

# Wearable electrochemical biosensors for monitoring performance athletes

19/08/11

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19/08/11



@cyrusmekon  
#Berkeley

# Contents

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- The need for wearable sensors.
- Wearable electrochemical sensors.
- Diverse material for sensing platforms.
  - Ionic Liquids
- Electrochemical biosensing: The road ahead.
  - Ionogels
- Conclusions.

# National Centre for Sensor Research

- Over 260 f/t researchers and support staff
- 23 affiliated faculty
- Investments and income since 1999 now approaching €100 million
- 1500 m<sup>2</sup> well-equipped specialist lab space and offices
- Phase II expansion completed 2008 (1300 m<sup>2</sup>)



**CLARITY**

The Centre for Sensor Web Technologies



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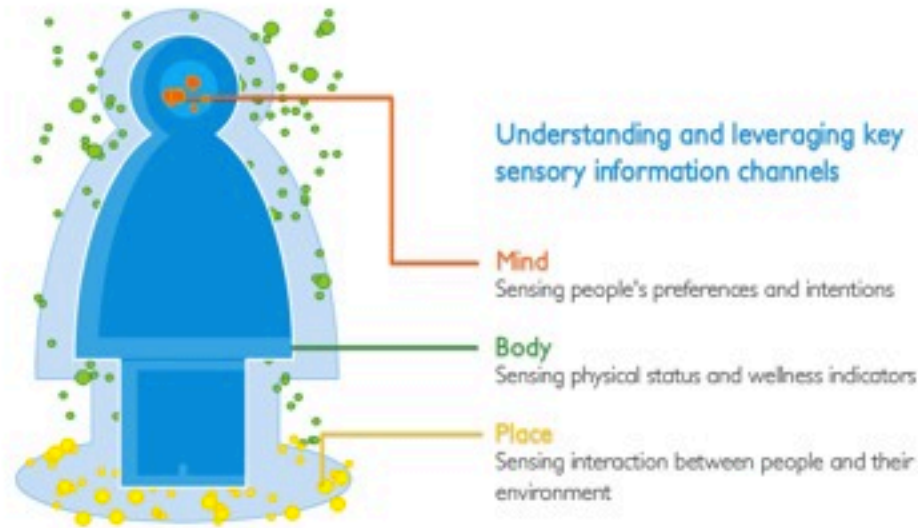


**CLARITY**

The Centre for Sensor Web Technologies



## Vision: Sensing Mind, Body & Place

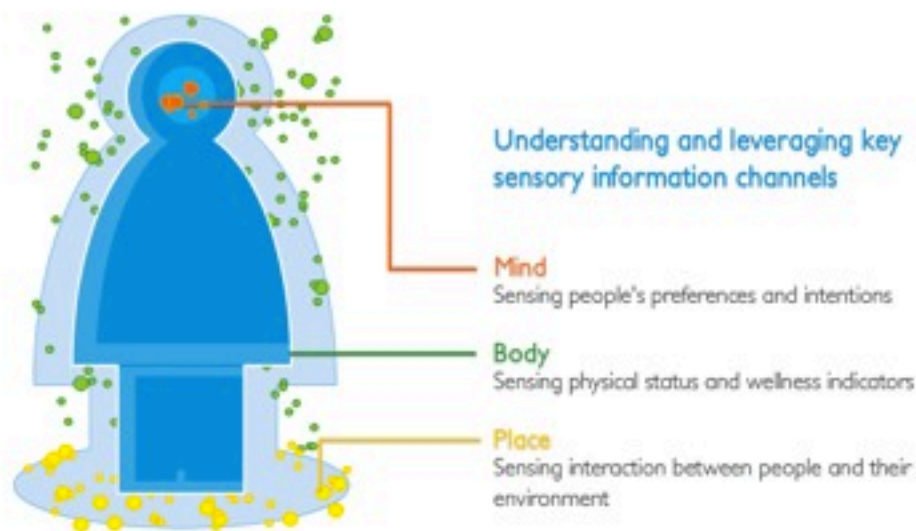


- 5-year, €16.4 million research program to develop next generation Sensor Web Technologies with significant environmental focus
- Brings together fundamental materials science, functional polymers, device prototyping, energy management, adaptive middleware, wearable sensors, distributed environmental monitoring.



[www.clarity-centre.org/](http://www.clarity-centre.org/)

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- 5-year, €16.4 million research program to develop next generation Sensor Web Technologies with significant environmental focus
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[www.clarity-centre.org/](http://www.clarity-centre.org/)

# The need for wearable sensors.

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- Wearable sensors allow the continuous monitoring of a person's physiology in a natural setting.
- Health-monitoring systems using electronic textiles are mainly targeting applications based upon physiological parameter measurements, such as body movements or electrocardiography (ECG).
- However, due to their relative complexity, there is very little activity in the development of real-time wearable chemo/bio sensing for sports applications.



# The need for wearable sensors.

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- Micro-Total-Analysis-Systems and Lab-on-a-Chip technology are widely used in analytical chemistry and biotechnology<sup>[1]</sup> but are still rarely used in other areas like sports science.
- In this field, wearable sensors are becoming increasingly employed, through the use of embedded transducers or smart fabrics for monitoring parameters like breathing rate, heart rate and footfall.
- These sensors require that the desired sample of analysis, usually a body fluid such as sweat is delivered to the sensor's active surface, whereupon a reaction happens and a signal is generated.

[1] K.-i. Ohno, K. Tachikawa and A. Manz, *ELECTROPHORESIS*, 2008, 29, 4443-4453.

[2] D. Diamond, S. Coyle, S. Scarmagnani and J. Hayes, *Chem. Rev.*, 2008, **108**, 652-679.

[3] P. Bhandari, T. Narahari and D. Dendukuri, *Lab on a Chip*, 2011, **11**, 2493-2499.

# The need for wearable sensors.

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- Moreover the system must be low cost, while still being robust, miniature, flexible, washable, reusable or disposable[2].
- All these requirements point to micro-fluidic devices as the key tools for improving wearable chemo-/bio-sensing[3].
- To open a dramatically wider field of applications, chemical measurements on body fluids (blood, sweat, saliva and urine) are needed.

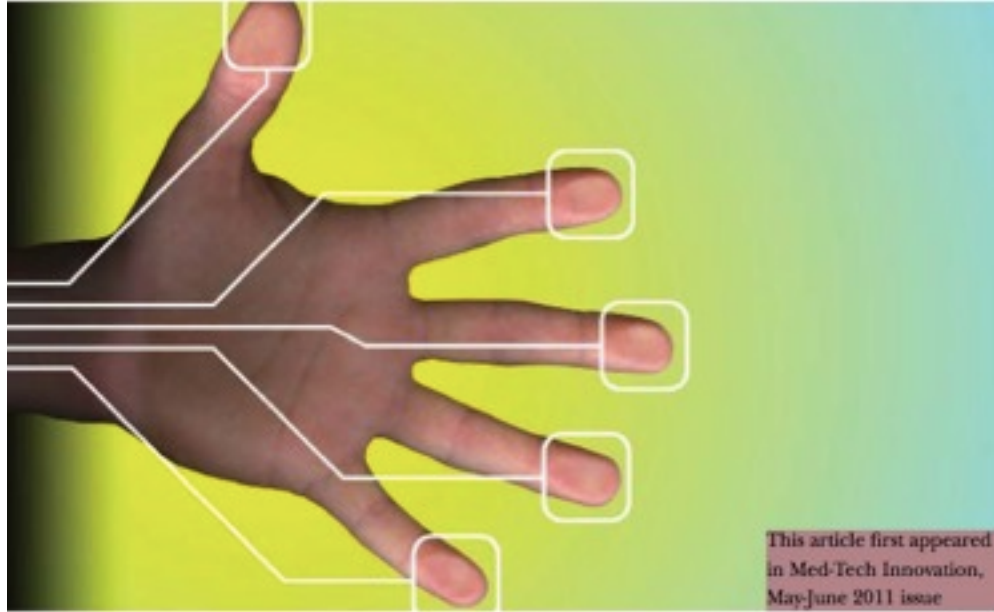
[1] K.-i. Ohno, K. Tachikawa and A. Manz, *ELECTROPHORESIS*, 2008, 29, 4443-4453.

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# The need for wearable sensors.

Med-Tech Innovation  
Design



Mid-tech Innovation  
May - June 2011



Press release

## Remote Sensing and the **AGEING POPULATION**

A research group at Dublin City University headed by Professor Dermot Diamond is investigating technologies that will provide new monitoring services in the home.

# The need for wearable sensors.

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- This area of research is unfortunately still poorly developed due to the difficulty in sampling such fluids. The BIOTEX project tackled some of these problems by developing a textile-based system to collect and analyze sweat by using a textile-based sensor capable of performing chemical measurements[2].
- The great advantage of analyzing sweat for health monitoring is that it is noninvasive, reasonably accessible, with the potential to provide valuable physiological information[4].
- However, advances in this direction have been limited due to the difficulty in obtaining uncontaminated samples.

[2] D. Diamond, S. Coyle, S. Scarmagnani and J. Hayes, *Chem. Rev.*, 2008, **108**, 652-679.

[4] J. Massie, K. Gaskin, P. V. Asperen and B. Wilcken, *Pediatric Pulmonology*, 2000, 29, 452-456.

# Wearable Electrochemical Sensors

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- Wearable sensors ideally should have the ability to monitor the physiology of the wearer and the surrounding environment.
- Wearable sensor may respond to physical changes, such as body temperature or movements of the joints.
- A chemical sensor (chemosensor) detects and measures a particular chemical in its environment.
- Biosensors are closely related to chemical sensors, distinguished by the molecular recognition element which is biological in nature (e.g. enzyme, receptor, DNA, antibody, or microorganism)[5]



[5] S. Coyle, F. Benito-Lopez, T. Radu, K. T. Lau and D. Diamond, *J. Text. App.*, 2010, **14**, 64.

## PHYSICAL SENSORS

Breath rate, heart rate, activity, posture, skin temperature...

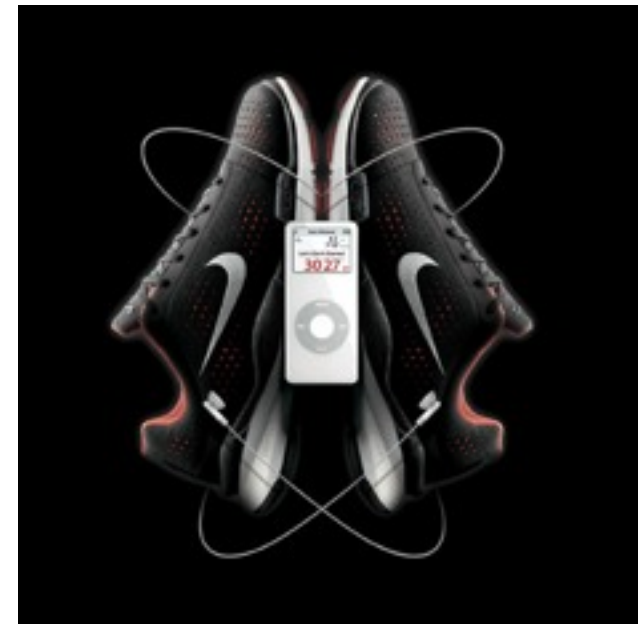
## PHYSICAL SENSORS

Breath rate, heart rate, activity, posture, skin temperature...



### TRAINTRAK™

heart rate, respiration rate, posture, activity, and GPS location



### NIKE-APPLE iPOD SPORTS KIT



LIFESHIRT®  
Bipolar affective disorder and schizophrenia  
'Activity'

# Current Wearable Sensors

Scosche myTrek sends workout vitals to your iPhone, starts shipping now for \$130 (video)

By Zach Honig posted Aug 9th 2011 9:40PM

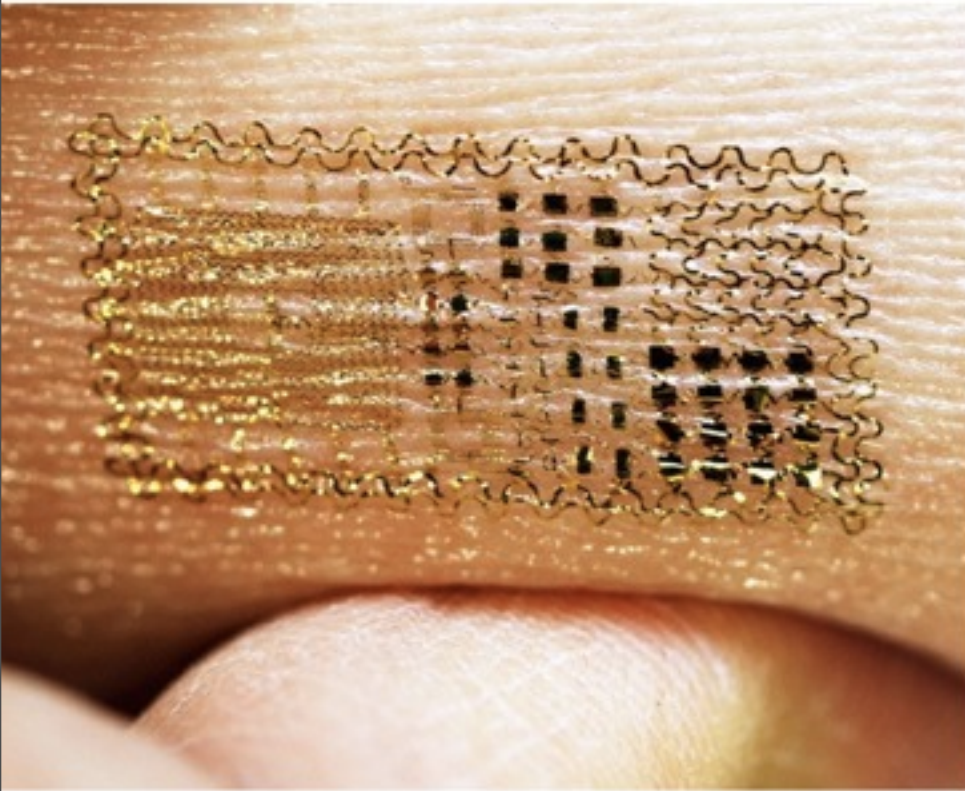


The myTREK utilizes two LEDs combined with a photo sensor to detect minute changes in the user's blood pressure to accurately measure pulse. A built-in accelerometer allows the myTREK to adjust for movement during exercise from the user's heartbeat allowing for an extremely accurate measurement of pulse and calories burned.



# Current Wearable Sensors

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John Rogers @ University of Illinois

11/08/2011

Ultra-thin, self-adhesive electronics device that can effectively measure data about the human heart, brain waves and muscle activity--all without the use of bulky equipment, conductive fluids or glues.



Link :[http://www.nsf.gov/news/news\\_summ.jsp?cntn\\_id=121343&org=NSF&from=news](http://www.nsf.gov/news/news_summ.jsp?cntn_id=121343&org=NSF&from=news)

# Wearable electrochemical Sensors

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## Why sweat?

- The great advantage of analyzing sweat for health monitoring is that it is noninvasive, easily accessible, and it offers valuable physiological information
- The sweat test previously used for the diagnosis of cystic fibrosis (CF)
- This is a once-off test that is performed in newborns and the diagnosis is based on sodium and chloride concentration levels.

# The BIOTEX project

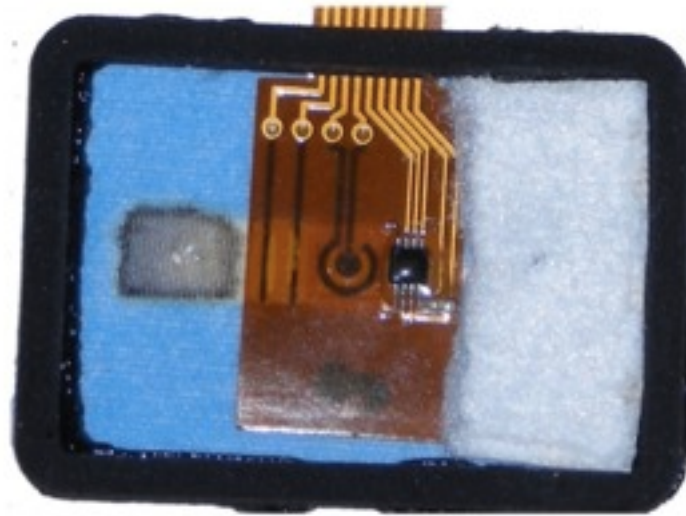
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- BIOTEX was an EU-funded project that aimed to develop textile sensors to measure physiological parameters and the chemical composition of body fluids, with a particular interest in sweat.
- Wearable sensing system had been developed that integrates a textile-based fluid handling system for sample collection and transport with a number of sensors including sodium, conductivity, and pH sensors.
- It was possible to monitor a number of physiological parameters together with sweat composition in real time.


 [6] S. Coyle *et al.*, *IEEE Transactions on Information Technology in Biomedicine*, **14** (2). pp. 364-370, 2010.

# The BIOTEX project

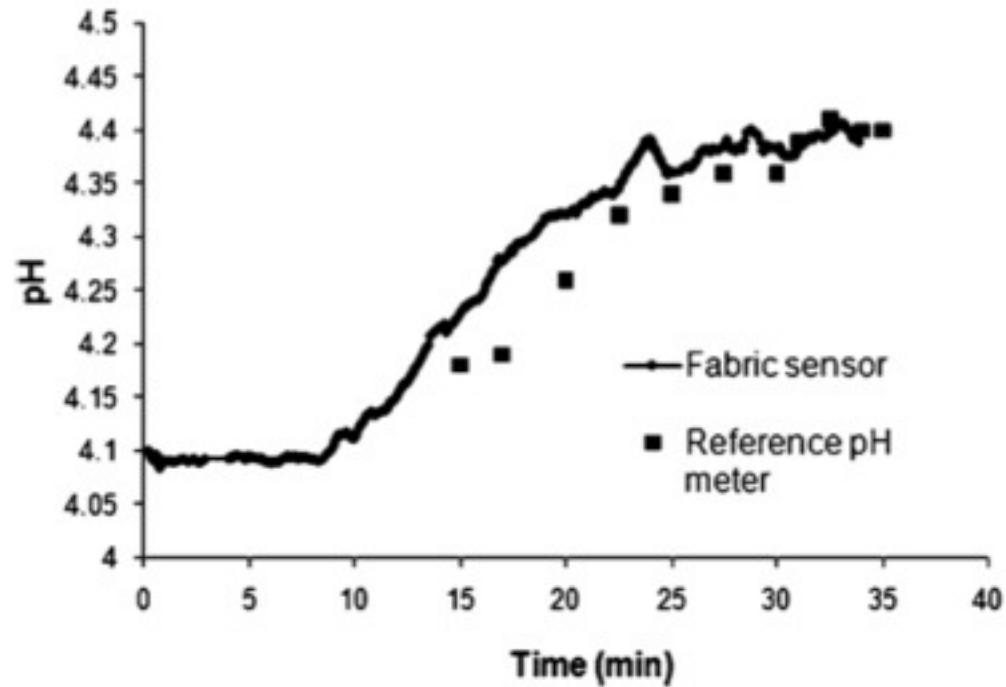
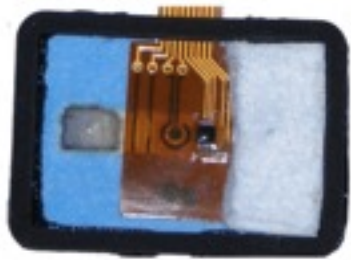
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- Multiparametric patch containing pH indicator, conductivity, sodium, and temperature sensors.

