

# **Inexpensive, Nonfluorinated (or Partially Fluorinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes**

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Project ID# es057

## Overview

### Timeline

Project Start: April 24, 2009  
Project End: March 31, 2012  
Percent Completed: 66%

### Budget

Total Project Funding:  
\$763,057  
Funding Received FY10:  
\$245,450  
Funding Received FY11:  
\$245,882

### Barriers

Low cost cell materials  
Abuse tolerance  
Low temperature performance

### Partners

Project Lead: Wesley Henderson  
Co-PIs: Michel Armand, Peter Fedkiw  
Collaborators:

- Kang Xu, Richard Jow (ARL)
- Patrick Judeinstein (Université Paris-Sud)
- Steve Greenbaum (Hunter College of CUNY )
- Patrik Johansson (Chalmers University)

## Objectives

- Develop techniques to synthesize electrolytes that allow for lower cost of production
- Develop low-cost, thermally stable electrolytes to replace ones now commonly used
- Develop electrolyte/additive combinations that will facilitate a more stable solid-electrolyte interphase (SEI) on the anode
- Develop additives that allow for the formation of protective coatings on the cathode (i.e., a cathode SEI) and enhances electrochemical stability above 4.3 V

## Milestones

<u>Milestone</u>	<u>Completion</u>
■ Characterization (properties/phase diagrams) of solvent-LiBF <sub>4</sub> mixtures as model electrolytes	ongoing
■ Characterization (properties/phase diagrams) of solvent-LiBOB and -LiDFOB mixtures to examine structural effects on solubility/properties	ongoing
■ Synthesis/characterization of ionic liquids containing cyanocarbanions and DFOB <sup>-</sup>	ongoing
■ Synthesis of new partially fluorinated anions (with new ligands) and cyanocarbanions	ongoing

## Approach

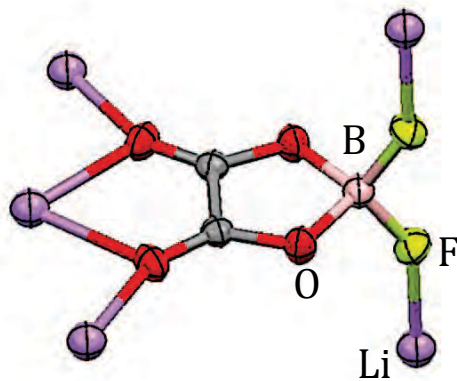
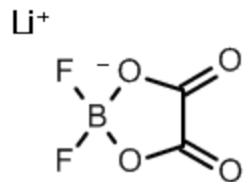
Synthesize and fully characterize two classes of nonfluorinated (or less fluorinated) anions:

- (1) chelated and non-chelated **organoborate anions** (related to bis(oxalato) borate or BOB<sup>-</sup>), and
- (2) Hückle-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic **cyanocarbanions**. Characterize the physical properties of these new anions, incorporated in both lithium salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as LiPF<sub>6</sub> and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imide anion (TFSI<sup>-</sup>).

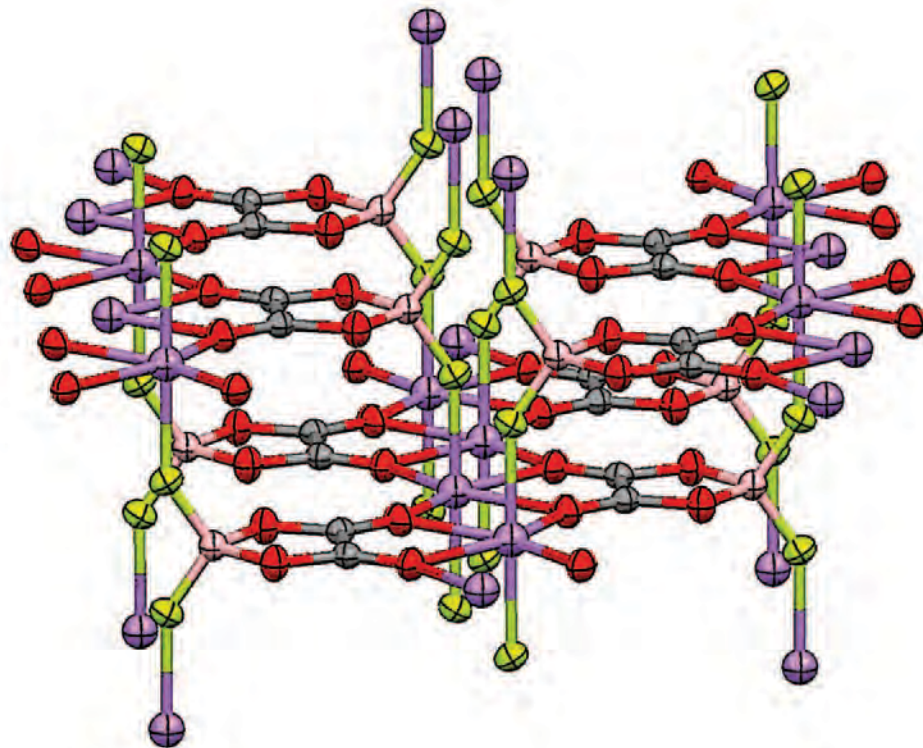
## Technical Accomplishments - Overview

- Prepared phase diagrams of solvent-LiBF<sub>4</sub> mixtures (acetonitrile, adiponitrile) to serve as a model system (for comparison with new salts)
- Synthesized high purity lithium difluoro(oxalato)borate (LiDFOB) – determined the crystal structure of the LiDFOB·2H<sub>2</sub>O dihydrate – prepared phase diagrams with a variety of solvents including carbonates, esters, sulfones and nitriles/dinitriles – numerous LiDFOB solvate crystal structures were determined providing insight into how the anion and solvent molecules interaction with Li<sup>+</sup> cations
- Characterized ionic liquid (IL) properties (conductivity, density, viscosity, diffusion coefficients) for ILs with cyanocarbanions: DCTA<sup>-</sup> (dicyanotriazolate) and DCA<sup>-</sup> (dicyanamide)

# Lithium Difluoro(oxalato)borate (LiDFOB)



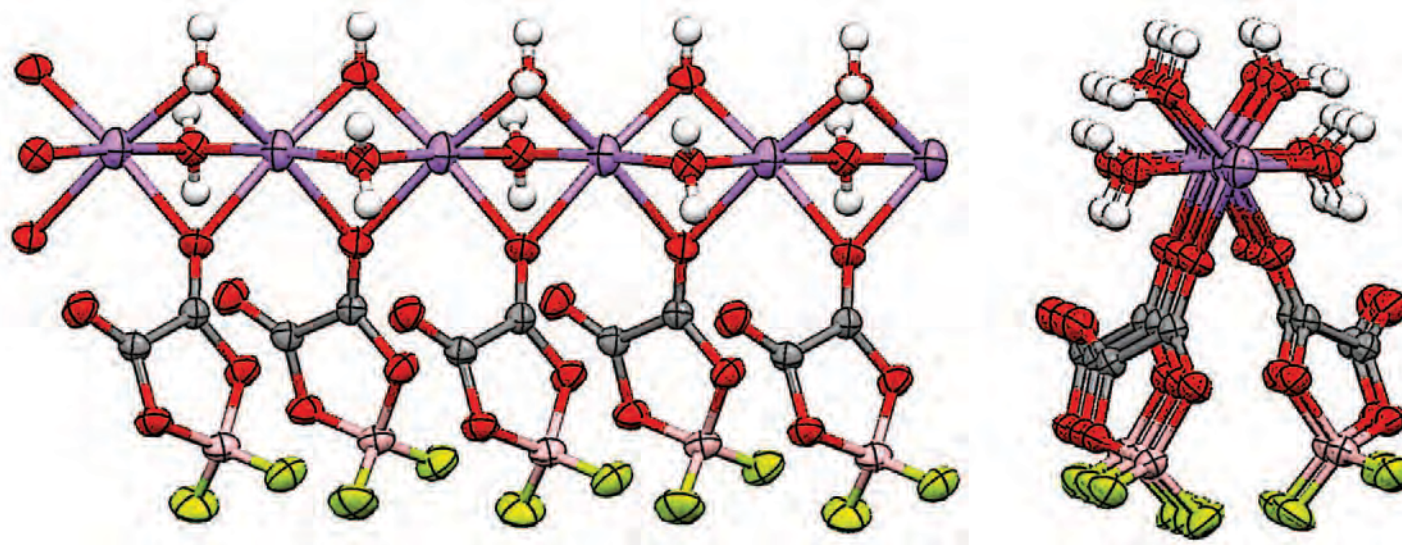
Crystal structure of LiDFOB



# LiDFOB·2H<sub>2</sub>O

Crystal structure of  
LiDFOB dihydrate

CIP (H<sub>2</sub>O)<sub>2</sub>:LiDFOB

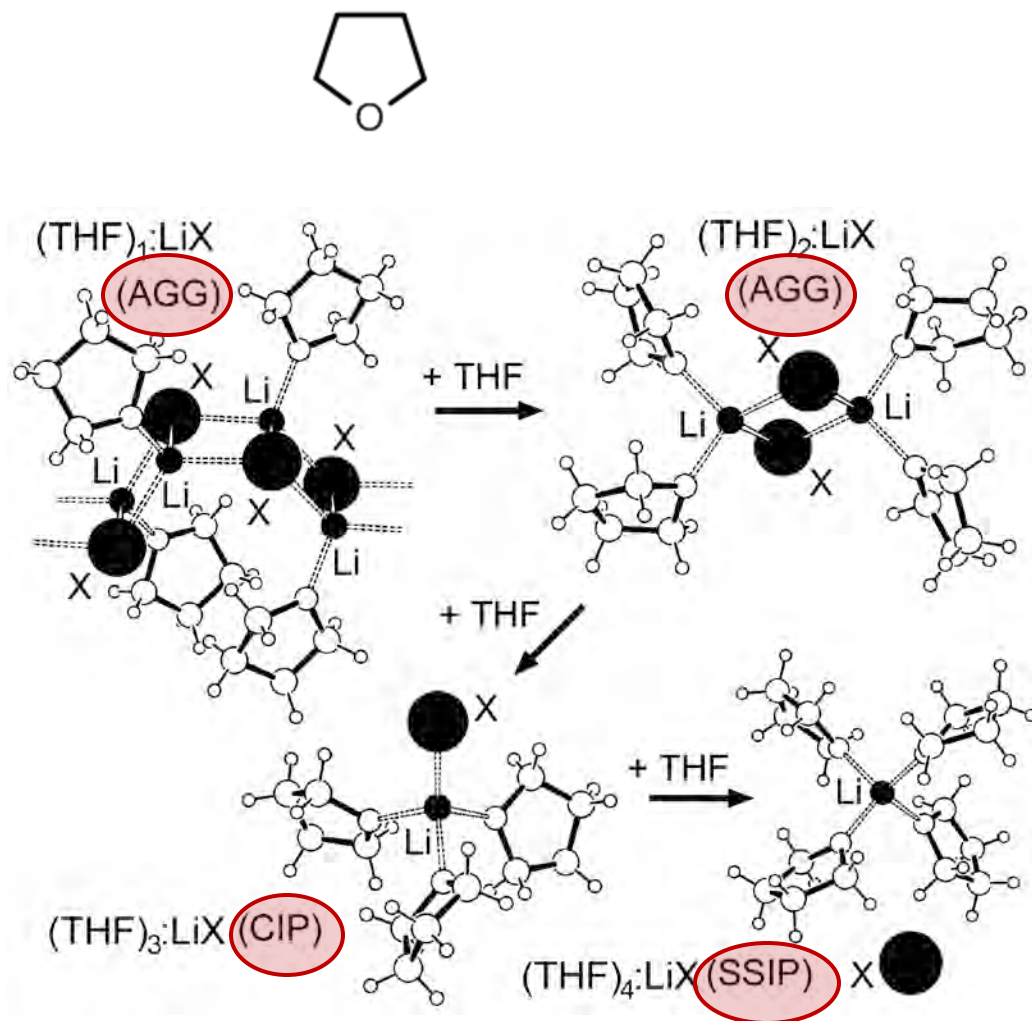


# (Solvent)<sub>n</sub>-LiX Mixtures: Ionic Association Interactions

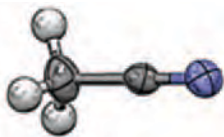
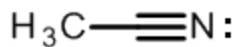
- Solvent-Separated Ion Pairs (SSIPs)  
(uncoordinated anions)
- Contact Ion Pairs (CIPs)  
(anion coordinated to 1 Li<sup>+</sup>)
- Aggregates (AGGs)  
(anion coordinated to 2 or more Li<sup>+</sup>)

