

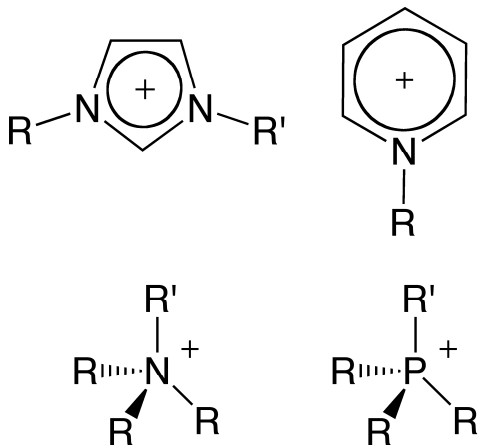
Electroactive Ionic Liquids: A New Approach To Flow Batteries

Date

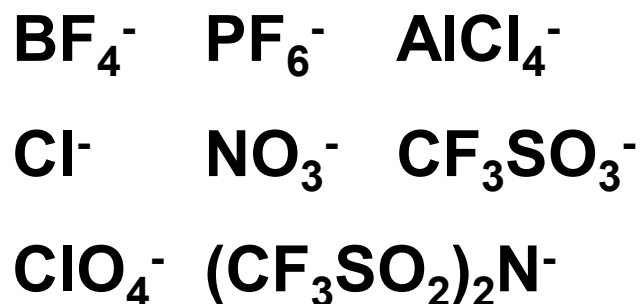
**Travis Anderson
David Ingersoll
Chad Staiger
Karen Waldrip**

Ionic Liquids

Common Cations



Common Anions

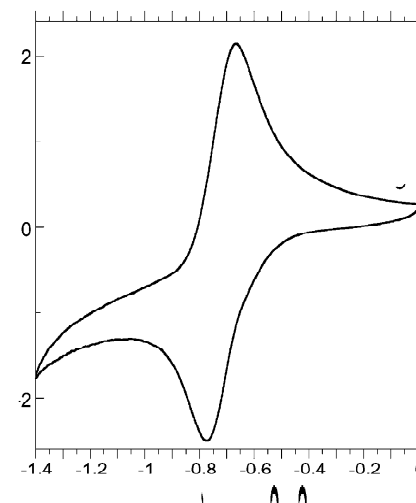
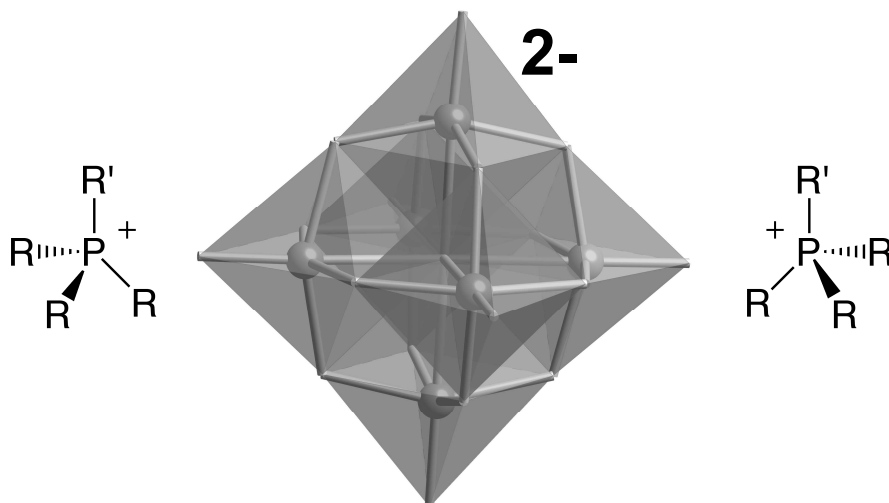


Synthetic “Targets”

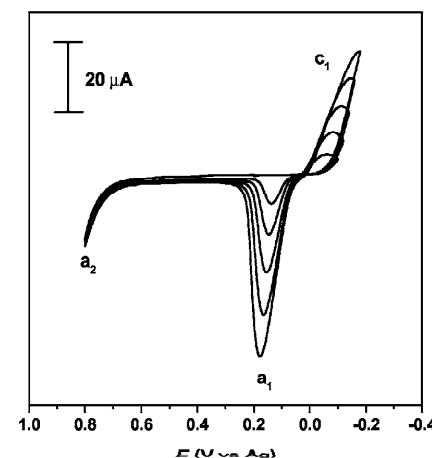
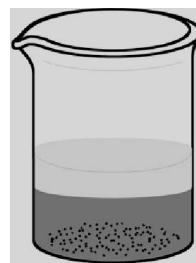
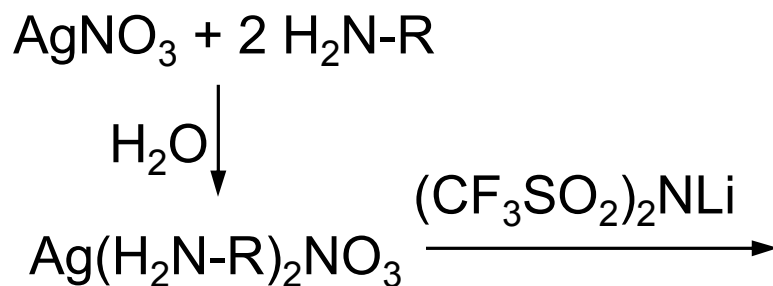
- Low symmetry
- Weak Intermolecular Interactions
- Low charge density

