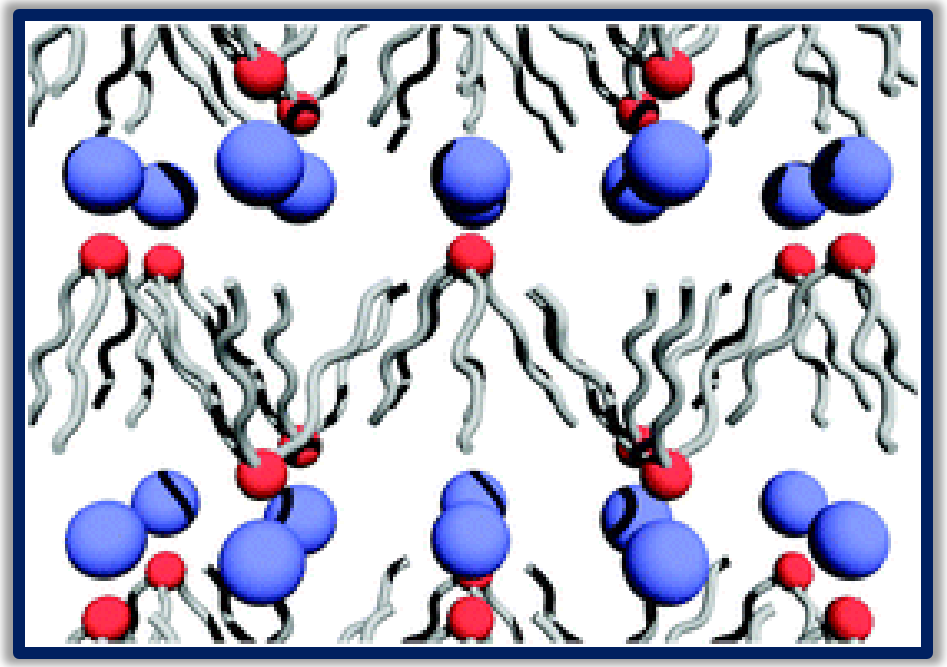


Phys. Chem. Chem. Phys., 2009,**11**, 5469-5475



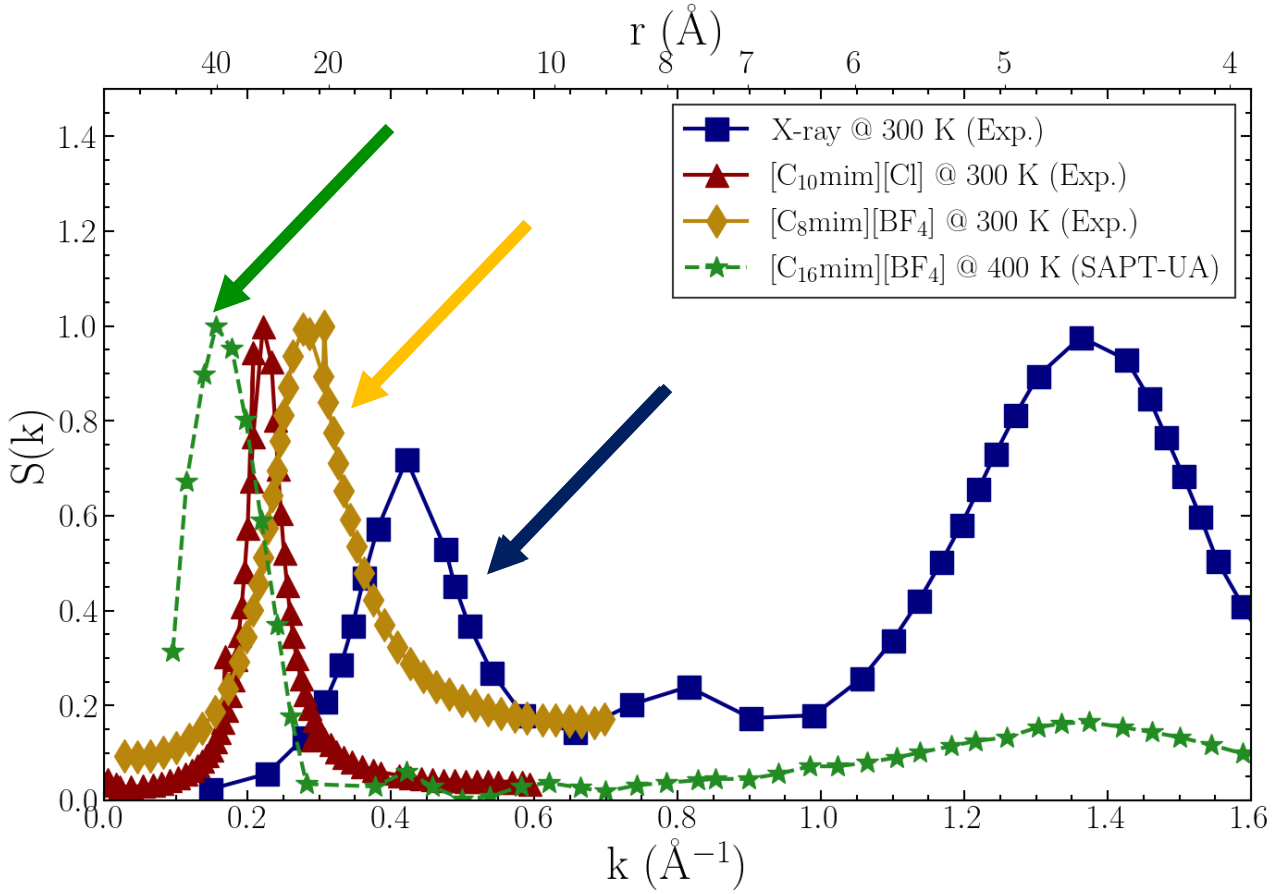
"mesoscopic" domains

J. Phys. Chem. Lett. 2012, 3, 1, 27−33

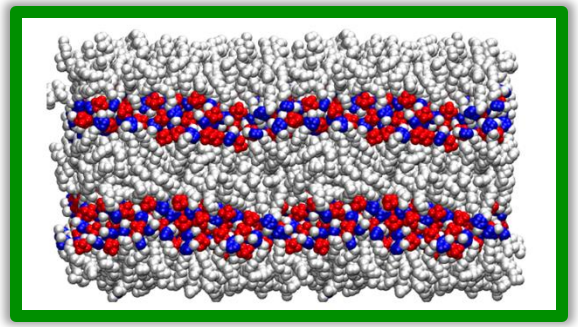


"disordered" smectic phase A?

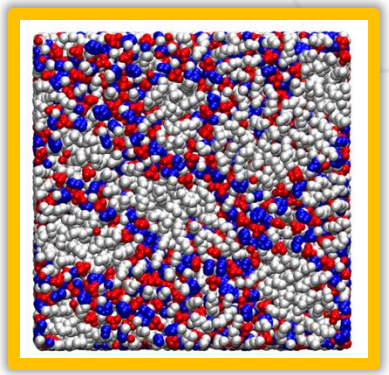
$[N_{1888}][TFSI]$: A Liquid Crystal?



