Ionic Liquids: A New Class of Sensing Materials

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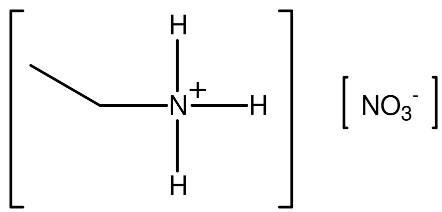
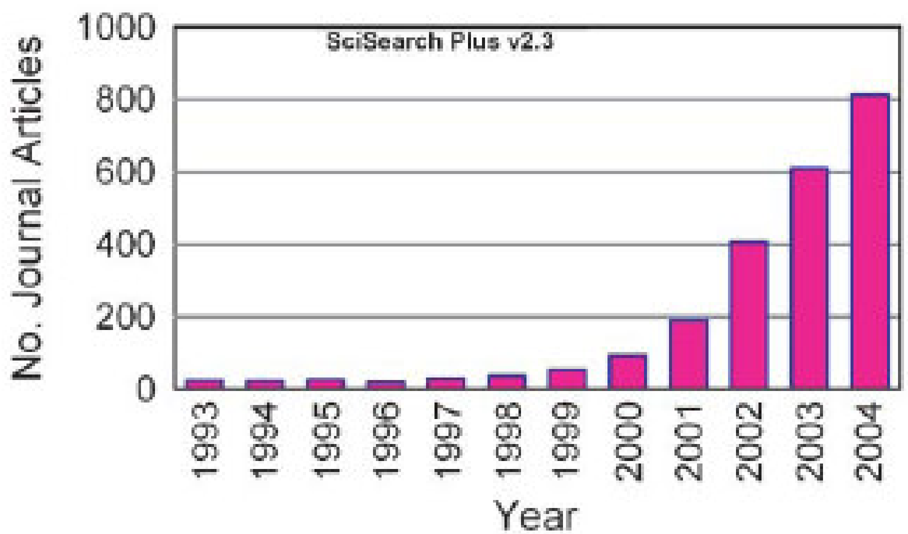
History and progress

- First ionic liquid: ethylammonium nitrate (1914, Paul Walden)



M.P. 12ºC

- Recent progress



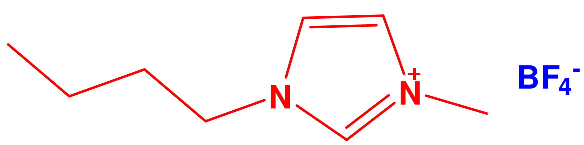
Bright et al. *Analyst*, **2005**, *130*, 800

Outline

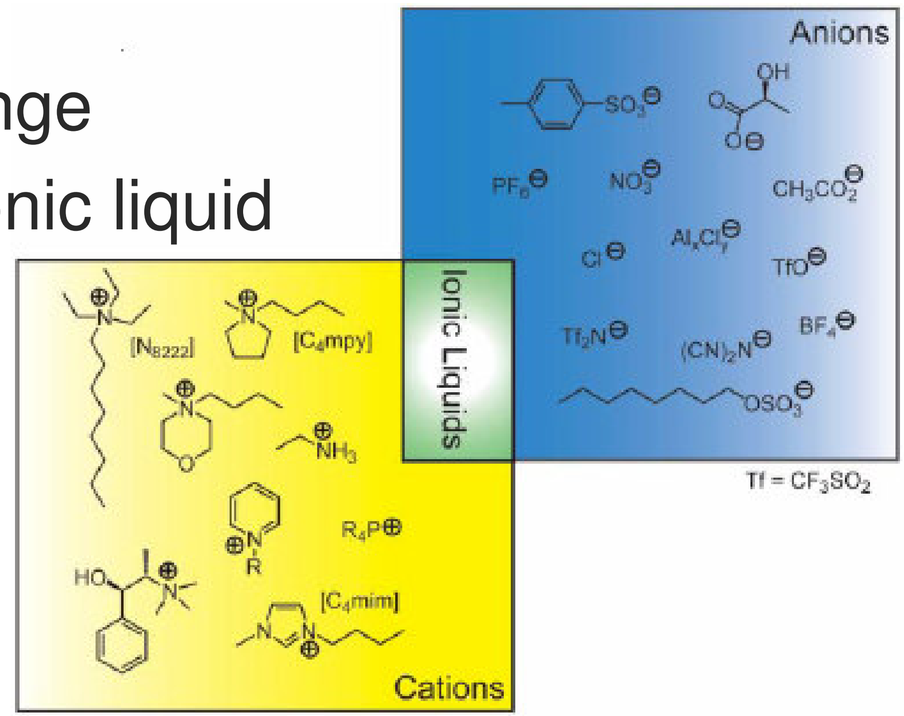
- Introduction
  - What is ionic liquid?
  - Features
  - Applications
- Sensor applications
  - Amperometric biosensor
- Conclusions