Electroactive Ionic Liquids

**ANL
Work**

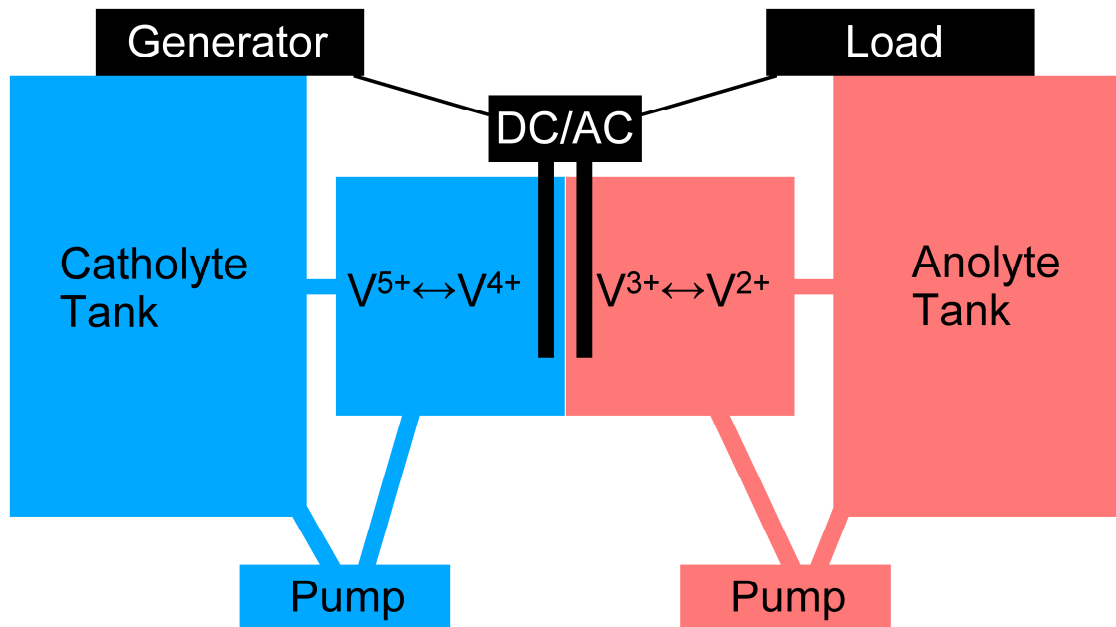


**ORNL
Work**



Flow Batteries

Vanadium Redox Battery (VRB)



vanadium redox couples are in both cells, separated by a proton exchange membrane

- No cross contamination
- Flexible layout
- High cycle life
- Large, tunable capacity
- Low maintenance

Energy Density

VRB 25 Wh/kg

Lead Acid 90-160 Wh/kg

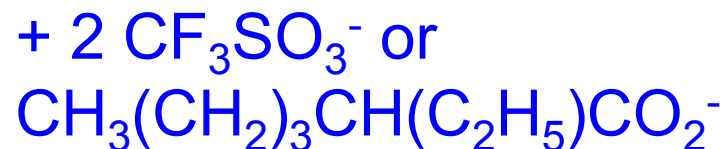
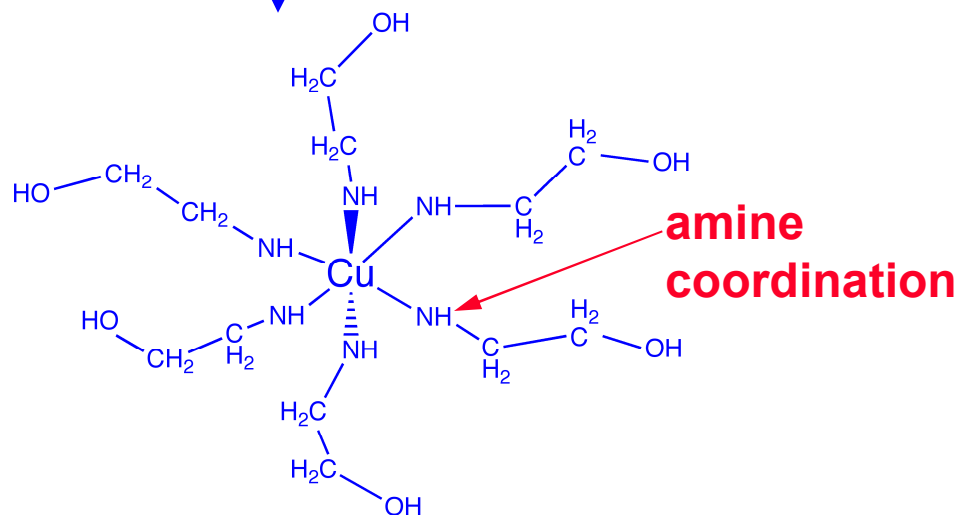
Zn-Br₂ 400 Wh/kg

Synthesis of Electroactive Ionic Liquids

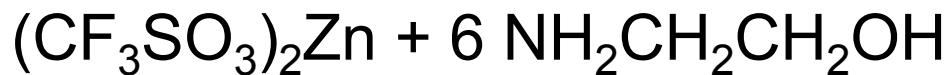


- scalable
- versatile
- low cost
- two functional groups

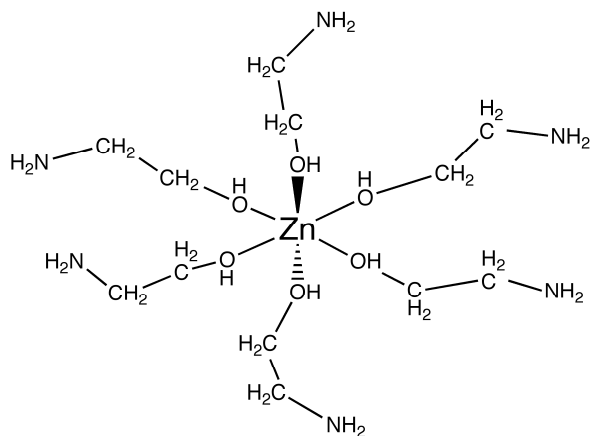
$\Delta 75^\circ\text{C}, 45 \text{ min}$