Phys. Chem. Chem. Phys., 2009,**11**, 5469-5475

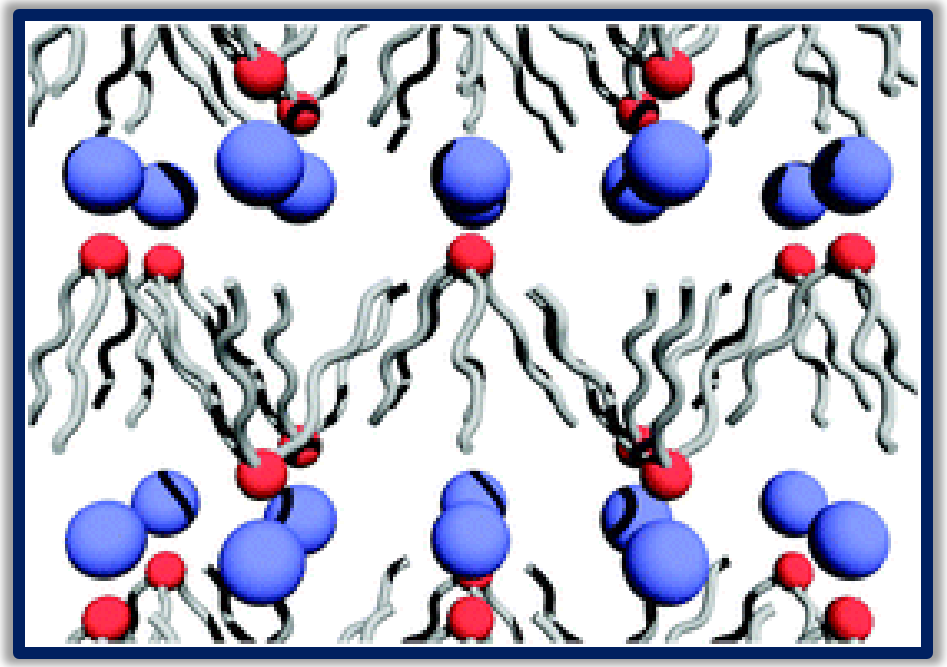


Liquid crystal



"mesoscopic" domains

J. Phys. Chem. Lett. 2012, 3, 1, 27−33



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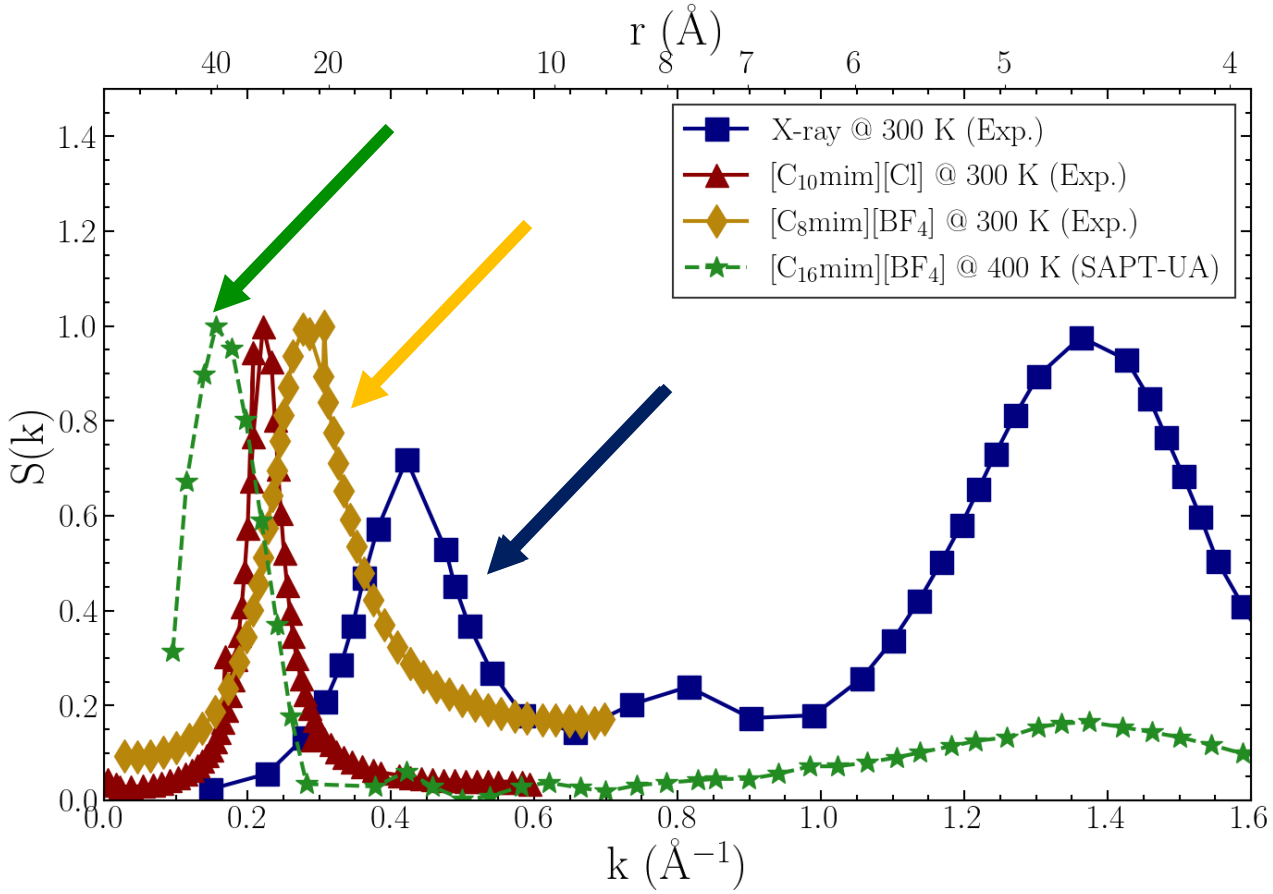
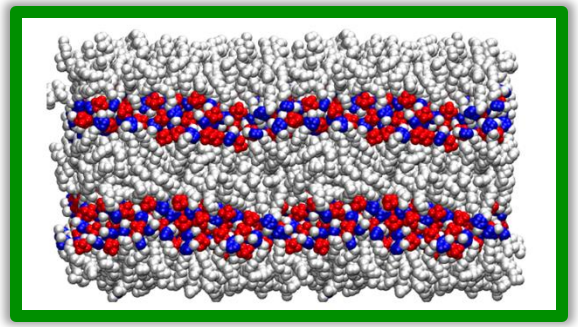
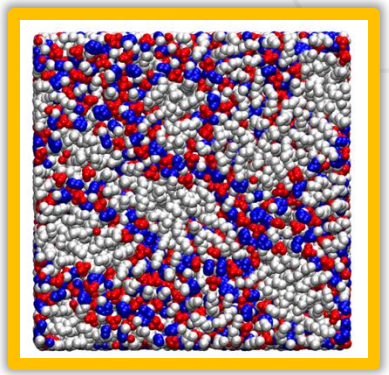