Introduction

- What is ionic liquid (IL)?
  - Molten salts (M.P. <100ºC)
  - (Semi)-organic
  - Appreciable liquid range
  - Room temperature Ionic liquid (RTIL) M.P. < 25ºC

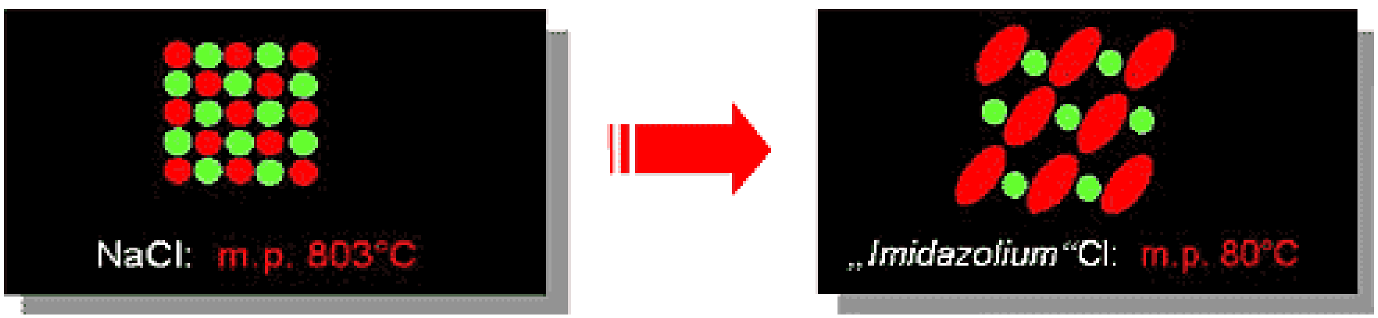


1-butyl-3-methylimidazolium hexafluorophosphate



Bright et al. *Analyst*, **2005**, *130*, 800

Why are ionic liquids “liquids”?



Traditional salts like sodium chloride are able to efficiently pack to form a crystal lattice

With ionic liquids, the cations are asymmetrically substituted with different length groups to prevent the packing of the cations/anions into a crystal lattice

Features

- Very low vapor pressure
- High thermal stability (~250-400ºC)
- Variable viscosity
- Hydrophobic or hydrophilic
- Capable of undergoing multiple solvation* interactions

*Solvation: attraction and association of solvent and solute
hydrogen bonding, ion-dipole and dipole-dipole attractions or
van der Waals forces.

Application

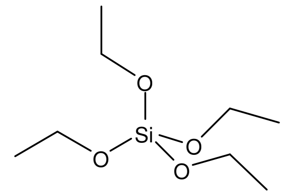
- Analytical extractions and separations
  - Liquid/liquid extraction and liquid phase microextraction
  - Mobile phase additives in HPLC
  - Stationary phases in GC
  - Run buffer additives in CE