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# The BIOTEX project

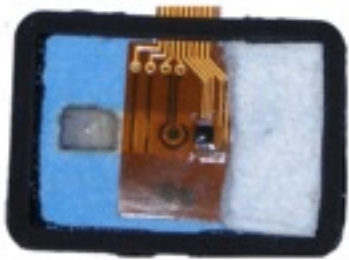


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# The BIOTEX project

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- The textile pump has been designed in such a way that it can successfully collect sweat from human subjects during exercise.



- Sweat is analyzed by pH, sodium, and conductivity sensors and stores the sample in an absorbent in such a way as to allow for a continuous flow of fresh sweat.

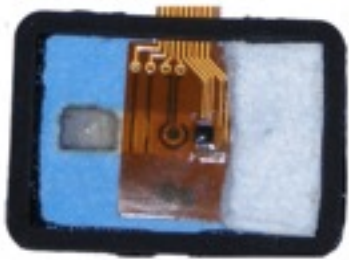
- The ability to measure changes in sweat electrolyte concentrations can assist people in choosing the correct level of hydration and avoid the need for medical intervention.

[6] S. Coyle *et al.*, *IEEE Transactions on Information Technology in Biomedicine*, **14** (2). pp. 364-370, 2010.

# The BIOTEX project

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<http://www.biotex-eu.com/>

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# In-house UV Sensor

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# In-house UV Sensor



2 hrs Sicily



# In-house UV Sensor



2 hrs Sicily



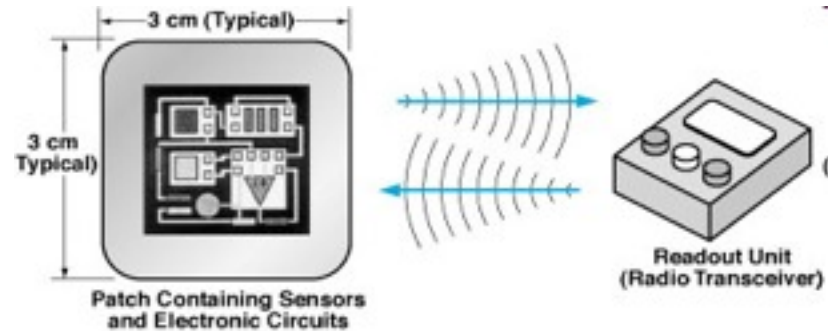
Dublin



# Current Wearable Sensors



Gluowatch



NASA: Wearable sensor patches



Abbot Freestyle Navigator

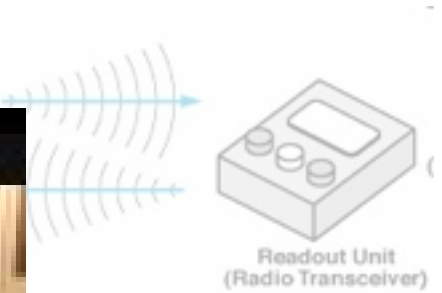


PharmChek Sweat Patch

# Current Wearable Sensors



Gluowatch



Multiple sensor patches



Abbot Freestyle Navigator

**SAMPLING BIG ISSUE!!!!**

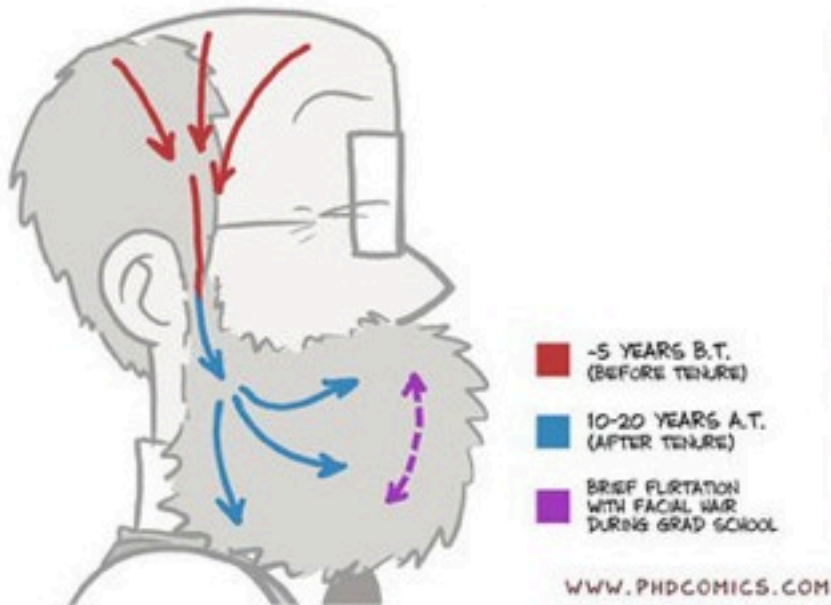
<http://www.youtube.com/watch?v=pmMo3AYKOk0>



PharmChek Sweat Patch

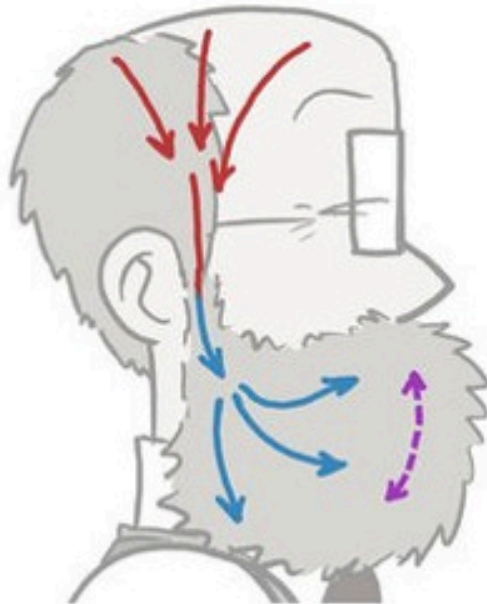
# For the Postgrads

HAIR MIGRATION PATTERN OF  
THE MALE PROFESSORIAT.



# For the Postgrads

HAIR MIGRATION PATTERN OF  
THE MALE PROFESSORIAT.



- -5 YEARS B.T.  
(BEFORE TENURE)
- 10-20 YEARS A.T.  
(AFTER TENURE)
- BRIEF FLIRTATION  
WITH FACIAL HAIR  
DURING GRAD SCHOOL

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# Ionic Liquids: A brief introduction

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## What is an Ionic Liquid (IL)?

- According to current convention, a salt melting below the normal boiling point of water is known as an “ionic liquid”



# Ionic Liquids: A brief introduction

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- The first IL was reported almost a century ago by Walden<sup>[7]</sup>, who protonated ethylamine with nitric acid to yield ethylammonium nitrate

[7] P. Walden, *Bull. Acad. Sci. St. Petersburg*, 1914, 405.

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- The first IL was reported almost a century ago by Walden<sup>[7]</sup>, who protonated ethylamine with nitric acid to yield ethylammonium nitrate
- The number of potential anion-cation combinations available reputedly equate to one trillion ( $10^{12}$ ) different ILs<sup>[8]</sup>

[7] P. Walden, *Bull. Acad. Sci. St. Petersburg*, 1914, 405.

[8] R. D. Rogers and K. R. Seddon, *Ionic Liquids as Green Solvents: Progress and Prospects*, American Chemical Society, 2003.

# Ionic Liquids: A brief introduction

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What is an Ionic Liquid (IL)?

De-localized charges

Asymmetric ion shape  
(poor packing)



Melting point below 100 °C

# Ionic Liquids: A brief introduction

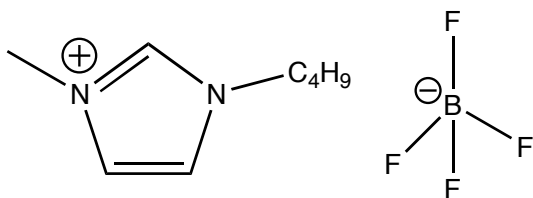
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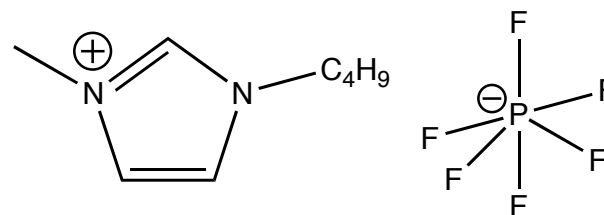
Asymmetric ion shape  
(poor packing)

Melting point below 100 °C

Typical ions to form ionic liquids

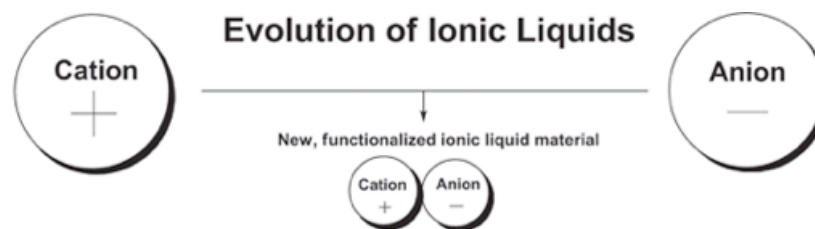


Hydrophilic  
T<sub>g</sub> -81°C only



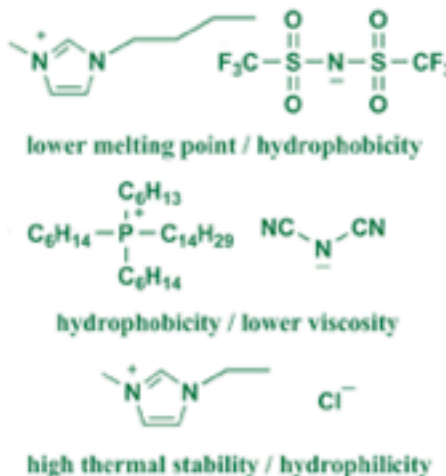
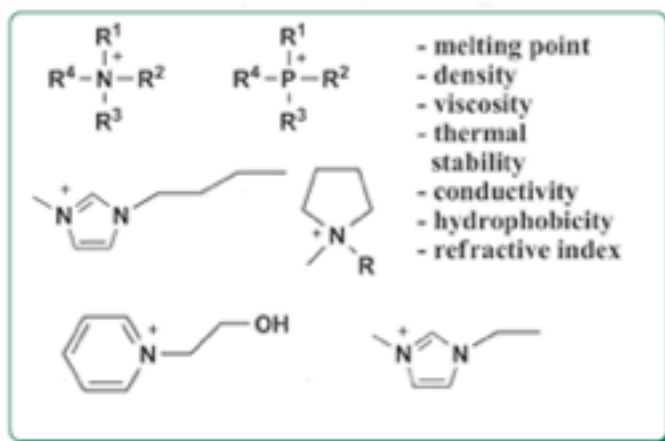
Hydrophobic  
M.P. of 6.4°C

# Ionic Liquids: A brief introduction

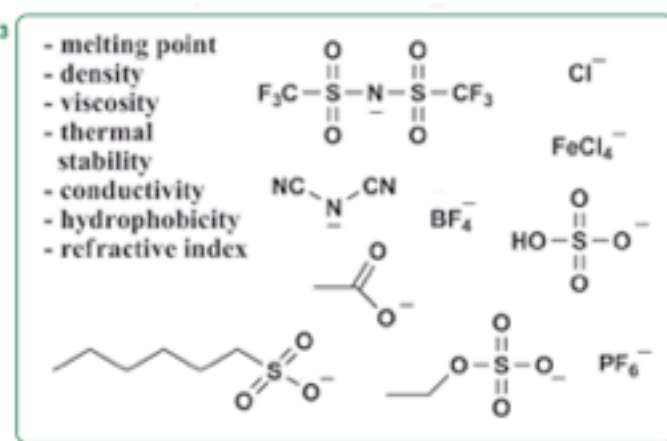


## Generation 1: ILs with unique tunable physical properties

### Physical property

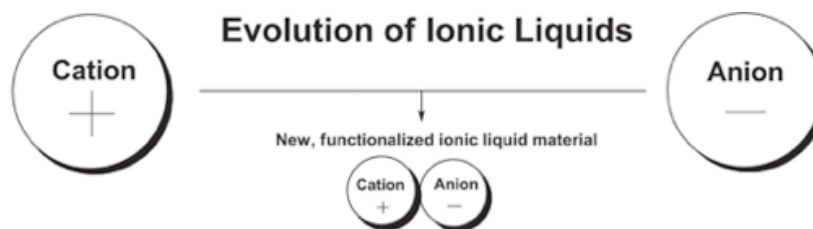


### Physical property



[9] W. L. Hough, M. Smiglak, H. Rodriguez, R. P. Swatloski, S. K. Spear, D. T. Daly, J. Pernak, J. E. Grisel, R. D. Carliss, M. D. Soutullo, J. H. Davis and R. D. Rogers, *New J. Chem.*, 2007, 31, 1429-1436.

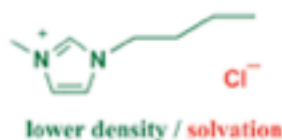
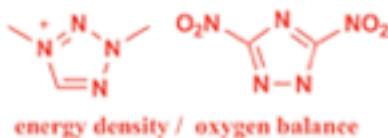
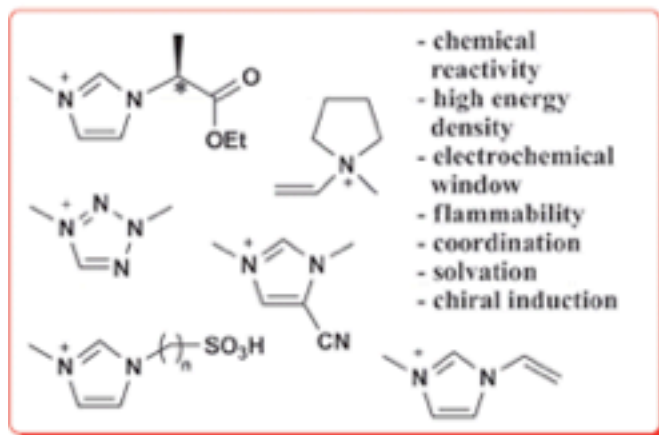
# Ionic Liquids: A brief introduction



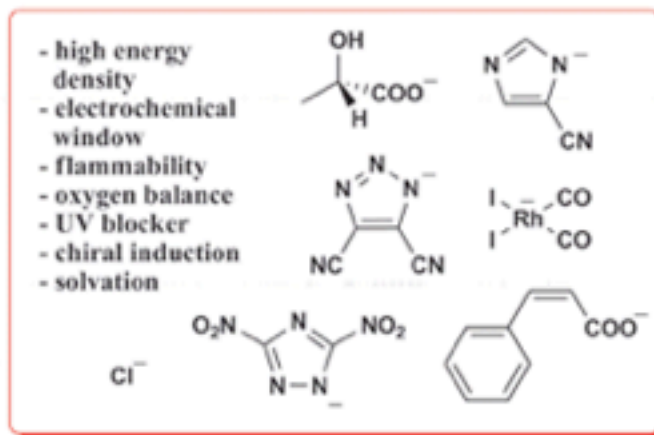
## Generation 2:

ILs with targeted chemical properties combined with chosen physical properties

### Chemical property

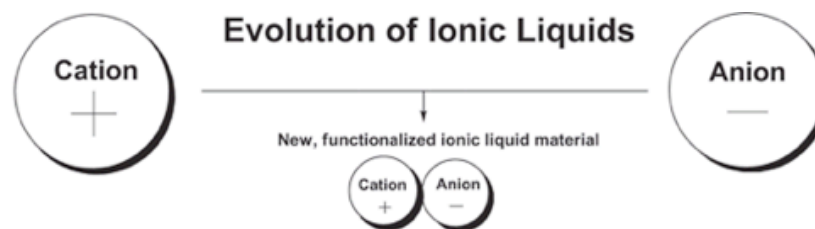


### Chemical property



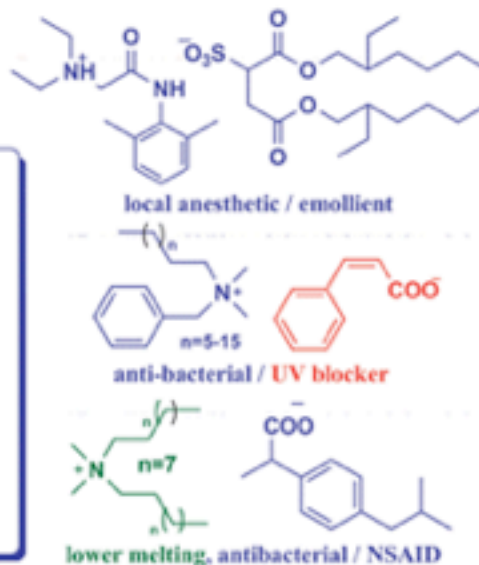
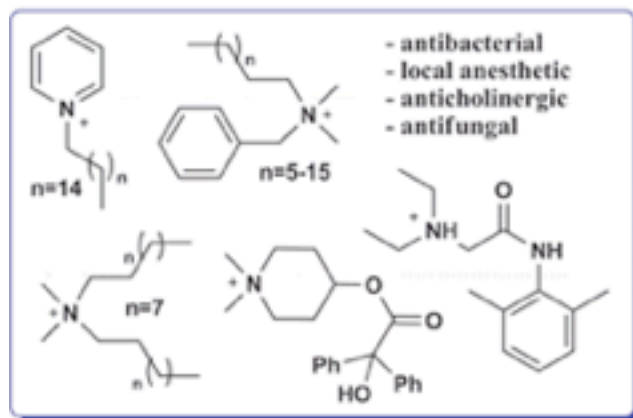
[9] W. L. Hough, M. Smiglak, H. Rodriguez, R. P. Swatloski, S. K. Spear, D. T. Daly, J. Pernak, J. E. Grisel, R. D. Carliss, M. D. Soutullo, J. H. Davis and R. D. Rogers, *New J. Chem.*, 2007, 31, 1429-1436.