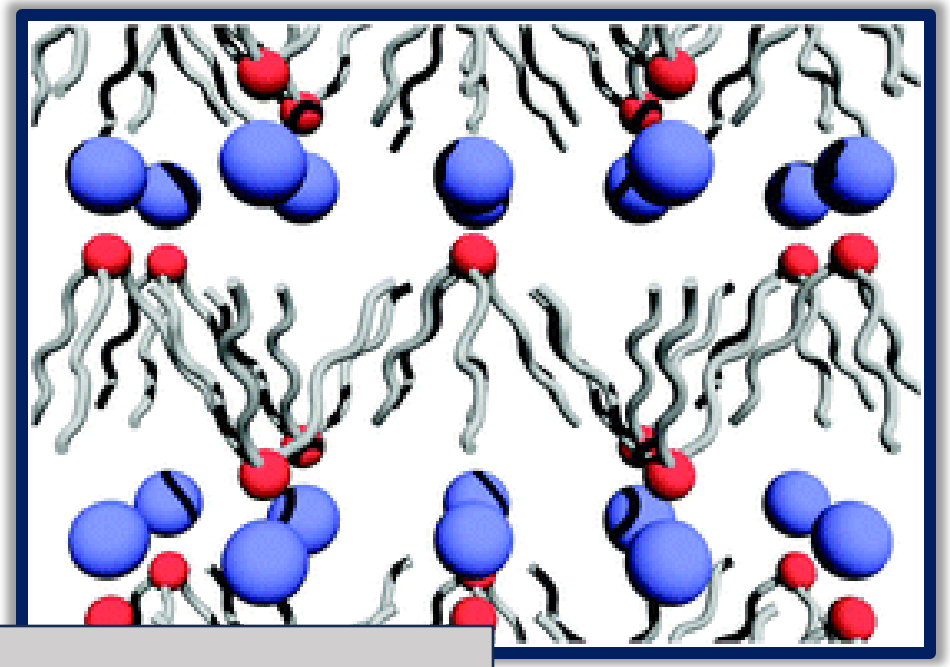


Liquid crystal



"mesoscopic" domains

J. Phys. Chem. Lett. 2012, 3, 1, 27−33

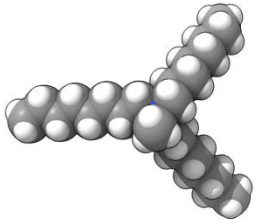


Phys. Chem

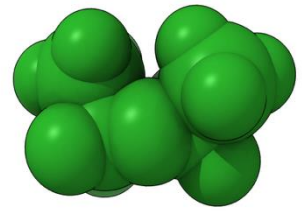
mectic phase A?

What is the bulk phase behavior of N_{1888}?

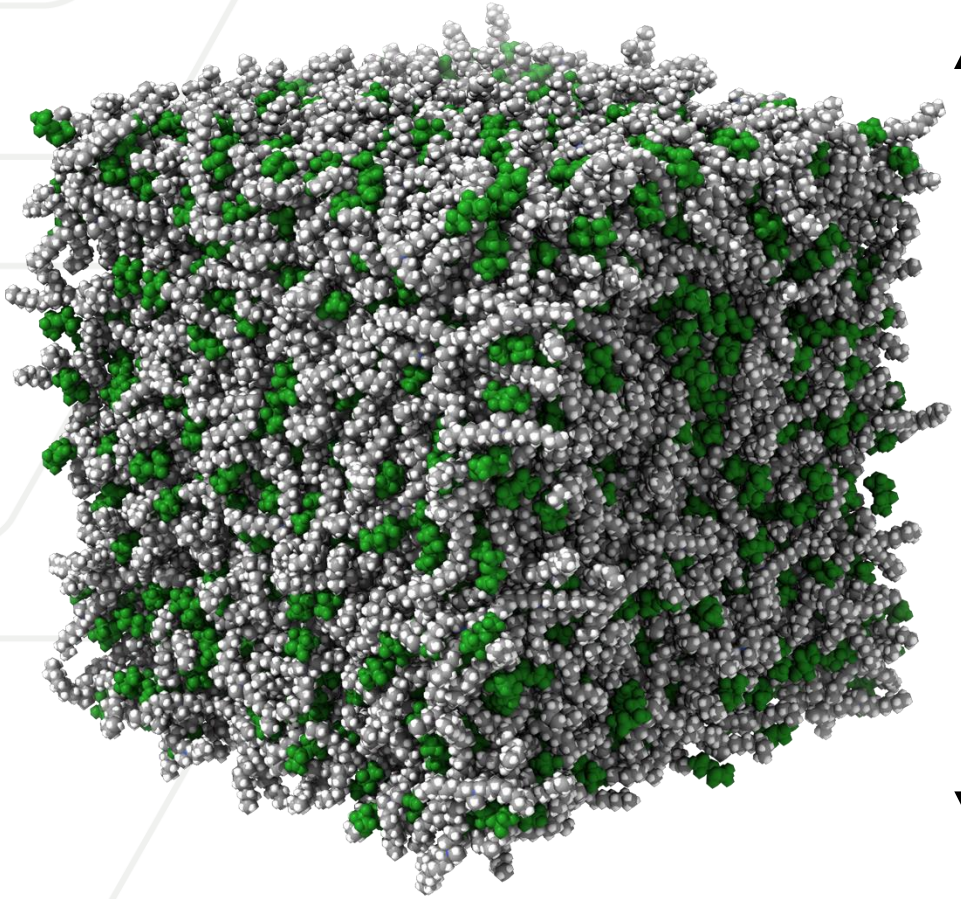
$[N_{1888}][TFSI]$ Simulation Setup



[N1888]



[TSFI]



~12 nm

- **Software**: OpenMM
- **Force Field**: SAPT-based ab initio FF
- **Conditions**:
  - **1600** ion pairs @ 300 – 500 K
  - NPT ensemble equilibration (~**1 µs**)

