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Title: Lanthanide based polymers and ionic liquids

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Abstract:

Novel optical materials have been prepared from ionic liquids and polymers containing inorganic centers, and in particular, lanthanide and rare earth-based clusters. These hybrid materials have potential applications in lighting, imaging, sensors, and photo-catalytic applications. These materials can be synthesized as room temperature ionic liquids, and transparent polymers, with high loadings of the lanthanide centers, resulting in highly luminscent materials.

Lanthanide-based Polymers and Ionic Liquids

Rico E. Del Sesto

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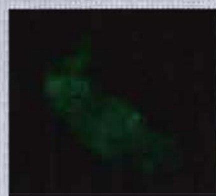
Los Alamos National Laboratory

March 22, 2009



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Polyoxometalate Liquids

- Optical and magnetic materials
- Take advantage of the O → W LMCT band to enhance emission
- Introduce Ln, organics dye to emitting materials
- Develop as ionic liquids for practical applications
- Phosphoniums have poor crystal packing – make most salts RTILs with larger PR_4^+ cations

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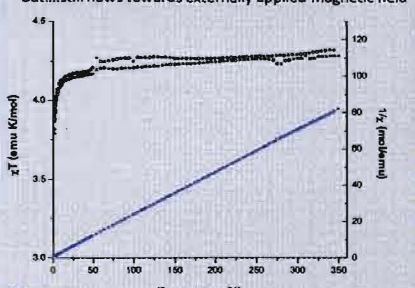
Magnetic Behavior in $[PR_4]_2[MnBr_4]$

- No indication of ferromagnetic behavior
- No indication of strong magnetic interactions in $1/\chi$
- But....still flows towards externally applied magnetic field



Chem. Commun., 2008, 447-449.

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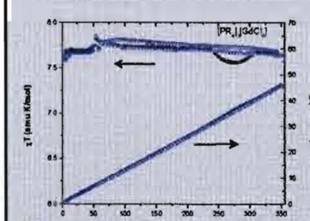
$[PR_4]_3[GdCl_6]$ Shows Interesting Behavior

If cooled rapidly from RT to 150K – interesting phase transitions seen
- transition not seen in slow cooling
- most likely due to glass formation of phosphoniums not seen in Im or Py

Not likely due to orientation effects of anion – tetrahedral symmetry doesn't allow for anisotropic favoring of magnetic alignment
No indication of magnetic particle formation



Chem. Commun., 2008, 447-449.

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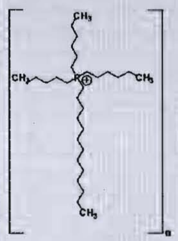
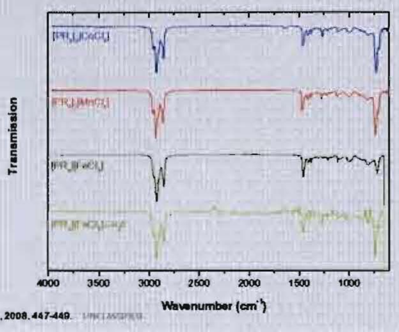
Phosphoniums Always Liquid at RT and Dry

- Hydrated metal halide salts are dehydrated with PR_4Cl
- Water comes out in separate layer





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Chem. Commun., 2008, 447-449.

Magnetic Fluids for Transport

$[PR_4][FeCl_4]$ in H_2O

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Chem. Commun., 2008, 447-449.

Magnetic Fluids for Transport

$[PR_4]_2[Co(SCN)_4]$ in silicon oil

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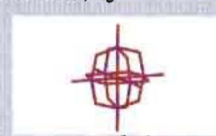
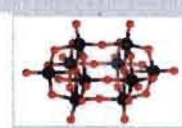
Polyoxometalate Clusters (POMs)

- Well-defined complexes formed by self-assembly
- Have interesting properties: electrochromism, photochromism, conductivity, redox activity, antimicrobial and antitumor properties.
- Structural diversity
- Easy tunability of their properties: from molecular shape to solubility
- Can be made in different sizes, e.g.

