

Electroactive Ionic Liquids:

A New Approach To Flow Batteries

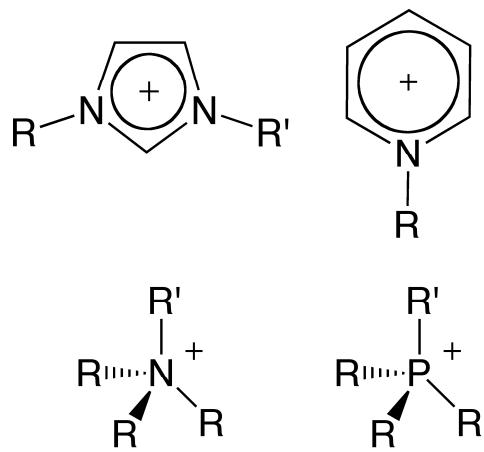
Date

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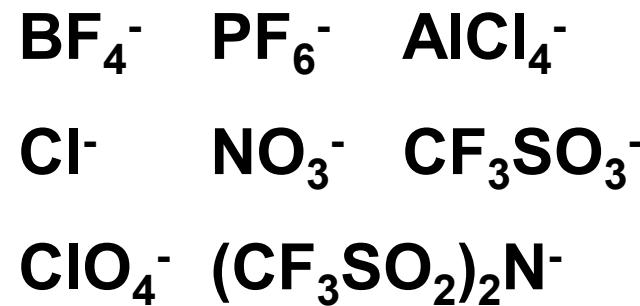


Ionic Liquids

Common Cations



Common Anions

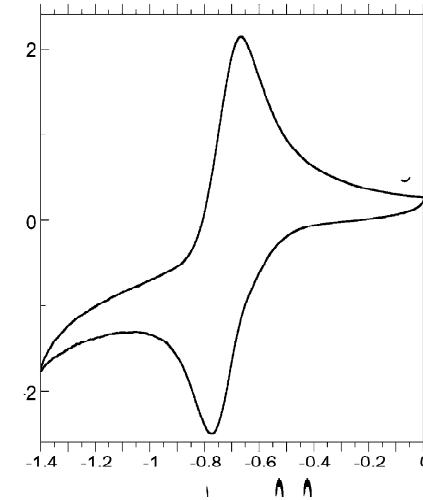
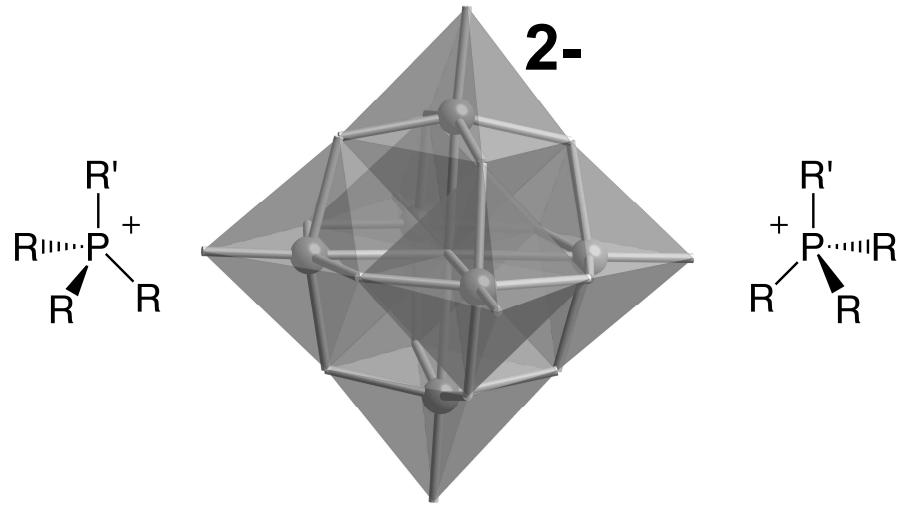


Synthetic “Targets”

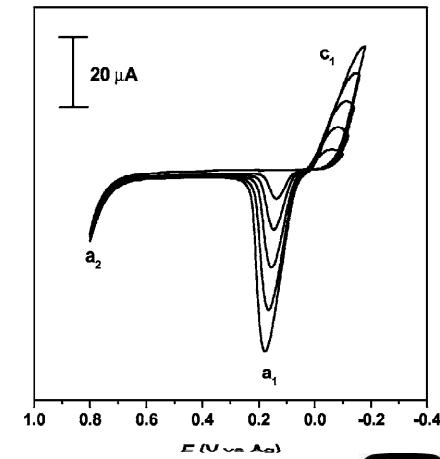
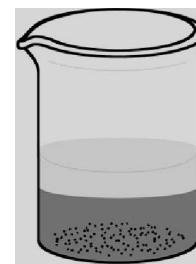
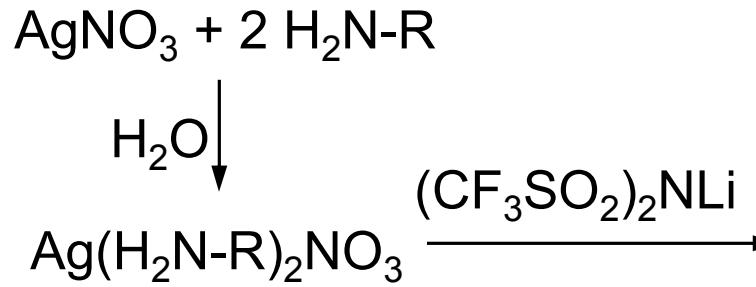
- Low symmetry
- Weak Intermolecular Interactions
- Low charge density