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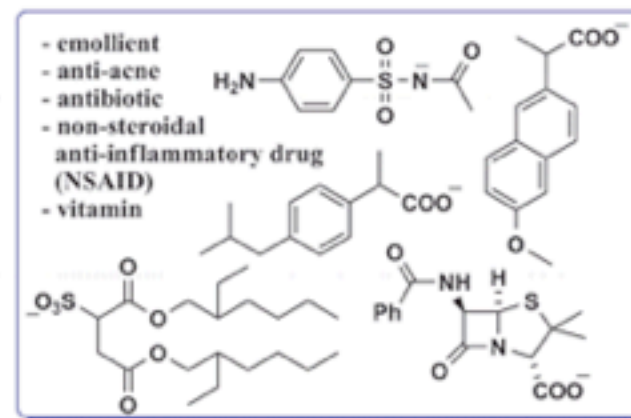


**Generation 3:**  
ILs with targeted biological properties combined with chosen physical and chemical properties

## Biological property



## Biological property

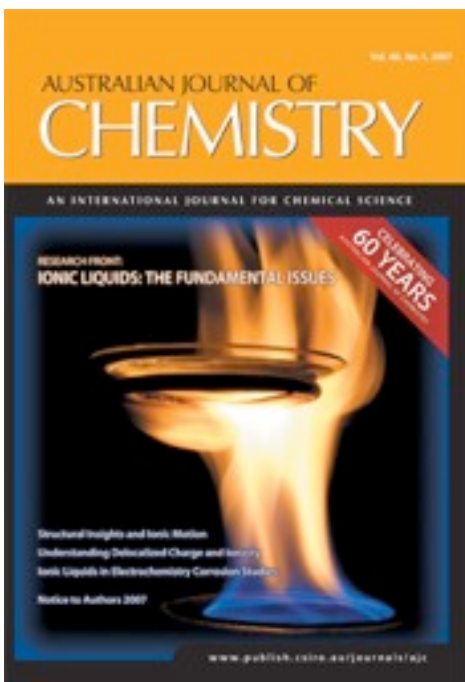


[9] W. L. Hough, M. Smiglak, H. Rodriguez, R. P. Swatloski, S. K. Spear, D. T. Daly, J. Pernak, J. E. Grisel, R. D. Carliss, M. D. Soutullo, J. H. Davis and R. D. Rogers, *New J. Chem.*, 2007, 31, 1429-1436.

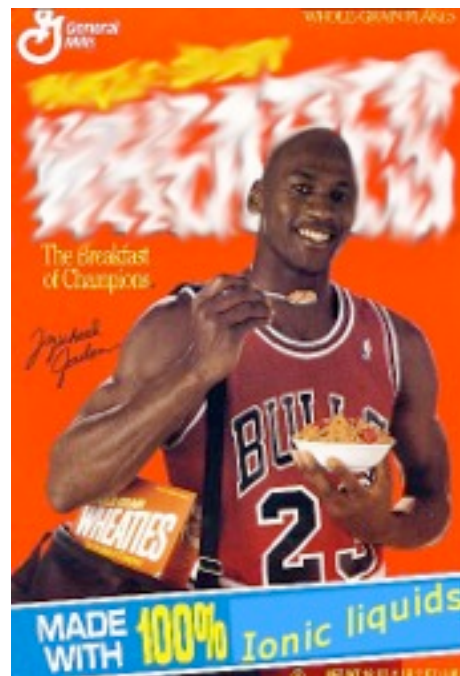
# Ionic Liquids: A brief introduction

## Subsets of ILs

- Phosphonium based ILs



- Bio compatible ILs





# Ionic Liquids: A brief introduction

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- Cytec<sup>R</sup> routinely produces tetraalkylphosphonium halides such as the ionic liquid trihexyl-tetradecyl phosphonium chloride

- Phosphonium based ILs



# Ionic Liquids: A brief introduction

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- Phosphonium based ILs



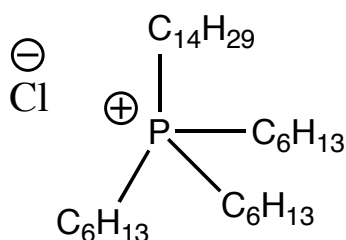
- Cytec<sup>R</sup> routinely produces tetraalkylphosphonium halides such as the ionic liquid trihexyl-tetradecyl phosphonium chloride
- Phosphonium ILs offer, in some cases, several advantages over other types of ILs, including, higher thermal stability, lower viscosity, and higher stability in strongly basic or strongly reducing conditions.
- Historically these compounds have been used as biocides<sup>[10]</sup> and phase transfer catalysts<sup>[11]</sup>

[10] D. Jerchel, *Chem. Ber.*, 1943, **76B**, 600.

[11] A. W. Herriott and D. Picker, *J. Am. Chem. Soc.*, 1975, **97**, 2345.

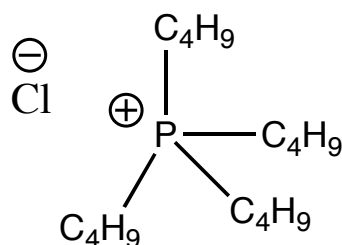
# Ionic Liquids: A brief introduction

- Phosphonium based ILs



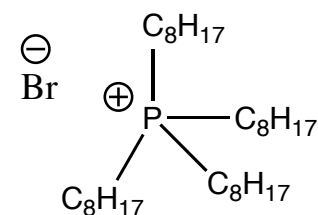
Trihexyl-tetradecyl phosphonium chloride,

Liquid at room temperature



Tetrabutyl phosphonium chloride

M.P 67 °C



Tetraoctyl phosphonium bromide

M.P 45 °C

# Ionic Liquids: A brief introduction

## Excellent Review



K. J. Fraser and D. R. MacFarlane,  
*Aust. J. Chem.*, 2009, **62**, 309-321.

### Phosphonium-Based Ionic Liquids: An Overview

Kevin J. Fraser<sup>A</sup> and Douglas R. MacFarlane<sup>A,B</sup>

<sup>A</sup>School of Chemistry, Monash University, Wellington, VIC 3800, Australia.

<sup>B</sup>Corresponding author. Email: Douglas.MacFarlane@sci.monash.edu.au

Phosphonium cation-based ionic liquids (ILs) are a readily available family of ILs that in some applications offer superior properties as compared to nitrogen cation-based ILs. Applications recently investigated include their use as extraction solvents, chemical synthesis solvents, electrolytes in batteries and super-capacitors, and in corrosion protection. At the same time the range of cation-anion combinations available commercially has also been increasing in recent years. Here, we provide an overview of the properties of these interesting materials and the applications in which they are appearing.

Manuscript received: 19 December 2008.

Final version: 9 March 2009.

#### Introduction

According to current convention, a salt that melts below the normal boiling point of water is known as an 'ionic liquid' (IL) or by one of many synonyms including low/melting/room temperature molten salt, ionic fluid, liquid organic salt, fused salt, and molten solvent.<sup>[1]</sup> The variation in properties between salts, even those with a common cation but different anions, is dramatic. For example, butylmethylimidazolium hexafluorophosphate [C<sub>4</sub>mim][PF<sub>6</sub>] is immiscible with water, whereas butylmethylimidazolium tetrakisfluoroborate [C<sub>4</sub>mim][TfF<sub>4</sub>] is water soluble.<sup>[2]</sup> This sort of variation in physical properties gave rise to Seddon's description of ILs as 'designer solvents'.<sup>[3]</sup> The number of potential anion-cation combinations possible reportedly equates to one trillion (10<sup>12</sup>) different ILs.<sup>[4]</sup> ILs have received much attention of late because of their potential application in green chemistry and as novel electrochemical materials. They have indeed become 'designer solvents', with many ILs now being designed for a specific application, for example as potential electrolytes for various electrochemical devices,<sup>[5-10]</sup> including rechargeable lithium cells,<sup>[11,12]</sup> solar cells,<sup>[13-15]</sup> actuators,<sup>[16-20]</sup> and double layer capacitors.<sup>[21-23]</sup>

Nitrogen-based cations, in particular *N*-methylimidazolium and pyrrolidinium salts, have been the subject of many of the publications in the field. A number of phosphonium cation-based ILs are also available and have a range of useful properties, but have been much less studied. Early reports regarding phosphonium ILs were published in the 1970s by Paretzki using stannate and germanate salts<sup>[24-26]</sup> and by Kocien et al.<sup>[24-40]</sup> in the 1980s centering on the use of molten tetrabutylphosphonium bromide as an ionic solvent. To some extent the slower uptake of work on phosphonium ILs can be attributed to the difficulty in synthesizing the starting materials, for example tetrabutylphosphine. Although phosphine derivatives have been available on a commercial scale since 1971, it was not until 1990 that tetrabutylphosphine became available on a large scale.<sup>[41]</sup> Since then tetrabutylphosphonium chloride and bromide have become widely available on a multi-ton scale, along with many other alkylphosphines and their corresponding quaternary phosphonium salts, in particular from Cytec Industries Inc.<sup>[42]</sup>

Variation of the four substituents on the phosphonium cation, along with the multitude of available anions, represents an enormous number of possible salts. Those commercially available as of November 2008, for example, can be found in Table 1.



Kevin J. Fraser received his B.Sc. in 2004 from the University of Aberdeen, Scotland. He recently completed his Ph.D. under the supervision of Professor D. R. MacFarlane entitled 'Physical Properties of Phosphonium Based Ionic Liquids' at Monash University, Melbourne. His current interests include air electrolysis for use in fuel cells and ionic liquid-based chemical sensors.

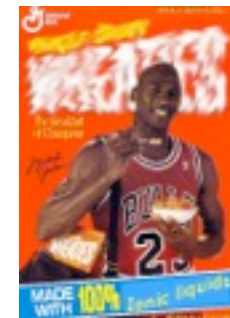


Professor Doug MacFarlane leads the Monash Ionic Liquids Group at Monash University. He is also the program leader of the Energy Program in the Australian Centre for Electromaterials Science. He was a Ph.D. graduate of Purdue University in 1992 and after postdoctoral work at Victoria University Wellington took up a faculty position at Monash University. Professor MacFarlane was recently awarded an Australian Research Council Federation Fellowship to extend his work on ionic liquids. He was elected to the Australian Academy of Sciences in 2007. His research interests include the chemistry and properties of ionic liquids and solids and their application in a wide range of technologies from electrochemical batteries, fuel cells, solar cells and corrosion prevention; to biotechnology (using ionic liquids and protein solubilization) and sugar processing.

# Ionic Liquids: A brief introduction

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## Bio compatible ILs

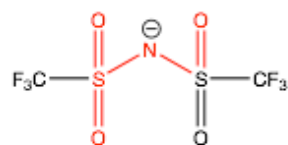


- In an attempt to steer away from fluoruous anions, a communication by Carter et al.<sup>[13]</sup> opened up a new field in the Ionic liquid world.
- The use of common sweeteners such as saccharin and acesulfamate were used in the formation of new ionic liquids.<sup>[13]</sup>
- These anions, in their alkali metal salt form, are widely used in foodstuffs and non-nutritive sweeteners



[13] E. B. Carter, S. L. Culver, P. A. Fox, R. D. Goode, I. Ntai, M. D. Tickell, R. K. Traylor, N. W. Hoffman and J. H. Davis, Jr., *Chem. Comm.*, 2004, 630.

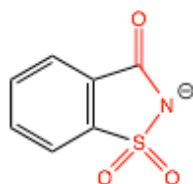
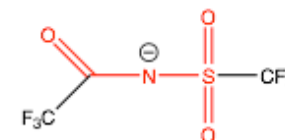
# Ionic Liquids: A brief introduction



Commonly used anion  
[NTf<sub>2</sub>]<sup>-</sup>

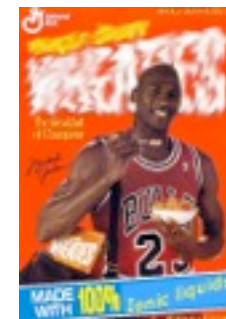
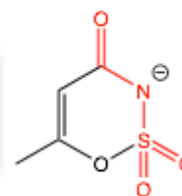
Exploring alternative  
analogues

2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide [TSAC]

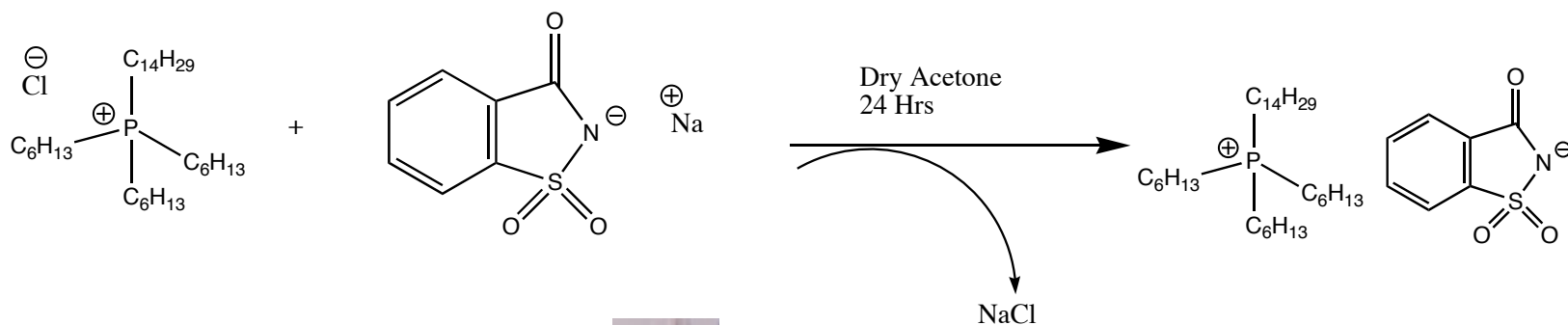


Saccharinate  
[Sacc]<sup>-</sup>

Acesulfamate  
[Ace]<sup>-</sup>

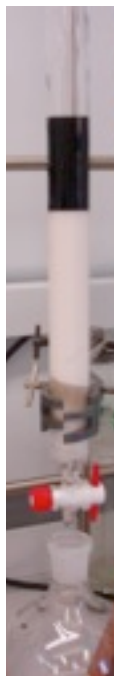


# Ionic Liquids: A brief introduction

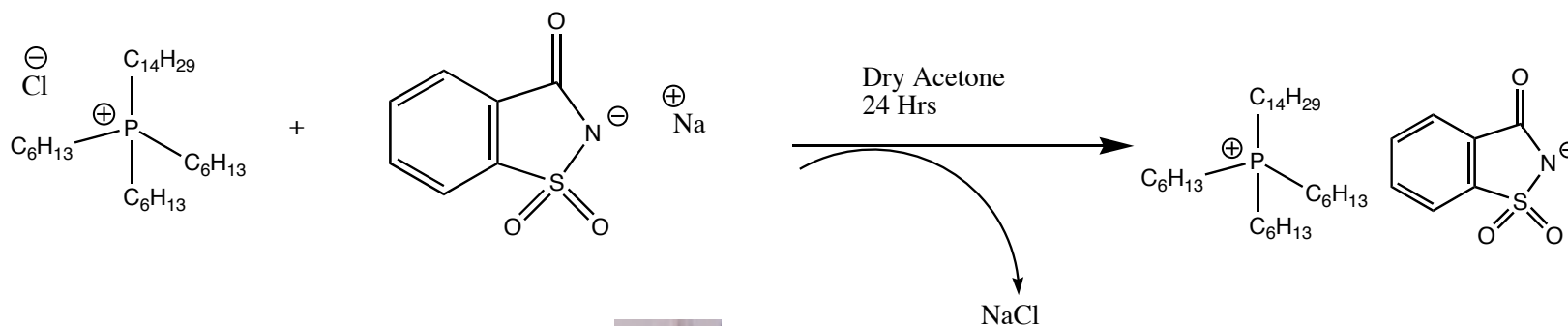


After which:

Micro filters,  
activated Carbon,  
alumina column

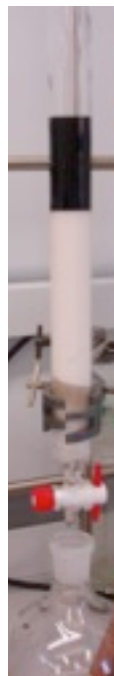


# Ionic Liquids: A brief introduction



After which:

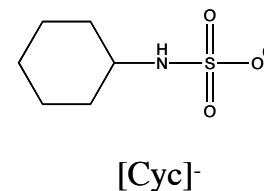
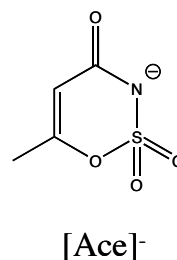
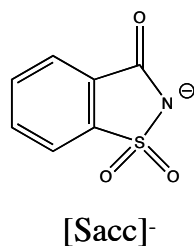
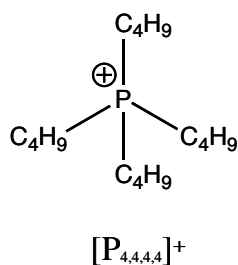
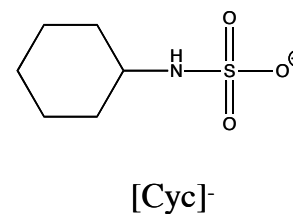
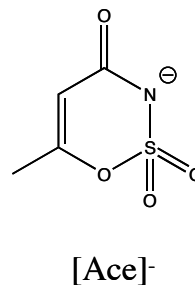
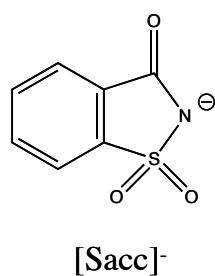
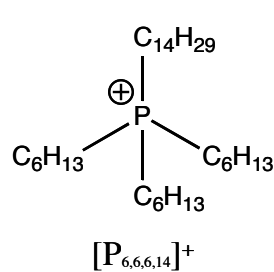
Micro filters,  
activated Carbon,  
alumina column





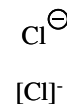
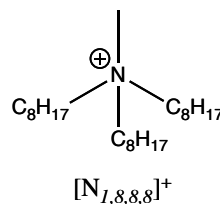
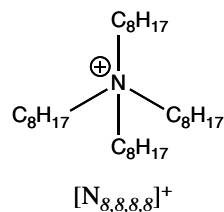
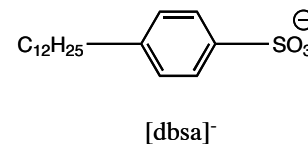
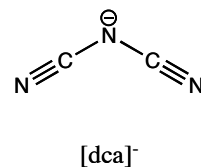
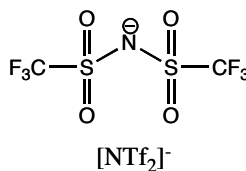
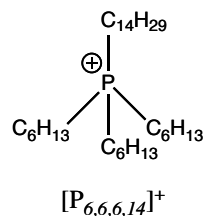
# Ionic Liquids: A brief introduction

6 new ILs.