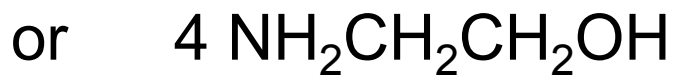
Versatile Synthesis



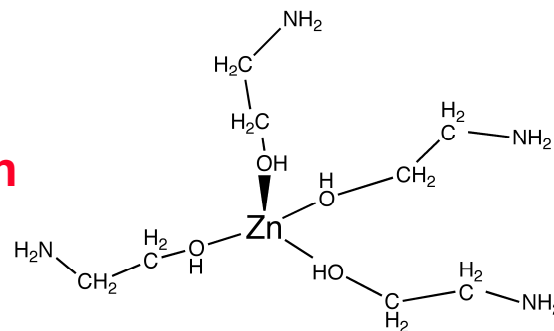
Δ 75 °C, 30 min



**alcohol
coordination**



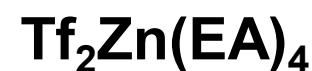
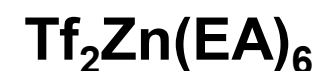
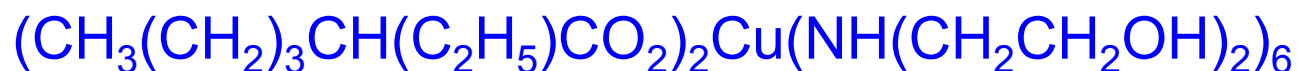
Δ 115 °C, 30 min



The coordination geometry can be varied by changing the reaction stoichiometry.



