Ionogel Materials for Fluid Control and Sensing in Microfluidic Devices

Fernando Benito Lopez

CLARITY Centre for Sensor Web Technologies

National Centre for Sensor Research

Dublin City University

10th February 2011, CNM, UAB

National Centre for Sensor Research

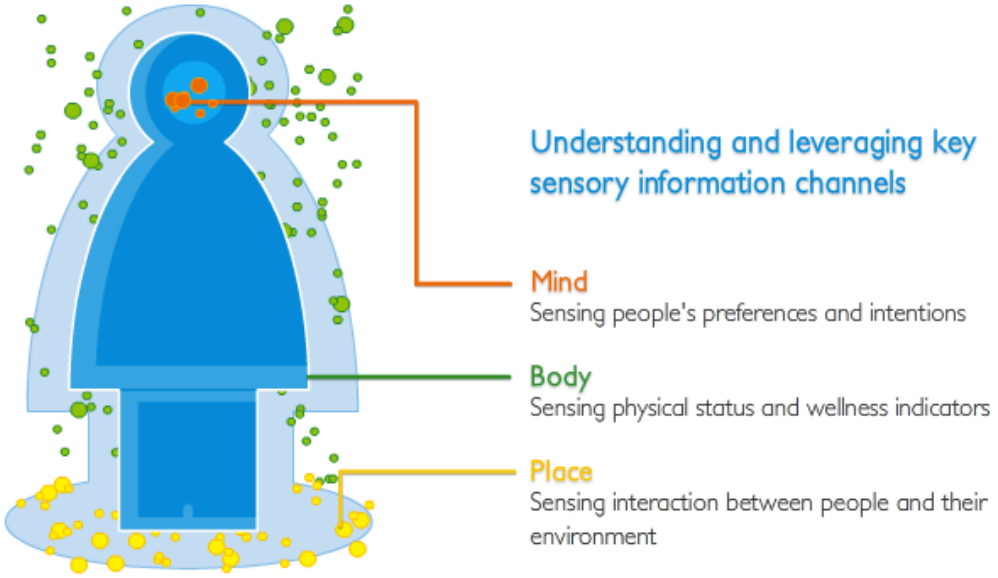
- OVER 260 RESEARCHERS AND SUPPORT STAFF
- 23 AFFILIATED FACULTY
- INVESTMENTS AND INCOME SINCE 1999 NOW APPROACHING €100 MILLION
- 1500 m^2 WELL-EQUIPPED SPECIALIST LAB SPACE AND OFFICE