$[Mo_2O_7]^{2-}$



$[Mo_6O_{19}]^{2-}$



$[W_{10}O_{32}]^{4-}$

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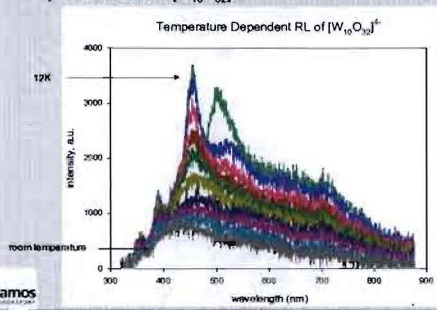
POM optical Properties

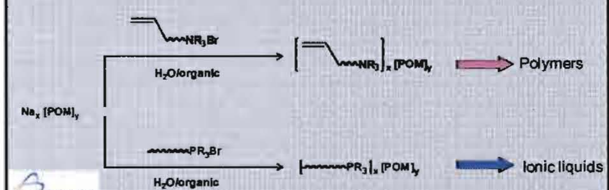
POM (O → W) excitation is 270 nm and only emits at low temperatures at 500 nm

X-ray luminescence of $[W_{10}O_{32}]^{-4}$:



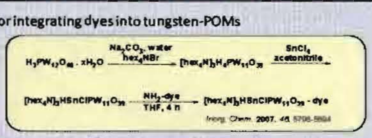
Cation Exchange to Isolate Organic-soluble POM materials

- POMs' solubility is often an issue
- Different cations can be used to promote their solubility in organic solvents for material development
- e.g. surfactants, monomer cations

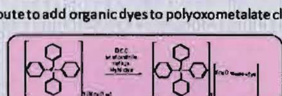


Integration of inorganic dyes into POMs

- Route for integrating dyes into tungsten-POMs



- Alternate route to add organic dyes to polyoxometalate clusters



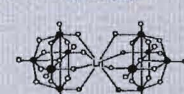
- Lanthanide as luminescence center

Integration of Lanthanides into Polyoxometalates

- lanthanides are often used in luminescent materials
- known to have a strong luminescent emission if the emission results from energy transfer
- explore the efficiency of energy transfer from POM clusters to lanthanide luminescent centers.

$$Na_2WO_4 \cdot 2H_2O \xrightarrow[Ln(NO_3)_3 \cdot 6H_2O]{\text{acetic acid (pH= 7.0-7.5)}} Na_9LnW_{10}O_{36}$$

$Ln = Ce^{3+}, Eu^{3+}, Tb^{3+}, Gd^{3+}$



POM as Host for Ce

$$Na_2WO_4 \cdot 2H_2O \xrightarrow[Ce(NO_3)_3 \cdot 6H_2O]{\text{acetic acid (pH= 7.0-7.5)}} Na_9CeW_{10}O_{36}$$ (X)

Obtained $Na_9CeW_{10}O_{36}$
Orange crystals
Ce(IV) is not luminescent

Ce(III) POMs are not stable- Ce(III) oxidizes to Ce(IV)

About 10 known Ce(III) POM structures

– most contain mixed anions and/or syntheses not well suited to incorporation in well-characterized materials.

- Some have very high charge but compensation is high number of Ce(III) ions

$[H_6Ce_2(H_2O)Cl(W_5O_{18})_3]^{7-}$
Inorg Chem. 2008, 47, 5612-5615.

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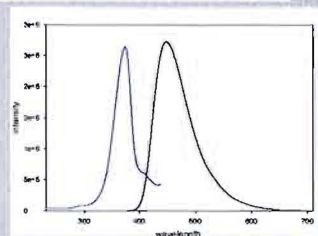
Emission from Ce(IV)

Emission and Excitation of PMMA-$CeW_{10}O_{36}$



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Energy Transfer within Ln-POM Ionic Liquids

O→W to Ln for most
Ln to O→ for Gd, maybe Ce?