LiTFSI, LiPF<sub>6</sub>  
 LiClO<sub>4</sub>, LiI  
 LiBF<sub>4</sub>  
 LiCF<sub>3</sub>SO<sub>3</sub>  
 LiCF<sub>3</sub>CO<sub>2</sub>

increasing  
 association

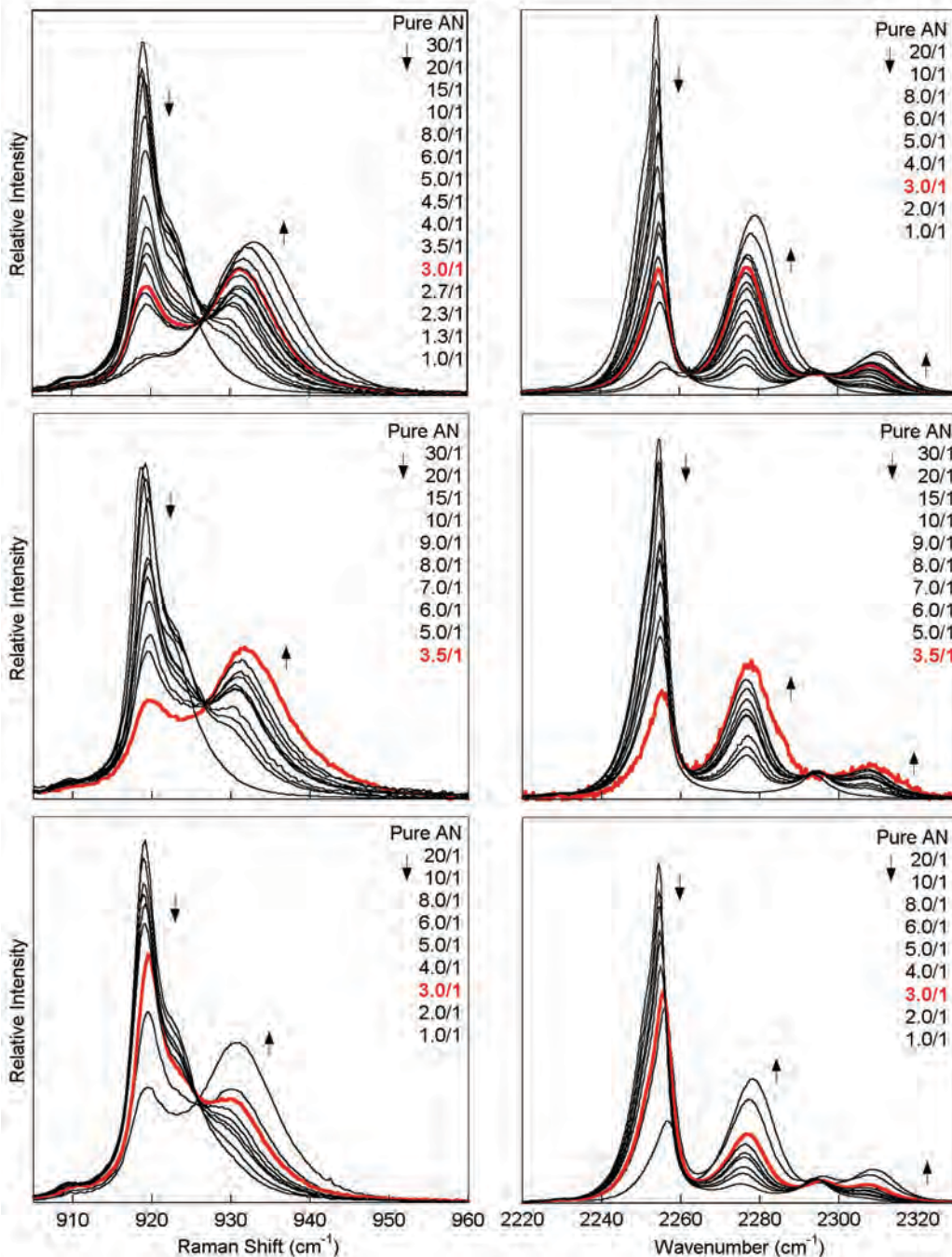


# AN-Li<sup>+</sup> Solvation

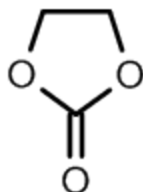


C-C stretching mode (920 cm<sup>-1</sup>)

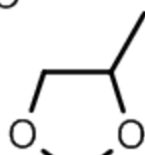
C≡N stretching mode (2250 cm<sup>-1</sup>)



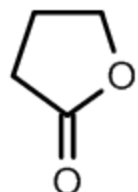
# Carbonate & Ester Solvents



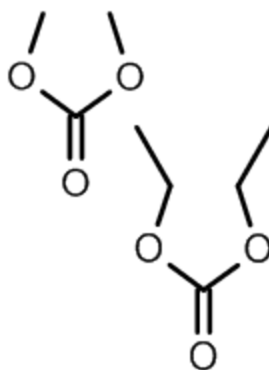
ethylene carbonate ( $T_m$  35°C,  $T_b$  244 C)



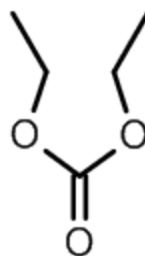
propylene carbonate ( $T_m$  -55°C,  $T_b$  242 C)



$\gamma$ -butyrolactone ( $T_m$  -44°C,  $T_b$  204 C)

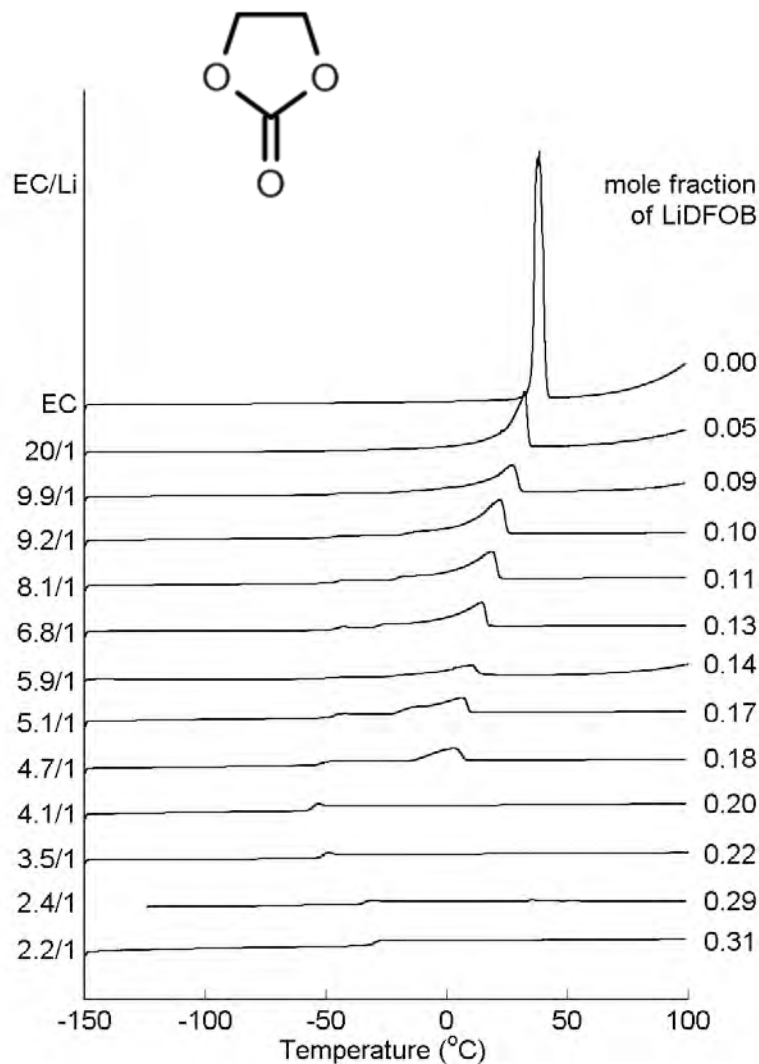
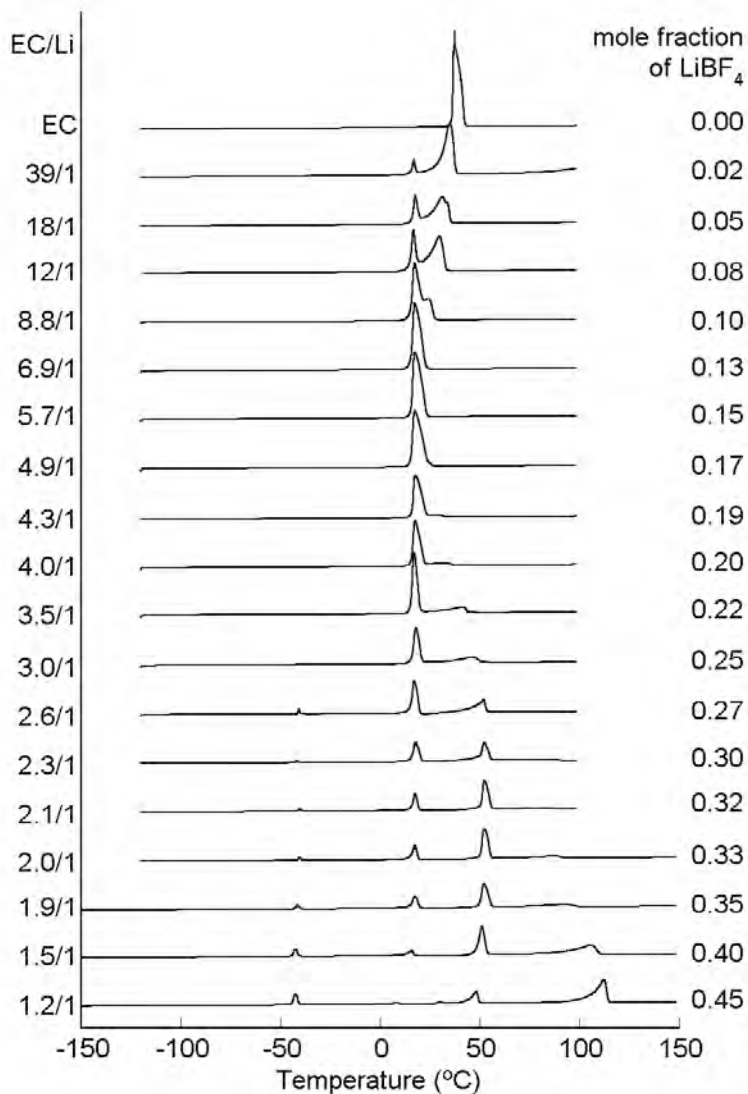


dimethyl carbonate ( $T_m$  5°C,  $T_b$  91 C)

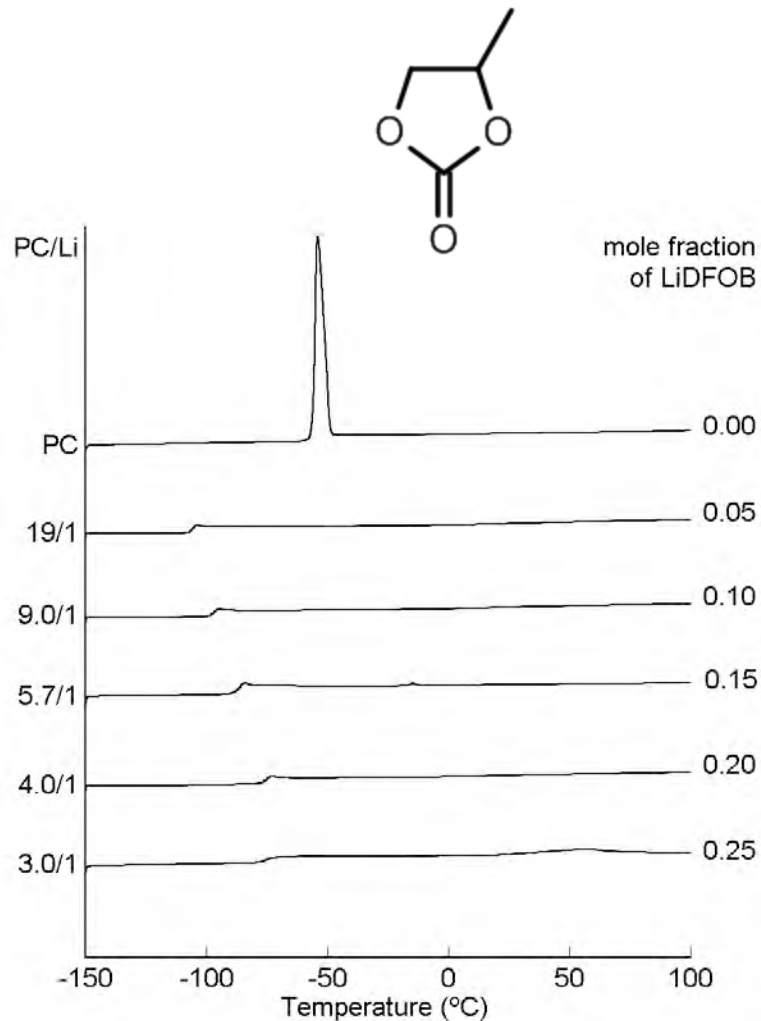
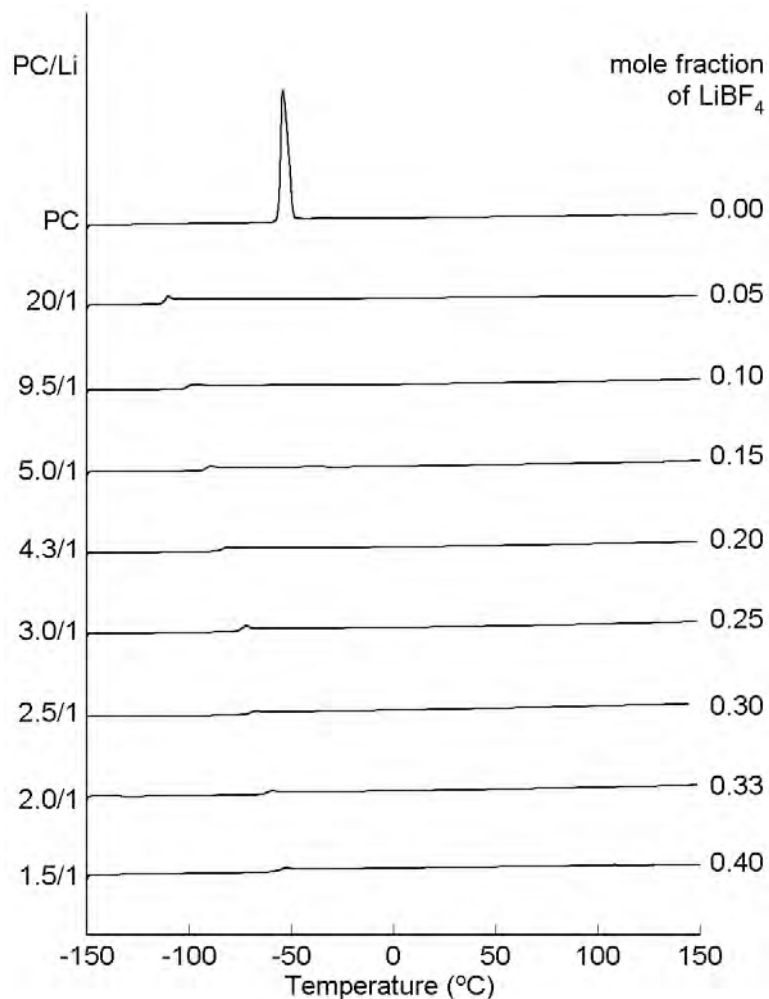