Seven New Electroactive Ionic Liquids





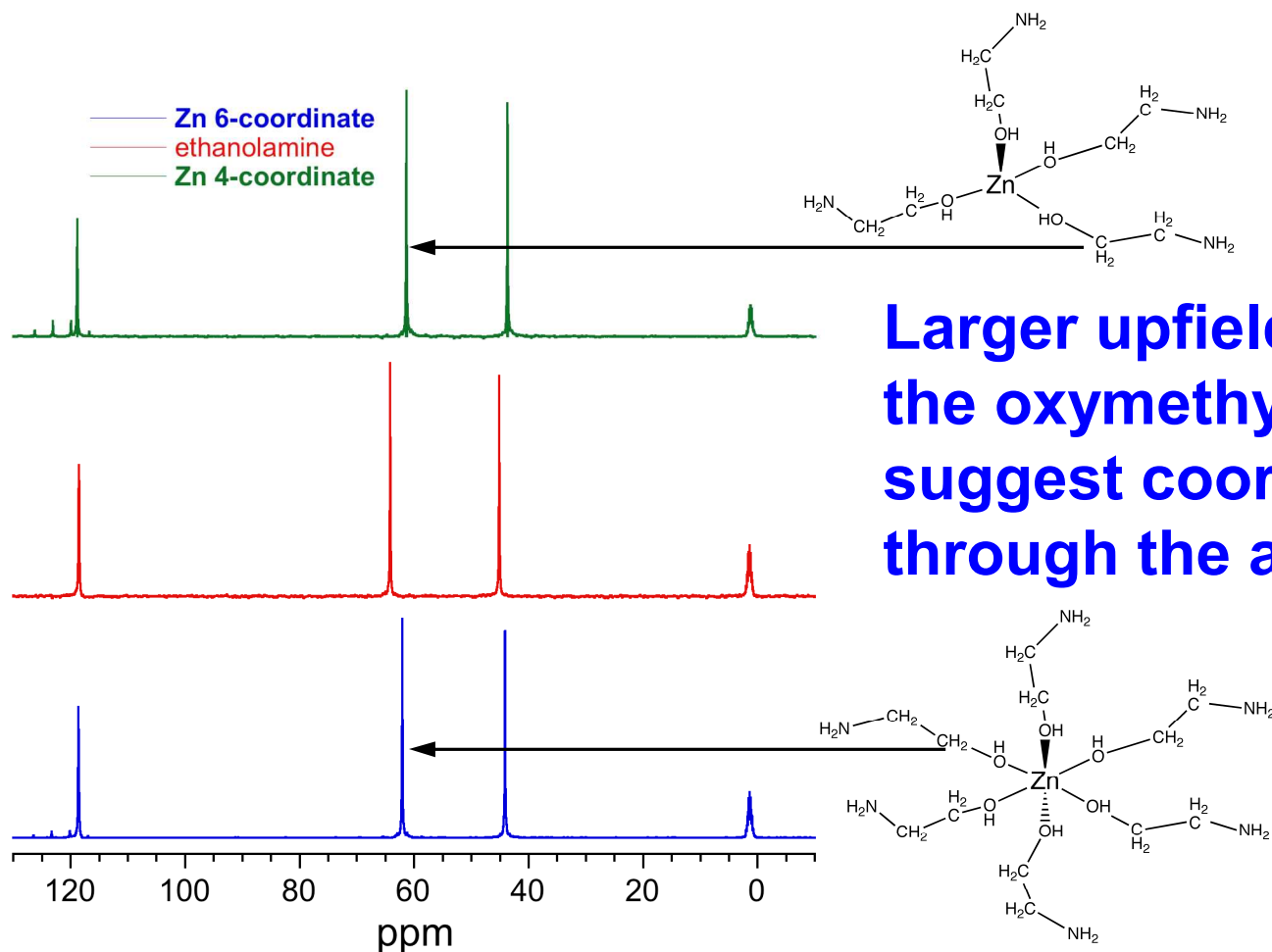
Magnetic Susceptibility Studies

<u>Compound</u>	<u>Calculated χ</u>	<u>Measured χ (± 0.05)</u>
$\text{Cb}_2\text{Cu}(\text{EA})_6$	1.73 BM	1.50 BM
$\text{Cb}_2\text{Cu}(\text{dEA})_6$	1.73 BM	1.69 BM
$\text{Cb}_2\text{Cu}(\text{tEA})_6$	1.73 BM	1.72 BM
$\text{Tf}_2\text{Cu}(\text{dEA})_6$	1.73 BM	1.60 BM
$\text{Tf}_2\text{Zn}(\text{EA})_6$	0	0
$\text{Tf}_2\text{Zn}(\text{EA})_4$	0	0
$\text{Tf}_3\text{Fe}(\text{dEA})_6$	5.90 BM	5.87 BM