Electroactive Ionic Liquids

ANL
Work



ORNL
Work

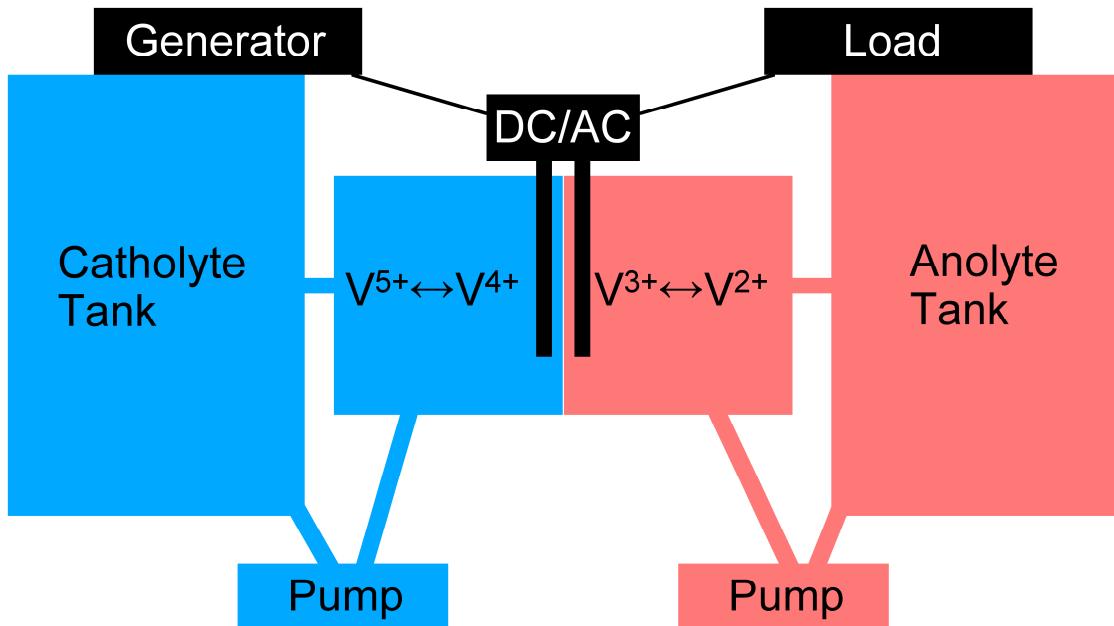


P. G. Rickert et al. *Dalton Trans.* **2007**, 529-531.

J.-F. Huang et al. *J. Electrochem. Soc.* **2006**, 153, J9-J13.

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

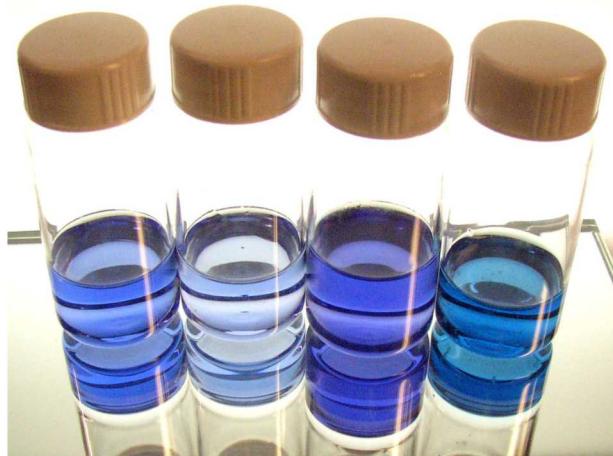
Lead Acid 90-160 Wh/kg

Zn-Br₂ 400 Wh/kg



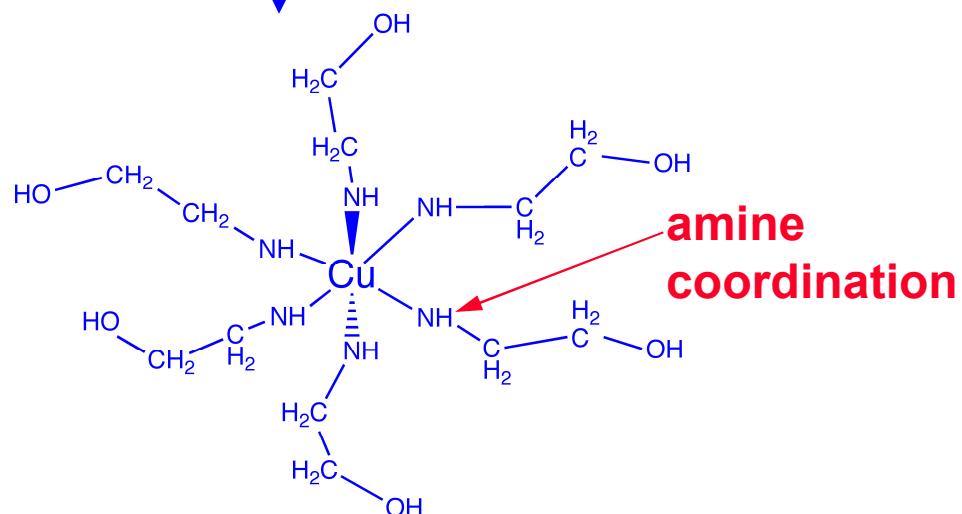
Synthesis of Electroactive Ionic Liquids