Application

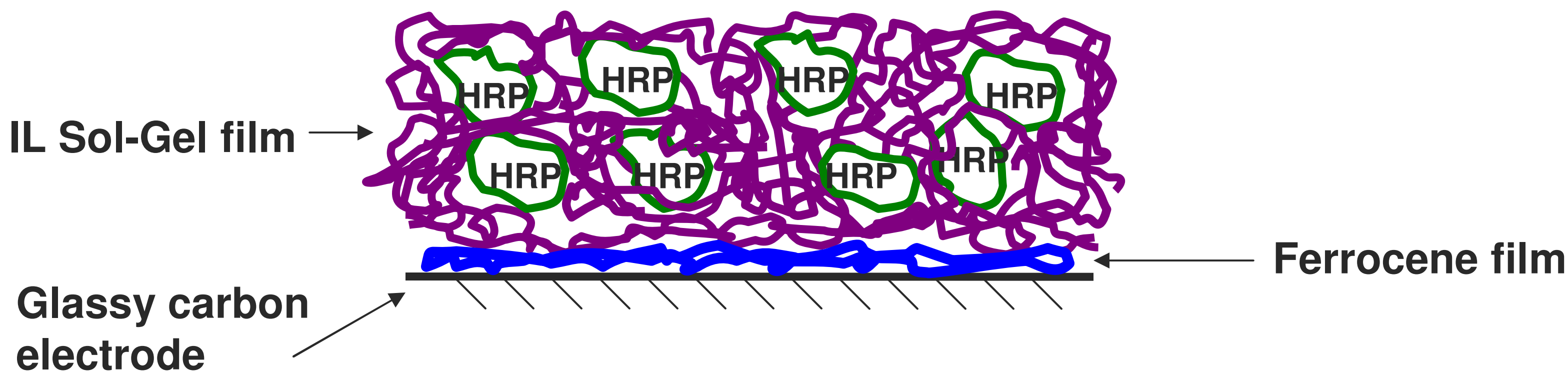
- An unorthodox matrix for analysis
  - Matrices for MALDI
- Sensor
  - QCM sensor
  - Optical sensor
  - Electrochemical sensor

Electrochemical sensor

- Ionic liquid sol–gel matrix
  - Tetraethyl orthosilicate (TEOS)

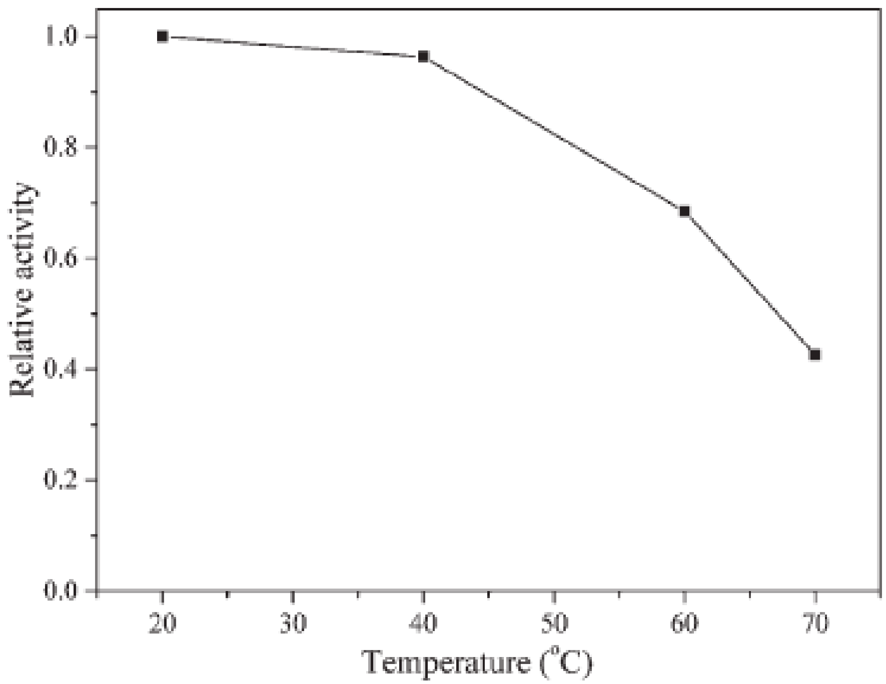


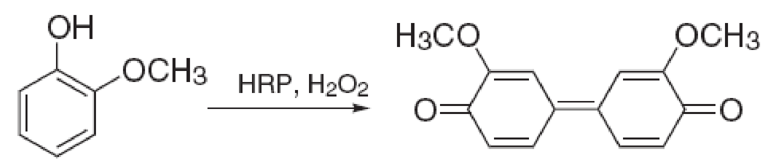
  - 1-Butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF4^-$)
  - Horseradish peroxidase (HRP)



Scheme 1 Sensor assembly. Li et al. *Chem. Commun.*, **2005**, *1778–1780*

Thermal stability





Guaiacol

Major product, UV@470nm

Kobayashi et al. *Chemistry Letters,* **2004,** *33(7),* 796.

