Pacific Northwest
NATIONAL LABORATORY

Predicting Functionality and Resiliency of Organic Redox Flow Battery

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U.S. DEPARTMENT OF ENERGY BATTELLE

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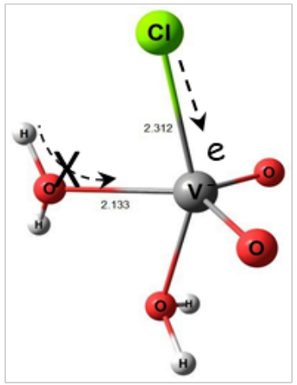
Objective: Design of Viable Redox Molecule

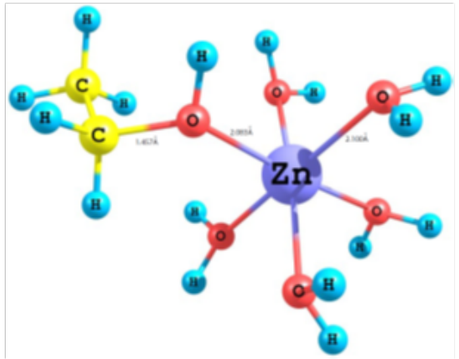
Our goal is to "*enable rapid design and screening of optimal redox molecules for targeted functionalities (such as solubility and stability) to build flow batteries with high energy density and long life-cycle*".