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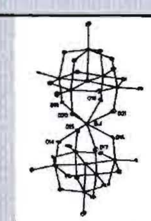
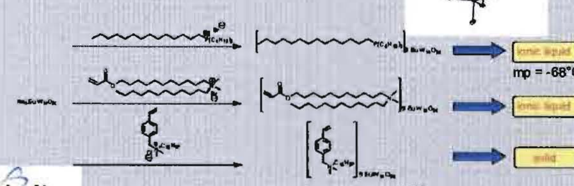
Eu(III) containing POM

$$Na_2WO_4 \cdot 2H_2O \xrightarrow[Eu(NO_3)_3 \cdot 6H_2O]{\text{acetic acid (pH= 7.0-7.5)}} Na_9EuW_{10}O_{36}$$

white crystals
Average Eu-O distance : 2.42 Å
D_{4d}





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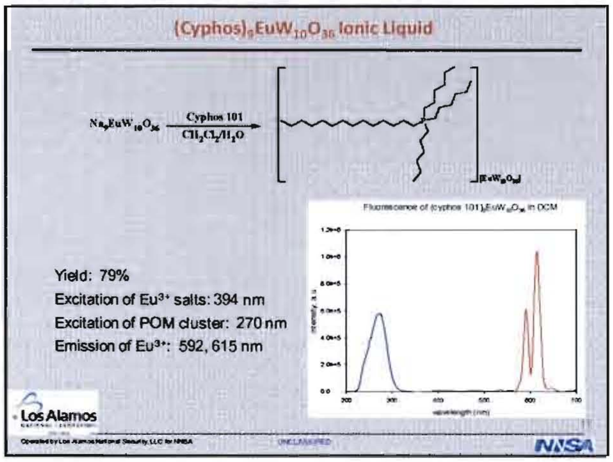

(Cyphos)$_9$EuW$_{10}$O$_{36}$ Ionic Liquid
Cyphos 101
CH$_2$Cl$_2$/H$_2$O
Yield: 79%
Excitation of Eu^{3+} salts: 394 nm
Excitation of POM cluster: 270 nm
Emission of Eu^{3+}: 592, 615 nm
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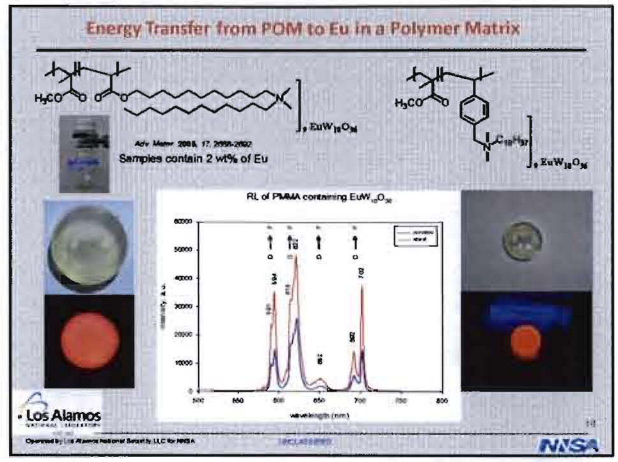

Energy Transfer from POM to Eu in a Polymer Matrix
Samples contain 2 wt% of Eu
RL of PMMA containing EuW$_{10}$O$_{36}$
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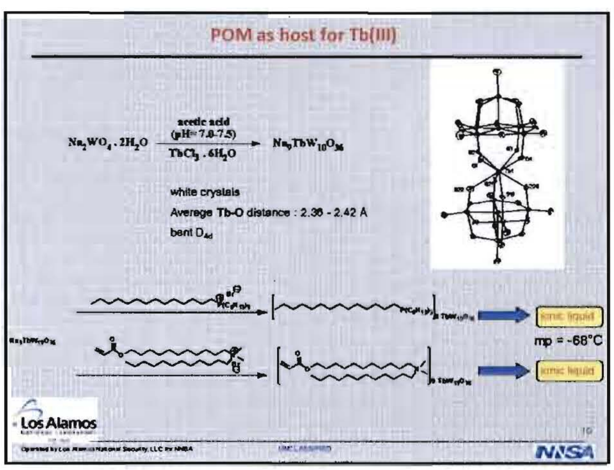

POM as host for Tb(III)
acetic acid
TbCl$_3$. 6H$_2$O
white crystals
Average Tb-O distance : 2.36 - 2.42 A
ionic liquid
mp = -68°C
ionic liquid
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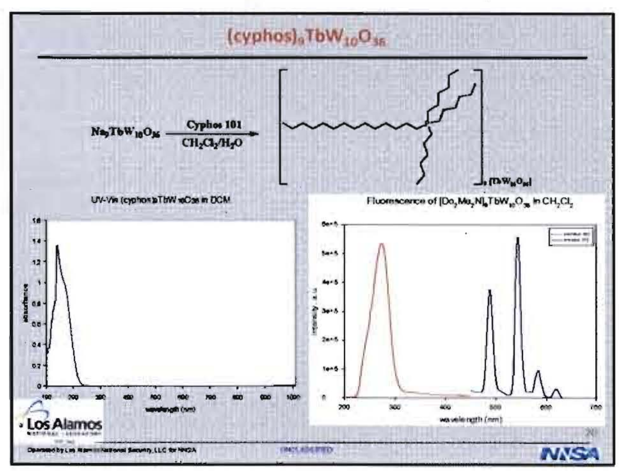