$(CF_3SO_3)_2Cu$ or $(CH_3(CH_2)_3CH(C_2H_5)CO_2)_2Cu + 6 NH_2CH_2CH_2OH$



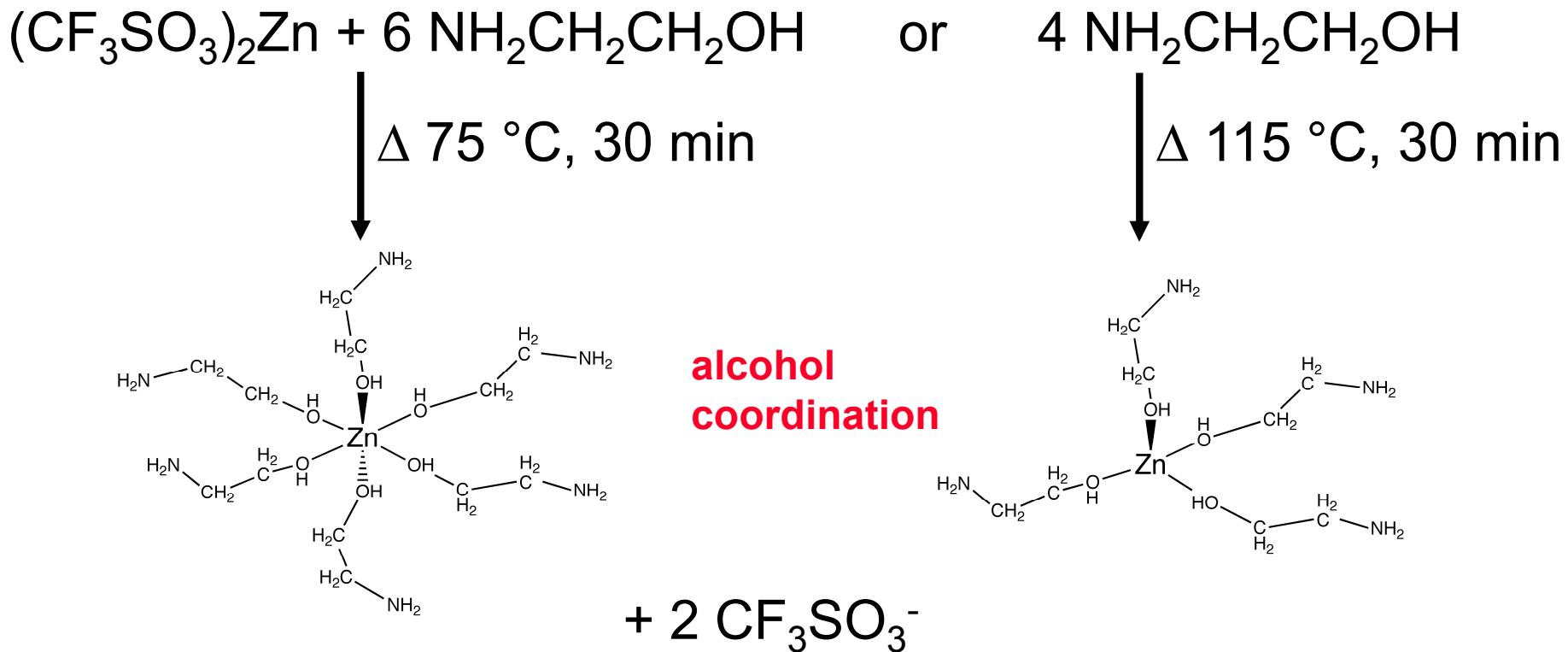
- scalable
- versatile
- low cost
- two functional groups