Mixed Acid



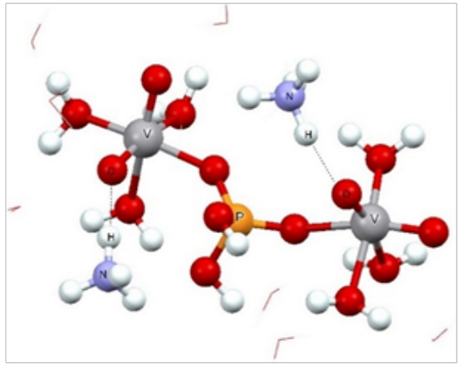
2011

Zn-I electrolyte



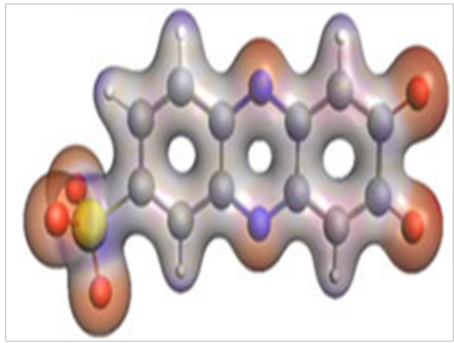
2013

Bi-additives



2016

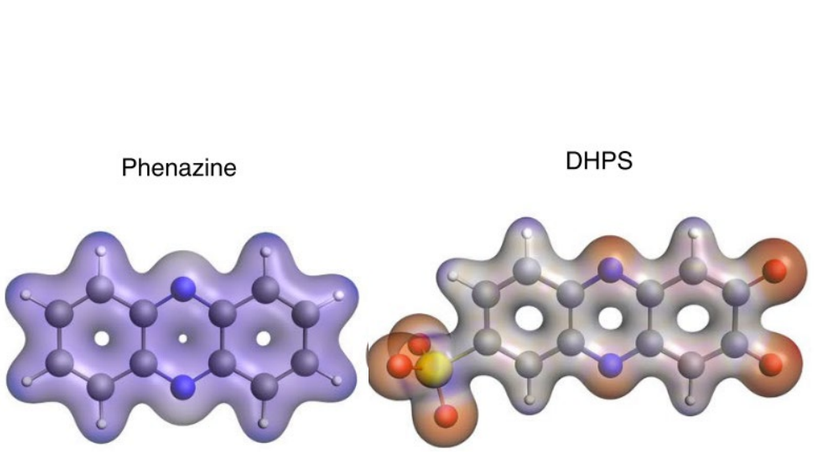
Organic-Flow

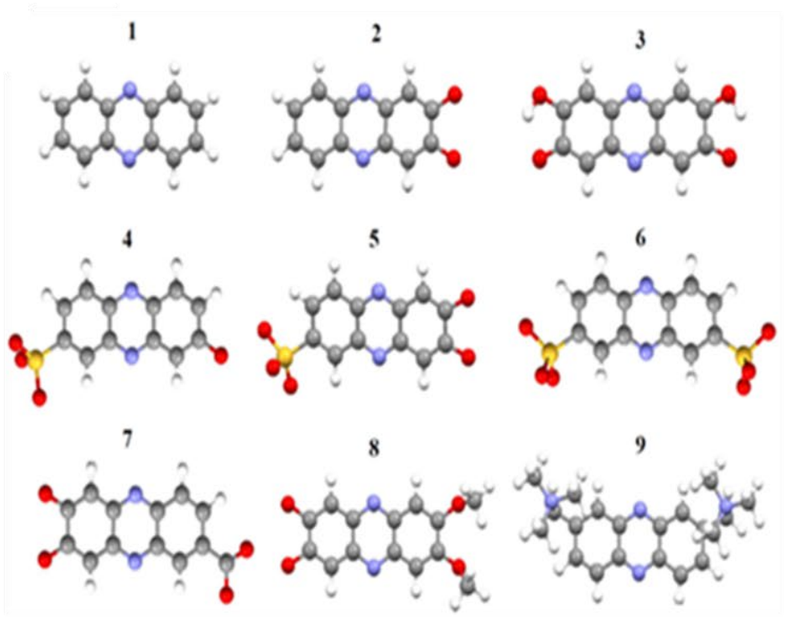


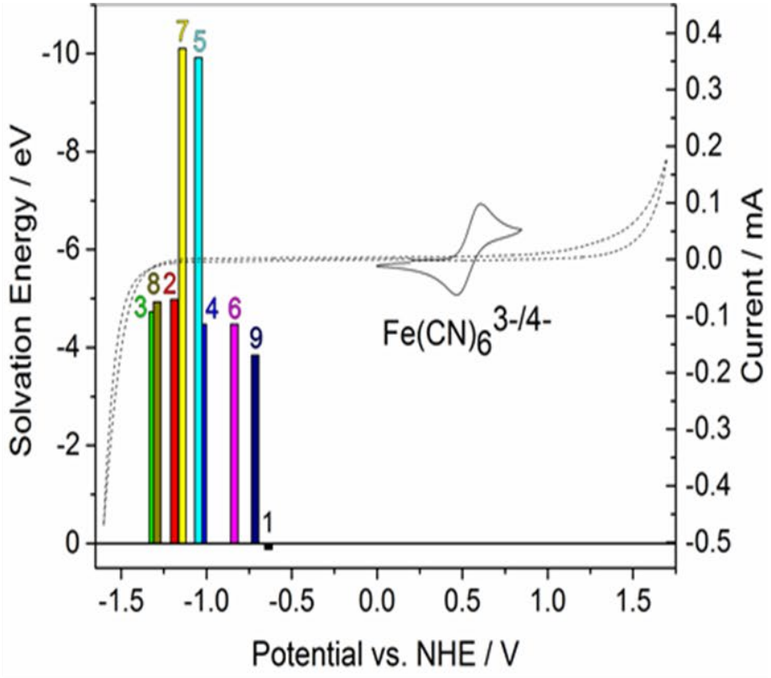
2018

Molecular design and engineering through tuning solvate structure and dynamics

Atomistic View of Redox Molecule Solubility







- Density functional theory (DFT) based calculations help us to predict redox potential and trends of aqueous solubility.
- Chemical identity and structural position of solubilizing functional groups (e.g. OH^-, SO_3^-, CO_2^-) are critically control many functional properties, including solubility and redox potentials.