~250,000 atoms for ~1 µs →

~ 1 GPU month

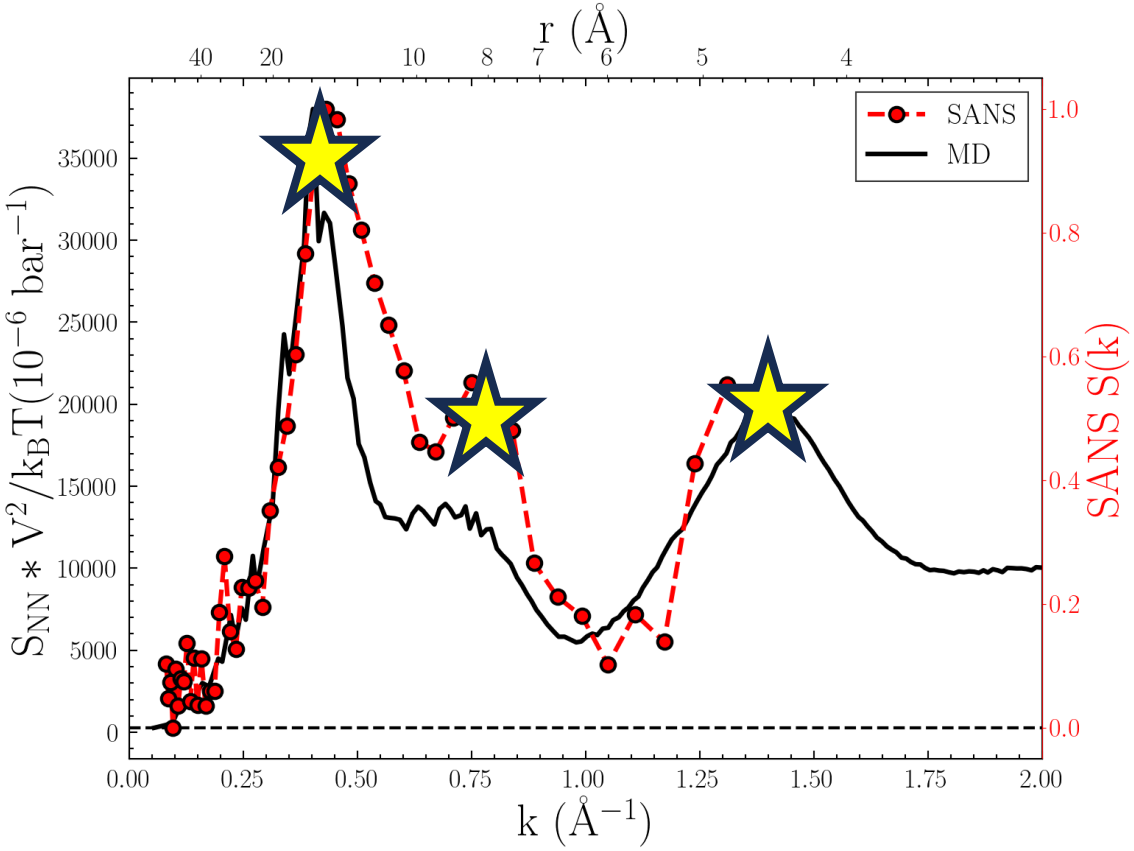
SMP et al. *J. Phys. Chem. B* 2024, 128, 45, 11313–11327