(cyphos)$_9$TbW$_{10}$O$_{36}$
Cyphos 101
CH$_2$Cl$_2$/H$_2$O
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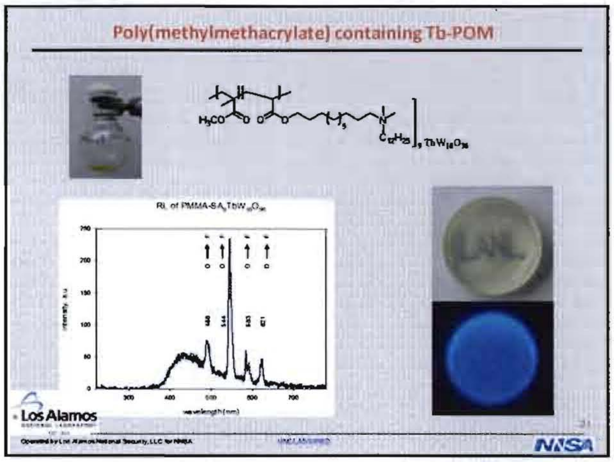
Poly(methylmethacrylate) containing Tb-POM
H_3CO
$C_{12}H_{25}$
$TbW_{10}O_{36}$
intensity, a.u.
wavelength (nm)
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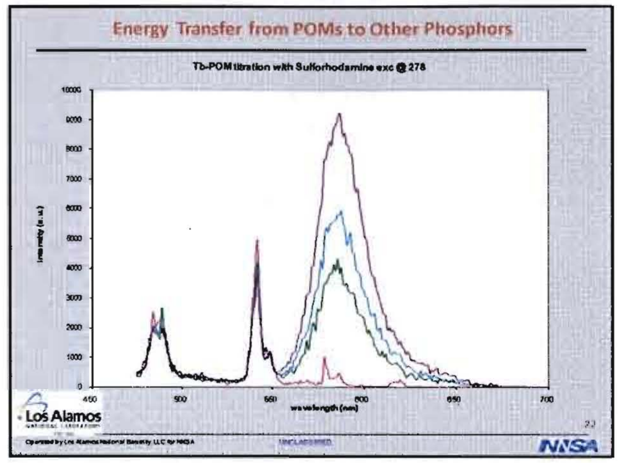
Energy Transfer from POMs to Other Phosphors
Tb-POM titration with Sulforhodamine exc @ 278
wavelength (nm)
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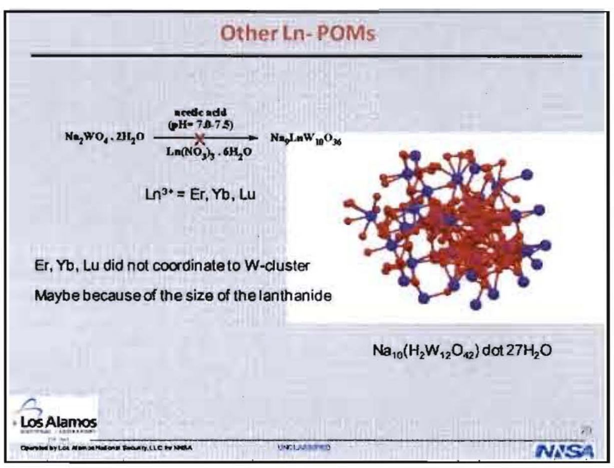
Other Ln- POMs
$Na_2WO_4 \cdot 2H_2O$
acetic acid (pH= 7.0-7.5)
$Ln(NO_3)_3 \cdot 6H_2O$
$Na_9LnW_{10}O_{36}$
Ln^{3+} = Er, Yb, Lu
Er, Yb, Lu did not coordinate to W-cluster
Maybe because of the size of the lanthanide
$Na_{10}(H_2W_{12}O_{42})$ dot $27H_2O$
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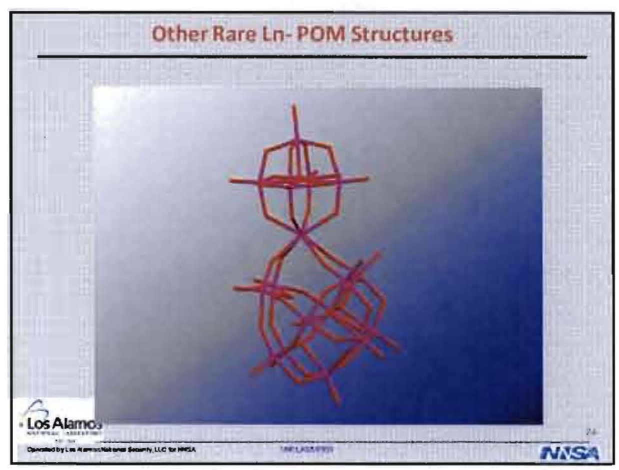
Other Rare Ln- POM Structures
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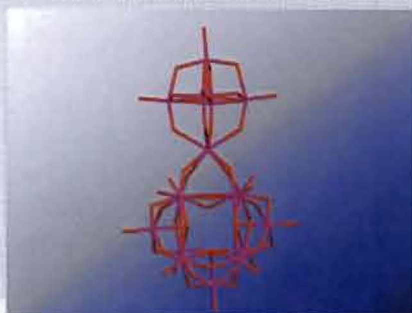
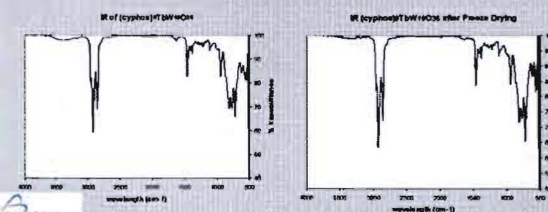
Other Rare Ln- POM Structures