# Ionic Liquids: A brief introduction

## Purchased ILs



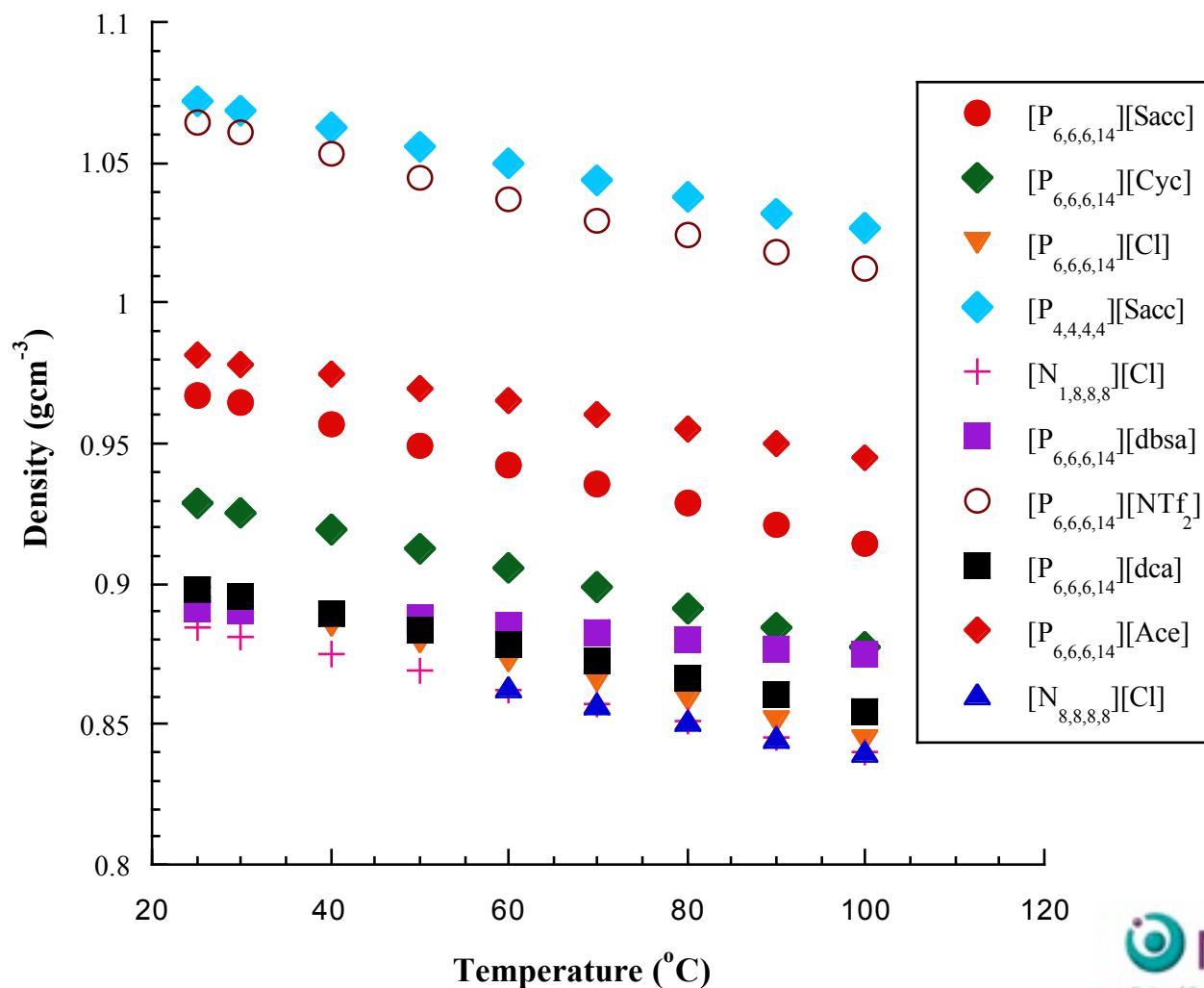
# Ionic Liquids: A brief introduction

## Thermal Properties

IL	$T_g / ^\circ\text{C}$	$T_{\text{dec}} / ^\circ\text{C}$
[P <sub>6,6,6,14</sub> ][Sacc]	-56	197
[P <sub>6,6,6,14</sub> ][Ace]	-61*	196
[P <sub>6,6,6,14</sub> ][Cyc]	-53	194
[P <sub>6,6,6,14</sub> ][NTf <sub>2</sub> ]**	-76	400
[P <sub>6,6,6,14</sub> ][dca]**	-67	395
[P <sub>6,6,6,14</sub> ][Cl]	-61	373
[P <sub>4,4,4,4</sub> ][Sacc]	-34	300
[P <sub>4,4,4,4</sub> ][Ace]	-47 ( $T_g$ ) 5 (crystallisation) 42 (melt, $\overline{\Delta S_f} = 43(10) \text{ JK}^{-1}\text{mol}^{-1}$ )	280
[P <sub>4,4,4,4</sub> ][Cyc]	-32	280
[N <sub>1,8,8,8</sub> ][Cl]		202
[N <sub>8,8,8,8</sub> ][Cl]	33 ( $S_{\text{III}} - S_{\text{II}} \overline{\Delta S_f} = 12(10) \text{ JK}^{-1}\text{mol}^{-1}$ ) 44 ( $S_{\text{II}} - S_{\text{I}} \overline{\Delta S_f} = 68(10) \text{ JK}^{-1}\text{mol}^{-1}$ ) 54 ( $T_{\text{melt}} \overline{\Delta S_f} = 59(10) \text{ JK}^{-1}\text{mol}^{-1}$ )	196

# Ionic Liquids: A brief introduction

## Density



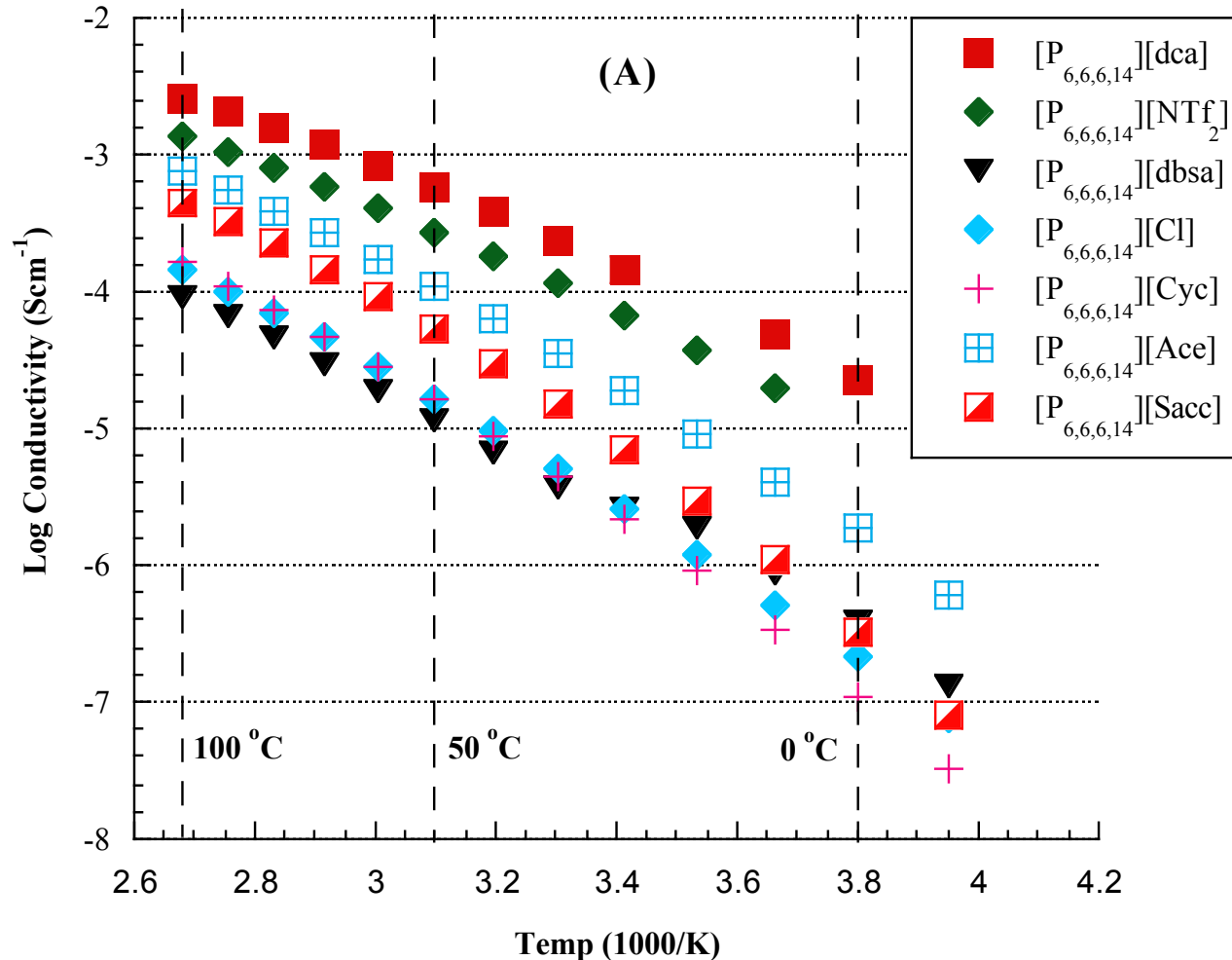
# Ionic Liquids: A brief introduction

## Transport

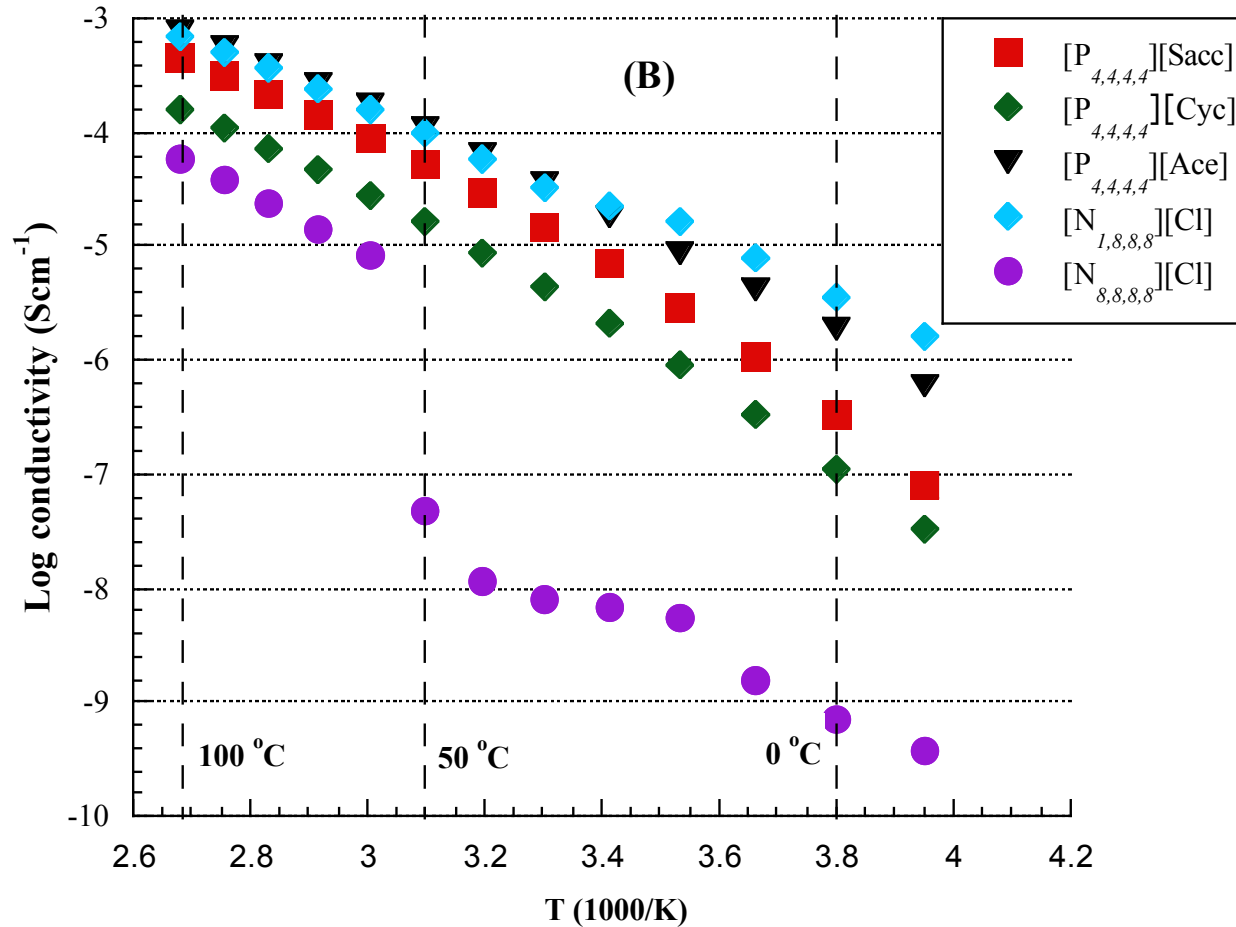
IL	Conductivity (S cm <sup>-1</sup> ) (40 °C)	Viscosity (Pa.s) (40 °C)
[P <sub>6,6,6,14</sub> ][Cl]	9.5 x 10 <sup>-6</sup>	0.70
[P <sub>6,6,6,14</sub> ][Cyc]	8.9 x 10 <sup>-6</sup>	0.62
[P <sub>6,6,6,14</sub> ][dbsa]	6.7 x 10 <sup>-6</sup>	0.95
[P <sub>6,6,6,14</sub> ][Ace]	6.4 x 10 <sup>-5</sup>	0.67
[P <sub>6,6,6,14</sub> ][Sacc]	3.0 x 10 <sup>-5</sup>	0.58
[P <sub>6,6,6,14</sub> ][NTf <sub>2</sub> ]	1.8 x 10 <sup>-4</sup>	0.15
[P <sub>6,6,6,14</sub> ][dca]	3.8 x 10 <sup>-4</sup>	0.12
[P <sub>4,4,4,4</sub> ][Sacc]	4.0 x 10 <sup>-5</sup>	1.58
[P <sub>4,4,4,4</sub> ][Ace]*	1.5 x 10 <sup>-4</sup>	--
[P <sub>4,4,4,4</sub> ][Cyc]*	8.7 x 10 <sup>-5</sup>	--
[N <sub>1,8,8,8</sub> ][Cl]	5.4 x 10 <sup>-5</sup>	0.57
[N <sub>8,8,8,8</sub> ][Cl]**	1.2 x 10 <sup>-8</sup>	--

# Ionic Liquids: A brief introduction

## Conductivity

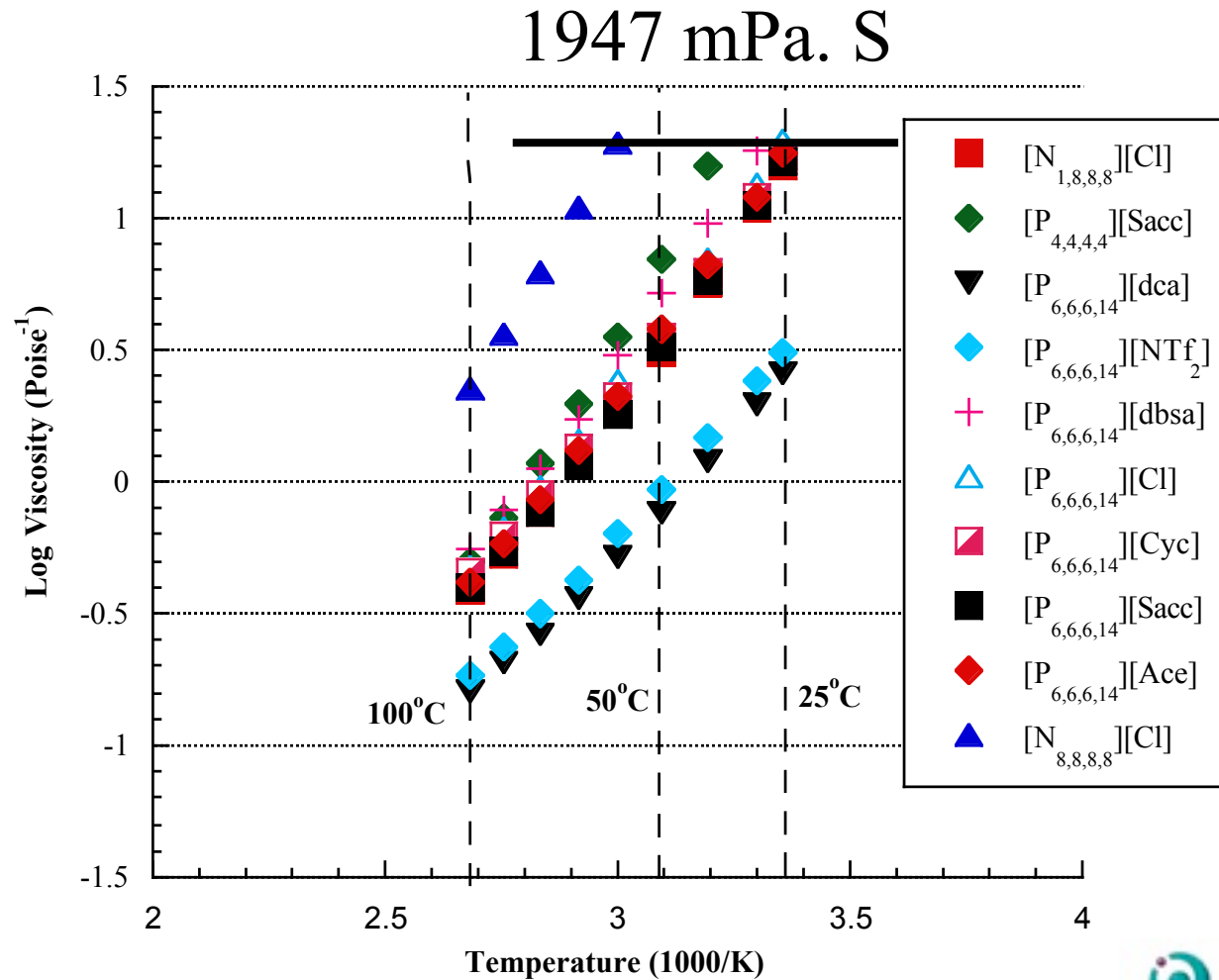


# Ionic Liquids: A brief introduction



# Ionic Liquids: A brief introduction

## Viscosity





# Ionic Liquids: A brief introduction

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- “How ionic is my ionic liquid” has become a question increasingly posed by scientists in the literature.
- To probe ion-ion interactions and “assess” the ionicity of ILs, test cases comprised of phosphonium cations paired with chloride or N-acyl-N-sulfonyl anions were prepared.



[14] K. J. Fraser, E. I. Izgorodina, M. Forsyth, J. L. Scott and D. R. MacFarlane, Chem. Commun., 2007, 3817-3819.