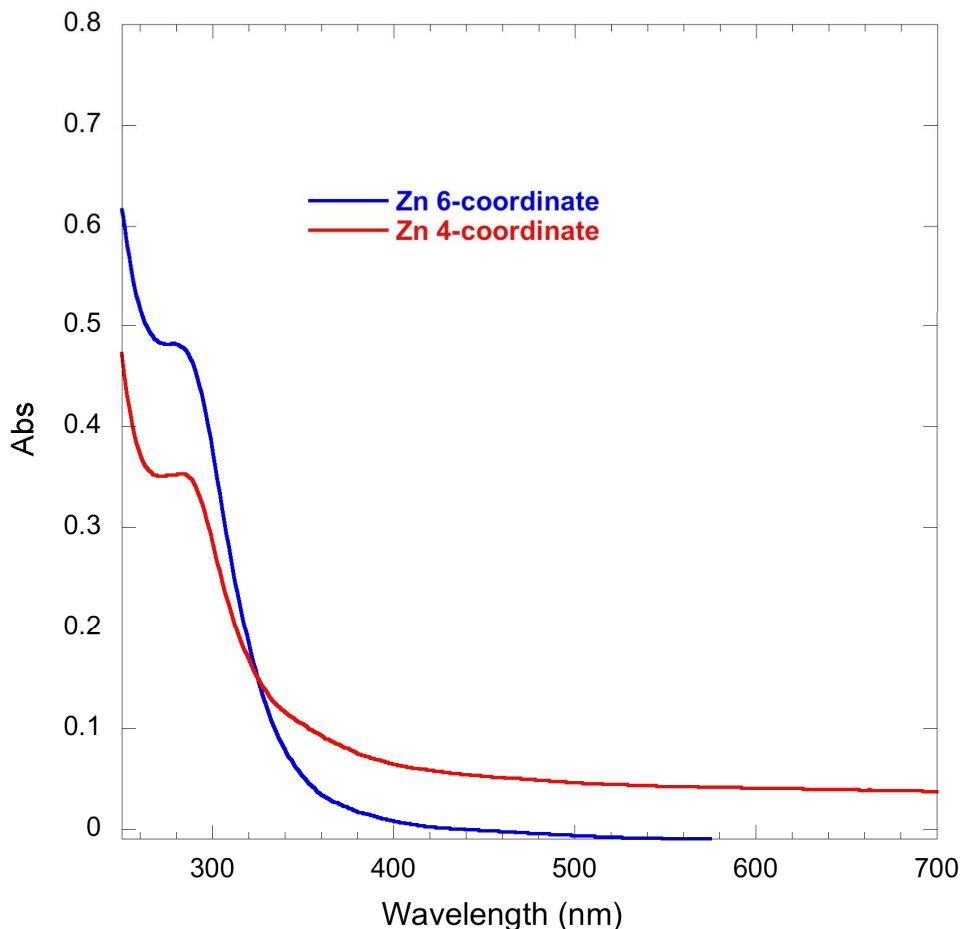
diamagnetic

-smaller ligands and anions promote
antiferromagnetic coupling

^{13}C NMR Studies

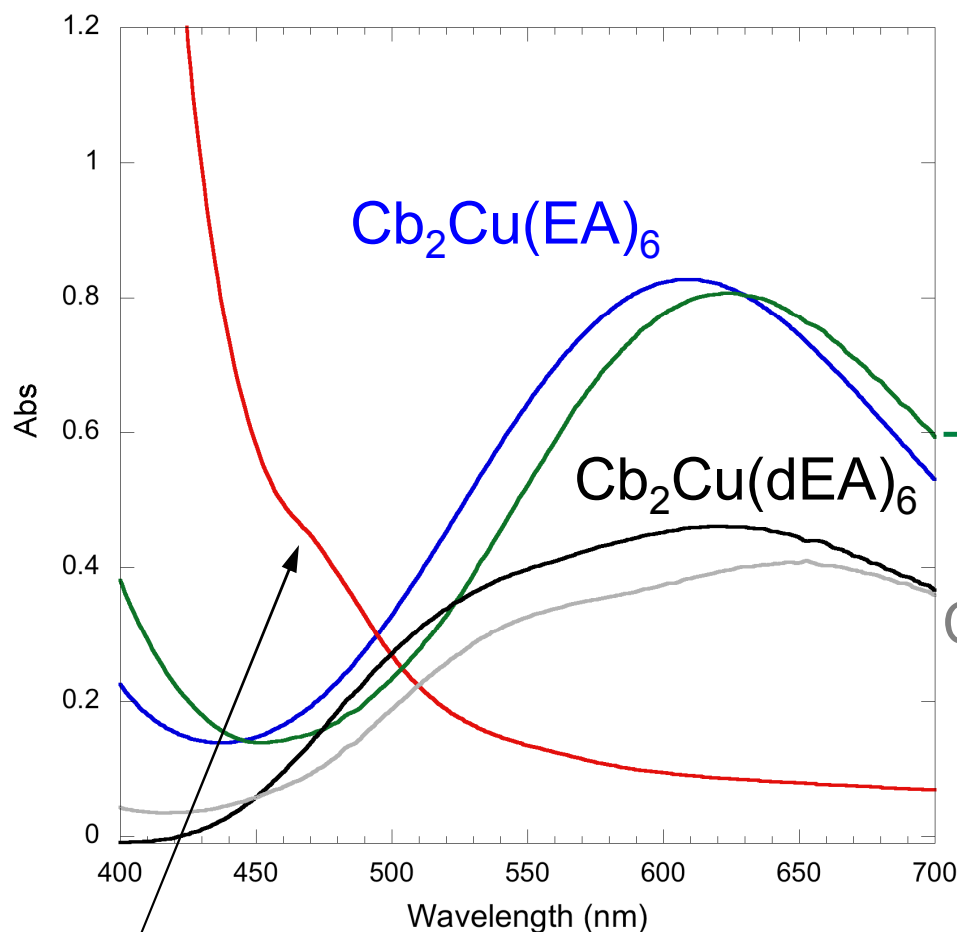


Electronic Absorption Studies



- Band is ligand-metal charge transfer
- 4-coordinate complex is blue-shifted due to the higher ligand field strength of tetrahedral geometry (versus pseudo-octahedral)

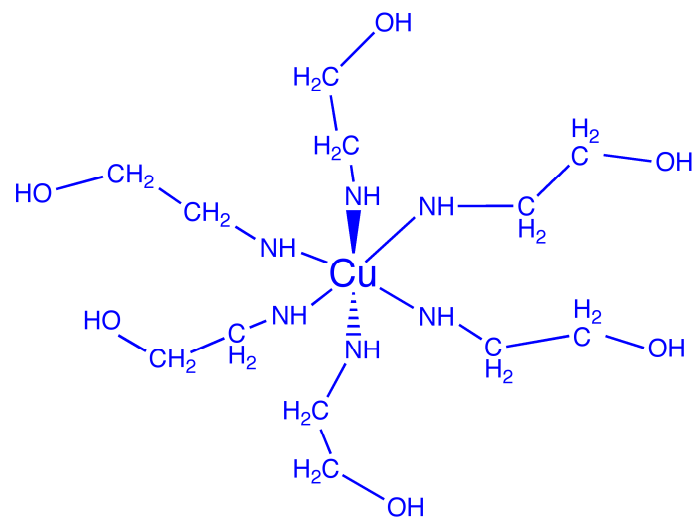
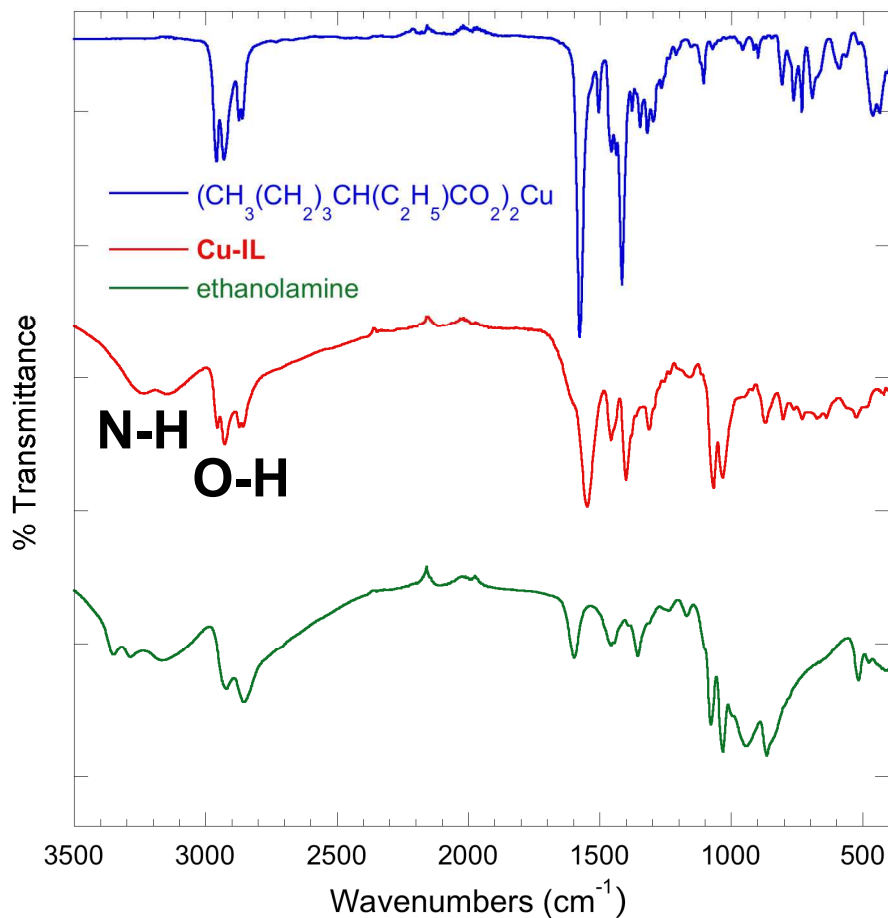
Electronic Absorption Studies



d-d transitions are red-shifted relative to Cb_2Cu , Tf_2Cu , and Tf_3Fe due to weakening of the ligand field upon coordination