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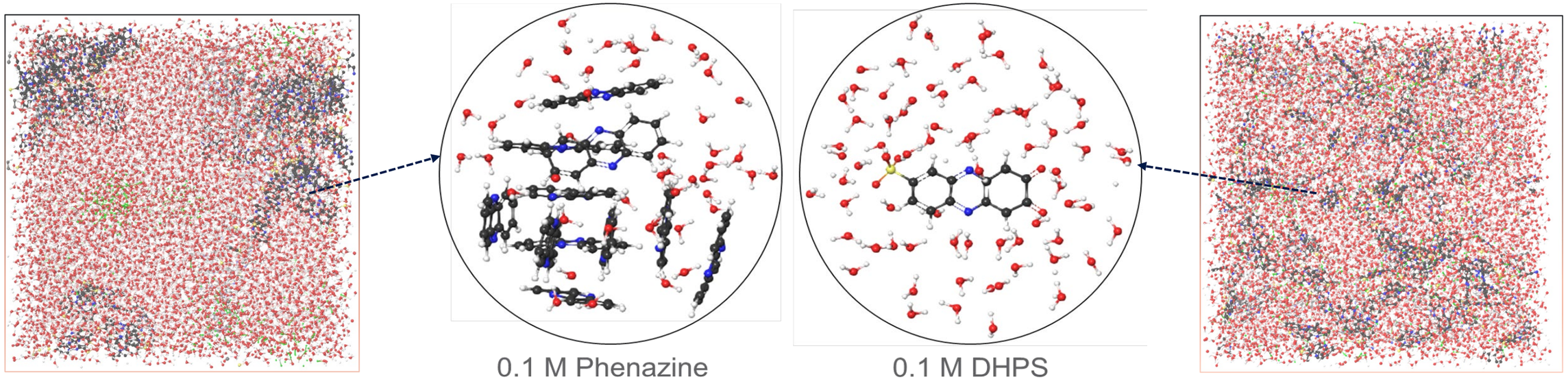
Mesoscopic View of Redox Molecule Solubility

(in collaboration with Prof. N.N. Rajput, Tufts University)



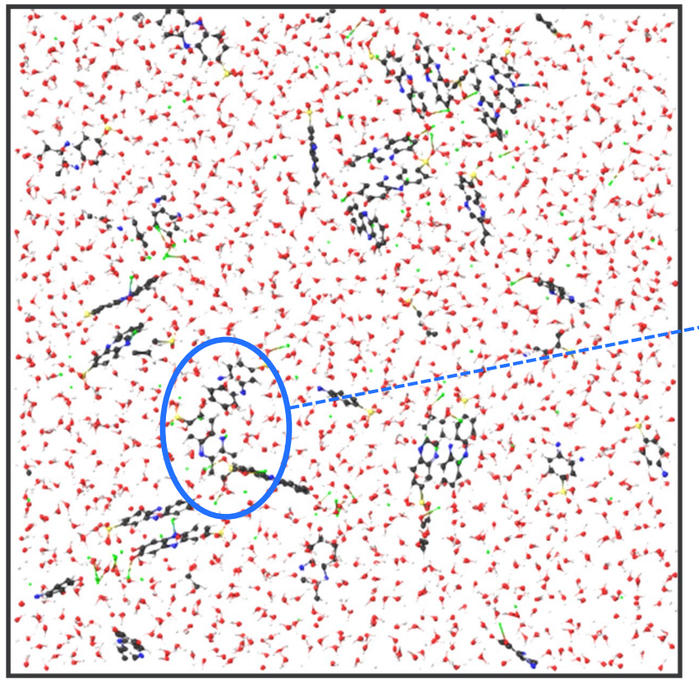
0.1 M Phenazine
Solubility <0.01M

0.1 M DHPS
Solubility ~1.4M

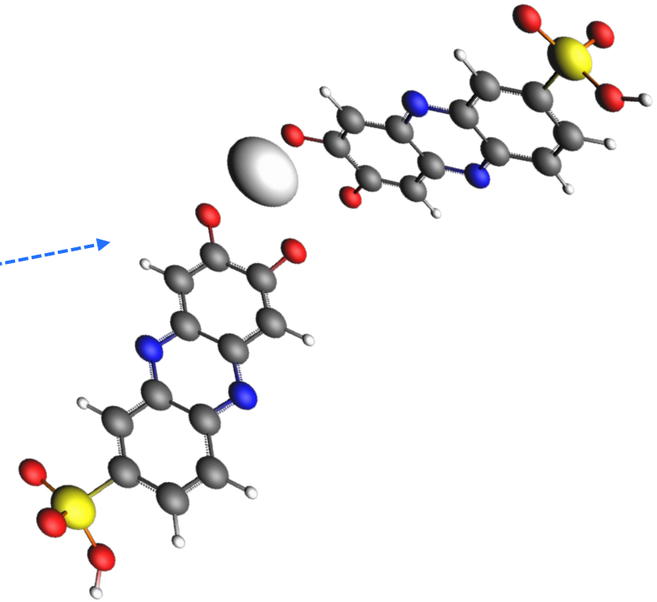
- Classic Molecular Dynamics (c-MD) based calculations help us to predict long range ordering across solvated structure of redox molecules and specific role of counter ions in electrolyte.
- Solvent and/or ion sharing between adjacent solvate structures can trigger clustering phenomena and lead to precipitation/solubility limit.