# Ionic Liquids: A brief introduction

## ChemComm

Chemical Communications

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Number 47 | 7 October 2007 | Pages 3817-3819



RSC Publishing

COMMUNICATION

Kevin J. Fraser, Ekaterina I. Izgorodina, Maria Forsyth, Janet L. Scott and Douglas R. MacFarlane  
Liquid Immiscibility between "Molecular" and "Ionic" Liquid Ion Pairs



[14] K. J. Fraser, E. I. Izgorodina, M. Forsyth, J. L. Scott and D. R. MacFarlane, Chem. Commun., 2007, 3817-3819.

# Ionic Liquids: A brief introduction

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Kevin J. Fraser, Ekaterina I. Izgorodina, Maria Forsyth, Janet L. Scott  
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Liquid Intermediate between "molecular" and "ionic" Liquid Ion Pairs?

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# Ionic Liquids: A brief introduction

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- Ionic liquids (ILs) have evolved as a new type of non-aqueous solvents for biocatalysis, mainly due to their unique and tunable physical properties <sup>[15]</sup>

Factors that affect Enzyme activity in ILs



[15] H. Zhao, *J. Chem. Tech. Biotech.*, 2010, **85**, 891-907.

# Ionic Liquids: A brief introduction

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- Ionic liquids (ILs) have evolved as a new type of non-aqueous solvents for biocatalysis, mainly due to their unique and tunable physical properties <sup>[15]</sup>

## Factors that affect Enzyme activity in ILs

IL polarity

Hydrogen bonding basicity

Viscosity

Ion kosmotropicity

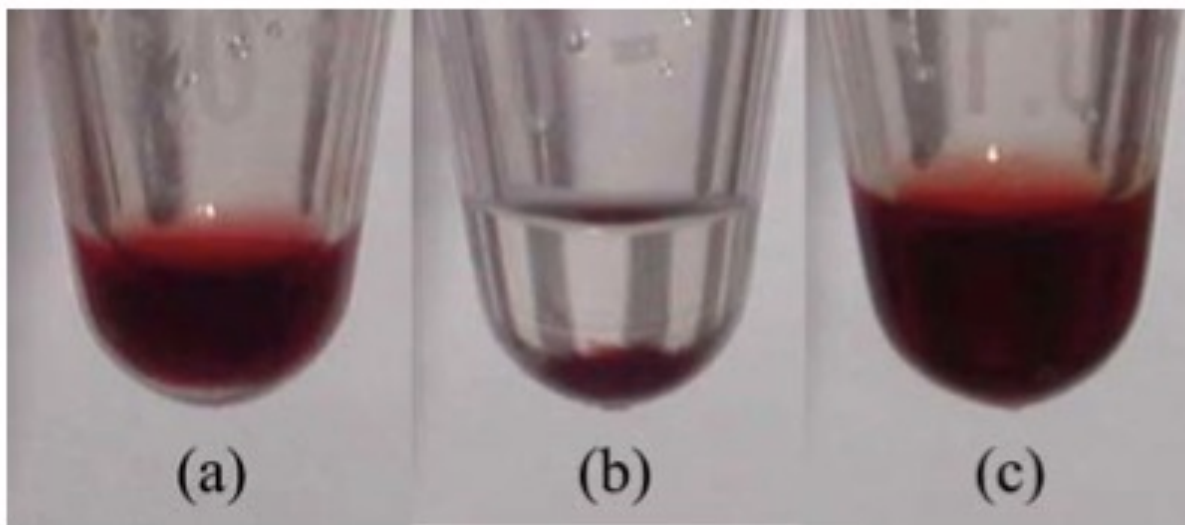
Enzyme dissolution



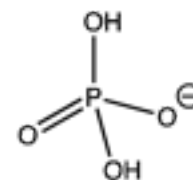
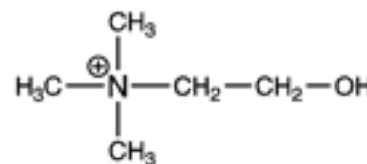
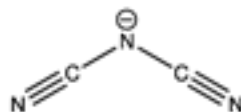
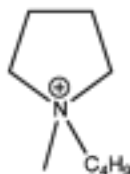
[15] H. Zhao, *J. Chem. Tech. Biotech.*, 2010, **85**, 891-907.

# Ionic Liquids: A brief introduction

Through smart design enzyme stability can be greatly enhanced



PBS



[16] K. Fujita, D. R. MacFarlane and M. Forsyth, *Chem. Commun.*, 2005, 4804-4806.

# Ionic Liquids: A brief introduction

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Through smart design enzyme stability can be greatly enhanced

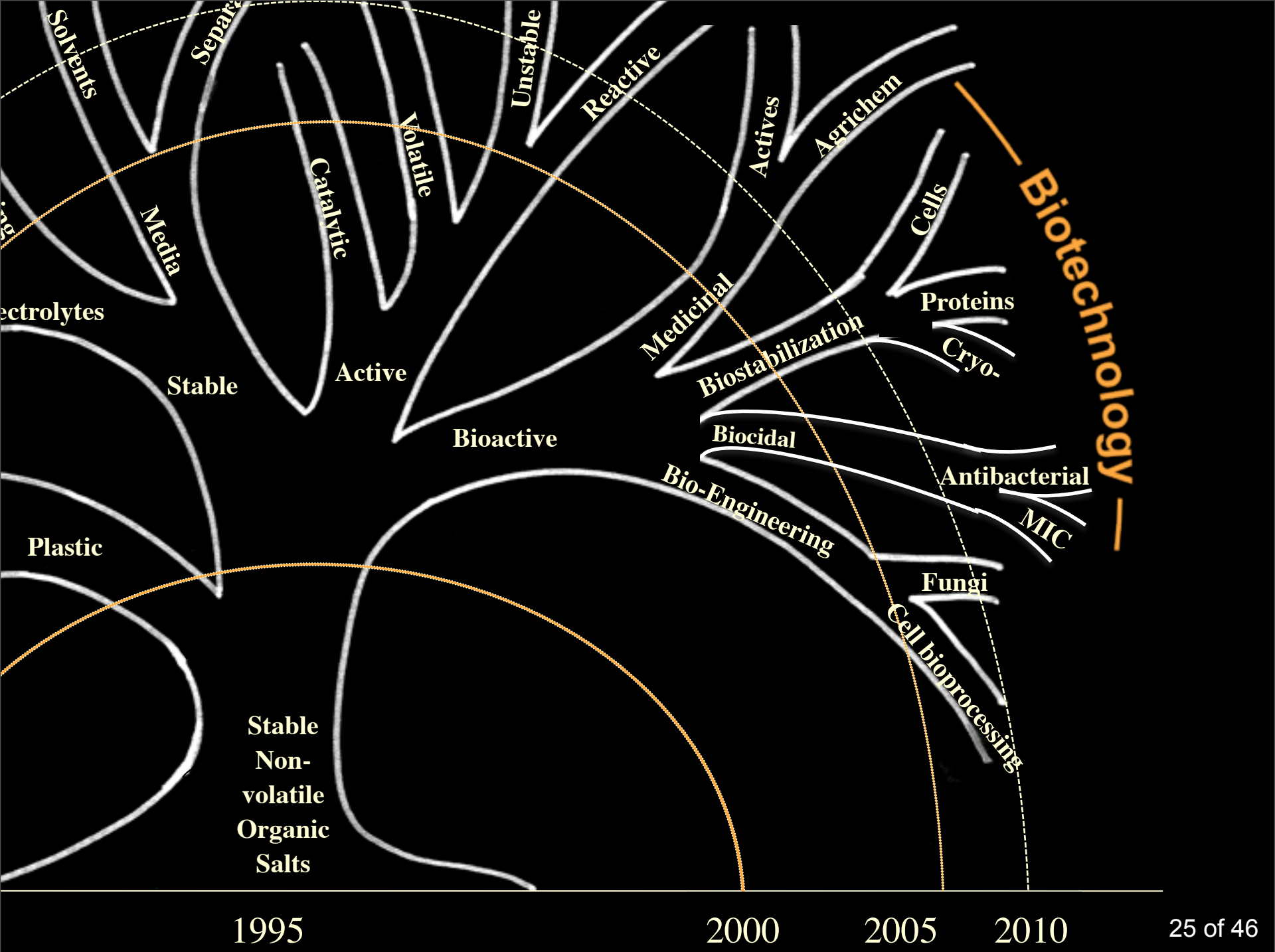
- Enhanced solubility of cytochrome c.
- dhp anion provided both a proton activity similar to that in neutral water as well as hydrogen bonding donor and acceptor sites.
- Choline DHP should enzyme stability up to 130 oC



[16] K. Fujita, D. R. MacFarlane and M. Forsyth, *Chem. Commun.*, 2005, 4804-4806.







1995

2000

2005

2010

# Sensing Platform: Ionic liquids

---

- Point-of-care (POC) glucose biosensors play an important role in the management of blood sugar levels in patients with diabetes.
- One of the most commonly used enzymes in glucose biosensors is Glucose Oxidase (GOx).
- Amperometric biosensors employing IL's have been reported previously, for example, ([C<sub>4</sub>mIm][BF<sub>4</sub>]) has been used as a mediator in a electrochemical H<sub>2</sub>O<sub>2</sub> biosensor<sup>[17]</sup>.



[17] Y. Liu, M. Wang, J. Li, Z. Li, P. He, H. Liu and J. Li, *Chem. Commun.*, 2005, 1778-1780.

# Sensing Platform: Ionic liquids

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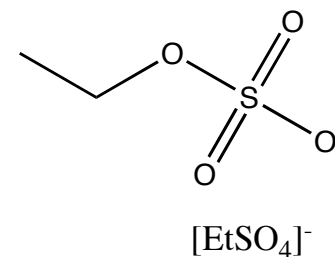
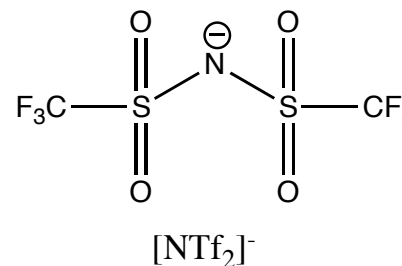
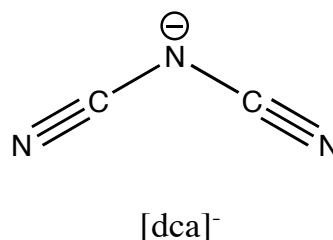
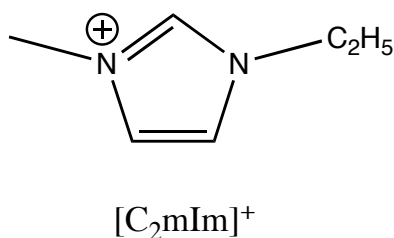
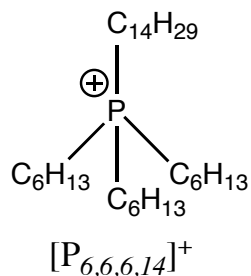
- This work investigates colorimetric and electrochemical methods of glucose detection by combining the enzyme's specificity, with the unique characteristics of IL's and either a chromogen (o-Dianisidine) or electrochemical mediator (ferrocene) to enhance the detection.
- This interest is driven by the need to find molecular environments in which enzymes are highly stabilized while retaining redox activity.



[17] Y. Liu, M. Wang, J. Li, Z. Li, P. He, H. Liu and J. Li, *Chem. Commun.*, 2005, 1778-1780.

# Sensing Platform: Ionic liquids

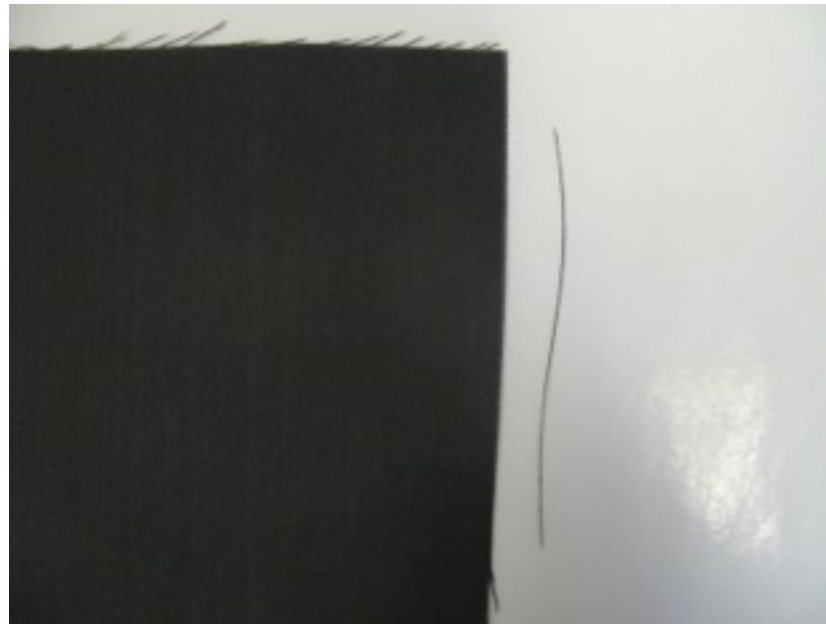
- Ionic liquids used in this study include  $[\text{C}_2\text{mIm}][\text{EtSO}_4]$ ,  $[\text{P}_{6,6,6,14}][\text{Cl}]$ ,  $[\text{P}_{6,6,6,14}][\text{dca}]$  and  $[\text{P}_{6,6,6,14}][\text{NTf}_2]$



# Sensing Platform: Ionic liquids

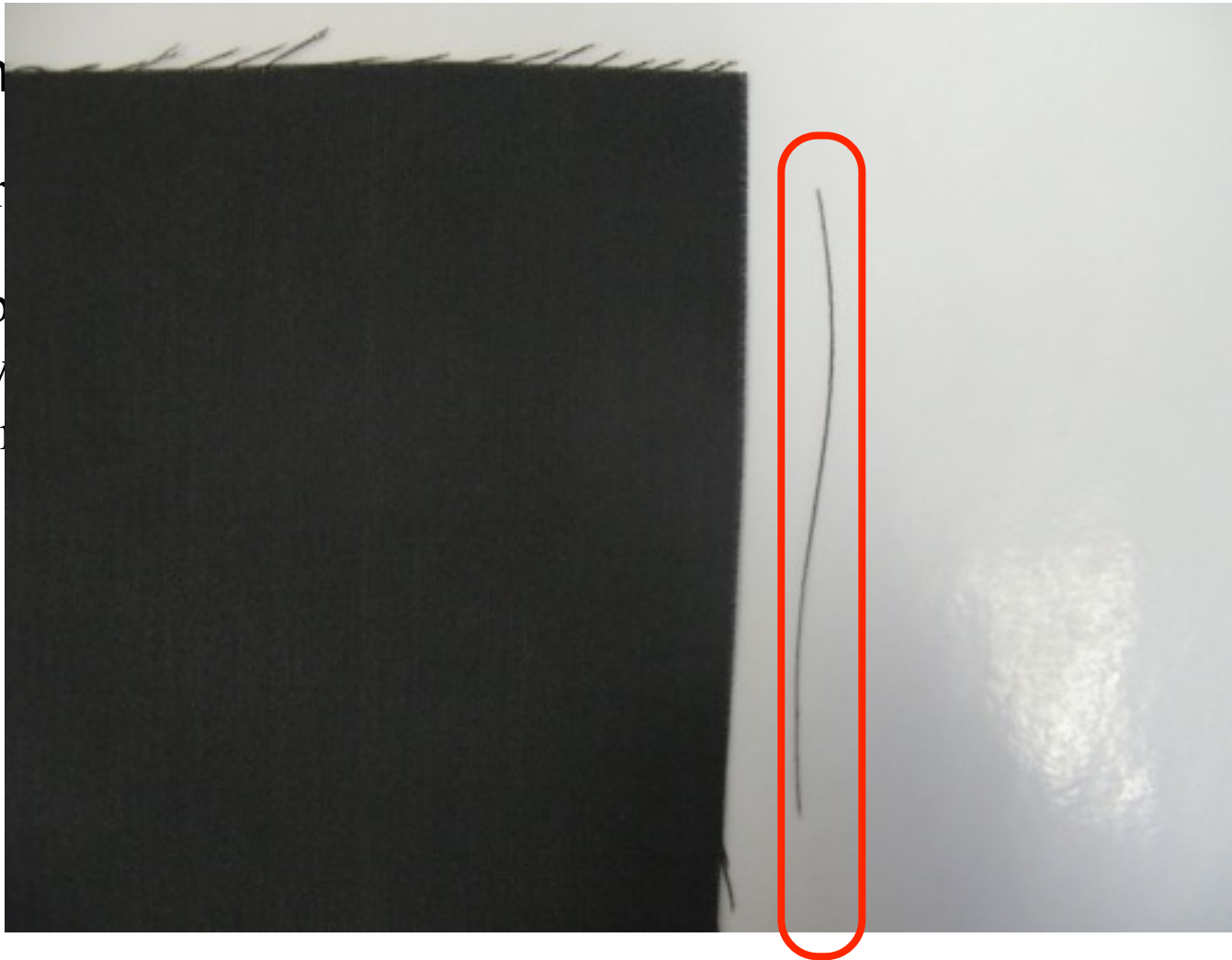
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- An alternative working electrode
- Carbon Cloth- Graphitized Spun Yarn Carbon Fabrics
- Fabric tailor-ability results from controlling the yield on rovings and yarns, and allows for a variety of finished composite thicknesses.