IR of POMs

- Water is hard to remove from POM ionic liquids
  - strong coordination of water to POM oxygens
  - POMs are highly charged
- Electrochem studies are in progress
  - study electrochromic and electrochemical behaviors
  - water has been an issue



Optical Purity of Ionic Liquids

- "Purity" is application-specific
- For optical studies and materials, they need to be extensively purified
- Commercially available and "spectroscopic grade"
- Many applications, off-the-shelf and commercially available are adequate

Application Specific Grades of Organic Solvents

n-Hexane, contains ca. 95% n-Hexane, for analysis

n-Hexane 97%, water <50 ppm, extra dry over molecular sieve

n-Hexane 97%, residue free, for electronic use

n-Hexane 96+%, water <20 ppm, extra dry

n-Hexane 98%, ECD tested halocarbons free grade

n-Hexane, for residue and pesticides anal., ca. 95% n-Hexane

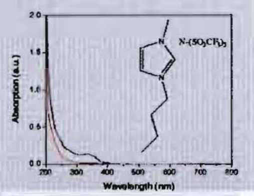
n-Hexane 95+%, extra pure

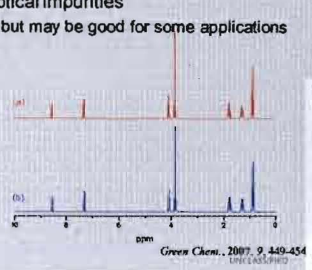
n-Hexane 99+%, for analysis

n-Hexane puriss. p.a., standard for GC, ≥99.7% (GC)

Optical Quality of Ionic Liquids

- For optical materials, need clean ILs!!
  - no background absorption, fluorescence
- NMR is not sensitive enough to detect optical impurities
  - but may be good for some applications

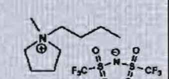


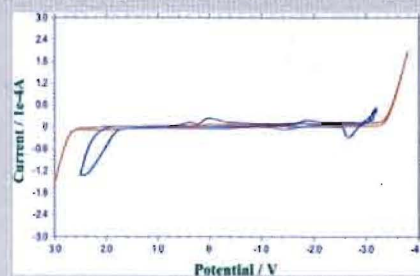


Green Chem., 2007, 9, 449-454

Optical Quality of Ionic Liquids

- For electrochromic materials, need clean ILs!!
  - no background electrochemical active species





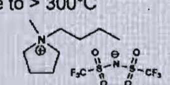
Green Chem., 2007, 9, 449-454.