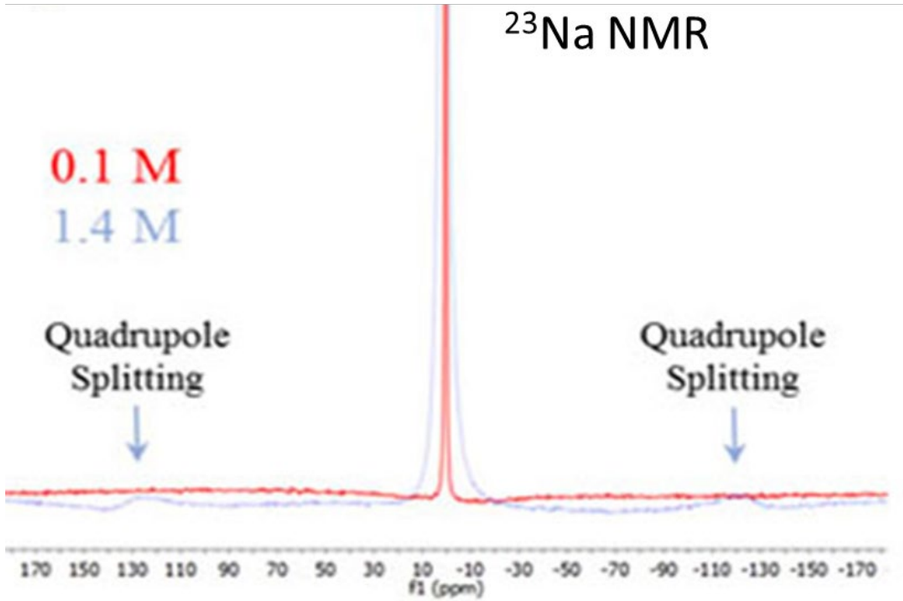
Solvate Clustering Limits DHPS solubility

(in collaboration with Prof. N.N. Rajput, Tufts University)