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



$+ 2 CF_3SO_3^-$ or
 $CH_3(CH_2)_3CH(C_2H_5)CO_2^-$

Versatile Synthesis



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



Seven New Electroactive Ionic Liquids



Cb₂Cu(EA)₆



Cb₂Cu(dEA)₆



Cb₂Cu(tEA)₆



Tf₂Cu(dEA)₆



Tf₂Zn(EA)₆



Tf₂Zn(EA)₄



Tf₃Fe(dEA)₆



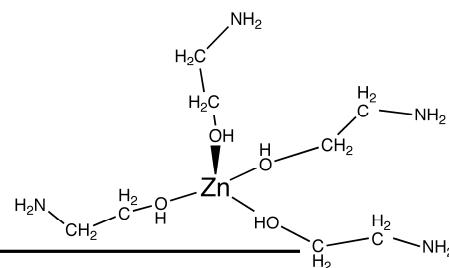
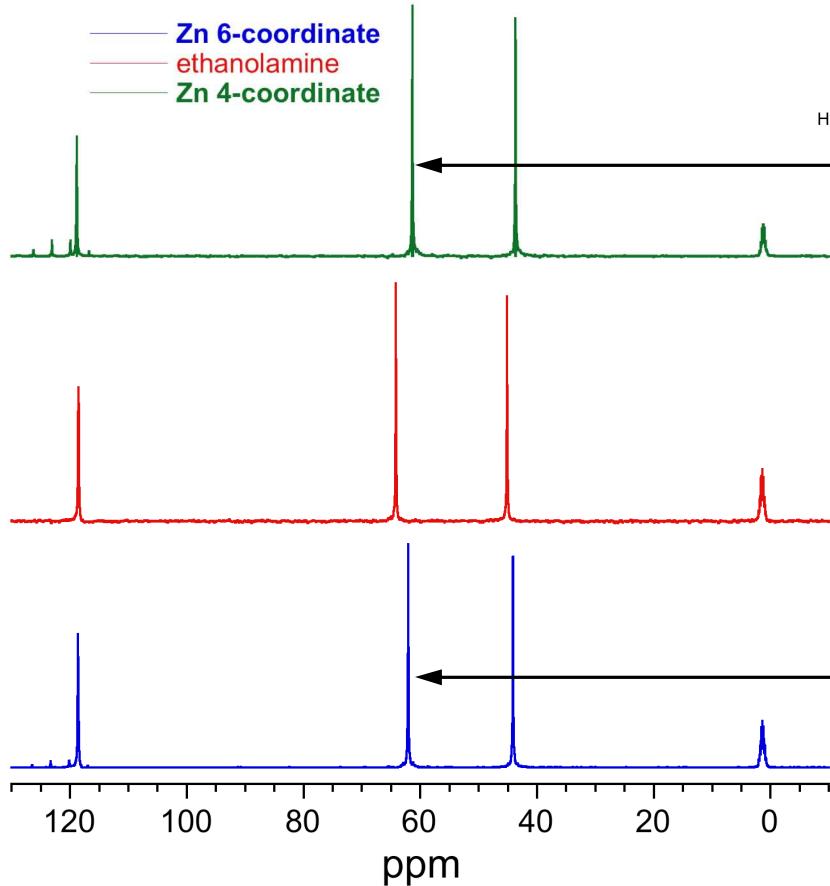
Magnetic Susceptibility Studies

<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

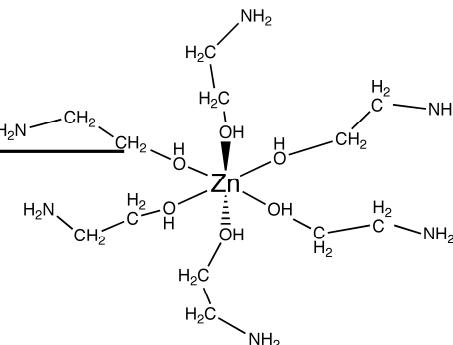
-smaller ligands and anions promote
antiferromagnetic coupling



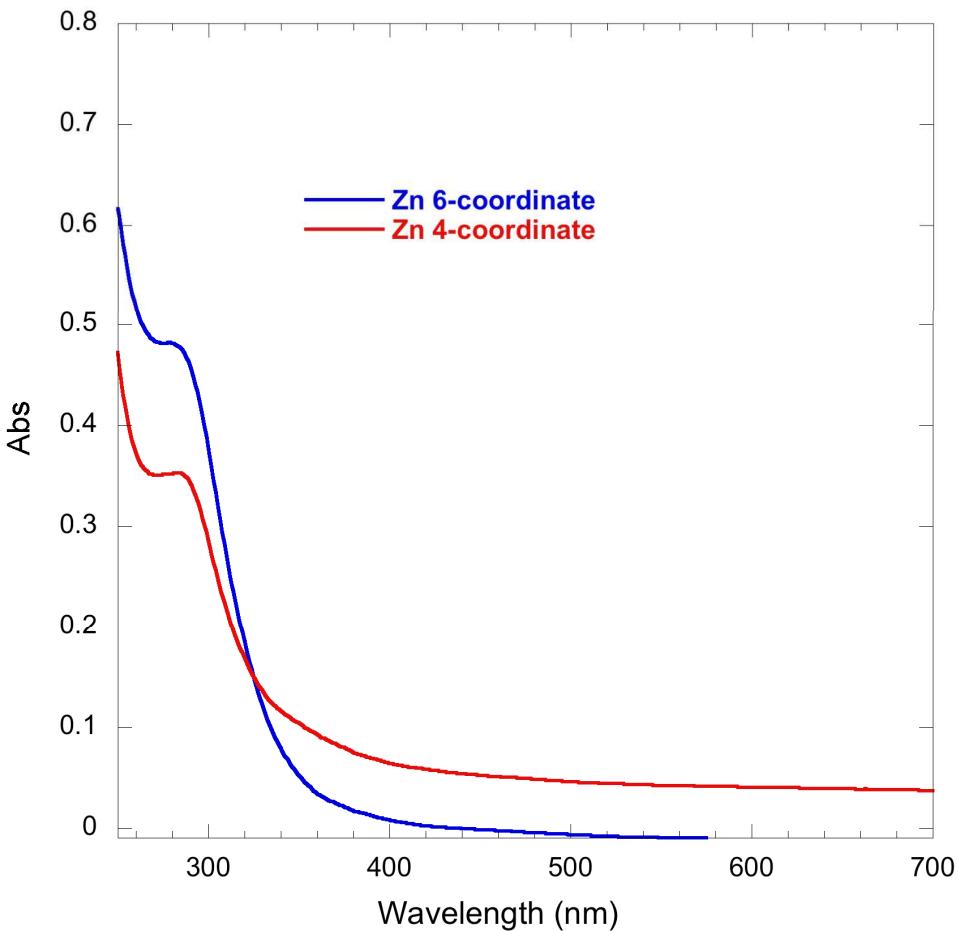
¹³C NMR Studies



Larger upfield shifts of the oxymethylene groups suggest coordination through the alcohol