Fig. 1 The thermal stability of HRP–IL@GEL. Each sample was treated at the stated temperature for 30 min. The activity assays were carried out in phosphate buffer solution (pH 6.86) with 1.5 mM of H_2O_2,1 mM of guaiacol and 5.7 mg of HRP–IL@GEL at ambient temperature. Li et al. *Chem. Commun.,* **2005**, *1778–1780*

Activity assay

- Colorimetric exp. with Guaiacol
  - UV every 2min for 60min
- 30-fold increase in activity
  - HRP–IL@GEL was assayed to be of 465U/gram HRP
  - Specific activity of the HRP@GEL was only 15.5U/per gram HRP

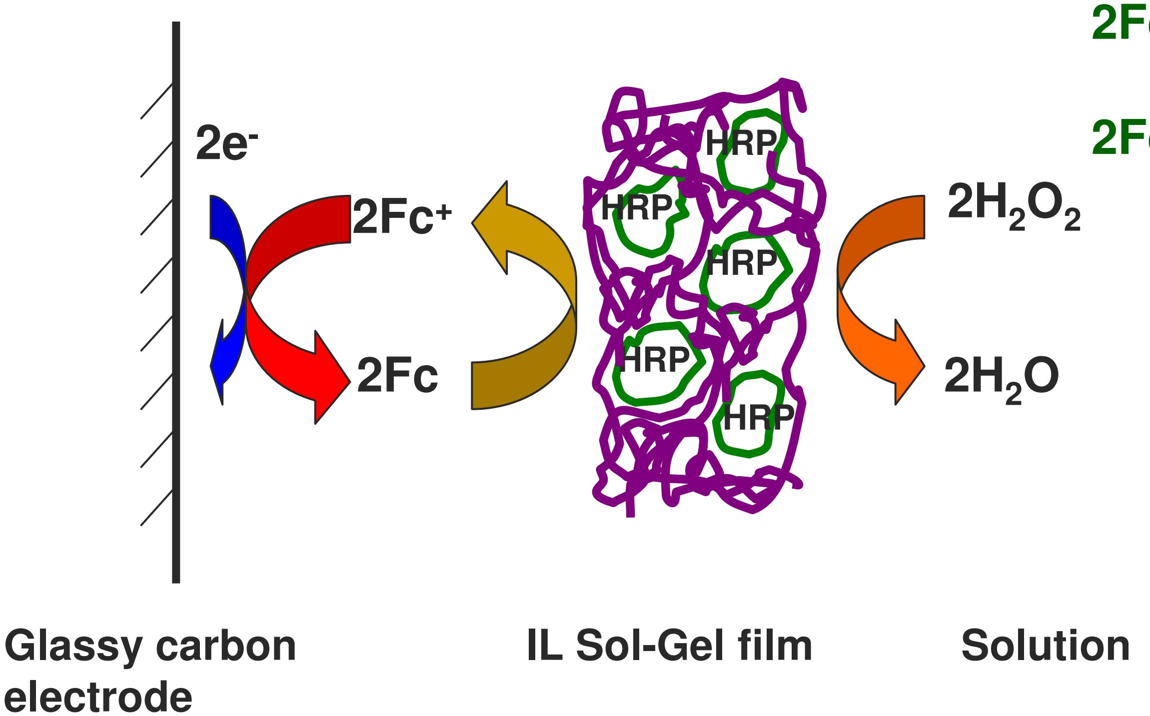
Li et al. *Chem. Commun.*, **2005**, *1778–1780*

Electrochemical process

HRP → HRP(ox) + 2e

2Fc + HRP(ox) → 2Fc+ + HRP

2Fc+ + 2e → Fc



Scheme 2 Electrochemical process. Li et al. *Chem. Commun.*, **2005**, *1778–1780*