1M DHPS, 4M $NaOH^-$ in water

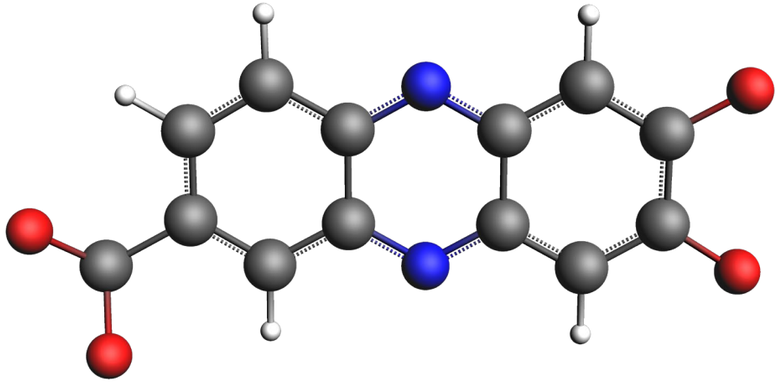




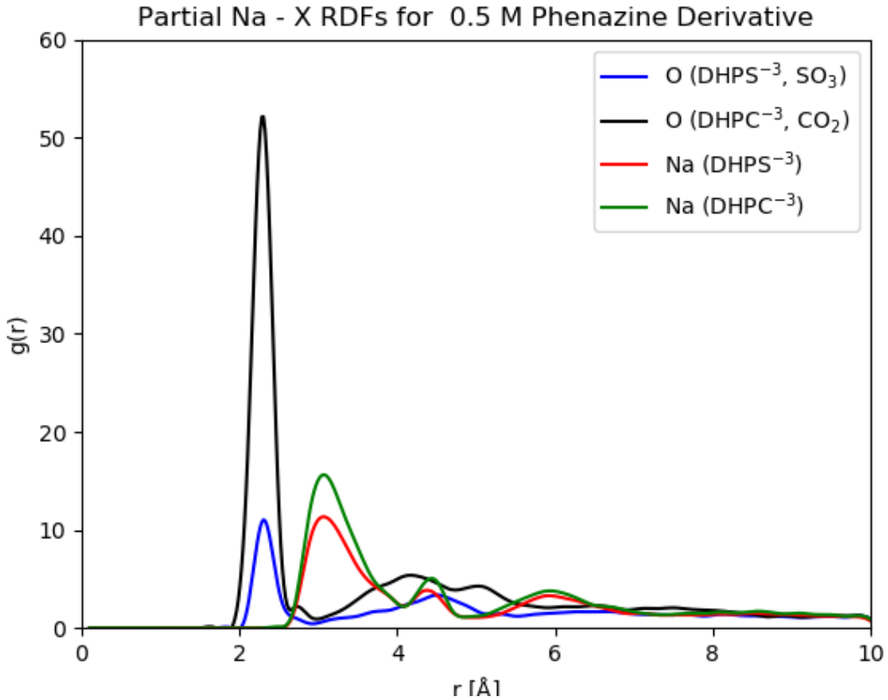
- c-MD based calculations reveals strong interactions between solvated structure of DHPS and Na^+ counter ions in electrolyte.
- More localized electron density at phenoxy (aryl-O) groups led to stronger interaction with Na^+ and subsequently triggers clustering phenomena.