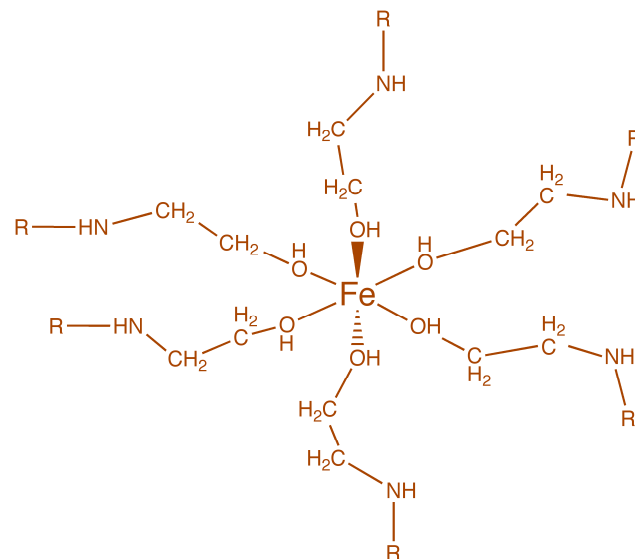
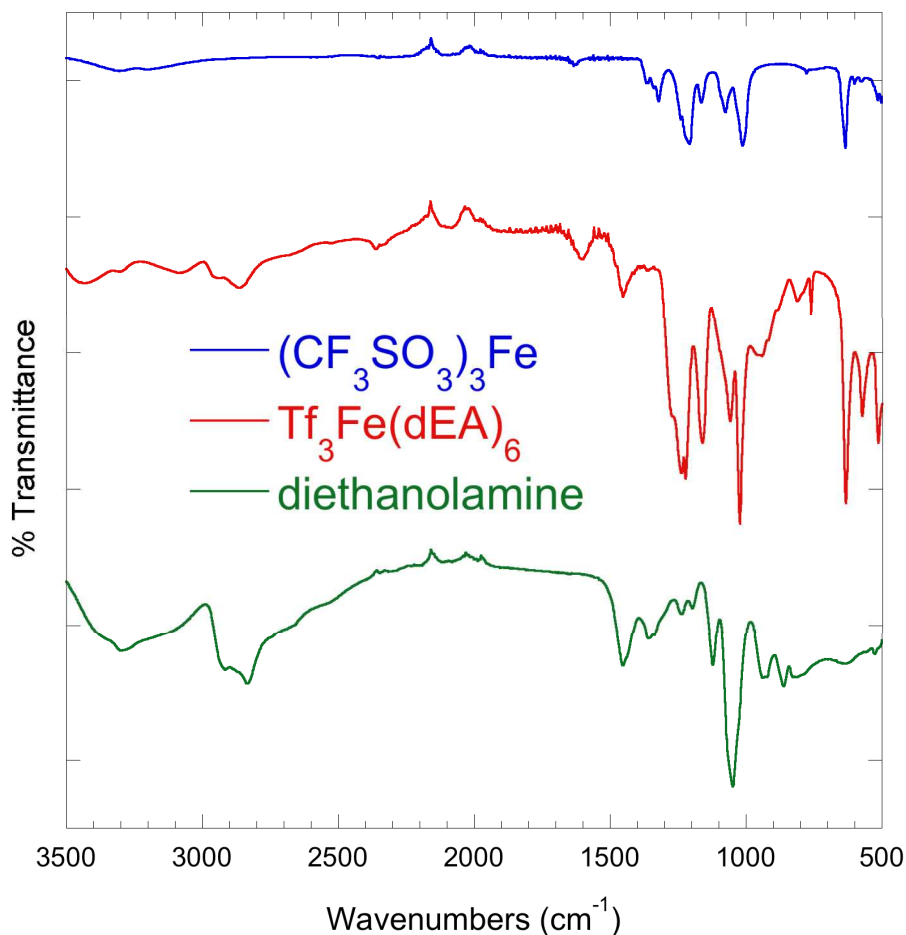
$\text{Cb}_2\text{Cu}(\text{dEA})_6$ and $\text{Cb}_2\text{Cu}(\text{tEA})_6$ have two peaks due to coordination with both alcohol and amine groups