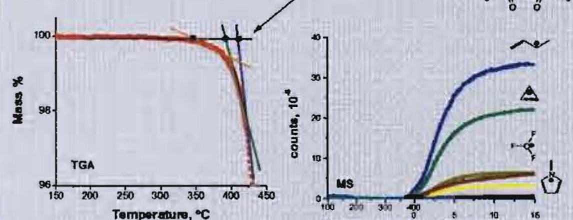
Thermal Stability of Ionic Liquids

- Drying of ionic liquids at elevated temperatures
  - Notice change in optical properties when drying
- Many ionic liquids "stable" to > 300°C and higher
- Therefore chemistry can be performed at elevated temperature with ionic liquids as solvents
- But "stability" is a relative term

Thermal Stability of Ionic Liquids

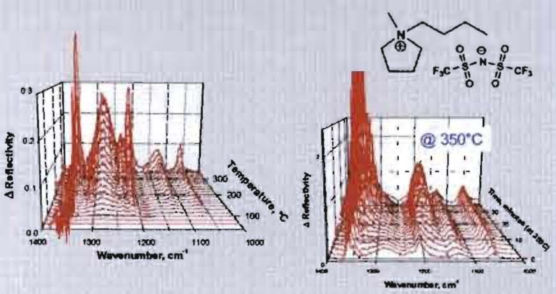
- Ionic liquids often considered thermally stable to > 300°C
- Decomposition determined by TGA "onset"





Thermal Stability of Ionic Liquids

- TGA measures decomposition by mass loss only
- See changes in IR at temp as low as 150°C - *irreversible*



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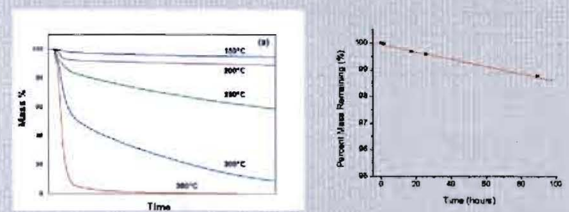
Isothermal Characterization

- Isothermal TGA to show stability at different temperatures
- $T_{0.01/10}$ - temperature at which 1% degradation – as determined by mass loss – occurs in 10 hours (271°C for [C4mpy][Tf_2N])

Wooster, T. J.; Johanson, K. M.; Fraser, K. J.; MacFarlane, D. R.; Scott, J. L. *Green Chem.*, 2006, 8, 691.



*R. A. Osteryoung, J. S. Wilkes, K. Seddon, R. Rogers, and many others

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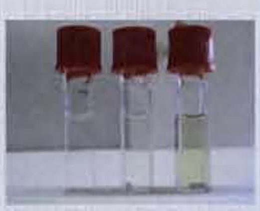
Purity is Application Specific

- Purity is application specific
- Consider effects of studying reaction in ILs at elevated temperatures
- If needed, check UV-Vis or fluorescence if using heating to dry ILs



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Exotic Ionic Liquid Materials for Optical and Magnetic Applications

- Large PR4 salts results almost entirely in RTILs
- Utilize stabilized organic radicals for electrochromic materials
- Paramagnetic ionic liquids can be manipulated with external H
- Response of ionic liquids to high intensity IR
- Purity is application specific
- Consider effects of studying reaction in ILs at elevated temperatures
- If needed, check UV-Vis or fluorescence if using heating to dry ILs

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Summary

- Synthesis of a number clusters as initial models for light emitting materials
- Synthesis of ionic liquid POM clusters containing Eu^{3+} and Tb^{3+}
- Synthesis of polymer containing Ln^{3+} sandwich POM clusters
- Study of the energy transfer of POM clusters to luminescent centers
- Strong collaboration – developing deep interactions with cross-disciplined team to develop several capabilities in application aspect of light emitting materials, and more fundamental capabilities in chemistry, materials, theory, and characterization

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Acknowledgements

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  - Materials Chemistry Group, LDRD
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  - National Academies of Science/National Research Council
- Cytec Canada
  - Phosphonium ILs (Al Robertson)

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