# Sensing Platform: Ionic liquids

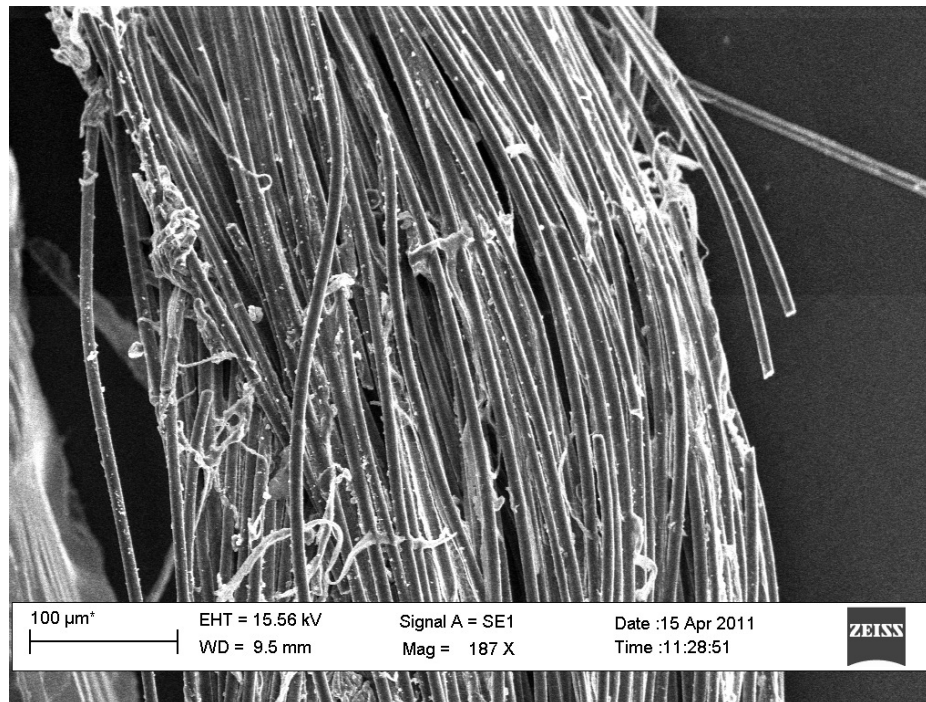
- An
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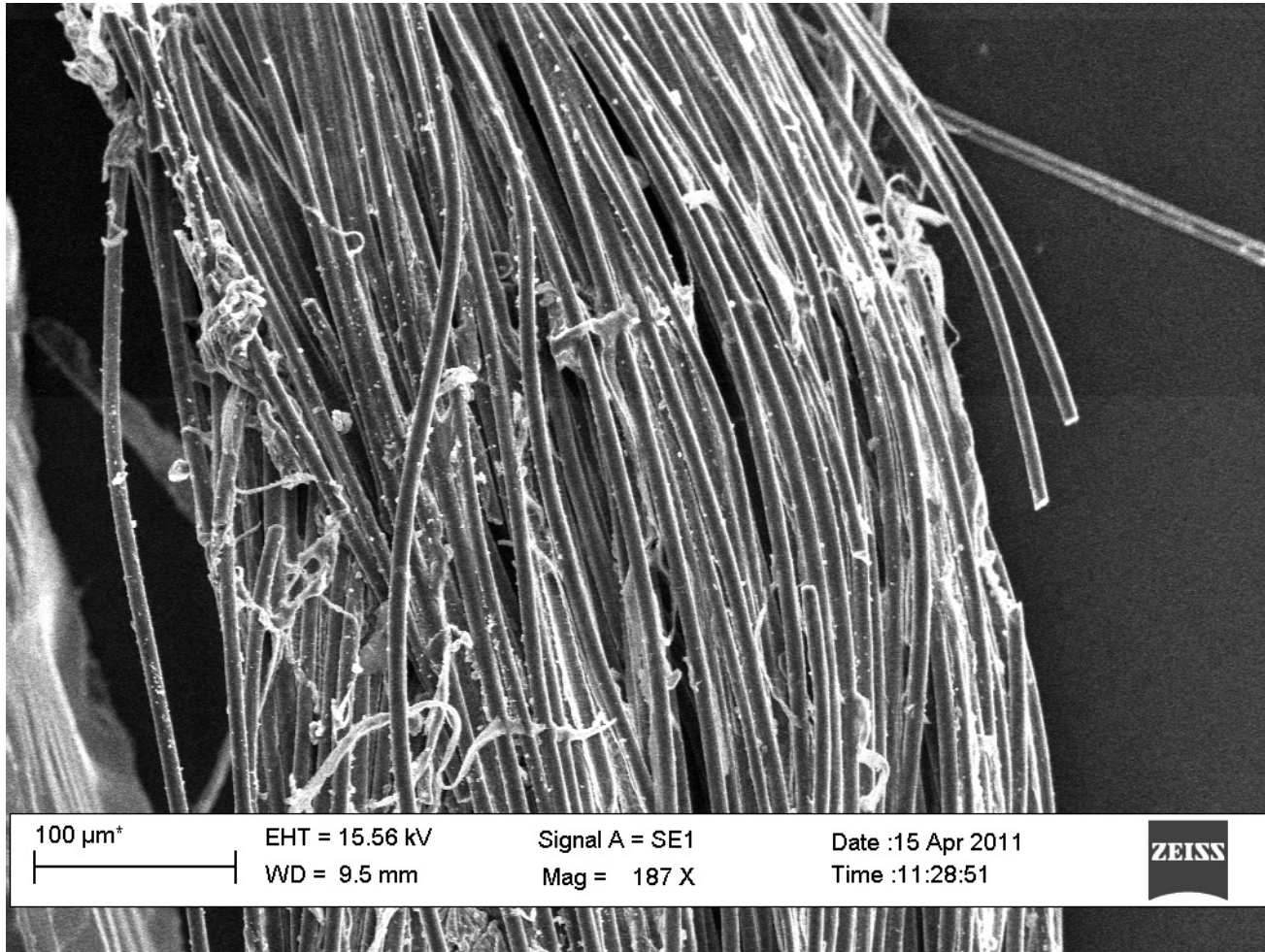
ings

# Sensing Platform: Ionic liquids

- Counter & working electrode consisted of carbon cloth graphitized Spun Yarn Carbon Fabrics
- 500  $\mu\text{m}$  threads consisting of a bundle of 10  $\mu\text{m}$  fibres. Allows for flexible substrates.



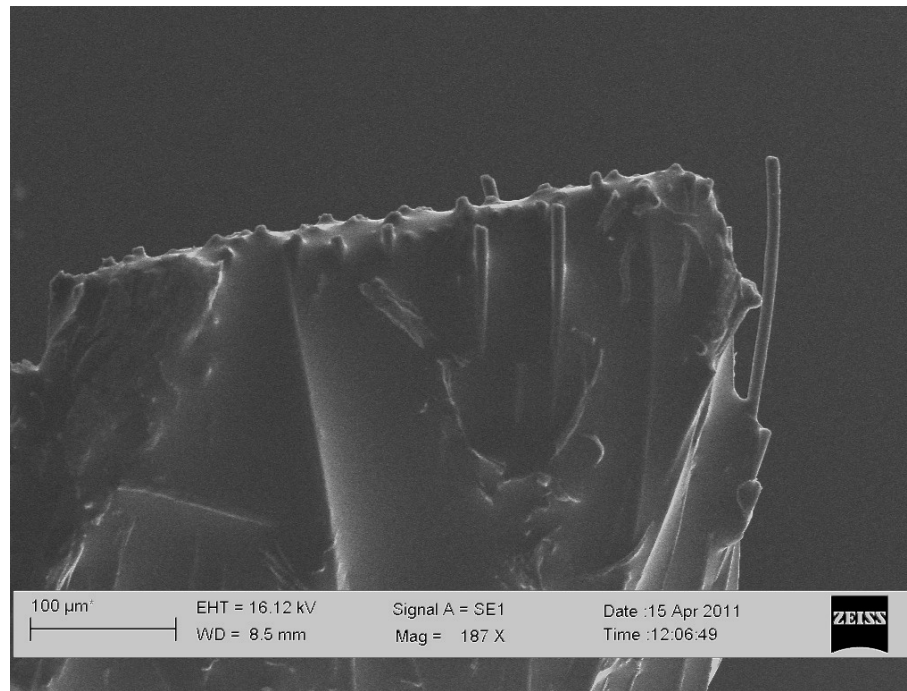
# Sensing Platform: Ionic liquids



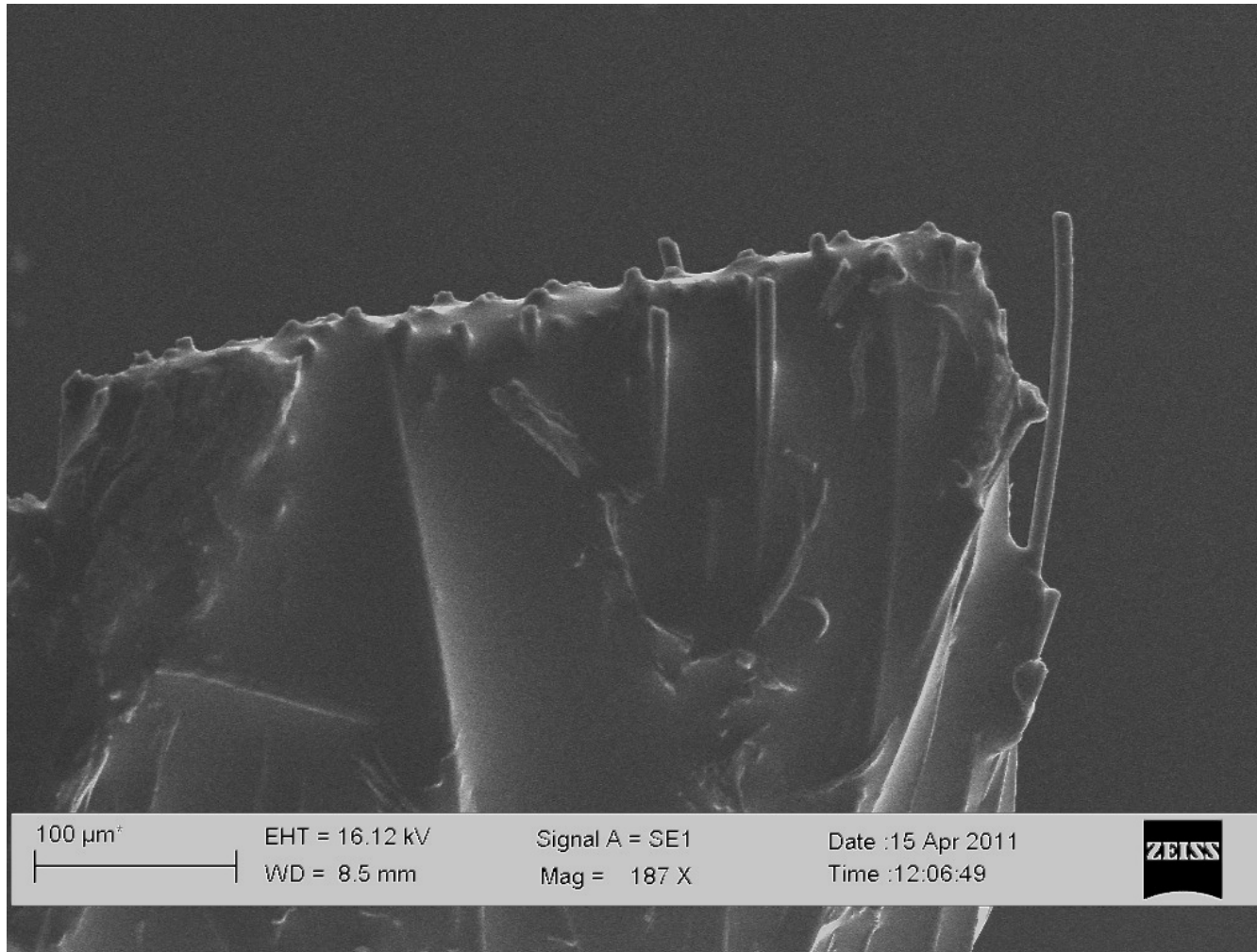


# Sensing Platform: Ionic liquids

- Potentials were against a Ag/AgCl reference electrode – 500  $\mu\text{m}$  silver wire chloridised in  $\text{FeCl}_3$ .
- Single threads were soaked in a IL / Ferrocene / GOx enzyme solution.



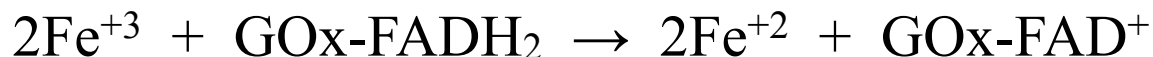
# Sensing Platform: Ionic liquids



# Sensing Platform: Ionic liquids

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- The electrochemical mechanism for glucose detection in a Ferrocene mediated system<sup>[18]</sup>:

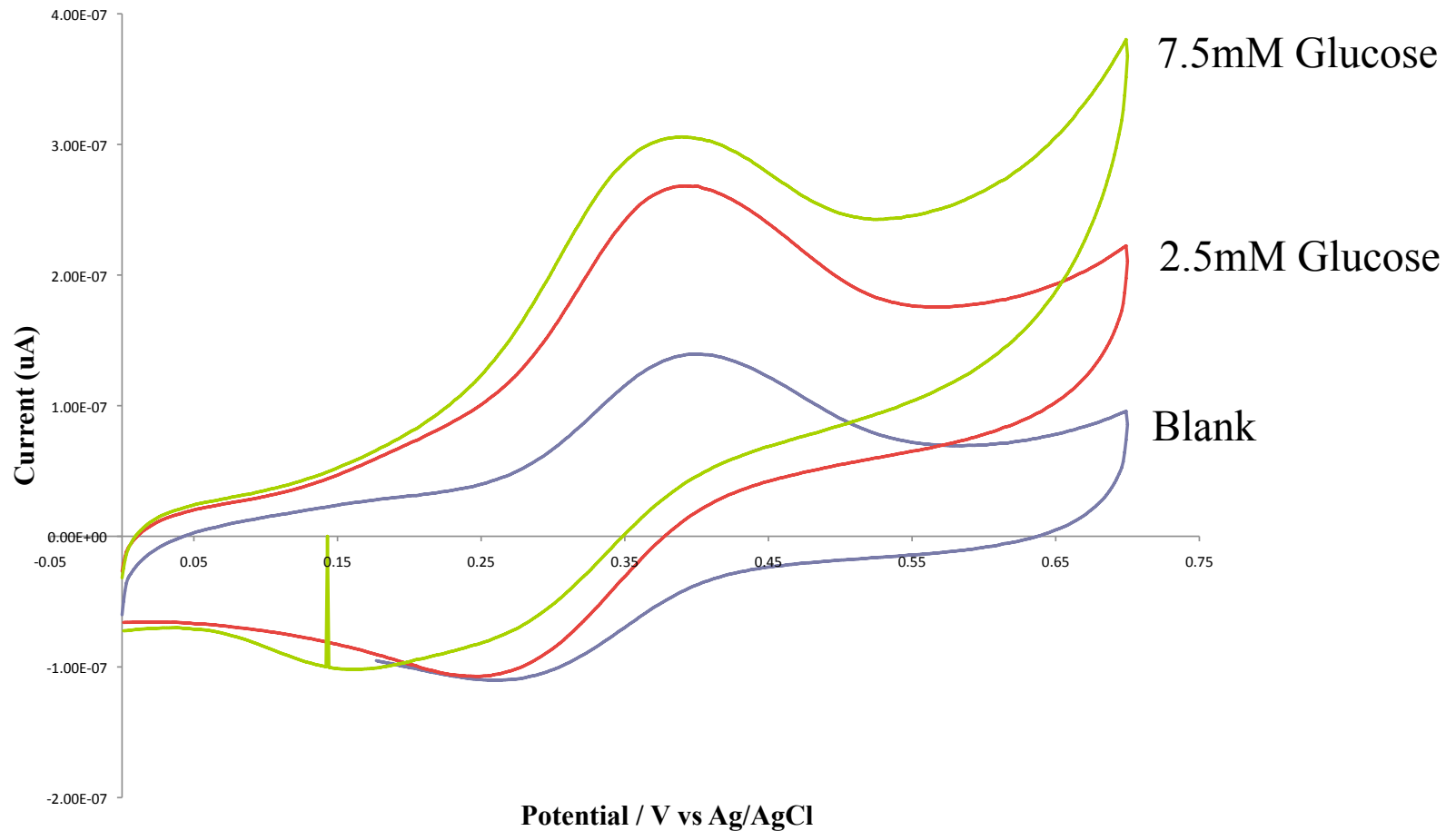


@ electrode surface



[18] J.F. Rusling, K Ito, *Analytica Chimica Acta*, **252**, (1991), 23-27.

# Sensing Platform: Ionic liquids



*CV of Glucose additions to  $[P_{6,6,6,14}][dca]/\text{Ferrocene}/\text{Gox}$  on carbon cloth. Scan rate 0.01 V/S*

# Sensing Platform: Ionic liquids

- Using the Anson equation, the calculated working area was approx 0.138 cm<sup>2</sup>.

$$Q = \frac{2nFAC_o D_o^{1/2}}{\pi^{1/2}} t^{1/2}$$

- Due to the hydrophobic nature of the cloth, [P<sub>6,6,6,14</sub>][dca] was chosen as the electrolyte.

## Quick summary

- Carbon cloth shows potential as a flexible working electrode.
- Can be woven into sports athletes clothing.
- Durable, flexible sensing platform.
- $[P_{6,6,6,14}][dca]$  as an electrolyte in the glucose system shows favourable limit of detection
- A flexible, wearable one shot sensor maybe produced using IL formulations

# Sensing Platform: Ionic liquids

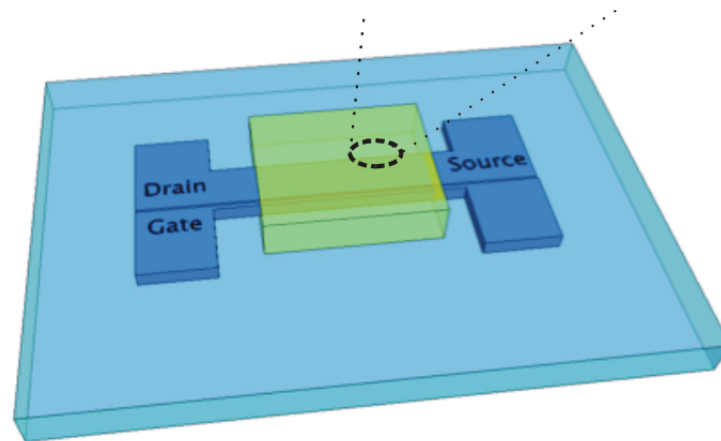
## Organic Electrochemical Transistors (OECTs)



# Sensing Platform: Ionic liquids

## The Aim:

- To develop an enzymatic sensor based on an OECT that uses an IL as an integral part of its structure.
- The strategy involves patterning the RTIL over the active area of the OECT, and using it as a reservoir for the enzyme and the mediator.





# Sensing Platform: Ionic liquids

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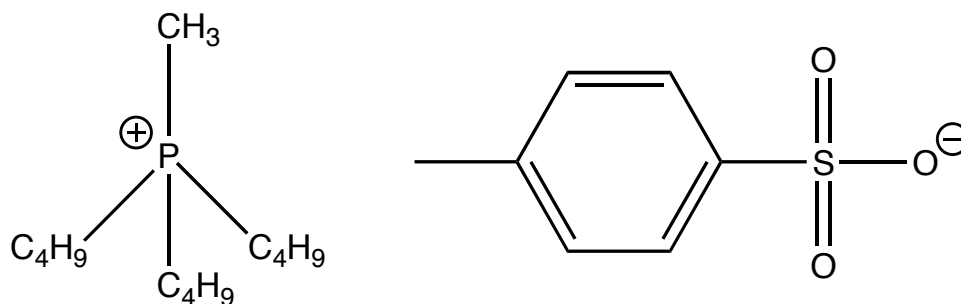
- Important properties of the electrolyte for this device must include wetting the PEDOT : PSS film.