Experiments & Simulation

OAK RIDGE National Laboratory

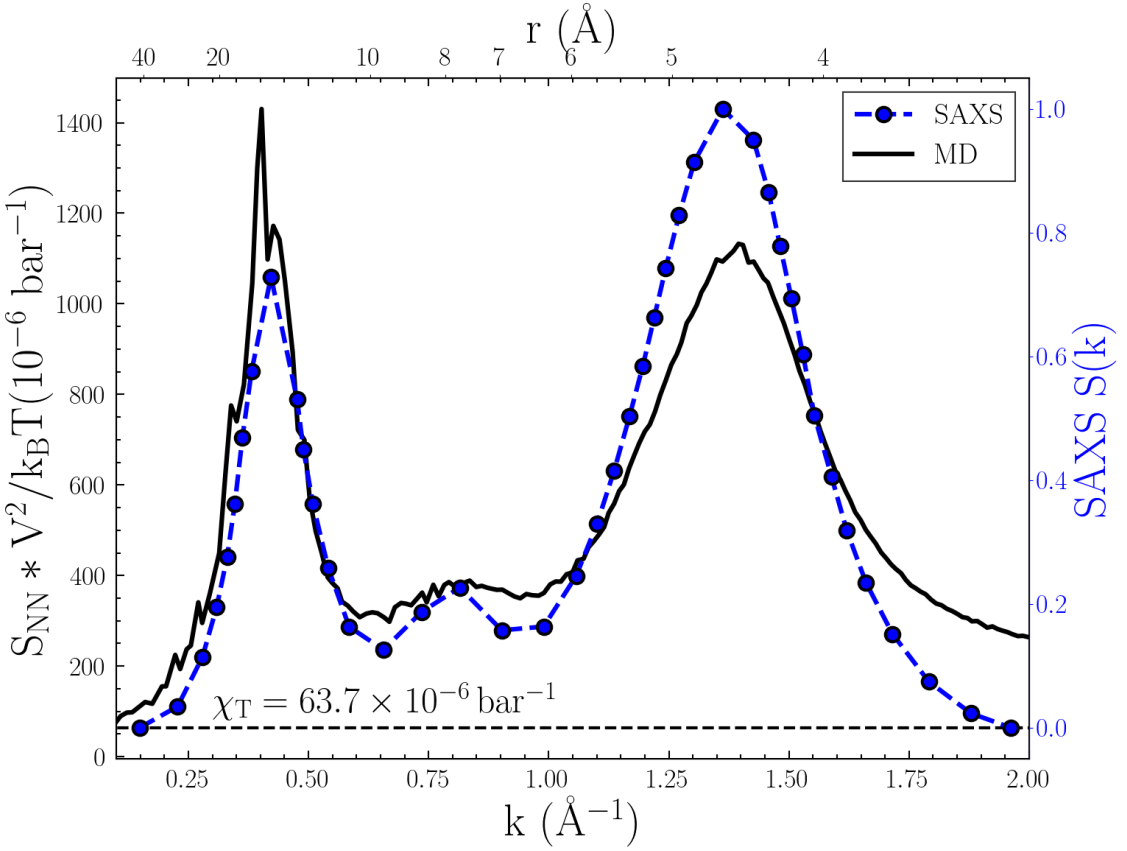
CASE SCHOOL OF ENGINEERING
CASE WESTERN RESERVE UNIVERSITY

Experiments by Dr. Changwoo Do, ORNL



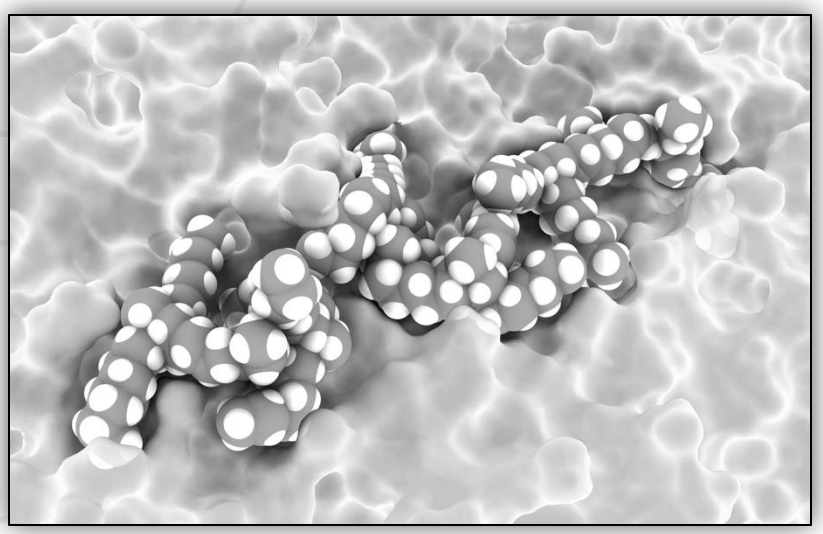
$$\rho_N(k) = \sum_{i=1}^{N} \boldsymbol{b_i^{coh}} e^{ik\cdot r_i}$$