Infrared Studies



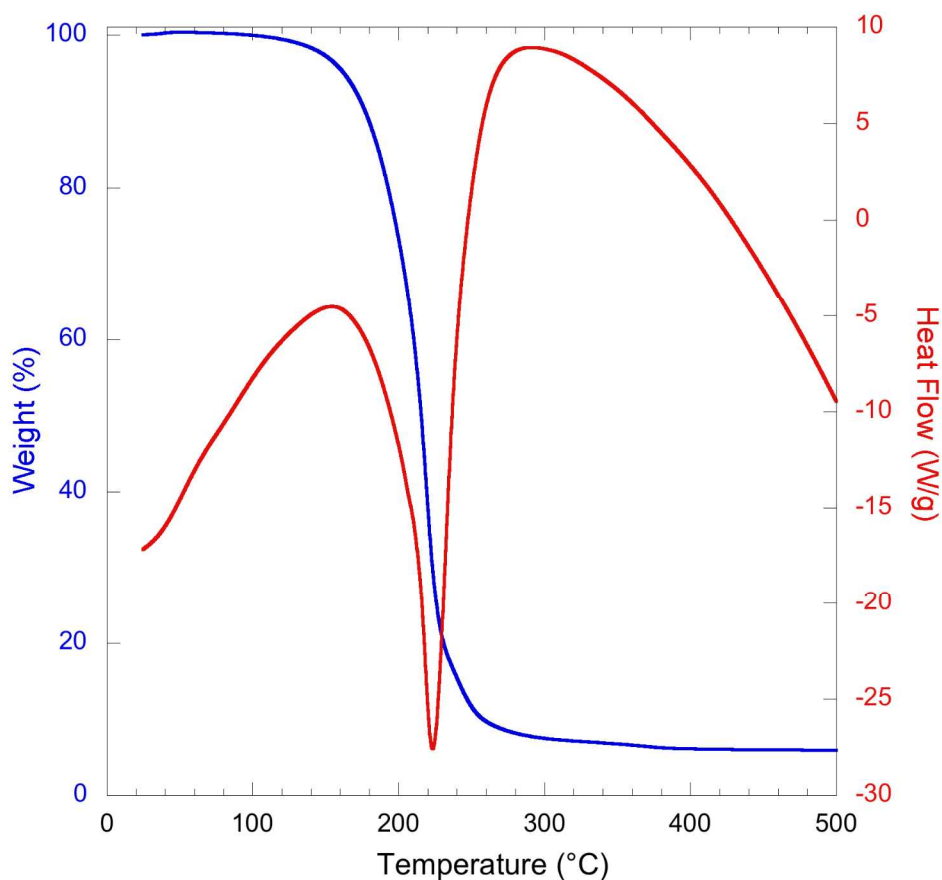
N-H band of $\text{Cb}_2\text{Cu}(\text{EA})_6$ at 3250 cm^{-1} is more red-shifted (relative to ethanolamine) than O-H band at 2900 cm^{-1}

Infrared Studies



Tf₃Fe(dEA)₆, Tf₂Zn(EA)₆,
and Tf₂Zn(EA)₄ preferentially
coordinate through the
alcohol group