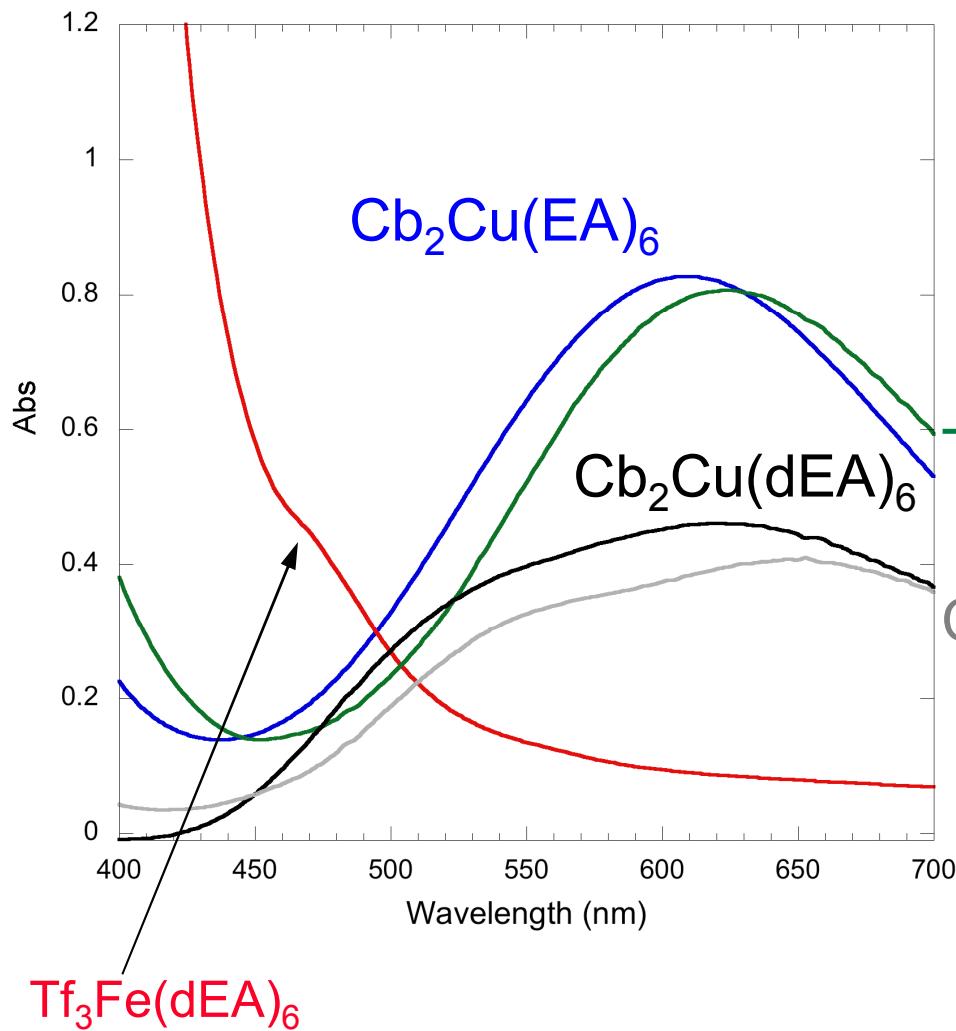
Electronic Absorption Studies



- 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 $\text{C}\text{b}_2\text{Cu}$, Tf_2Cu , and Tf_3Fe due to weakening of the ligand field upon coordination

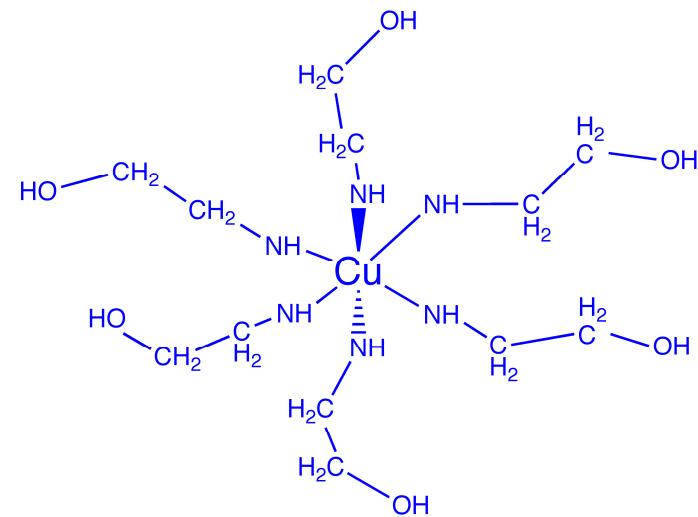
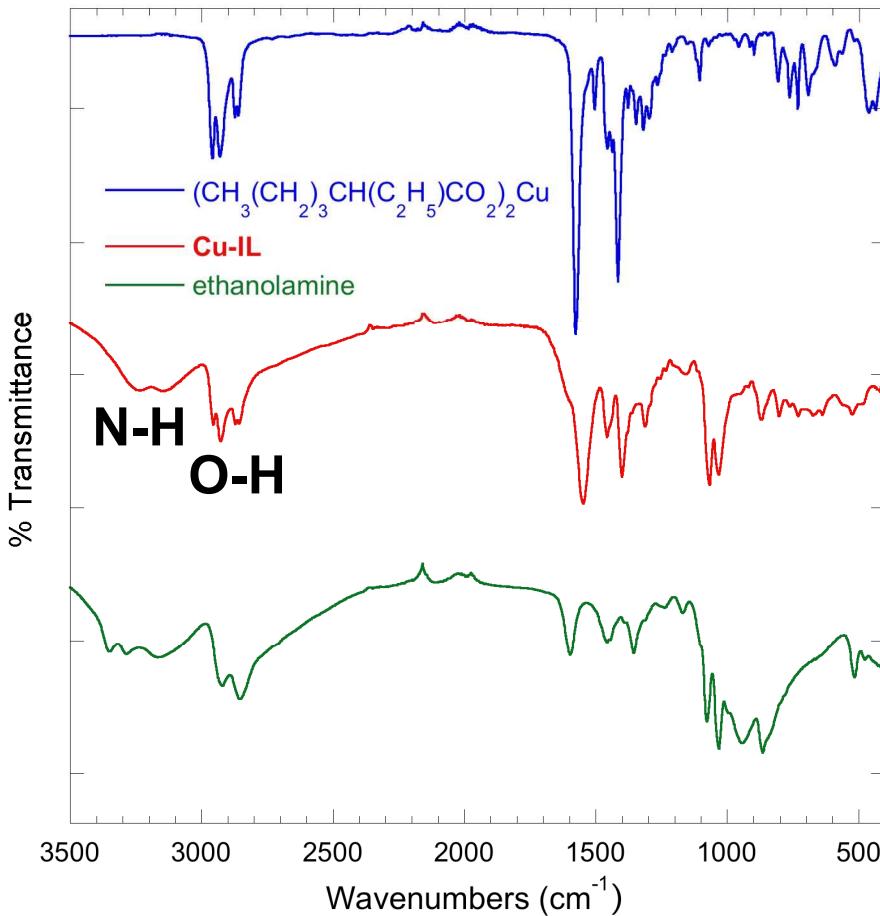
$\text{Tf}_2\text{Cu}(\text{dEA})_6$