[19] S. Y. Yang, F. Cicoira, R. Byrne, F. Benito-Lopez, D. Diamond, R. A. Owens and G. G. Malliaras, *Chem. Commun.*, 2010, **46**, 7972-7974.

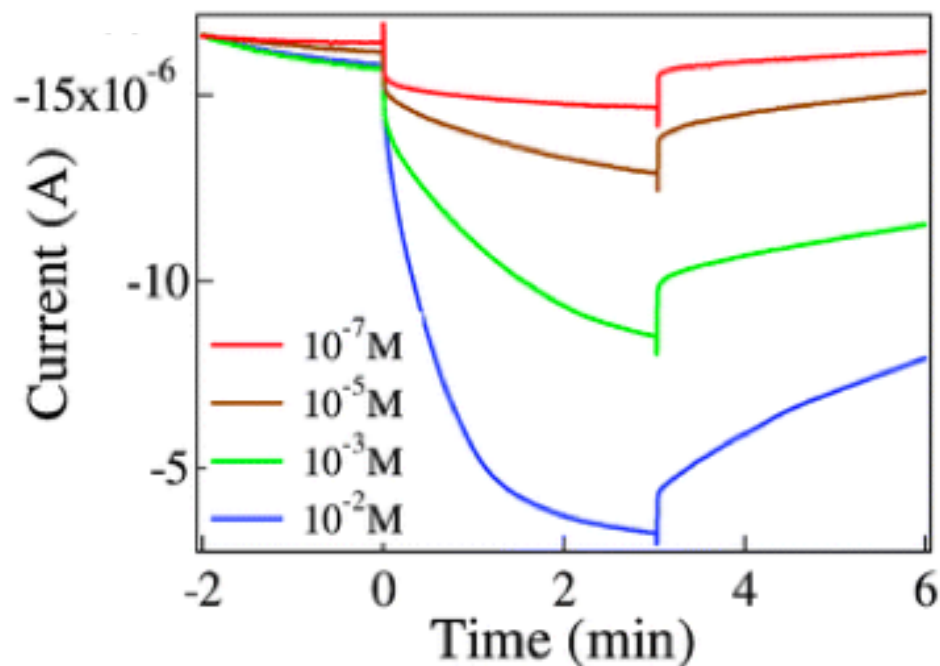
# Sensing Platform: Ionic liquids

- Important properties of the electrolyte for this device must include wetting the PEDOT : PSS film.
- This allows the enzyme and the mediator to be patterned over the active area of the device.
- The IL should be miscible with the aqueous phase (PBS).
- Triisobutyl(methyl)phosphonium Tosylate ( $[P_{1,4,4,4}][Tos]$ ) due to the hydrophilic nature of the cation / anion.



[19] S. Y. Yang, F. Cicoira, R. Byrne, F. Benito-Lopez, D. Diamond, R. A. Owens and G. G. Malliaras, *Chem. Commun.*, 2010, **46**, 7972-7974.

# Sensing Platform: Ionic liquids



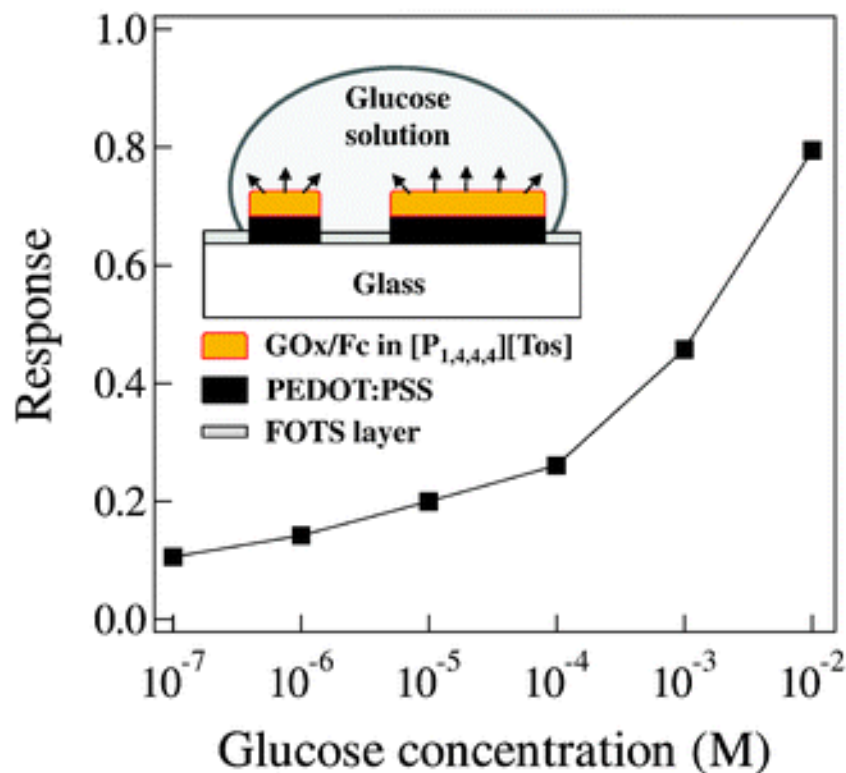
- The transient response of the drain current of an OECT upon application of a gate voltage of 0.4 V and duration of 3 min. The drain voltage was -0.2 V.



[19] S. Y. Yang, F. Cicoira, R. Byrne, F. Benito-Lopez, D. Diamond, R. A. Owens and G. G. Malliaras, *Chem. Commun.*, 2010, **46**, 7972-7974.

# Sensing Platform: Ionic liquids

- Current modulation of the OECT as a function of glucose concentration.

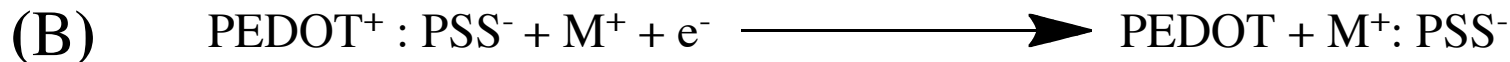
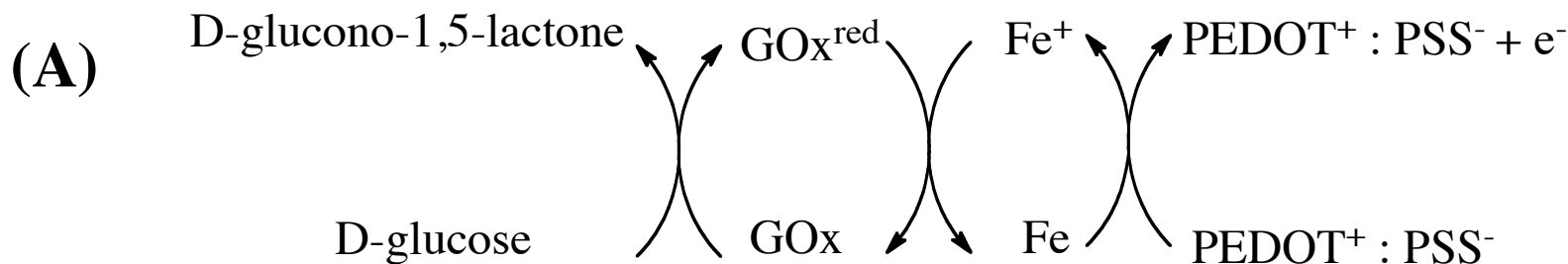


- Inset shows the concept of device operation, and the arrows indicate the dissolution of the RTIL carrying the enzyme and the mediator into the analyte solution.

[19] S. Y. Yang, F. Cicoira, R. Byrne, F. Benito-Lopez, D. Diamond, R. A. Owens and G. G. Malliaras, *Chem. Commun.*, 2010, **46**, 7972-7974.

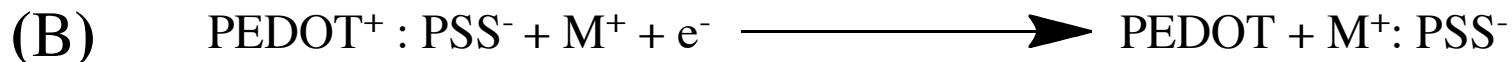
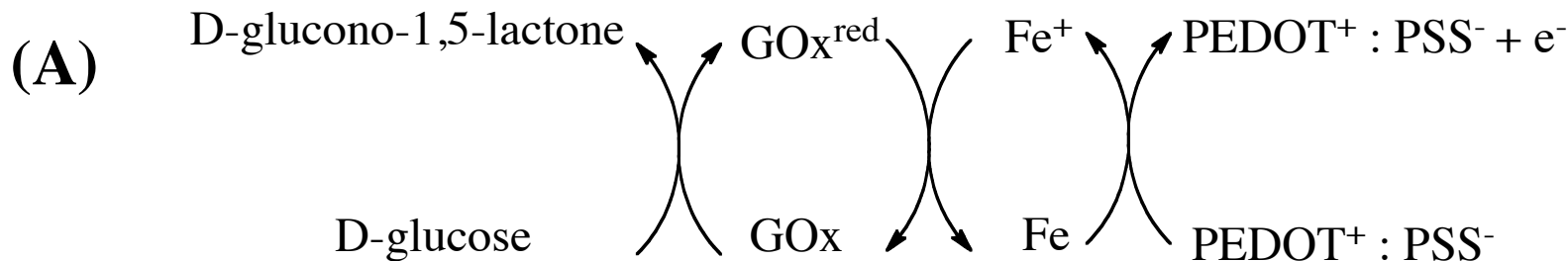
# Sensing Platform: Ionic liquids

- The data show the characteristic decrease of drain current upon gating which has been understood on the basis of the reactions shown below



Reactions at the gate electrode **(a)** and at the channel **(b)** of the OEET.

# Sensing Platform: Ionic liquids



- As glucose in the solution is oxidised, the enzyme (GOx) itself is reduced, and cycles back with the help of the Fc/ferricenium ion (Fc<sup>+</sup>) couple, which shuttles electrons to the gate electrode (A).
- For example, for 10<sup>-2</sup> M of glucose, this cascade of reactions causes a current of 8x10<sup>-8</sup> A to flow to the gate electrode.
- At the same time, cations from the solution (M<sup>+</sup>) enter the PEDOT : PSS channel and dedope it. (B)

# Sensing Platform: Ionic liquids

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## Conclusions:

- Successful integration of an OECT with an IL as electrolyte.

# Sensing Platform: Ionic liquids

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## Conclusions:

- Successful integration of an OECT with an IL as electrolyte.
- The ionic liquid was confined on the surface of the transistor using a photolithographically patterned hydrophobic monolayer.
- The enzyme was in a dispersed state in the ionic liquid, which may prove to be a good strategy for improving long-term storage.
- Using the glucose/ glucose oxidase pair as a model, it was demonstrated the analyte detection in the  $10^{-7}$  to  $10^{-2}$  M concentration range.





# Electrochemical biosensing: The road ahead



- Currently for applications in materials science, there is a growing interest in ‘ionogels’.
- Polymers with ionic liquids integrated such that they retain their specific properties within the polymer/gel environment.

# Electrochemical biosensing: The road ahead

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Ionogel synthesis:

Inorganic route: Oxides, Sol-Gel.<sup>[20]</sup>

- Applications in catalysis & photonics.



[20] M.-A. Nouze, J. L. Bideau, P. Gaveau, S. Bellayer and A. Vioux, *Chem. Mater.*, 2006, **18**, 3931-3936.

## Ionogel synthesis:

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Organic route: Polymers, Acrylamide gels <sup>[21]</sup>

- Applications in solid state electrolytes and separations



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[21] T. Ueki and M. Watanabe, *Macromolecules*, 2008, **41**, 3739-3749.

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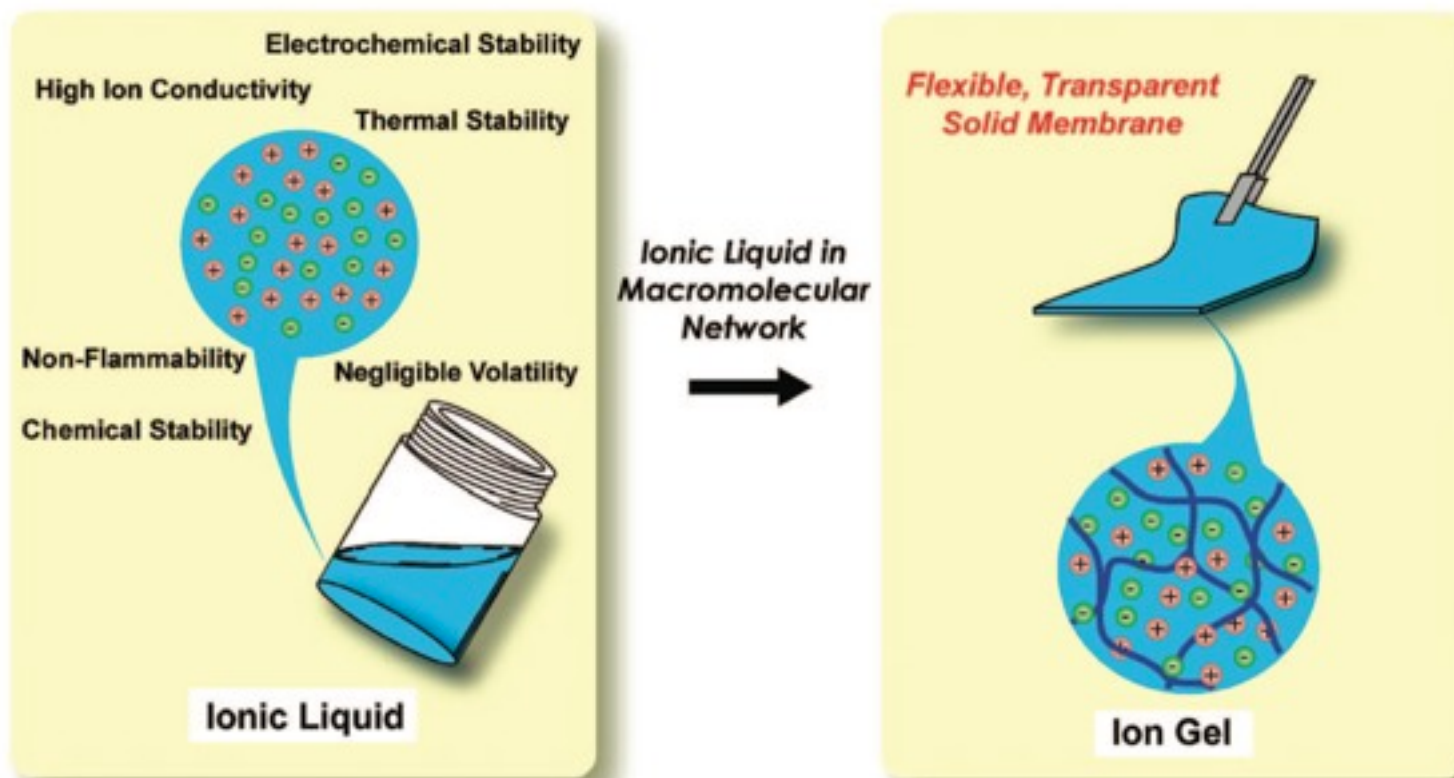
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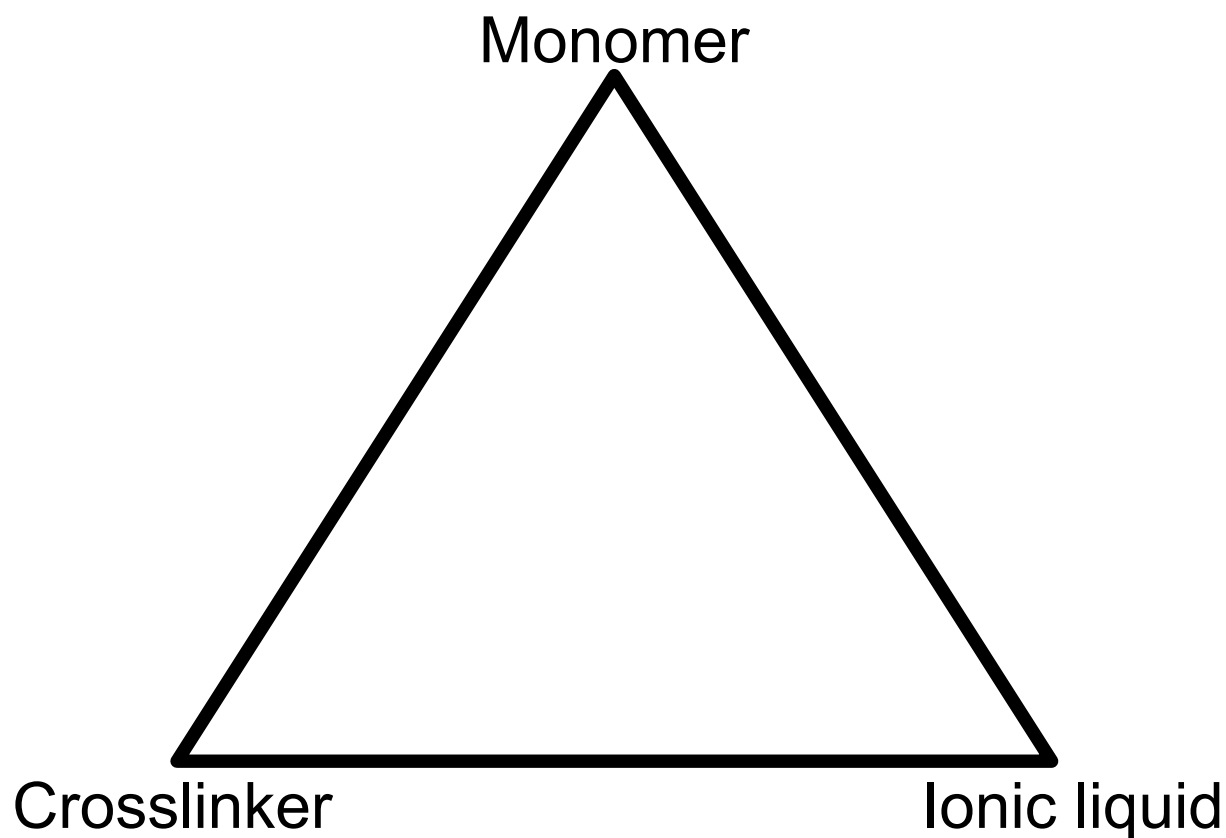
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[21] T. Ueki and M. Watanabe, *Macromolecules*, 2008, **41**, 3739-3749.