Experiments from Pott and Méléard, 2009

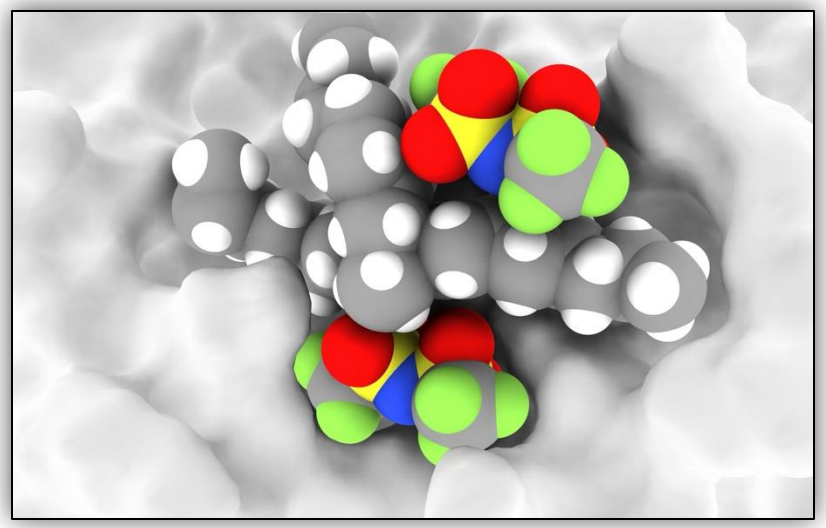


$$\rho_N(k) = \sum_{i=1}^{N} \boldsymbol{f_i(k)} e^{ik\cdot r_i}$$

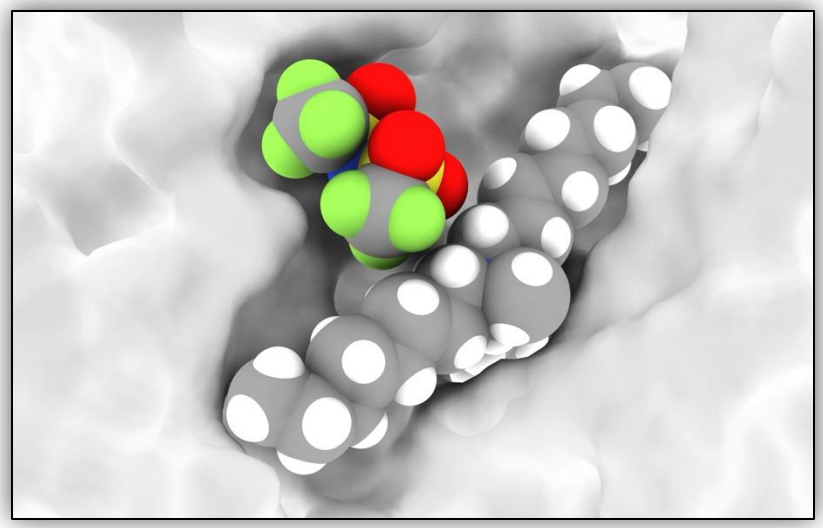
Summary: Bulk Phase Behavior of $[N_{1888}][TFSI]$



$k \approx 0.4$ Å^{-1} (r ≈ 16 Å)



$k \approx 0.7$ Å^{-1} (r ≈ 9 Å)