$\text{C}\text{b}_2\text{Cu}(\text{tEA})_6$

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



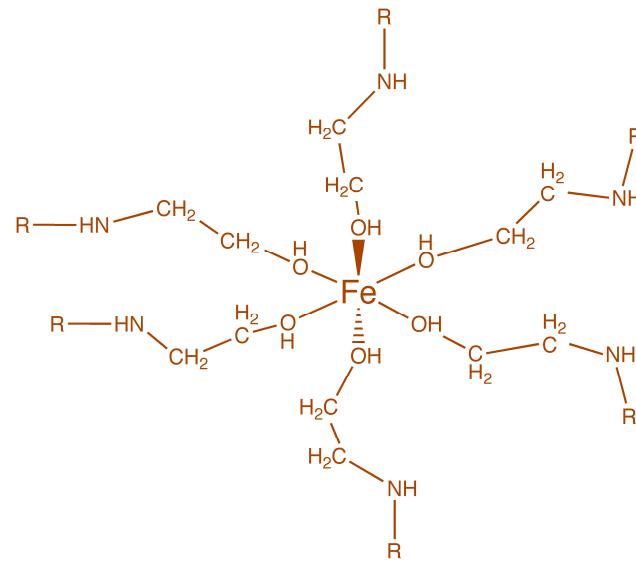
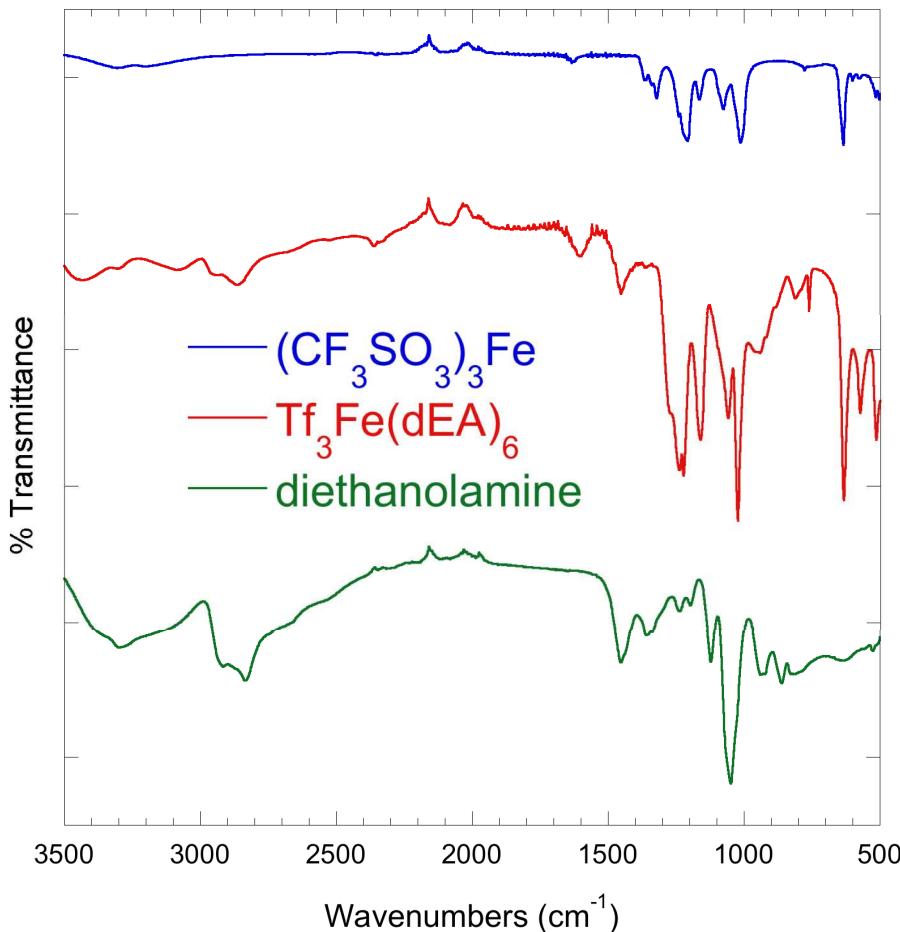
Infrared Studies