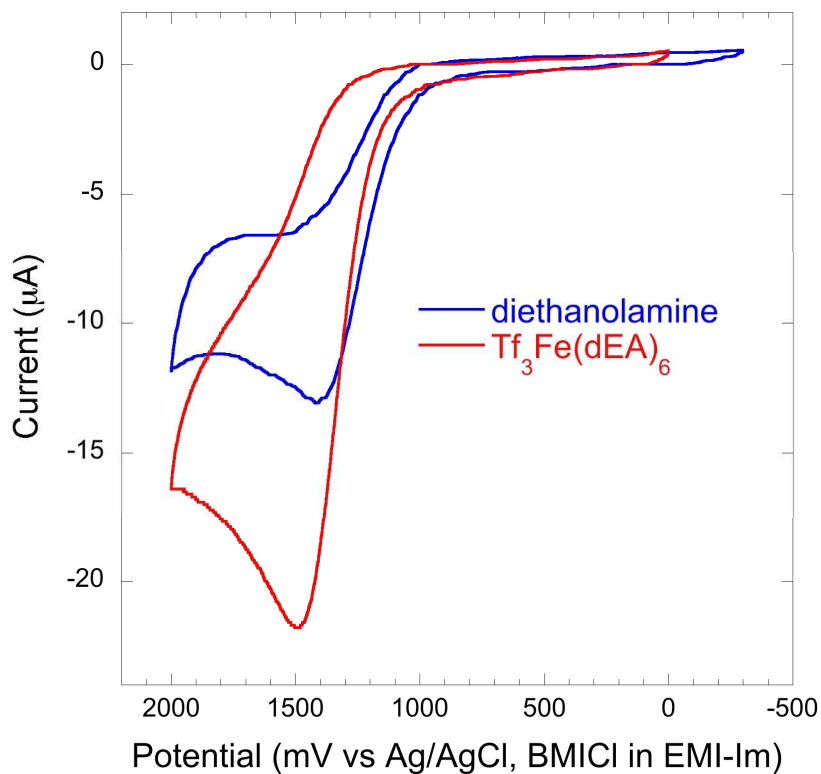
Thermal Stability Studies



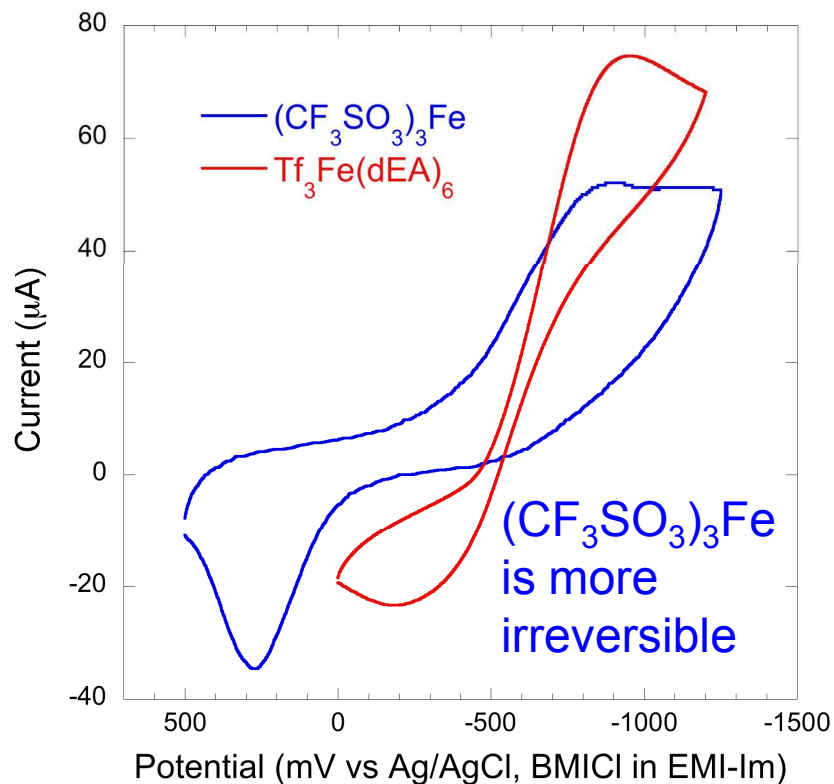
Complex	Disassociation Temperature
$\text{Tf}_2\text{Zn}(\text{EA})_4$	150 °C
$\text{Tf}_2\text{Zn}(\text{EA})_6$	150 °C
$\text{Cb}_2\text{Cu}(\text{EA})_6$	185 °C
$\text{Tf}_2\text{Cu}(\text{dEA})_6$	210 °C
$\text{Cb}_2\text{Cu}(\text{dEA})_6$	225 °C
$\text{Cb}_2\text{Cu}(\text{tEA})_6$	250 °C
$\text{Tf}_3\text{Fe}(\text{dEA})_6$	255 °C

Cyclic Voltammetry

Ligand Oxidation



Metal Redox



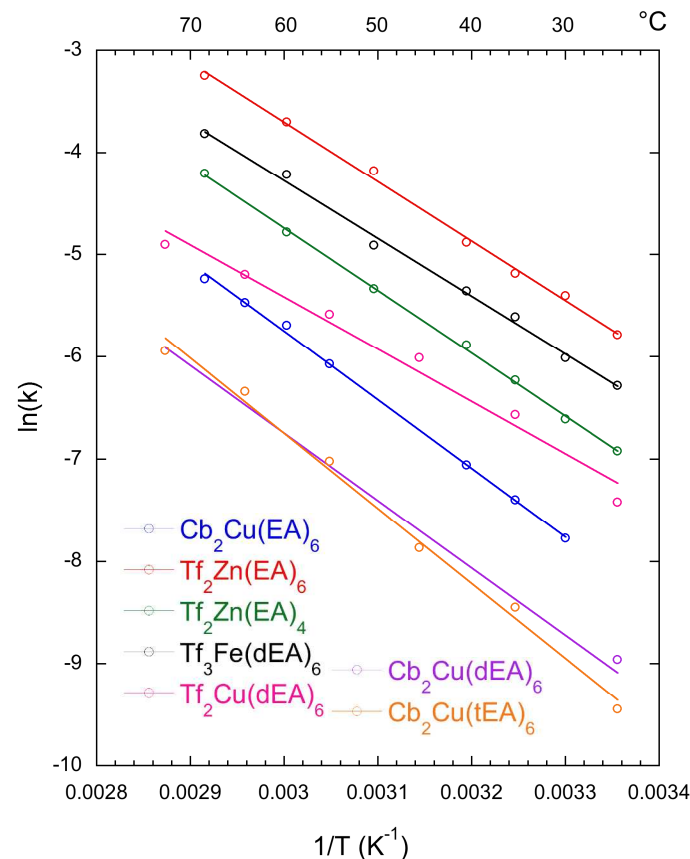
Conditions: Pt working electrode, 1 M TEABF_4 in CH_3CN

Conductivity Studies

Complex	Specific Conductivity ($\mu\text{S cm}^{-1}$) at 25 °C	Activation Energy (kcal mol^{-1})
$\text{Cb}_2\text{Cu}(\text{tEA})_6$	8.77	13.3
$\text{Cb}_2\text{Cu}(\text{dEA})_6$	14.3	11.6
$\text{Cb}_2\text{Cu}(\text{EA})_6$	44.6	12.2
$\text{Tf}_2\text{Cu}(\text{dEA})_6$	66.7	11.2
$\text{Tf}_2\text{Zn}(\text{EA})_4$	101	8.9
$\text{Tf}_3\text{Fe}(\text{dEA})_6$	207	13.1
$\text{Tf}_2\text{Zn}(\text{EA})_6$	341	14.6

the specific conductivity of common battery electrolytes at 25 °C is $\sim 0.5\text{-}1 \text{ S cm}^{-1}$

E_a of aqueous (and molten) metal salt $\sim 3\text{-}5 \text{ kcal mol}^{-1}$



conductivity is low: suggests significant ion pairing

Conclusions and Future Work

- Although we have demonstrated the compounds may serve as a **liquid electrode** they are not yet appropriate as the **electrolyte**
- Future work on the electroactive ionic liquids will focus on both new **ligands** and new **anions** to increase hydrophobicity
- Evaluate the effect of hydrophobicity on the fundamental electrochemical characteristics