Cyclic voltammetry

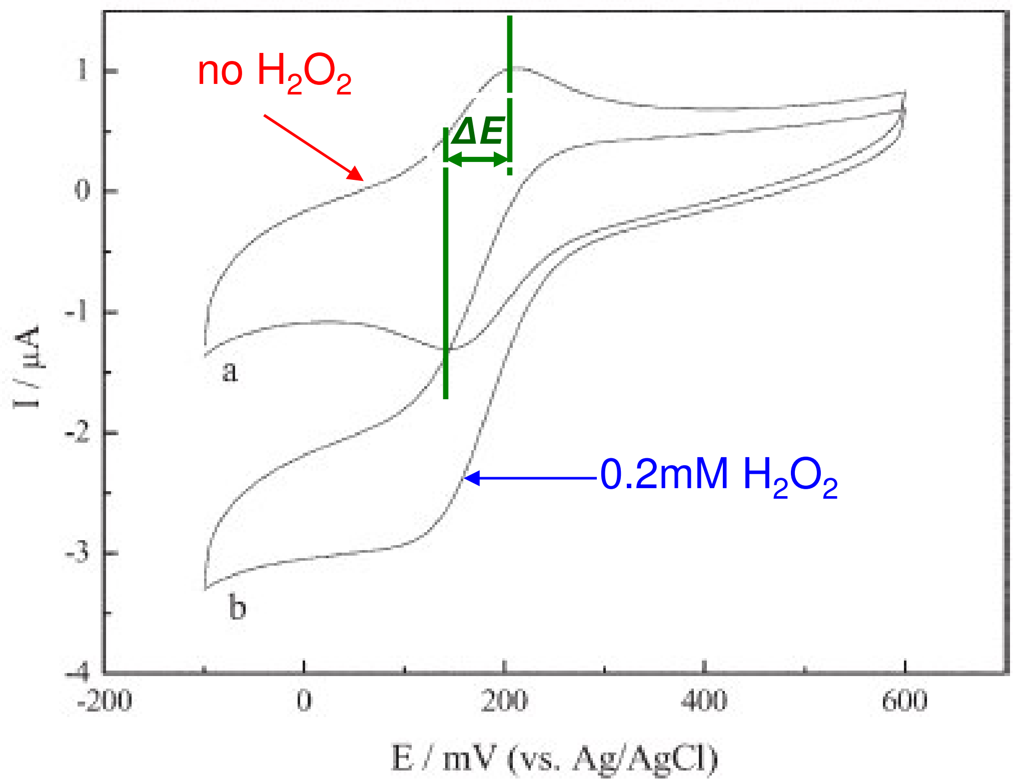
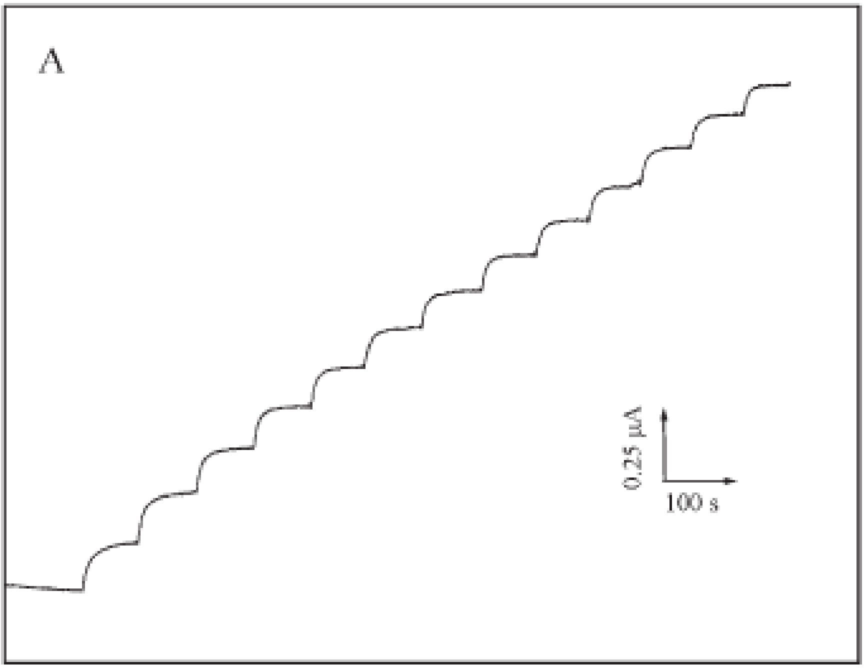


Fig. 2 Cyclic voltammograms of the IL enzyme electrode at a scan rate of 50 mV/s in 0.05MPBS (pH 7.0) containing (a) 0, (b) 0.2mM H_2O_2.
Li et al. *Green Chem.,* **2005**, *7*, 655.