diethyl carbonate ( $T_m$  -74°C,  $T_b$  126 C)

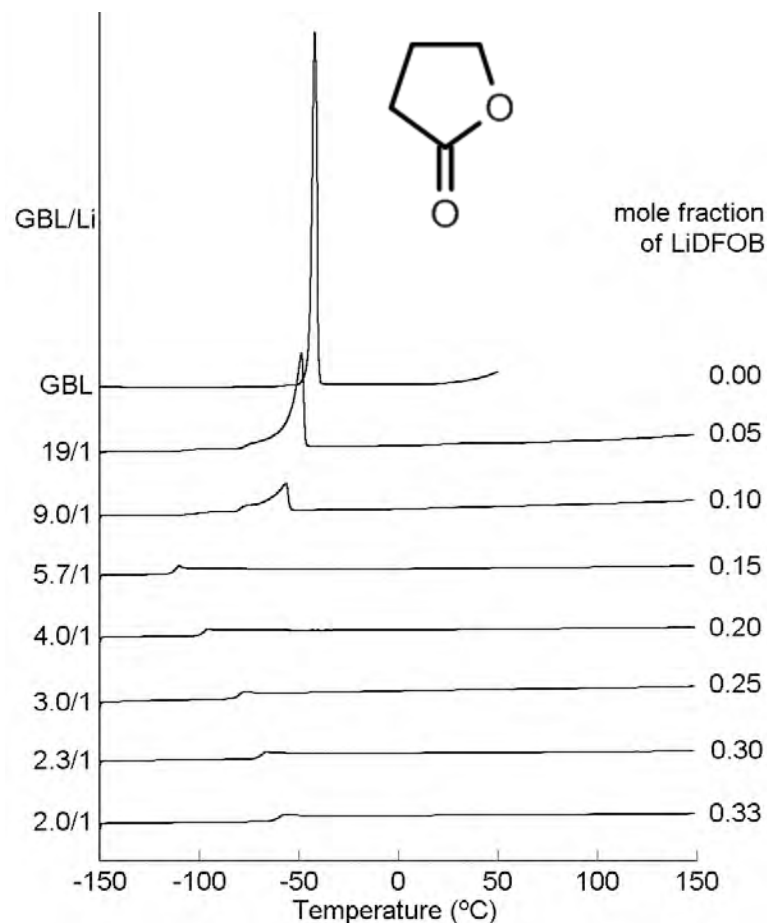
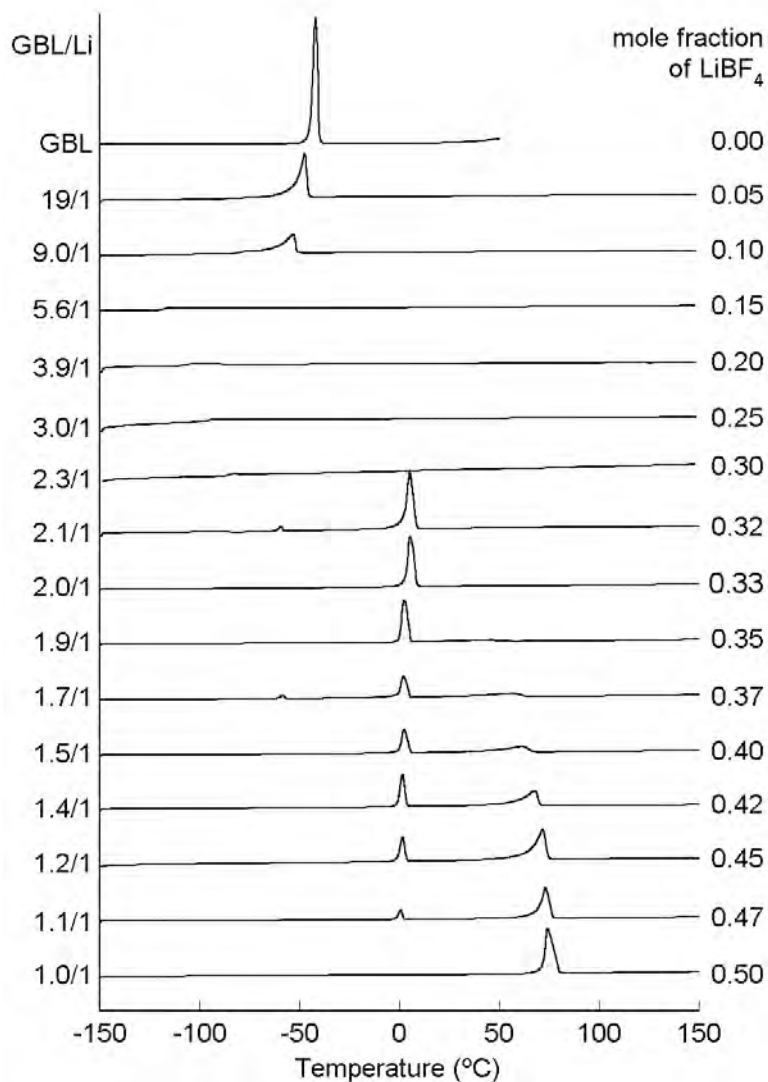
# Ethylene Carbonate (EC)<sub>n</sub>-LiX Phase Behavior



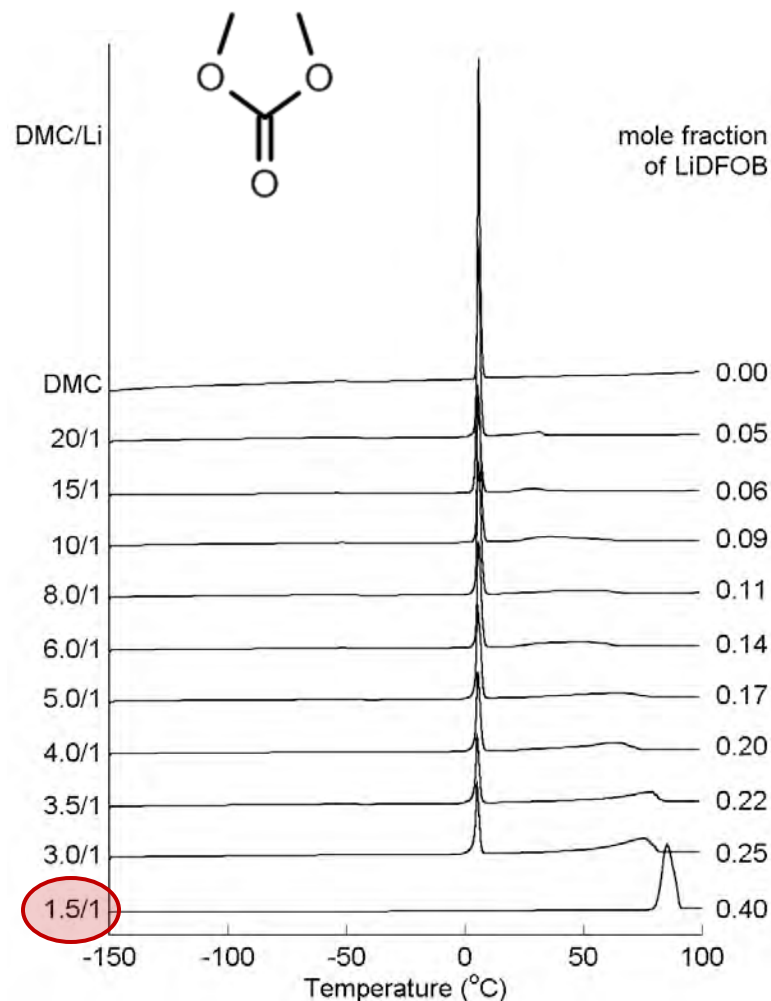
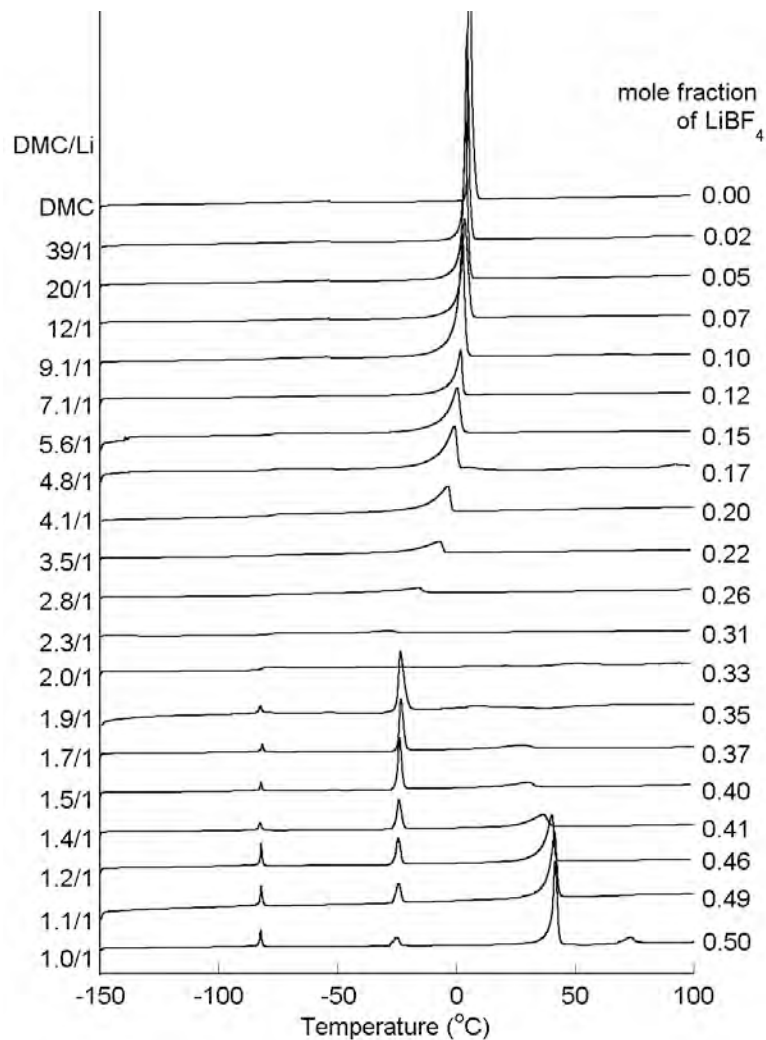
# Propylene Carbonate (PC)<sub>n</sub>-LiX Phase Behavior