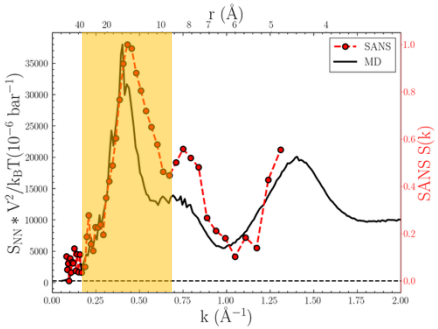


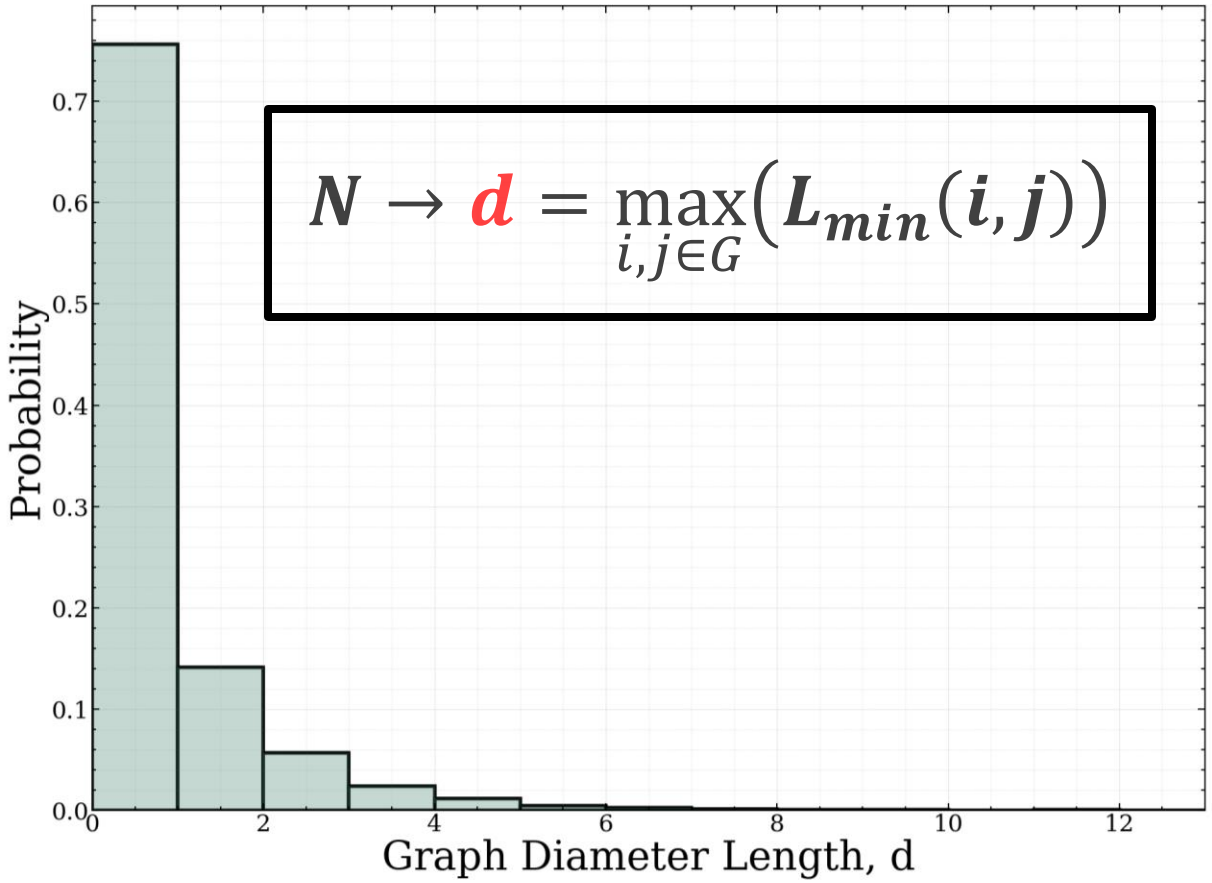
$k \approx 1.4$ Å^{-1} (r ≈ 4.5 Å)

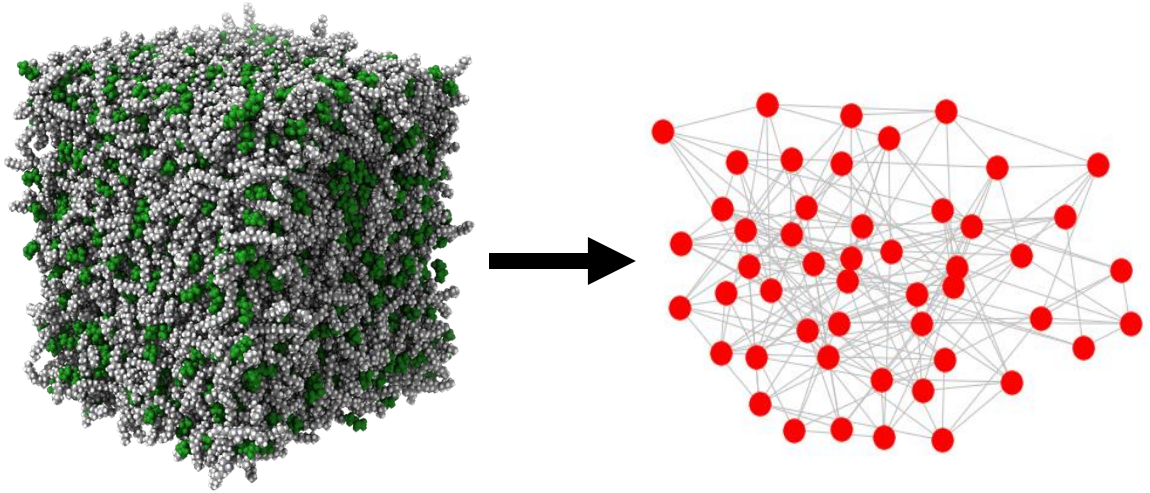
Bulk phase behavior of N_{1888} is governed by the alternation of polar/apolar, charge, and adjacent domains.