Challenges with Structural and Chemical Asymmetry

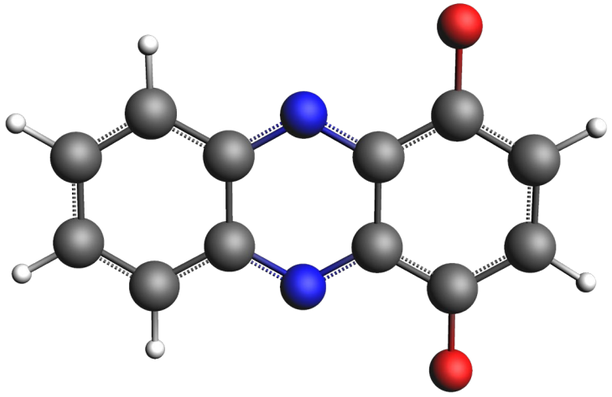
DHPC



Solubility ~0.9M



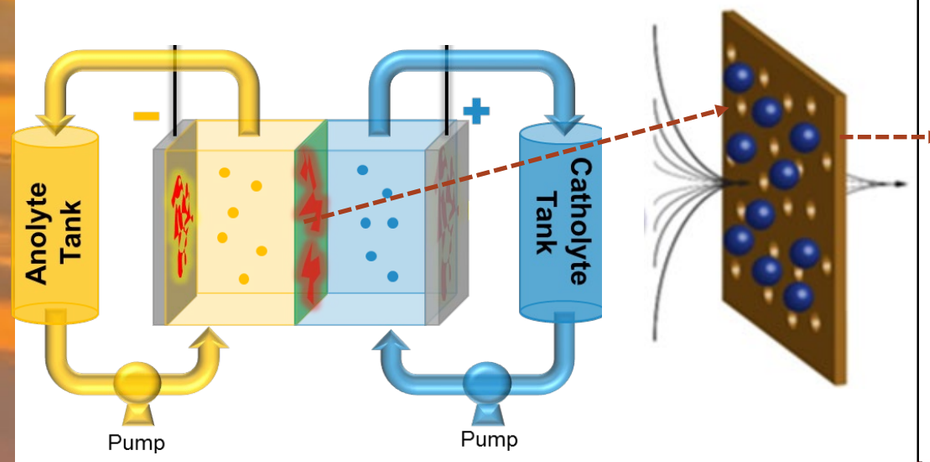
1,4-DHP

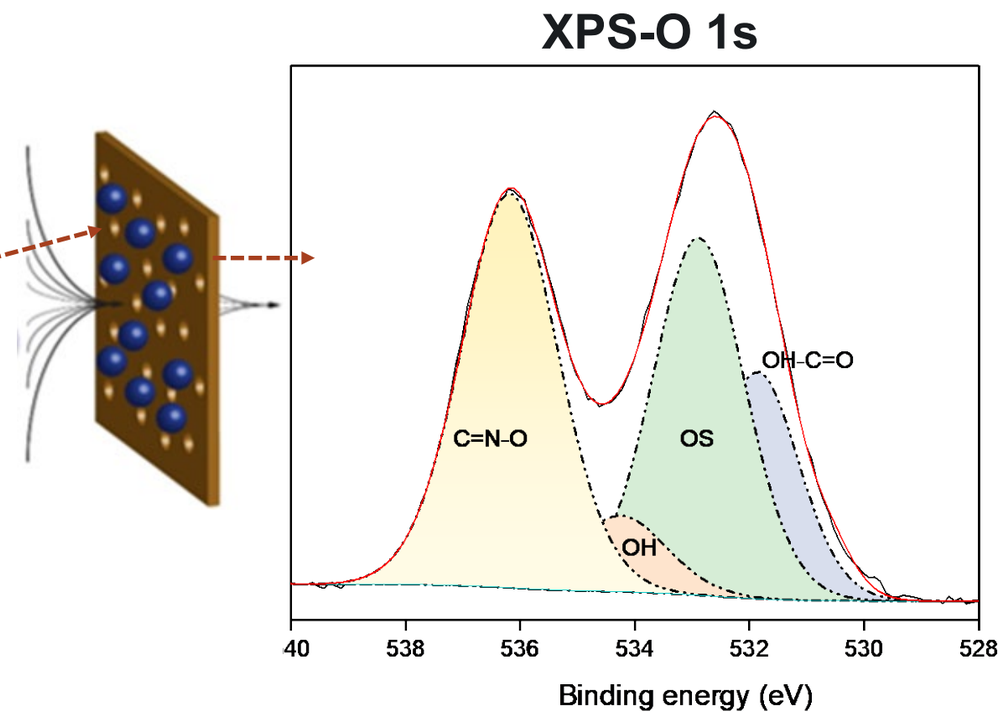


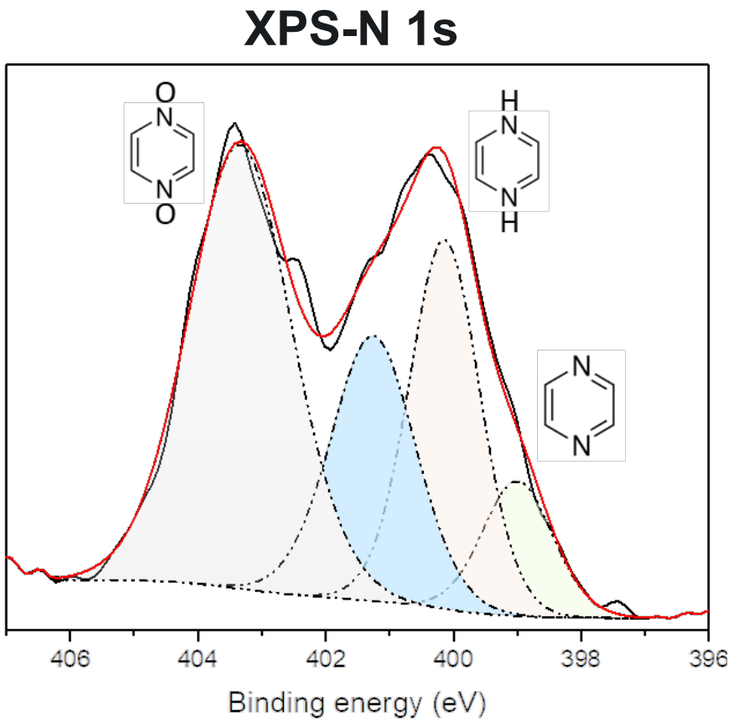
Solubility ~0.5M

- c-MD based calculations reveals stronger interactions of Na^+ counter ions with carboxyl groups than phenoxy (aryl-O) groups within DHPC.
- Isomeric changes with functional group placements can drastically change solubility and long term stability.

Reactivity Induced Fouling in Membranes







- Pores in membranes can be active regime of catholyte and anolyte reaction, leading to unique decomposition pathways and fouling process.
- Fouling of membranes can block charge transport and ultimately increase the resistance and battery performance degradation.

Acknowledgements

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Tufts University, Boston