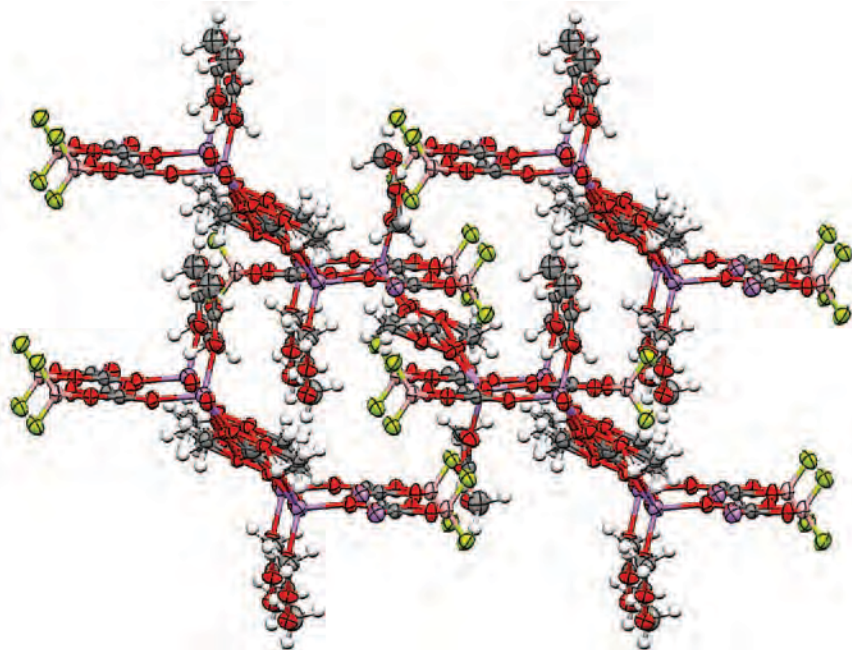
# $\gamma$ -Butyrolactone (GBL)<sub>n</sub>-LiX Phase Behavior



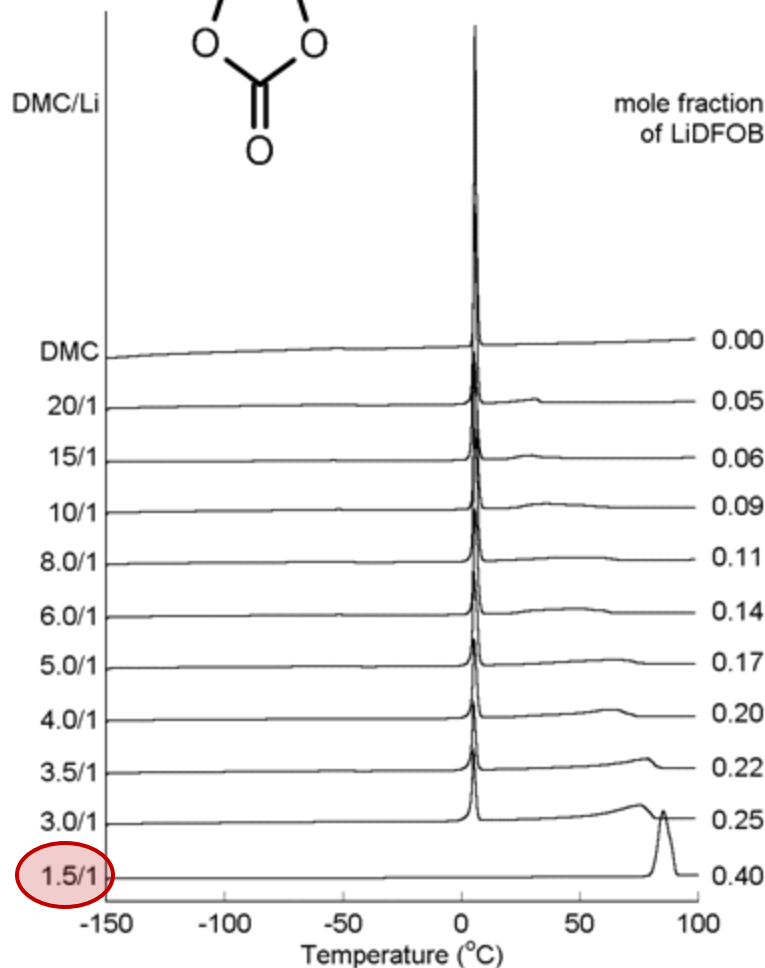
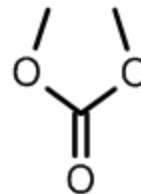
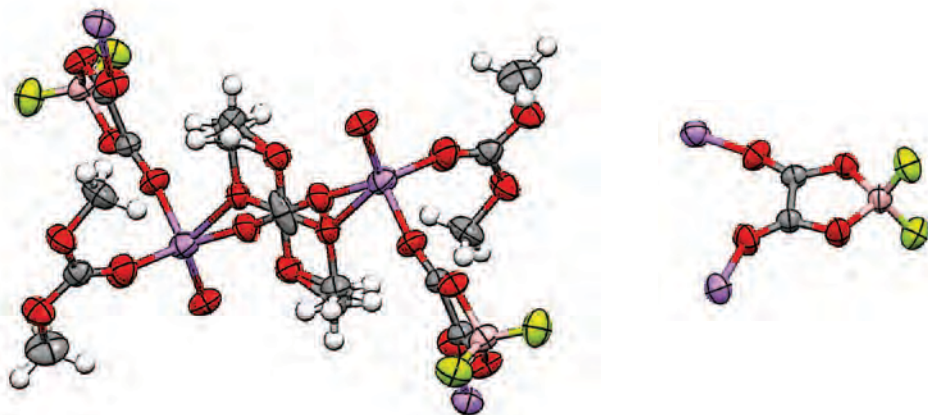
# Dimethyl Carbonate (DMC)<sub>n</sub>-LiX Phase Behavior



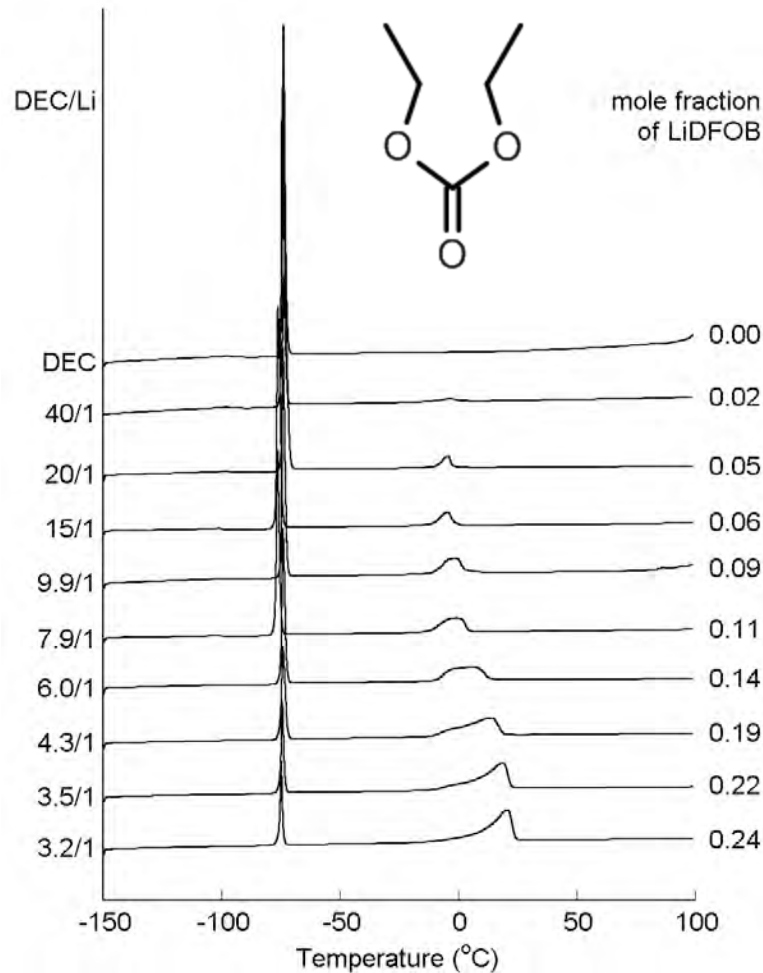
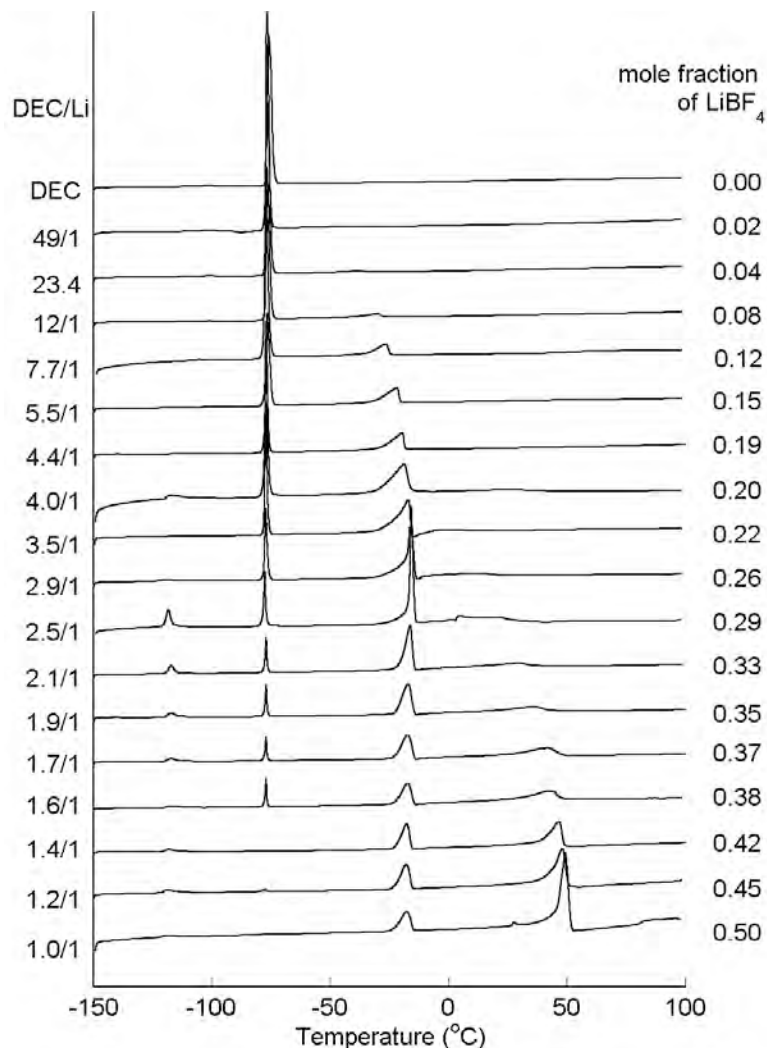
# Dimethyl Carbonate (DMC)<sub>n</sub>-LiX Phase Behavior



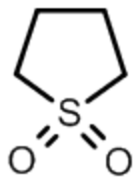
AGG (DMC)<sub>3/2</sub>:LiDFOB



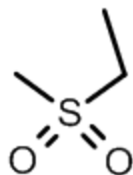
# Diethyl Carbonate (DEC)<sub>n</sub>-LiX Phase Behavior



# Sulfone Solvents for High-Voltage Electrolytes



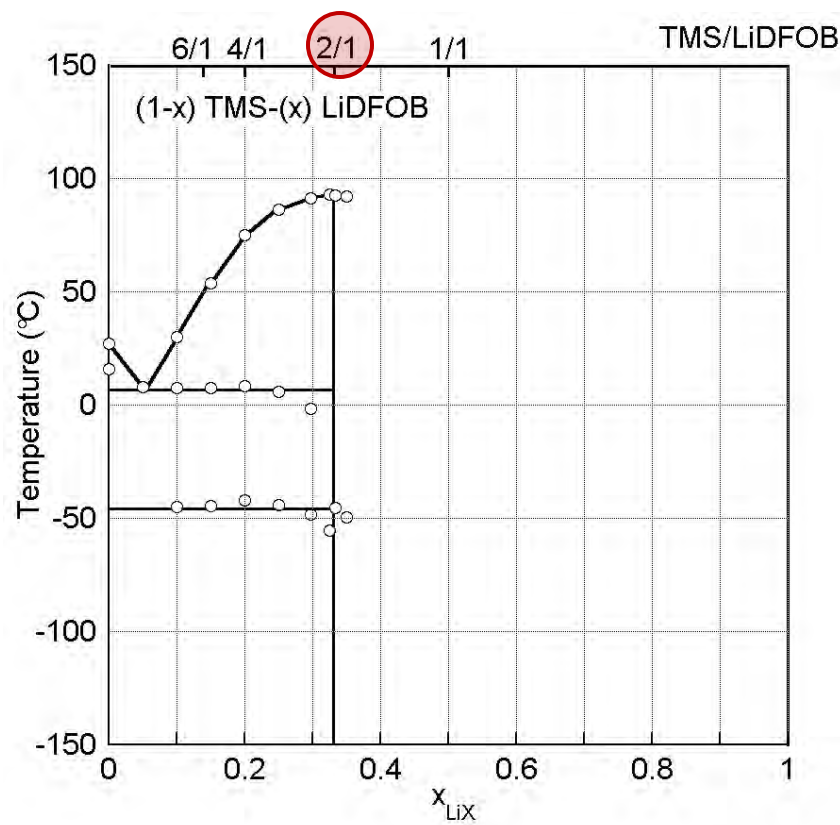
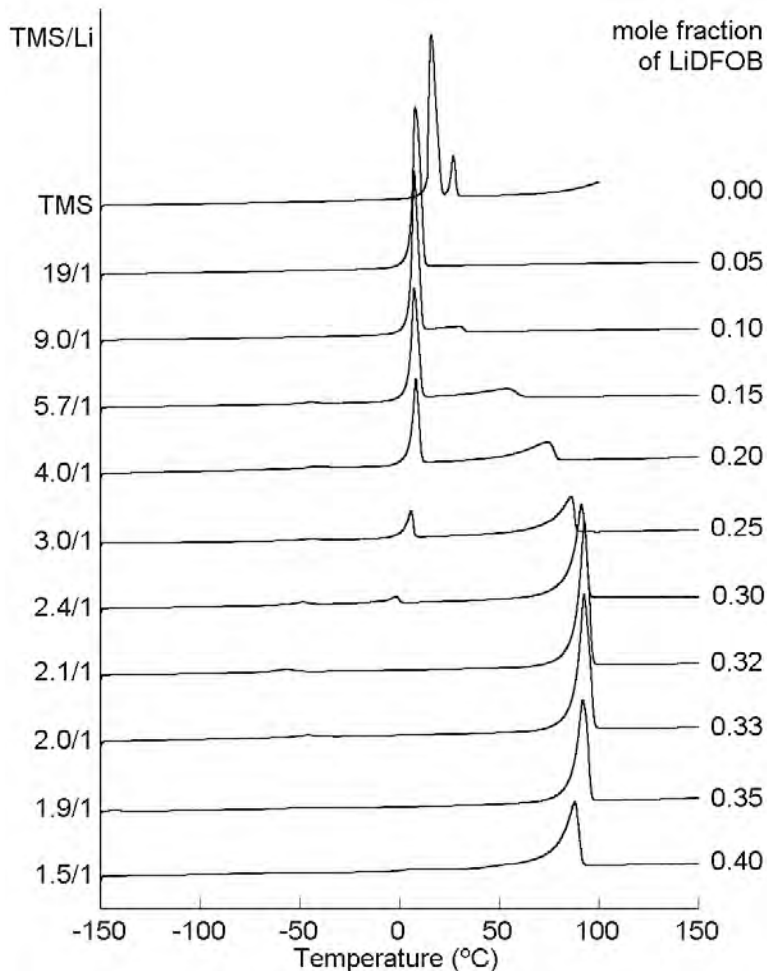
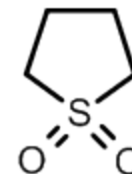
tetramethylene sulfone ( $T_m$  27°C,  $T_b$  285 C)