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

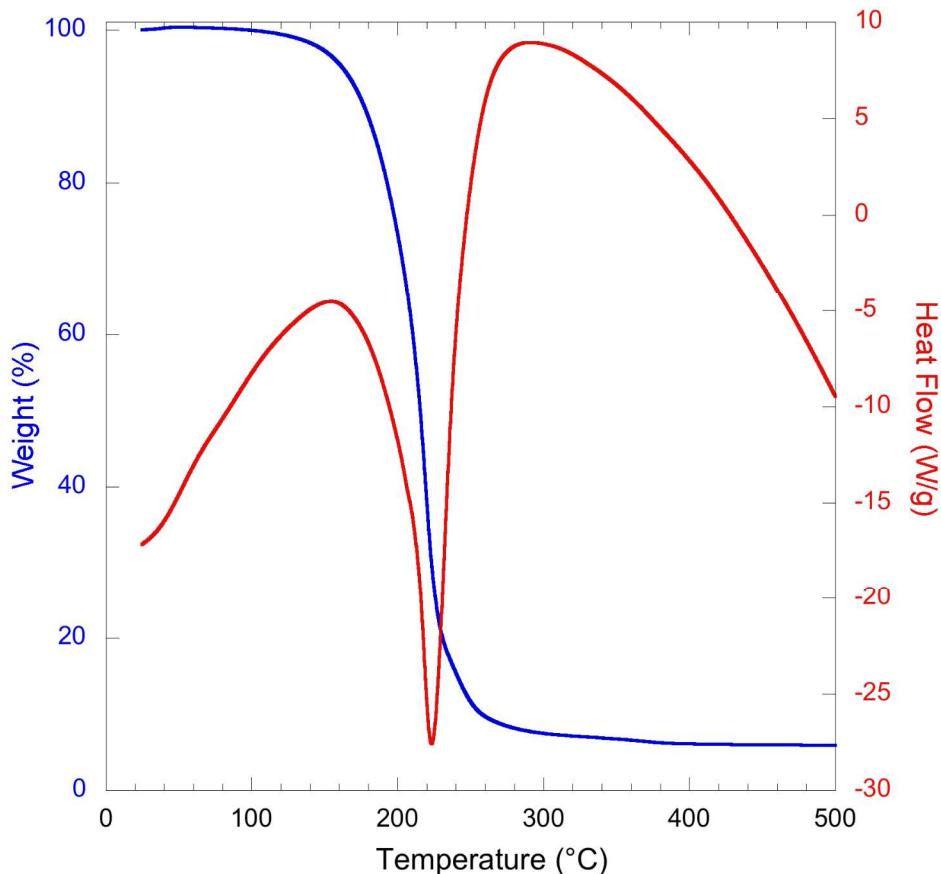


$Tf_3Fe(dEA)_6$, $Tf_2Zn(EA)_6$, and $Tf_2Zn(EA)_4$ preferentially coordinate through the alcohol group