## Ionogel synthesis: Organic route



# Electrochemical biosensing: The road ahead

## Ionogel synthesis: Organic route

Tea leaves



Water

Milk



Chem Soc Rev

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Cite this: DOI: 10.1039/c0cs00059k

[www.rsc.org/csr](http://www.rsc.org/csr)

**CRITICAL REVIEW**

## Ionogels, ionic liquid based hybrid materials†

Jean Le Bideau,<sup>a</sup> Lydie Viau<sup>b</sup> and André Vioux<sup>\*b</sup>

Received 30th July 2010

DOI: 10.1039/c0cs00059k

An excellent review by Le Bideau *et. al.*[22]

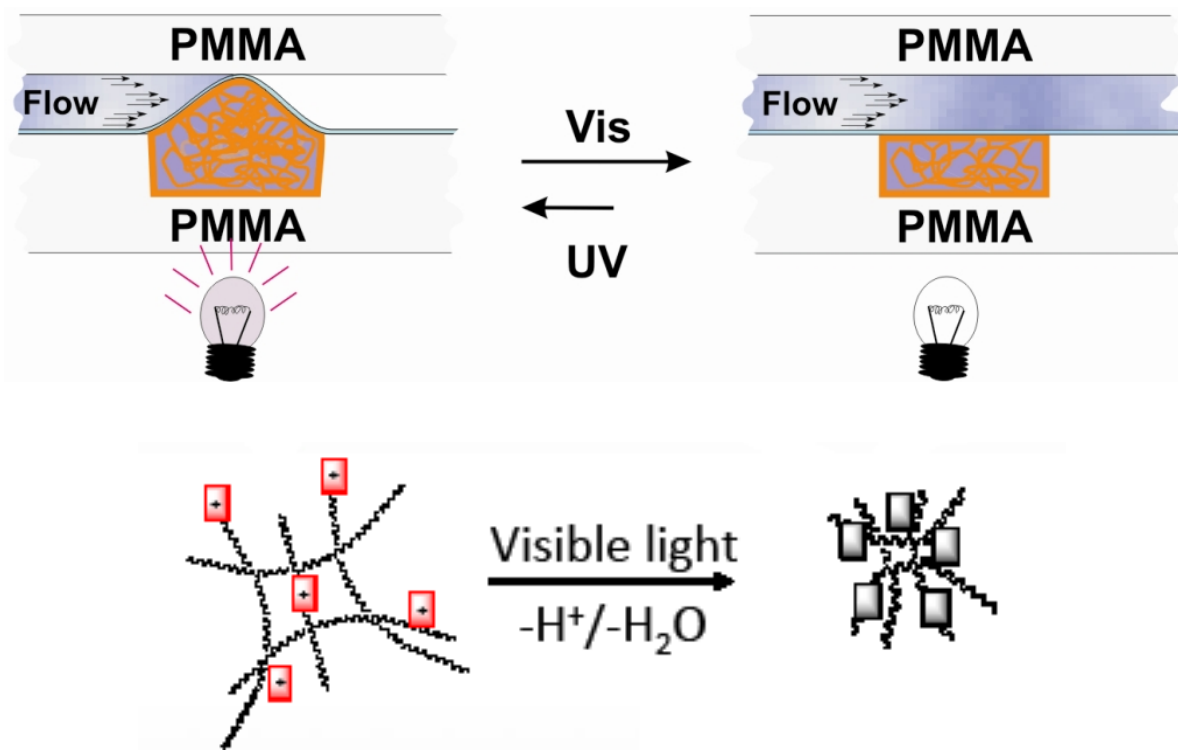


[22] J. Le Bideau, L. Viau and A. Vioux, *Chem. Soc. Rev.*, 2011, **40**, 907-925.



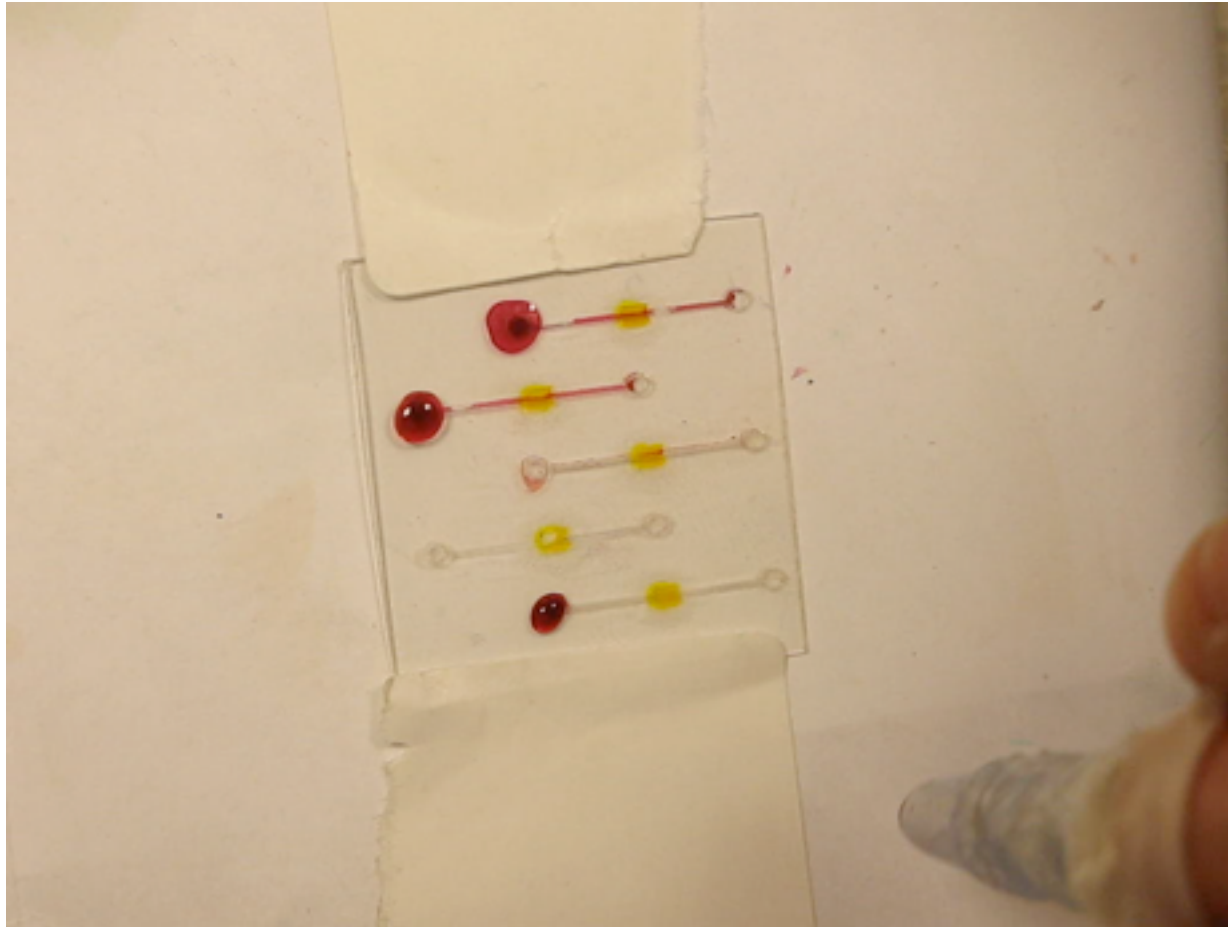
# Ionogels: Applications in sensors & actuators

## Actuation



# Ionogels: Applications in sensors & actuators

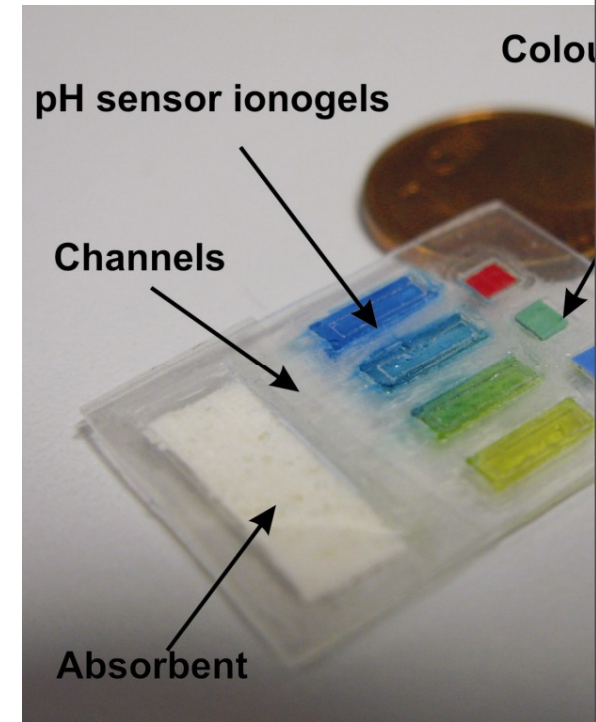
## Actuation



## Sensing

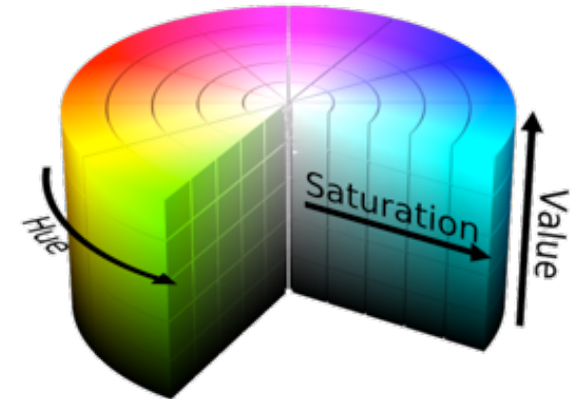
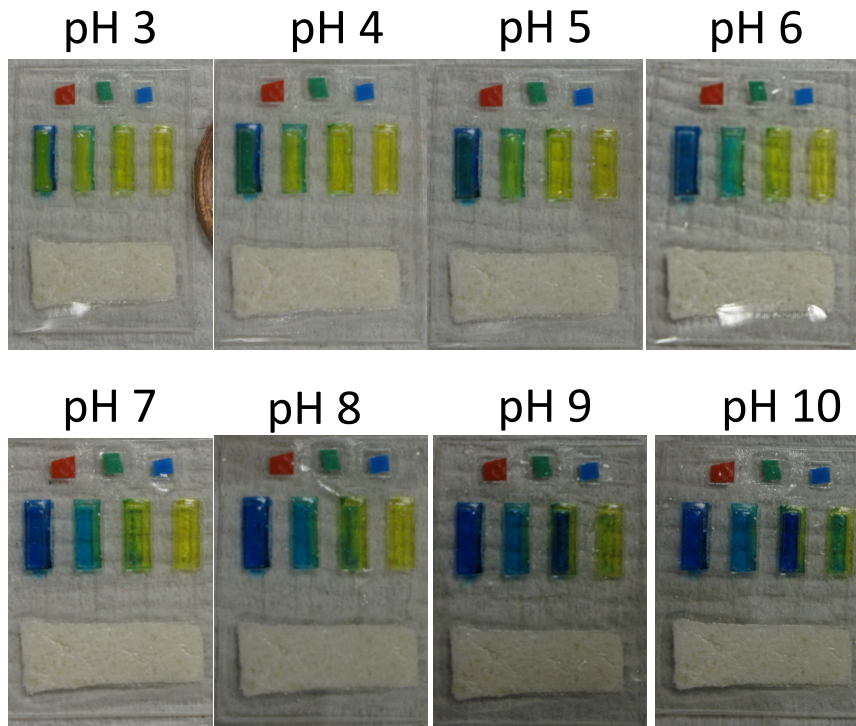
### Characteristics:

- Ionogel/dyes
- Image data analysis
- Absorbent = passive pump
- Electronics is not required



# Ionogels: Applications in sensors & actuators

Sensing



## Hue

“the degree to which a stimulus can be described”



# Ionogels: Applications in sensors & actuators

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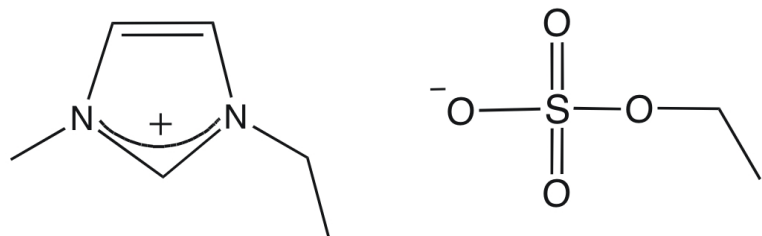
## Sensing



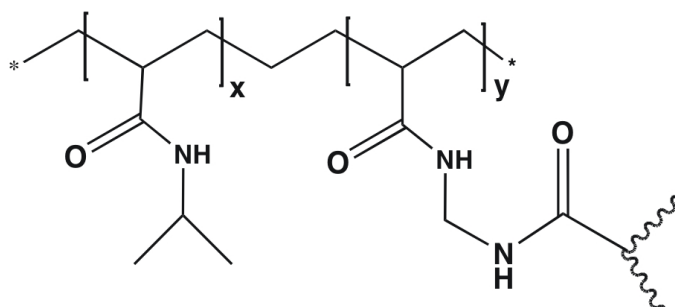
Visiting Berkley Oct 2011

# Electrochemical biosensing: The road ahead

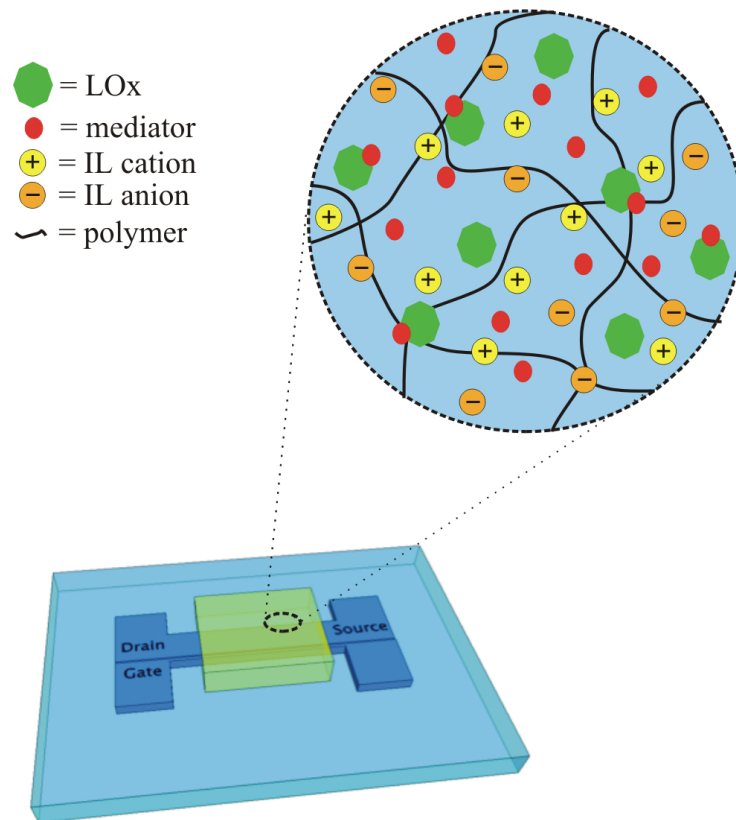
- Incorporate printable formulations onto OECTs for biosensing



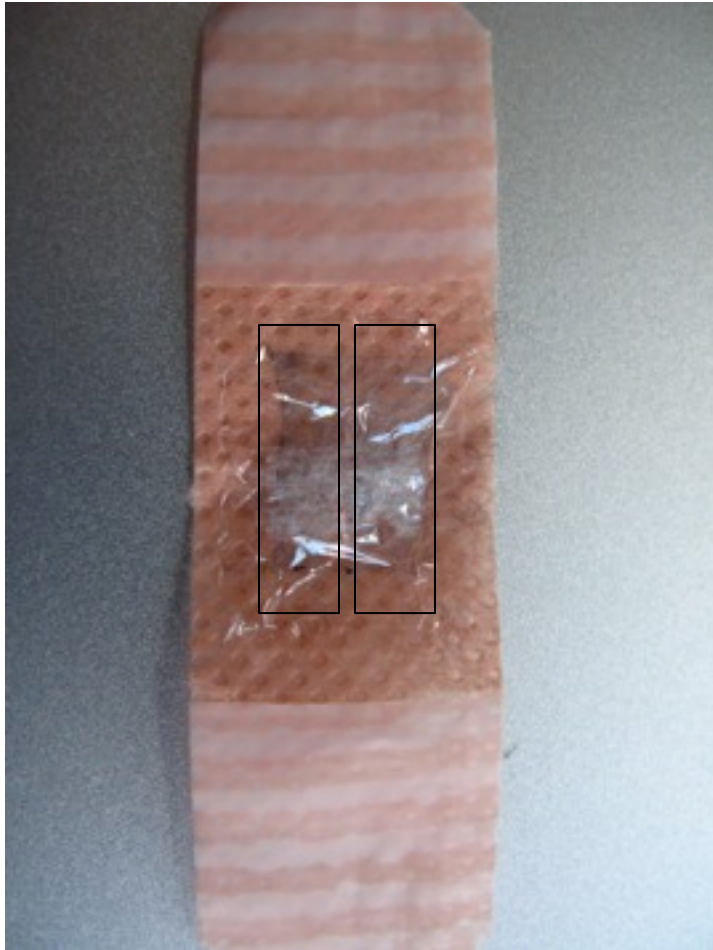
1-Ethyl-3-methylimidazolium (EMIM) cation ethyl sulfate (EtSO<sub>4</sub>) anion



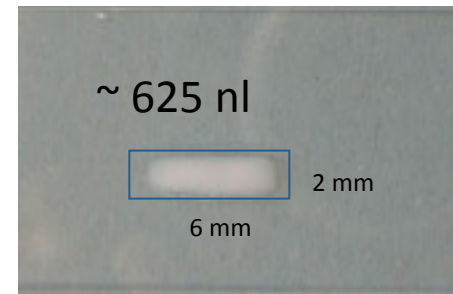
poly(*N*-isopropylacrylamide-co-*N,N'*-methylenebisacrylamide)



## Flexible Wearable Transistor



## Printing Ionogel



150  $\mu\text{m}$  thickness

## Advantages of Ionogels

- Control the Ratio of cross linker to IL.



## Advantages of Ionogels

- Control the Ratio of cross linker to IL.
- Less crosslinker, less dense polymer. Diffusion is improved
- Catalytically active proteins and enzymes may also be confined.
- It is therefore proposed that having “Ionogels” is a particularly attractive strategy in the field of biosensing.
- These materials, in theory, will inherit all of the favourable IL properties whilst being in a solid, semi-solid gel like structure.

# Acknowledgments

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Dr Shirley Coyle

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Caroline Barry

Dr Susan Warren

Dr Eithne Dempsey

Prof Douglas MacFarlane

Prof Dermot Diamond

IL / Transistor work

Dion Khodagholy

Prof George Malliaras

Prof Róisín Owens

Prof Dermot Diamond

Dr Fernando Benito-Lopez

Dr Robert Byrne

# Acknowledgments

## Funding Agencies



# CLARITY Centre & Ecosystem

## INDUSTRY COLLABORATORS



## SOCIAL/AGENCY COLLABORATORS



# Thanks for your attention

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## QUESTIONS?



Presentation available for  
download (@Cyrusmekon)



<http://tinyurl.com/3pc2b9v>