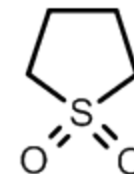
ethyl methyl sulfone ( $T_m$  32-37°C,  $T_b$  ??? C)

- A. Abouimrane, I. Belharouak, K. Amine, *Electrochem. Commun.* **2009**, 11, 1073

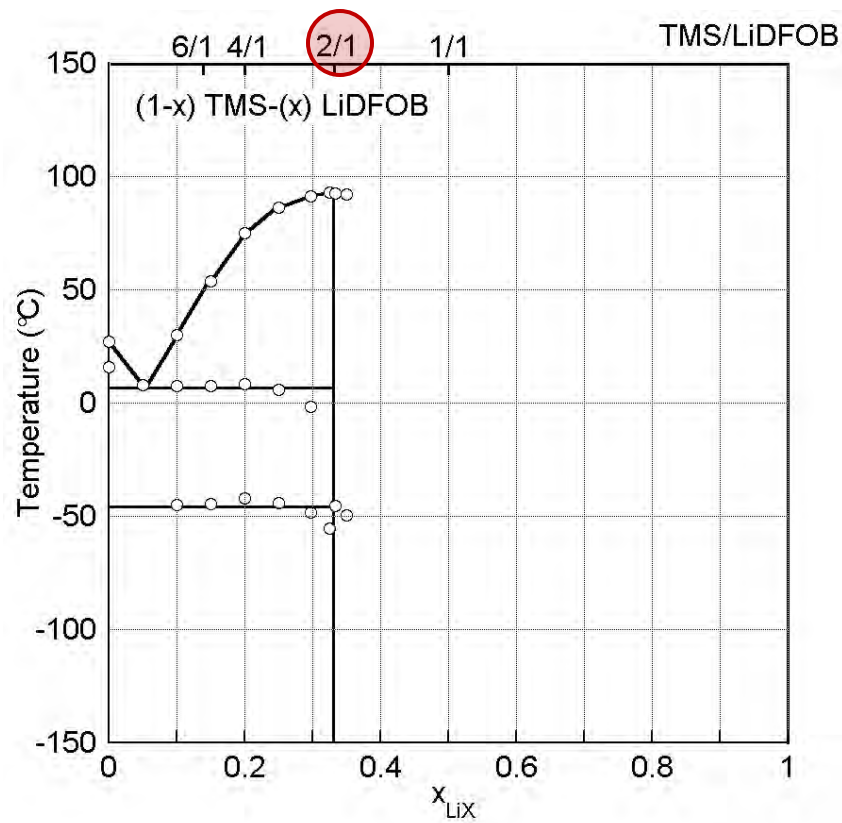
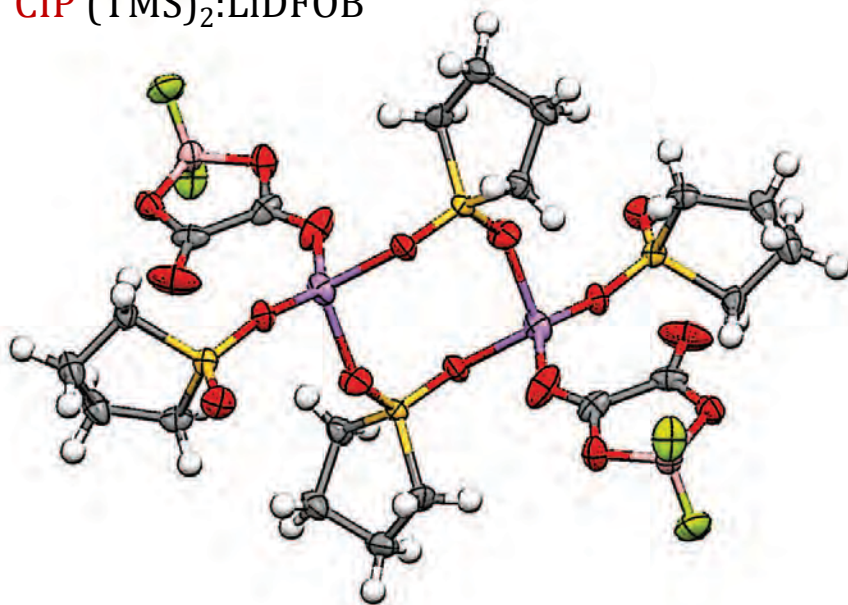
# Sulfone-LiDFOB Phase Behavior



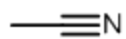
# (TMS)<sub>n</sub>-LiDFOB Phase Behavior



CIP (TMS)<sub>2</sub>:LiDFOB



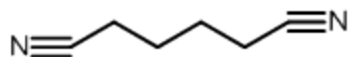
# Nitrile/Dinitrile Solvents for High-Voltage Electrolytes



acetonitrile ( $T_m$   $-45^\circ\text{C}$ ,  $T_b$  **82** C)



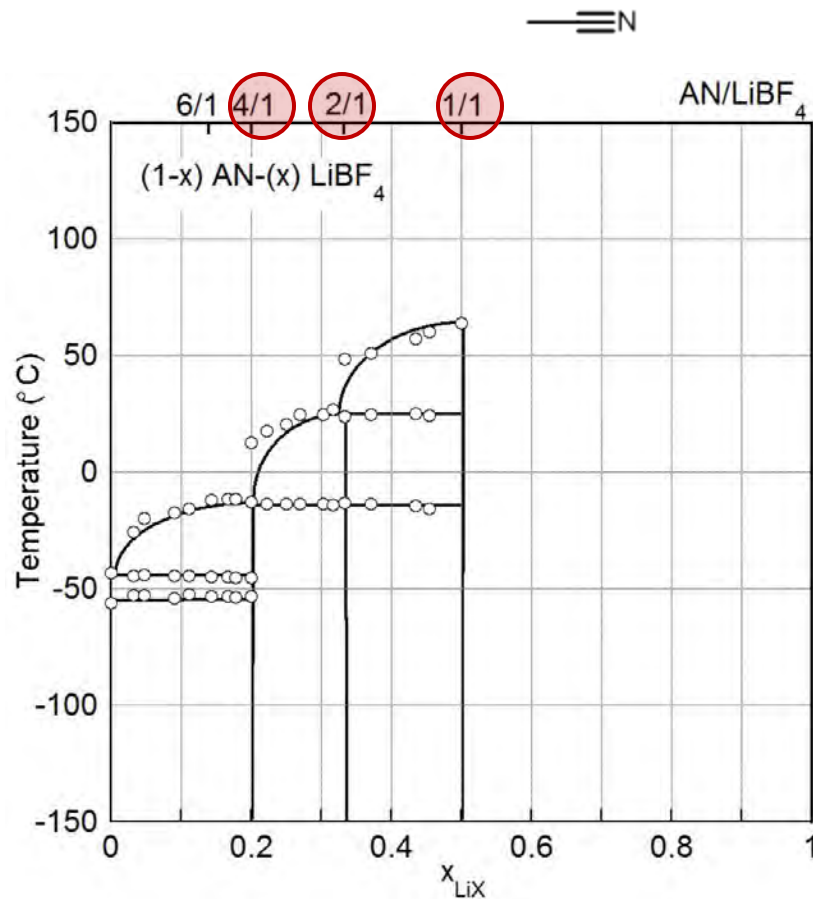
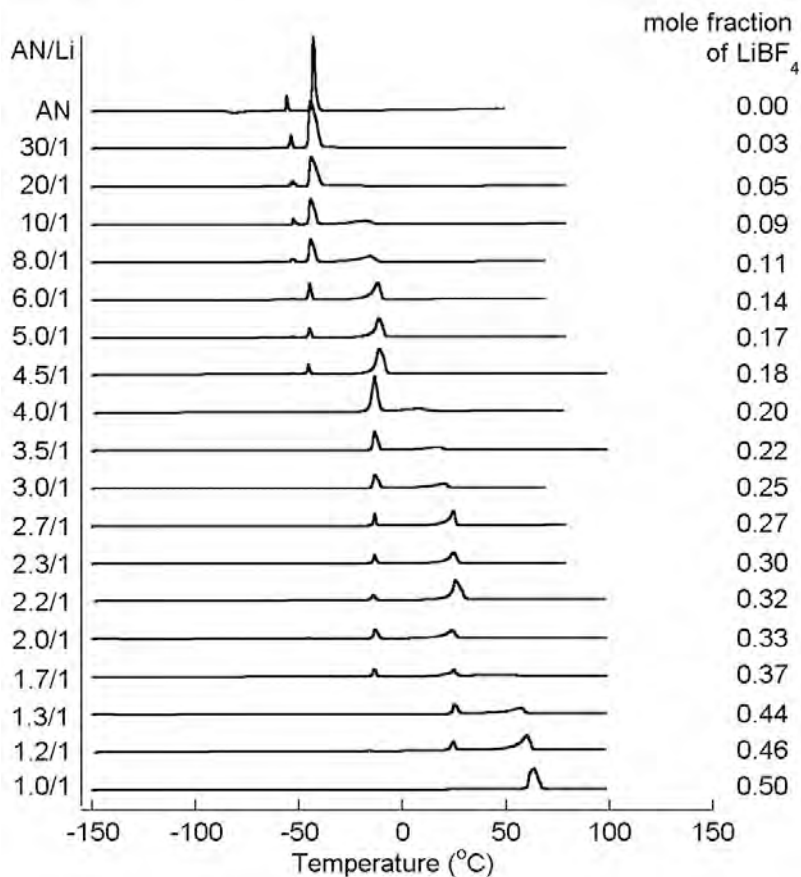
glutaronitrile ( $T_m$   $-29^\circ\text{C}$ ,  $T_b$  286 C)



adiponitrile ( $T_m$   $4^\circ\text{C}$ ,  $T_b$  **295** C)

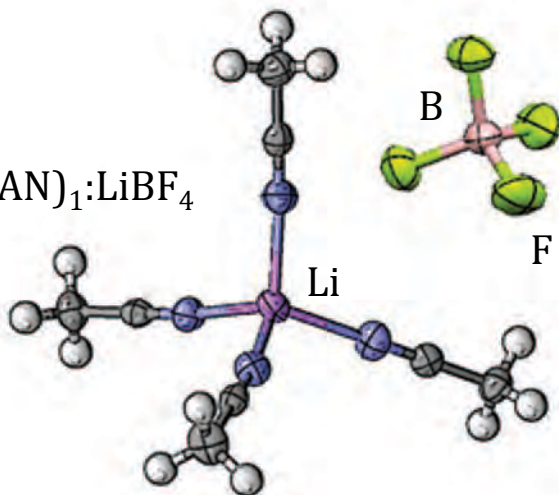
- Y. Abu-Lebdeh and I. Davidson, *J. Electrochem. Soc.* **2009**, 156, A60