ΔE = 64mV ~ 59mV
good one electron reversible process
$Fc \leftrightarrow Fc^+ + e$

$HRP \rightarrow HRP(ox) + 2e$
$2Fc + HRP(ox) \rightarrow 2Fc^+ + HRP$
$2Fc^+ + 2e \rightarrow Fc$

Amperometric response

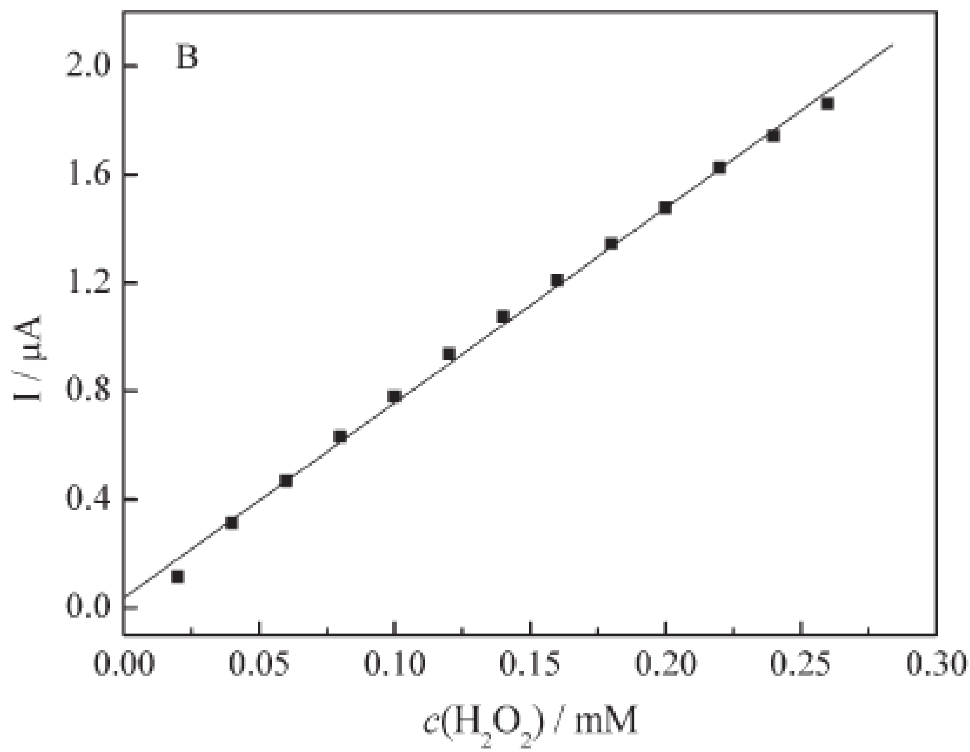


Response was faster than previous study: achieve steady state current within 10s vs 16s (Tan et al. *Analyst,* **1997**, *122,* 1431.)

Uniform porous structure of the IL sol-gel matrix, and conductivity of IL

Fig. 3 (A)Typical current–time response curves for the biosensor upon successive additions of 0.02 mM H_2O_2 into pH 7.0 PBS. Applied potential, 0 mV (vs. Ag/AgCl). Li et al. *Green Chem.*, **2005**, *7*, 655.

Amperometric response



Sensitivity: 7.2 μA/mM H_2O_2
vs 67μA/mM H_2O_2
(Tan et al. *Analyst,* **1997**, *122,* 1431.)

Detection limit of the biosensor was 1.1 mM at a S/N of 3.

Fig. 3 (B)The resulting calibration plot for the biosensor upon successive additions of 0.02 mM H_2O_2 into pH 7.0 PBS. Applied potential, 0 mV (vs. Ag/AgCl). Li et al. *Green Chem.,* **2005**, *7*, 655.

Summary

- Unique structures of IL-HRP@GEL
  - OH net work
  - Reduced deactivating or denaturing thermal motion
  - hydrogen bond and the electrostatic interaction between IL and enzyme resulted in a high kinetic barrier for the unfolding of the enzyme

Conclusions

- Figure of merits
  - Good thermal stability
  - Improved activity
  - Short response time
  - Dramatically increased sensitivity
- Predict a new class of sensing materials

Reference

1. Bright et al. *Analyst*, **2005**, *130*, 800.
2. Li et al. *Chem. Commun*., **2005**, 1778.
3. Kobayashi et al. *Chemistry Letters,* **2004,** *33(7),* 796.
4. Li et al. *Green Chem.,* **2005**, *7*, 655.
5. Tan et al. *Analyst,* **1997***, 122,* 1431.

Thank you for your attention!!

Enzyme assay

- Enzyme units
  - SI unit: katal, 1 katal = 1 mol s^{-1}
  - 1 enzyme unit (EU) = 1 μmol min^{-1}
- Types of assay
  - Initial rate experiments
  - Progress curve experiments
  - Transient kinetics experiments
  - Relaxation experiments

http://en.wikipedia.org/wiki/Enzyme_assay