Thermal Stability Studies

$\text{Tf}_2\text{Cu(dEA)}_6$

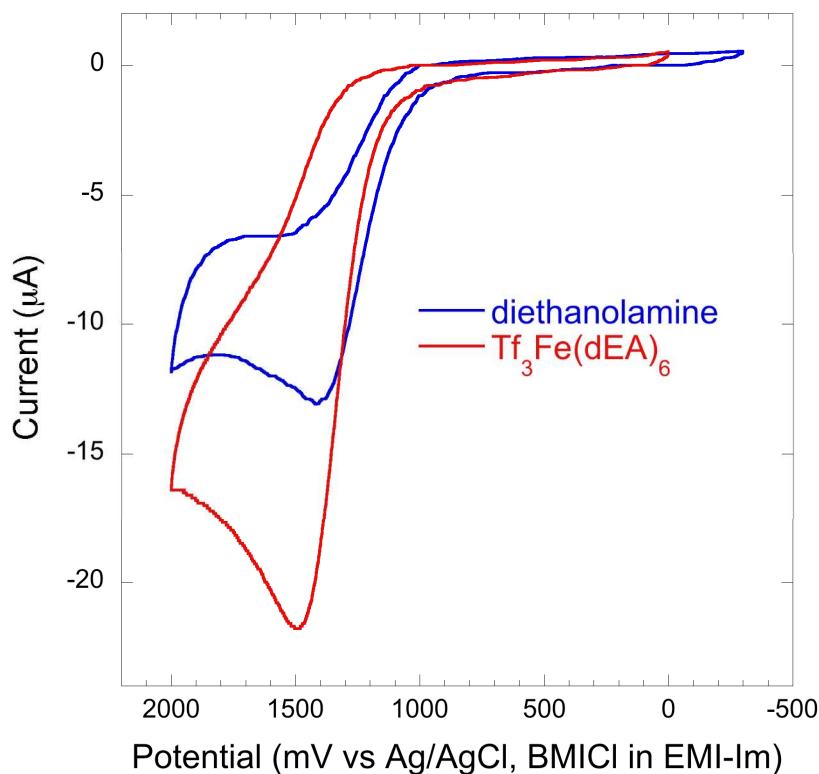


Complex	Disassociation Temperature
$\text{Tf}_2\text{Zn(EA)}_4$	150 °C
$\text{Tf}_2\text{Zn(EA)}_6$	150 °C
$\text{Cb}_2\text{Cu(EA)}_6$	185 °C
$\text{Tf}_2\text{Cu(dEA)}_6$	210 °C
$\text{Cb}_2\text{Cu(dEA)}_6$	225 °C
$\text{Cb}_2\text{Cu(tEA)}_6$	250 °C
$\text{Tf}_3\text{Fe(dEA)}_6$	255 °C

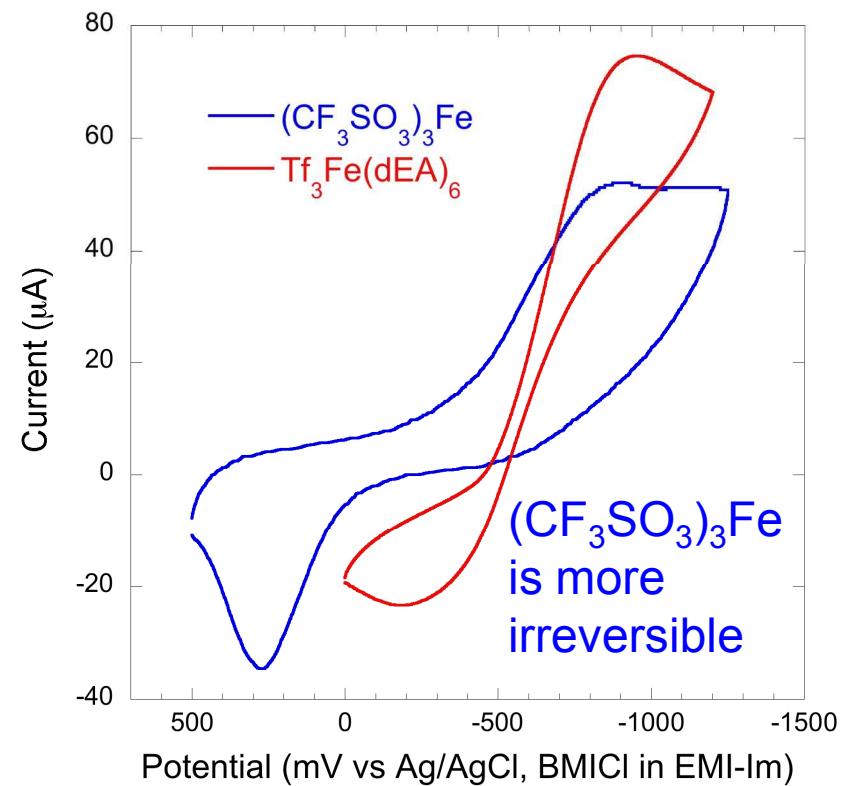


Cyclic Voltammetry

Ligand Oxidation



Metal Redox



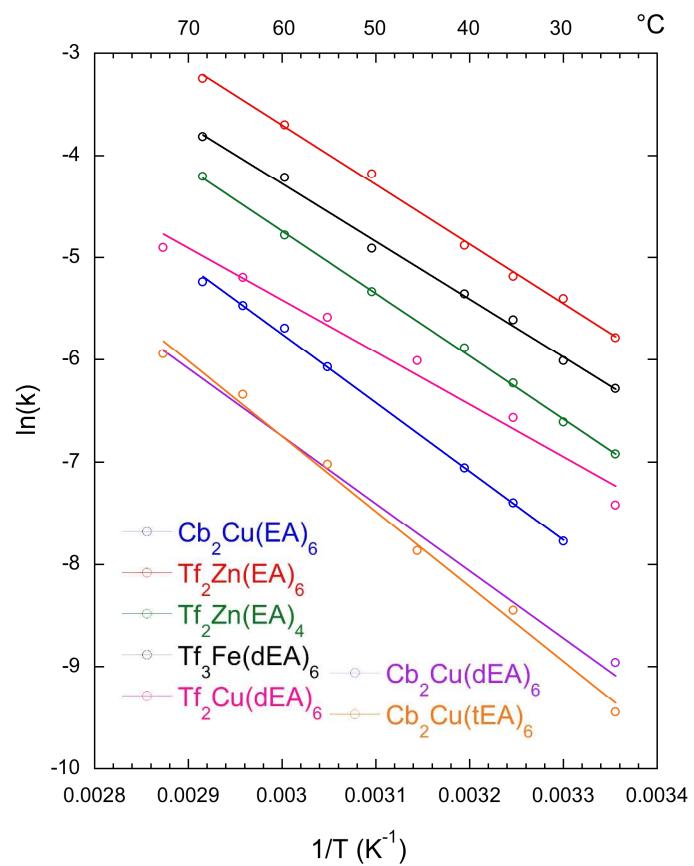
Conditions: Pt working electrode, 1 M TEABF₄ in CH₃CN

Conductivity Studies

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

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

E_a of aqueous (and molten) metal salt ~3-5 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