# Acetonitrile (AN)-LiBF<sub>4</sub> Phase Behavior

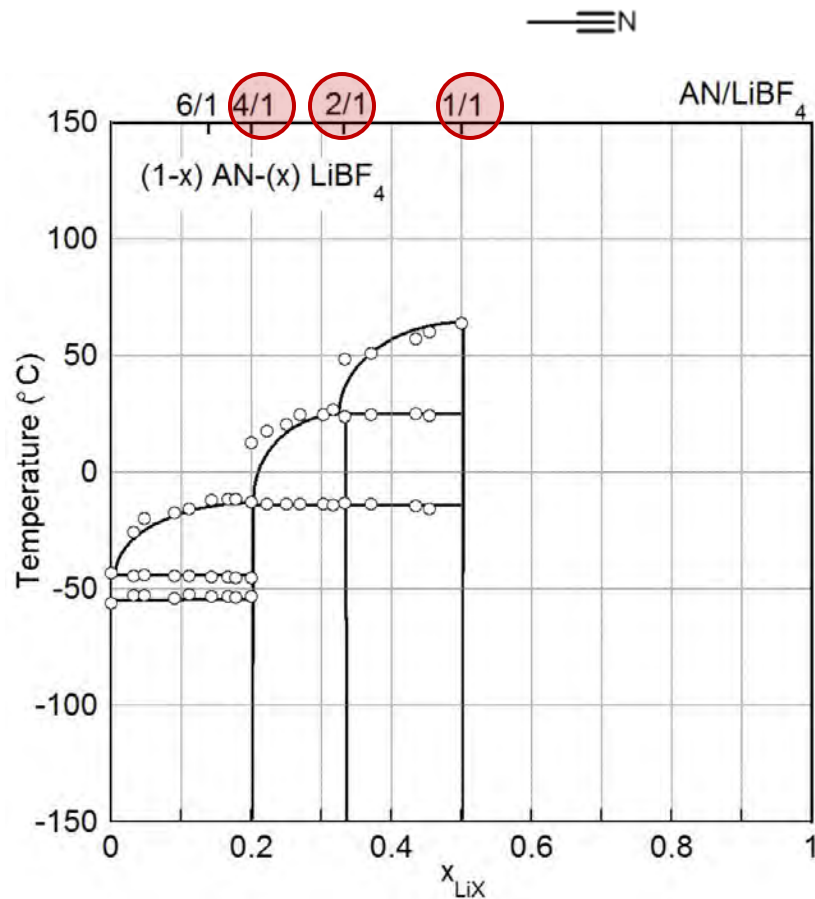
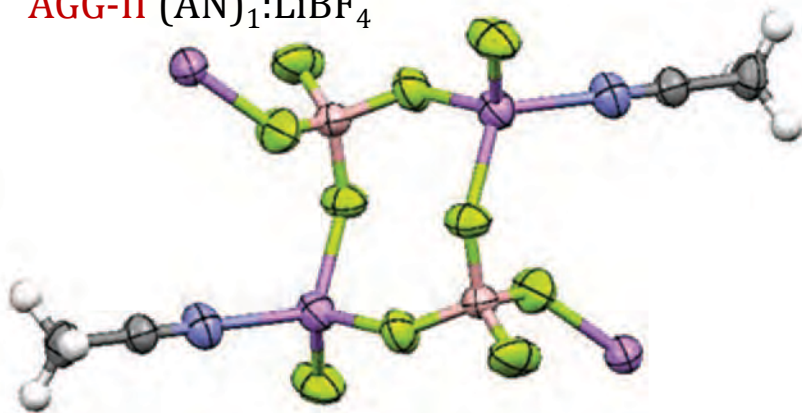


# Acetonitrile (AN)<sub>n</sub>-LiBF<sub>4</sub> Phase Behavior

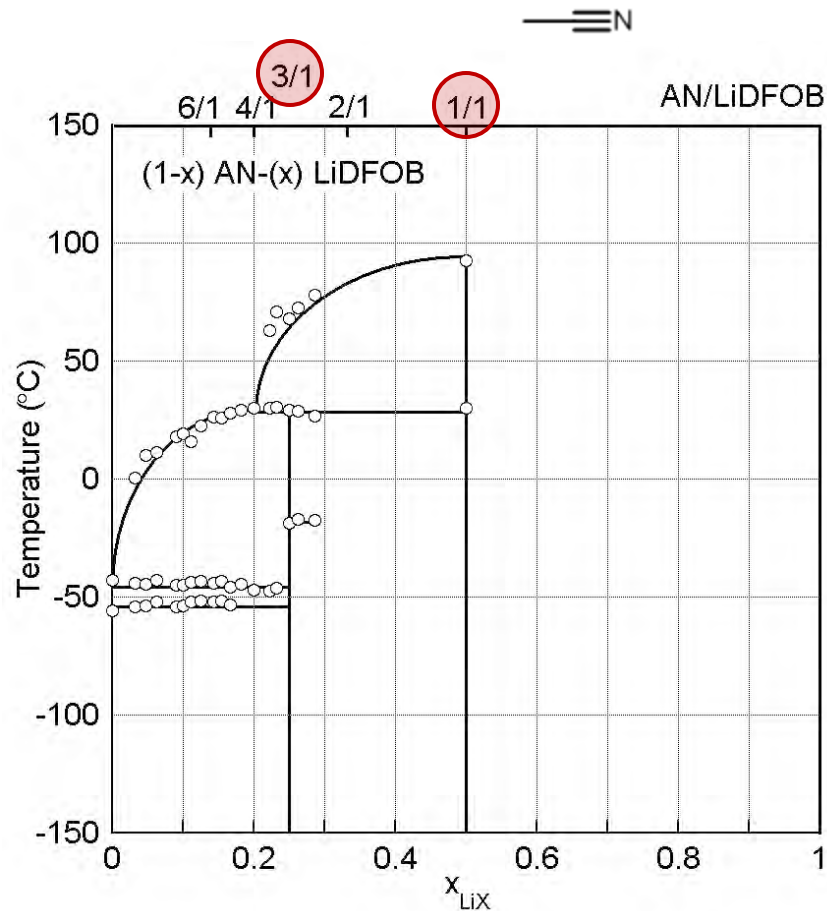
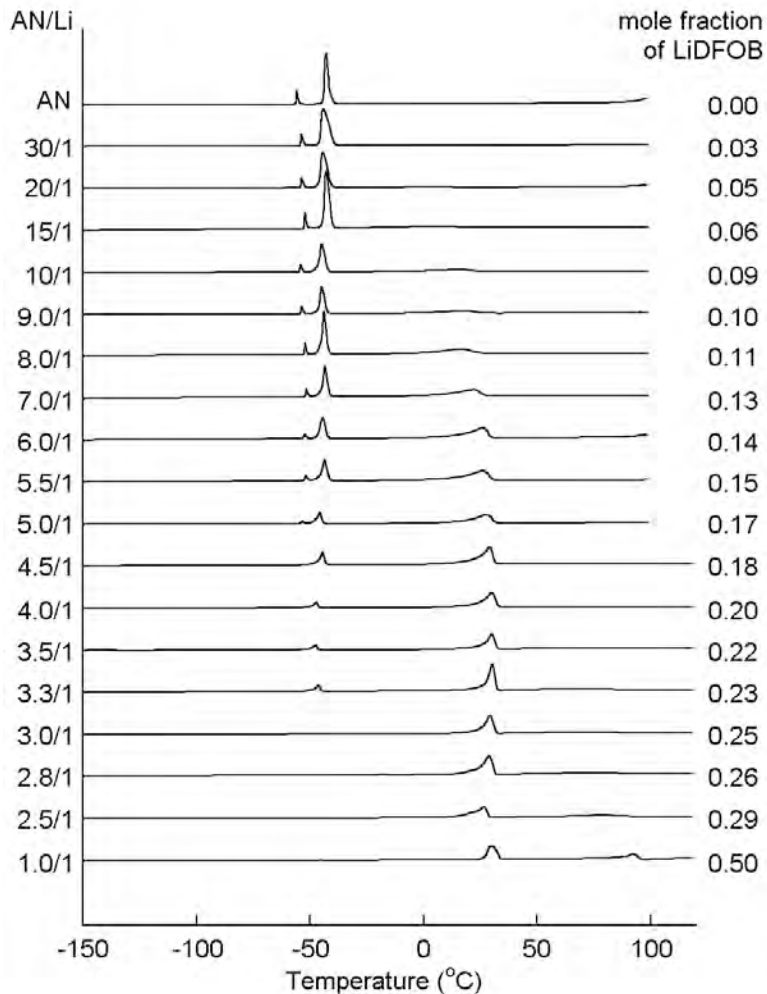
SSIP (AN)<sub>1</sub>:LiBF<sub>4</sub>



AGG-II (AN)<sub>1</sub>:LiBF<sub>4</sub>

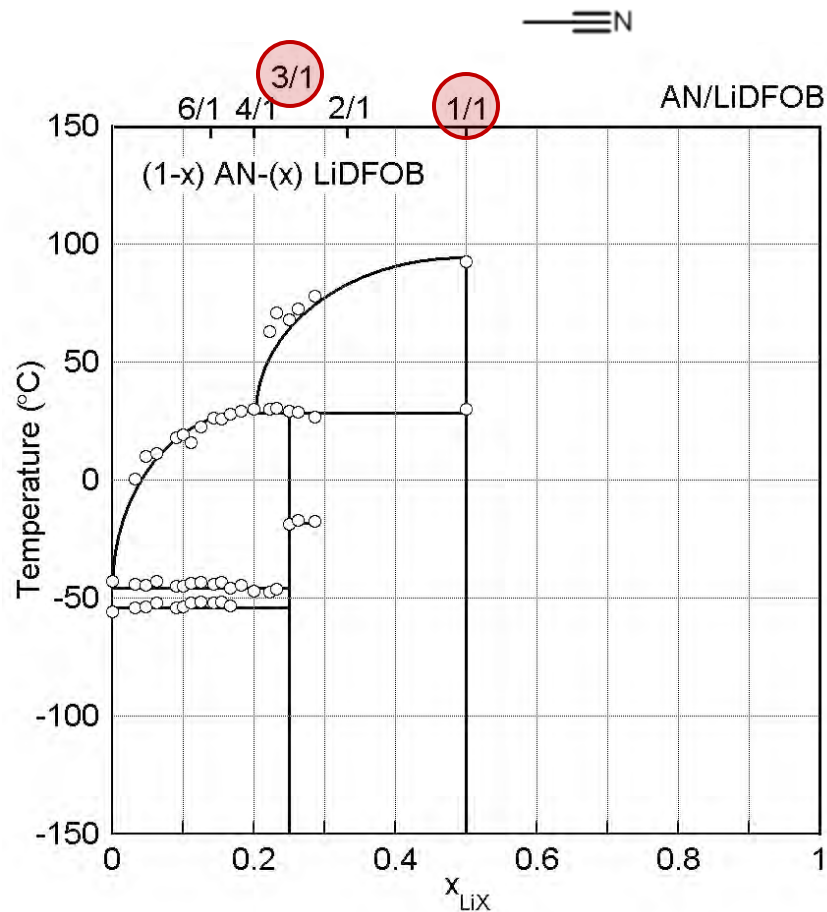
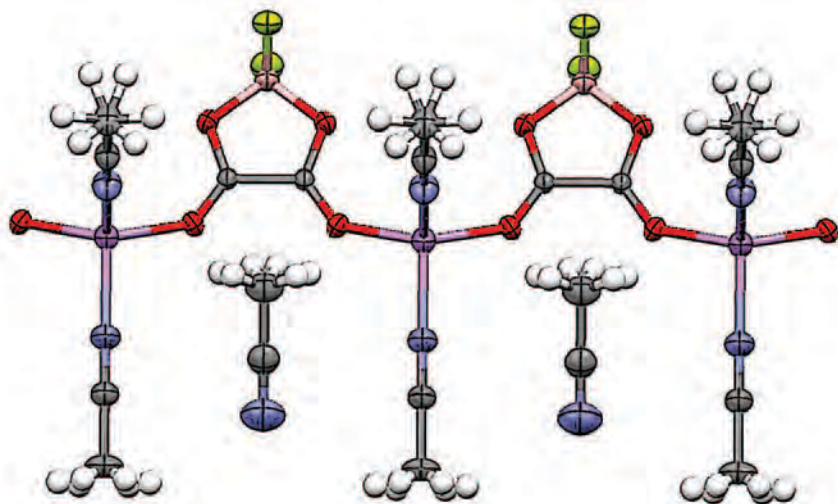