Polarity Domain

$k \approx 0.4\ \text{Å}^{-1}$ (r ≈ 16 Å)





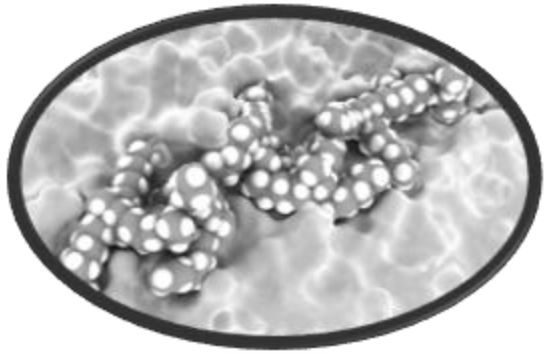


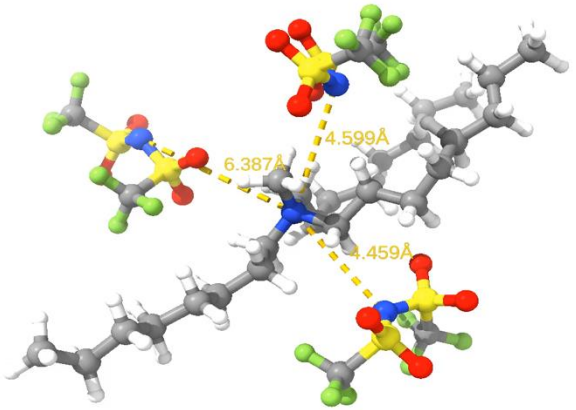
https://github.com/shehan807/graph-network-analysis

NetworkX
Network Analysis in Python

Graph network analysis quantifies (real space) *spatial extent* of apolar network; no indication of smectic behavior of interdigitation.

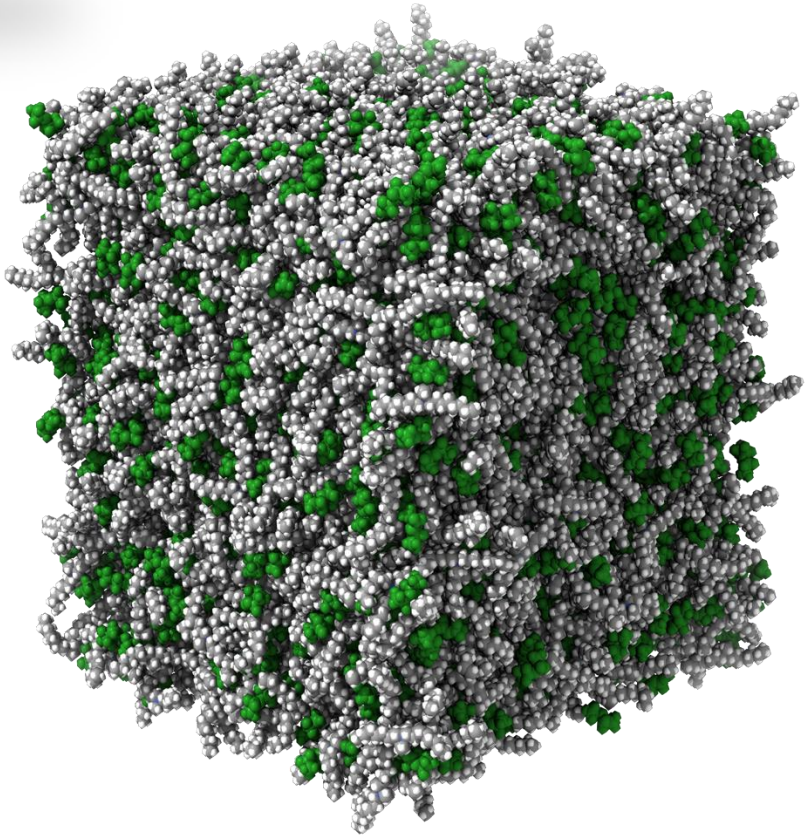
Conclusions





Summary:

- High-throughput screening workflow spots unique ionic liquid candidates for battery applications
- Bulk-phase structure consists of three domains (polarity, charge, & adjacency)



Future Work:

- Understand solid/liquid interface
- Develop design principles for ionic liquid electrolytes

Acknowledgements

- Prof. Jesse McDaniel
- Prof. Burcu Gurkan
- Dr. Changwoo Do
- Air Force Research Laboratory
- McDaniel Research Group Members!

DOE CSGF

U.S. AIR FORCE

OAK RIDGE National Laboratory