# Acetonitrile (AN)<sub>n</sub>-LiDFOB Phase Behavior



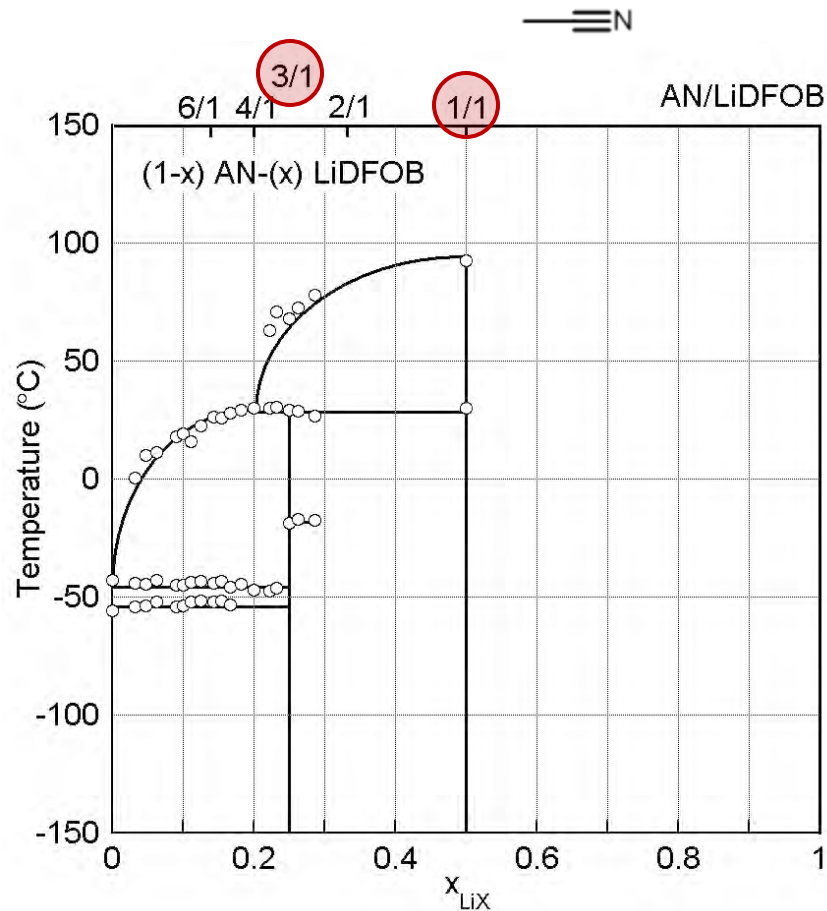
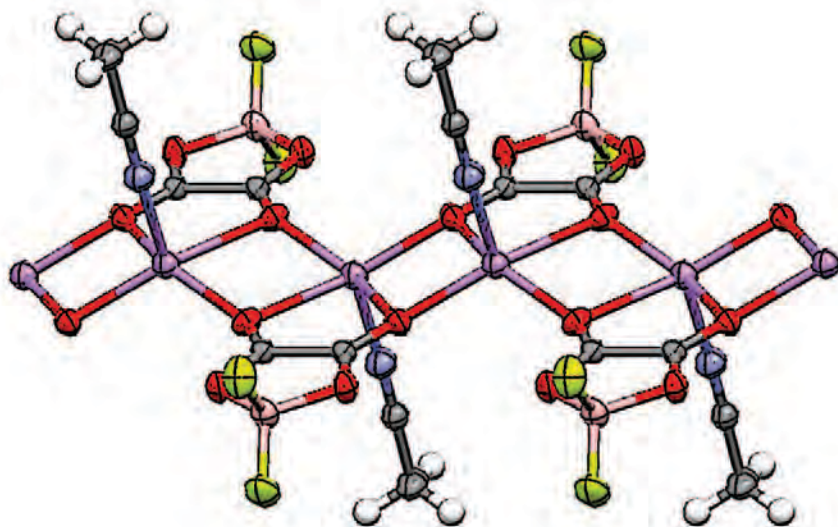
# Acetonitrile (AN)<sub>n</sub>-LiDFOB Phase Behavior

AGG (AN)<sub>3</sub>:LiDFOB

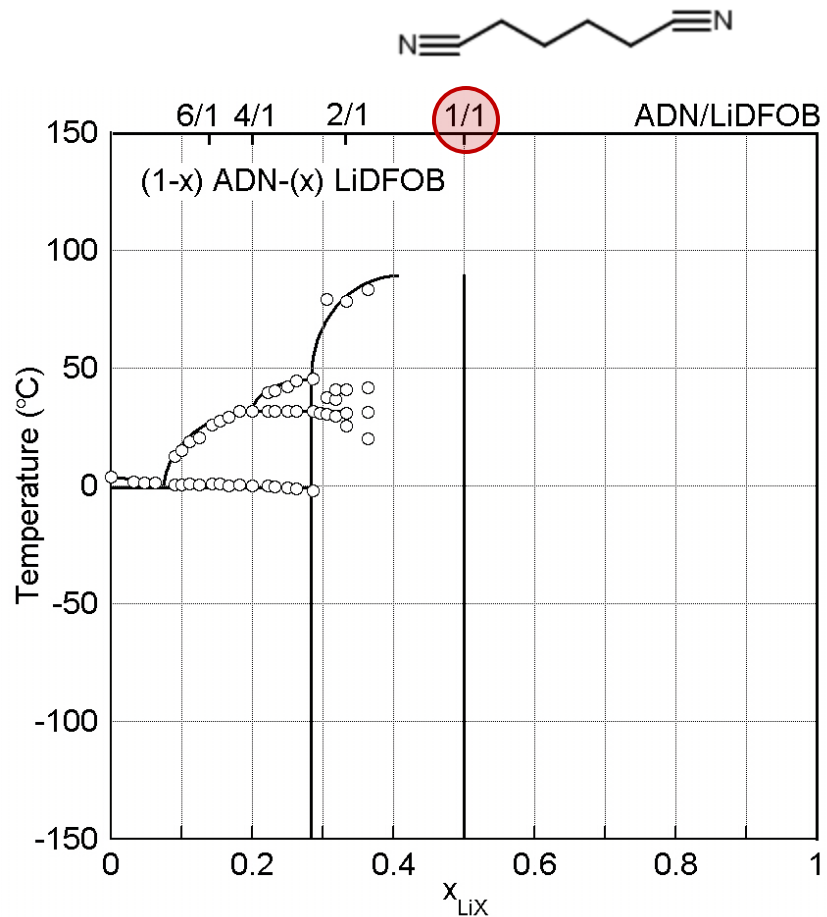
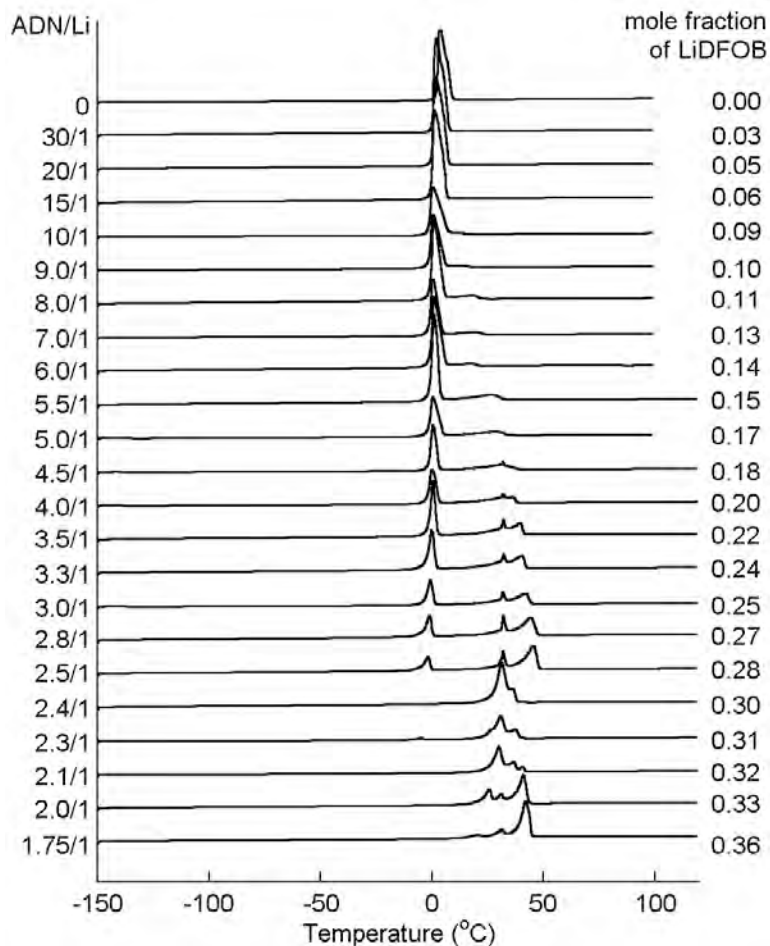


# Acetonitrile (AN)<sub>n</sub>-LiDFOB Phase Behavior

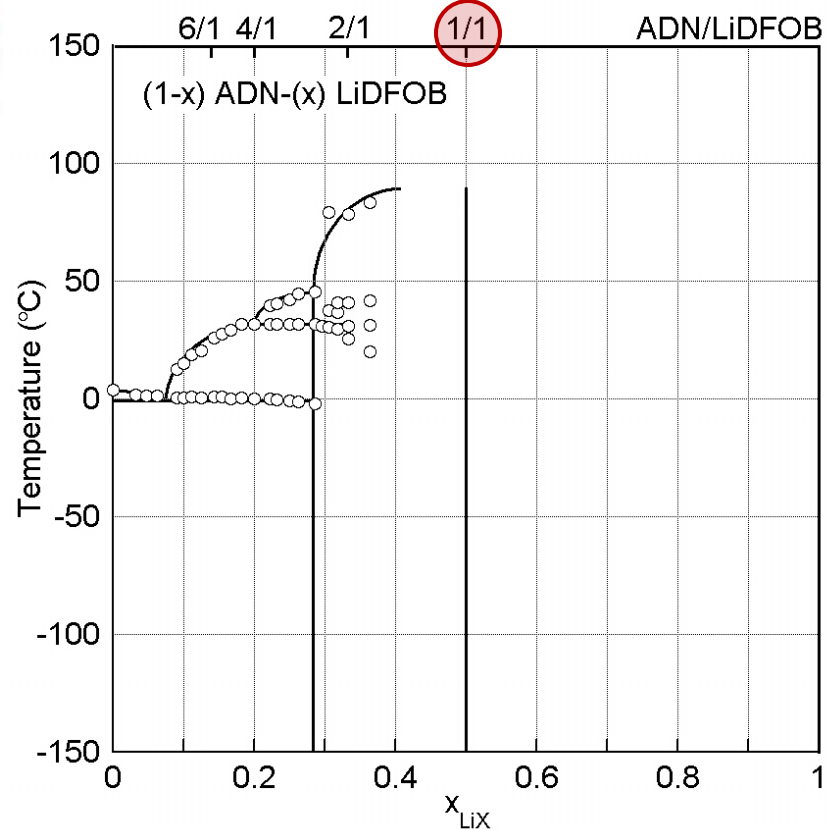
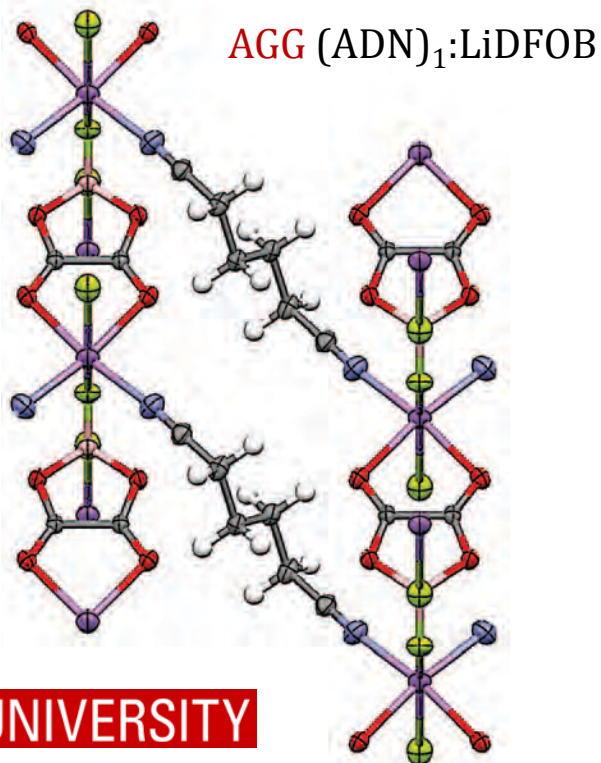
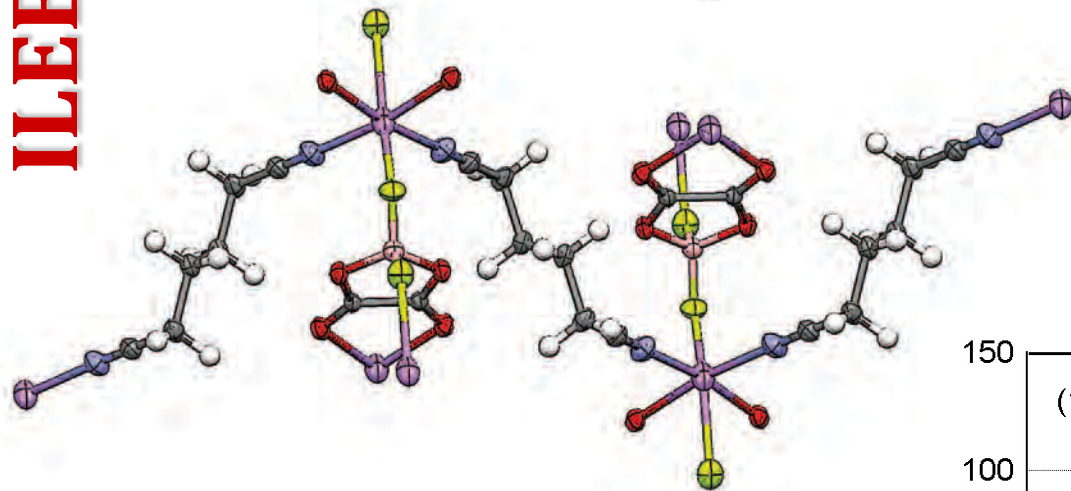
AGG (AN)<sub>1</sub>:LiDFOB



# Adiponitrile (ADN)<sub>n</sub>-LiDFOB Phase Behavior

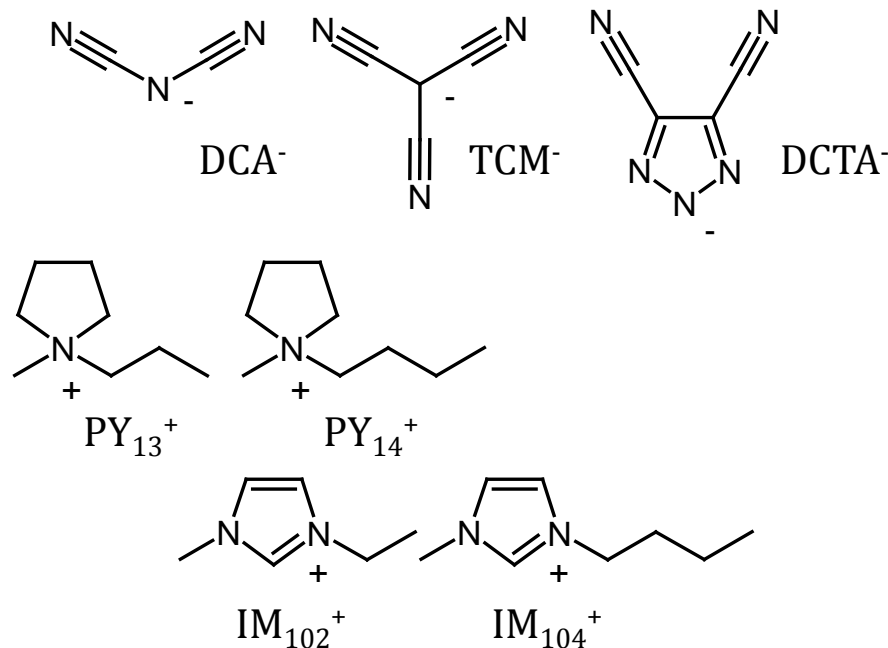
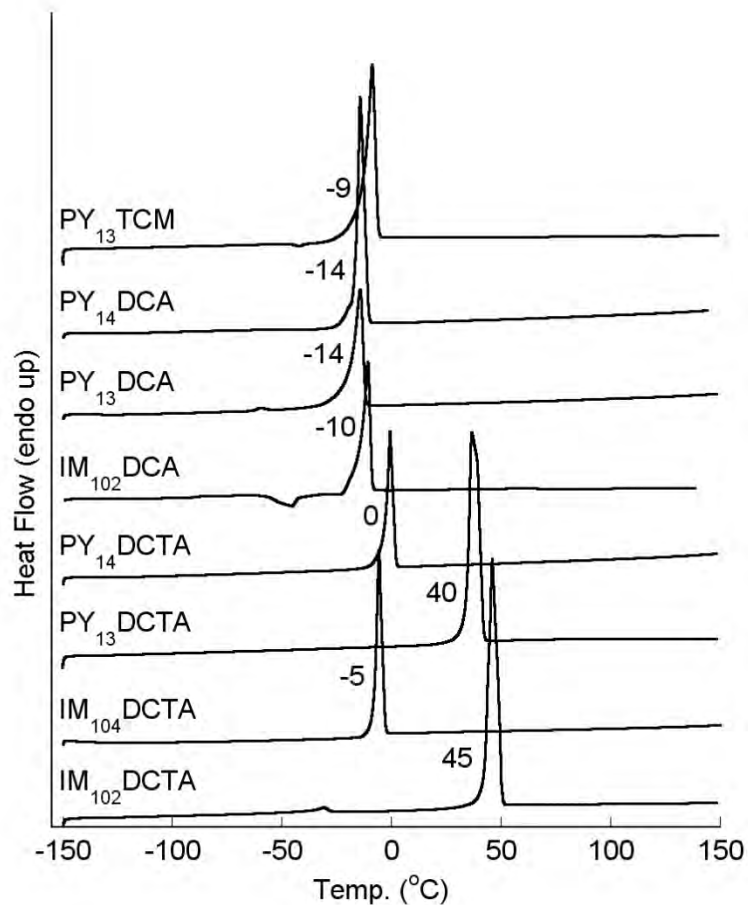


# ILEET Adiponitrile (ADN)<sub>n</sub>-LiDFOB Phase Behavior



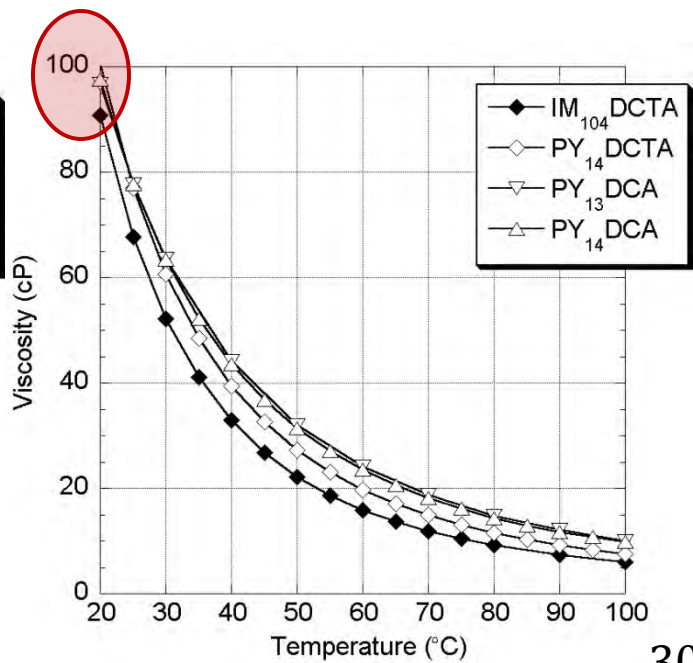
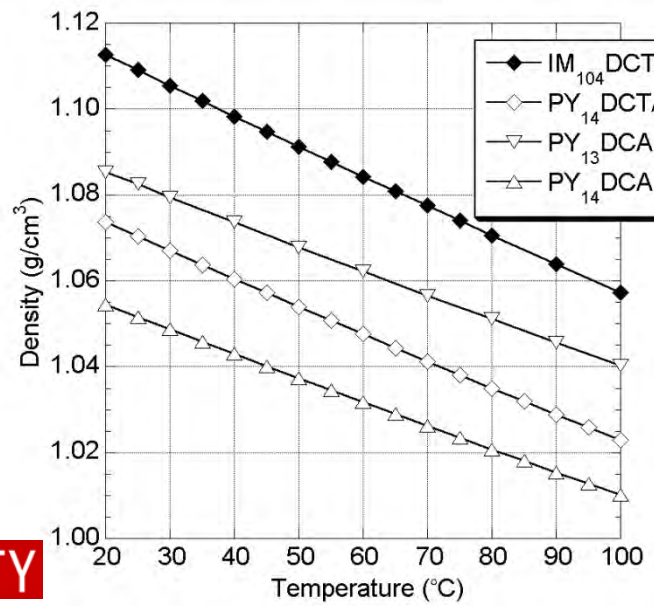
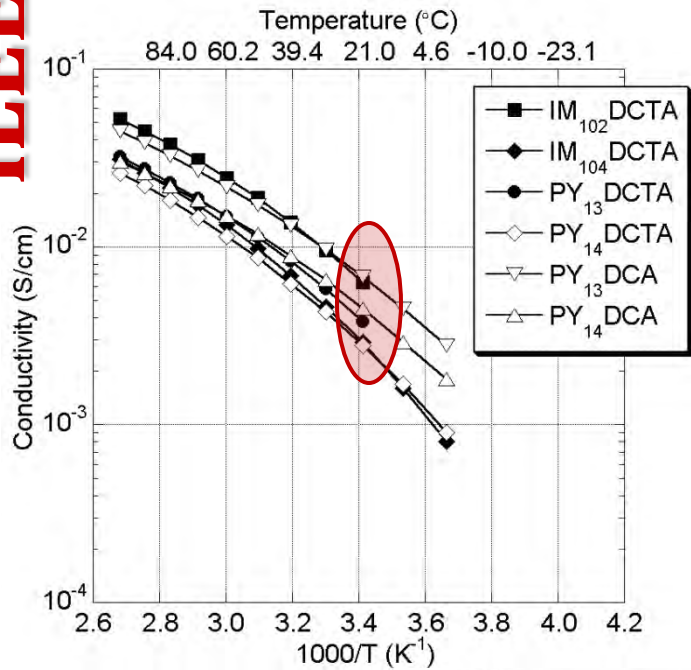
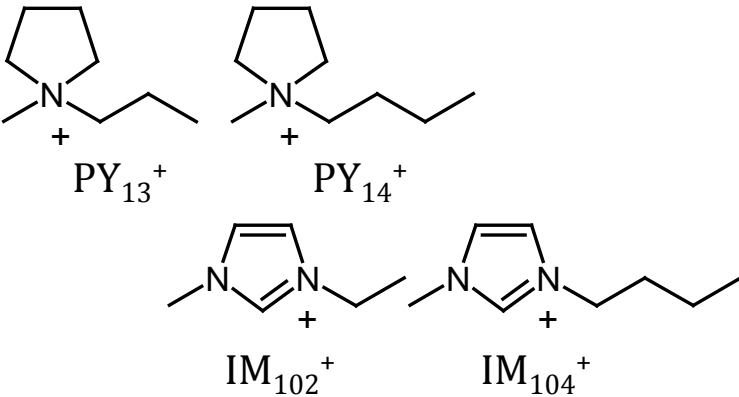
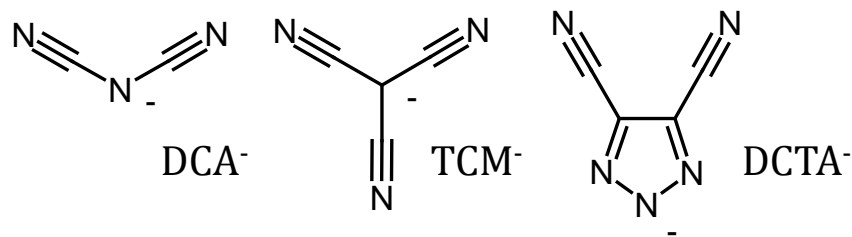
# Ionic Liquids (ILs)

A number of ILs have been synthesized and their properties are currently being characterized



★ IM<sub>10R</sub>X ILs prepared for comparison with PY<sub>1R</sub>X ILs rather than as electrolyte materials

# Ionic Liquids (ILs)



## Collaborations/Coordination with Other Institutions

**Army Research Laboratory (ARL)** – Joshua Allen (a graduate student) spent several weeks last year with **Kang Xu** and **Richard Jow** and will spend several months this year at ARL testing the properties of the salts

**Université Paris-Sud & Hunter College of CUNY** – **Patrick Judeinstein** and **Steve Greebaum** have performed NMR diffusion measurement on the ILs

**Chalmers University, Sweden** – **Patrik Johansson** is utilizing the known LiDFOB solvate structures to computationally analyze the Raman and IR vibrational bands for the different DFOB<sup>-</sup> solvate structures

## Future Work

- Continue with the phase diagram characterization of  $\text{LiBF}_4$  and  $\text{LiDFOB}$  with a wide variety of solvents – extend this to include  $\text{LiPF}_6$  and additional organoborate anions
- Utilize Raman spectroscopy to further characterize the solvent and anion interactions in both the solid and liquid state...correlate this work with the phase diagrams and solvate crystal structures
- Measure the transport properties (viscosity, conductivity, diffusion coefficients) of the solvent- $\text{LiX}$  mixtures to determine the link between properties and structure (solvent and anion)
- Prepare/characterize ILs based upon the  $\text{DFOB}^-$  anion with varying cations – prepare phase diagrams of IL- $\text{LiX}$  mixtures
- Test solvent- $\text{LiX}$  (nitrile/dinitrile) and IL- $\text{LiX}$  mixtures in half and full cells

## Summary

- Phase diagrams have been prepared for (solvent)<sub>n</sub>-LiBF<sub>4</sub> and -LiDFOB mixtures to characterize the solid-liquid thermal phase behavior – these diagrams, in concert with solvate crystal structures, provide tremendous insight into the solvent...Li<sup>+</sup> and anion...Li<sup>+</sup> interactions
- The phase diagrams and solvate structures also greatly aid in interpreting Raman vibrational spectroscopic data used to characterize the solvent and anion interactions in both the solid and liquid phase – this enables the direct exploration of detailed solution structural information – a daunting challenge to date
- Characterization of the thermal and transport properties ( $T_m$ , density, viscosity, conductivity, diffusion coefficients) of ILs is underway

# Acknowledgements



## Researchers:

- Sam Delp (postdoctoral fellow)
- Joshua Allen (graduate student)
- Sang-Don Han (graduate student)

Dr. Venkat Srinivasan, the staff at LBNL, the BATT Program and the U.S. DOE's Vehicle Technologies Program are gratefully acknowledged for support for this research