Beaufort, SmartCoast, SmartBay, Strive

CLARITY – SFI CSET

CLARITY
clarity-centre.org

Vision: Sensing Mind, Body & Place



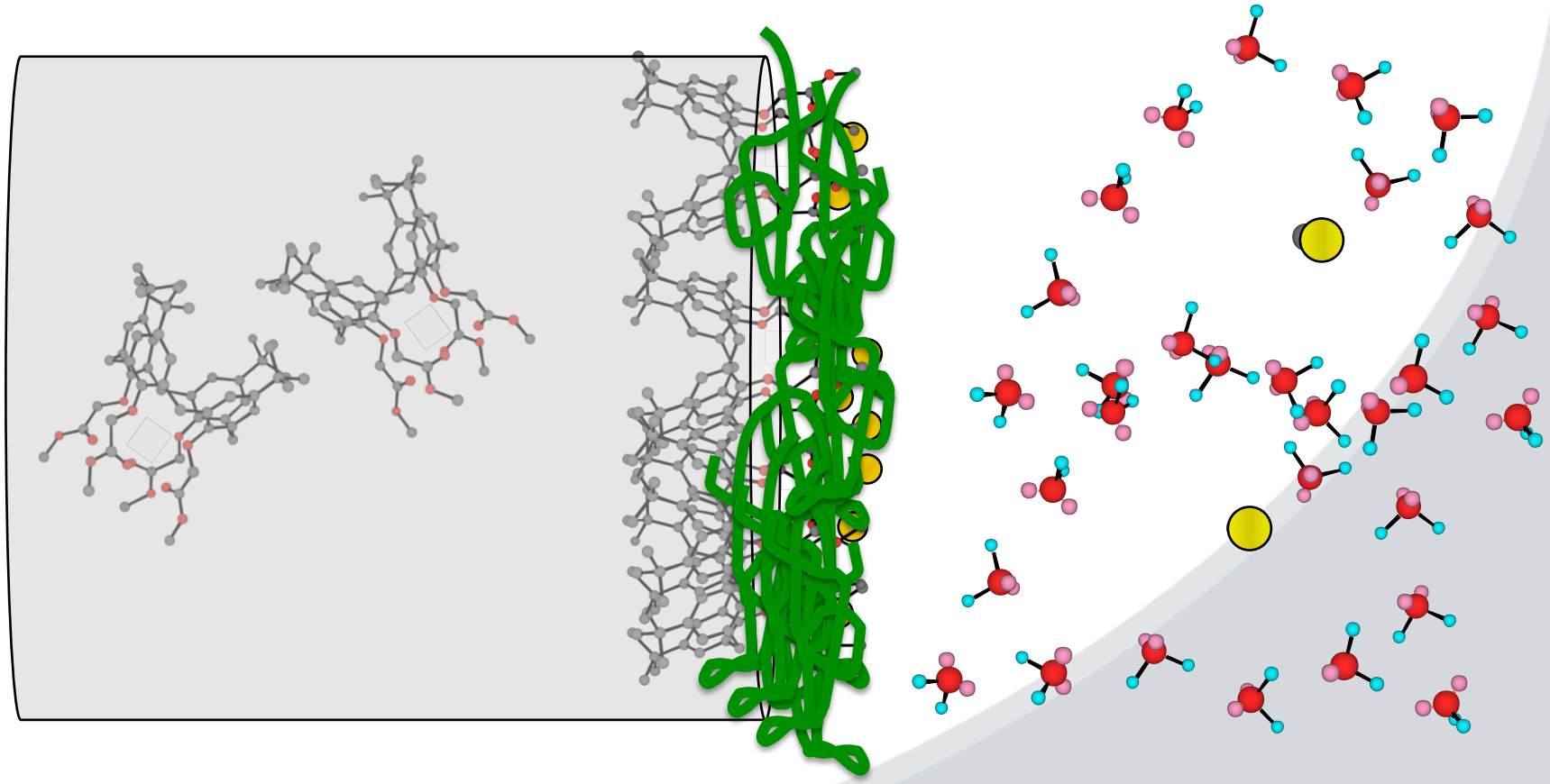
- **5-YEAR, €16.4 MILLION RESEARCH PROGRAM TO DEVELOP NEXT GENERATION SENSOR WEB TECHNOLOGIES WITH SIGNIFICANT ENVIRONMENTAL FOCUS**
- **BRINGS TOGETHER FUNDAMENTAL MATERIALS SCIENCE, FUNCTIONAL POLYMERS, DEVICE PROTOTYPING, ENERGY MANAGEMENT, ADAPTIVE MIDDLEWARE, WEARABLE SENSORS, DISTRIBUTED ENVIRONMENTAL MONITORING ….**

Sensor Hierarchy

- **PHYSICAL TRANSDUCERS – THE GOOD GUYS; LOW COST, RELIABLE, LOW POWER DEMAND, LONG LIFE-TIME**
  - THERMISTORS (TEMPERATURE), MOVEMENT, LOCATION, POWER,, LIGHT LEVEL, CONDUCTIVITY, FLOW, SOUND/AUDIO, ……
- **CHEMICAL SENSORS – MORE COMPLICATED, MISBEHAVE, NEED REGULAR CALIBRATION, MUCH MORE COSTLY TO IMPLEMENT**
  - ELECTROCHEMICAL, OPTICAL, .. FOR METAL IONS, PH, ORGANICS…
- **BIOSENSORS – THE WORST OF ALL, VERY DIFFICULT TO WORK WITH, DIE QUICKLY, SINGLE SHOT (DISPOSABLE) MODE**
  - DUE TO THE DELICATE NATURE OF ENZYMES, ANTIBODIES….

BUT CAN WE USE THESE SENSORS IN CONTINUOUS DIRECT CONTACT WITH REAL SAMPLES TO PROVIDE LOW COST, AUTONOMOUS SENSING PLATFORMS...

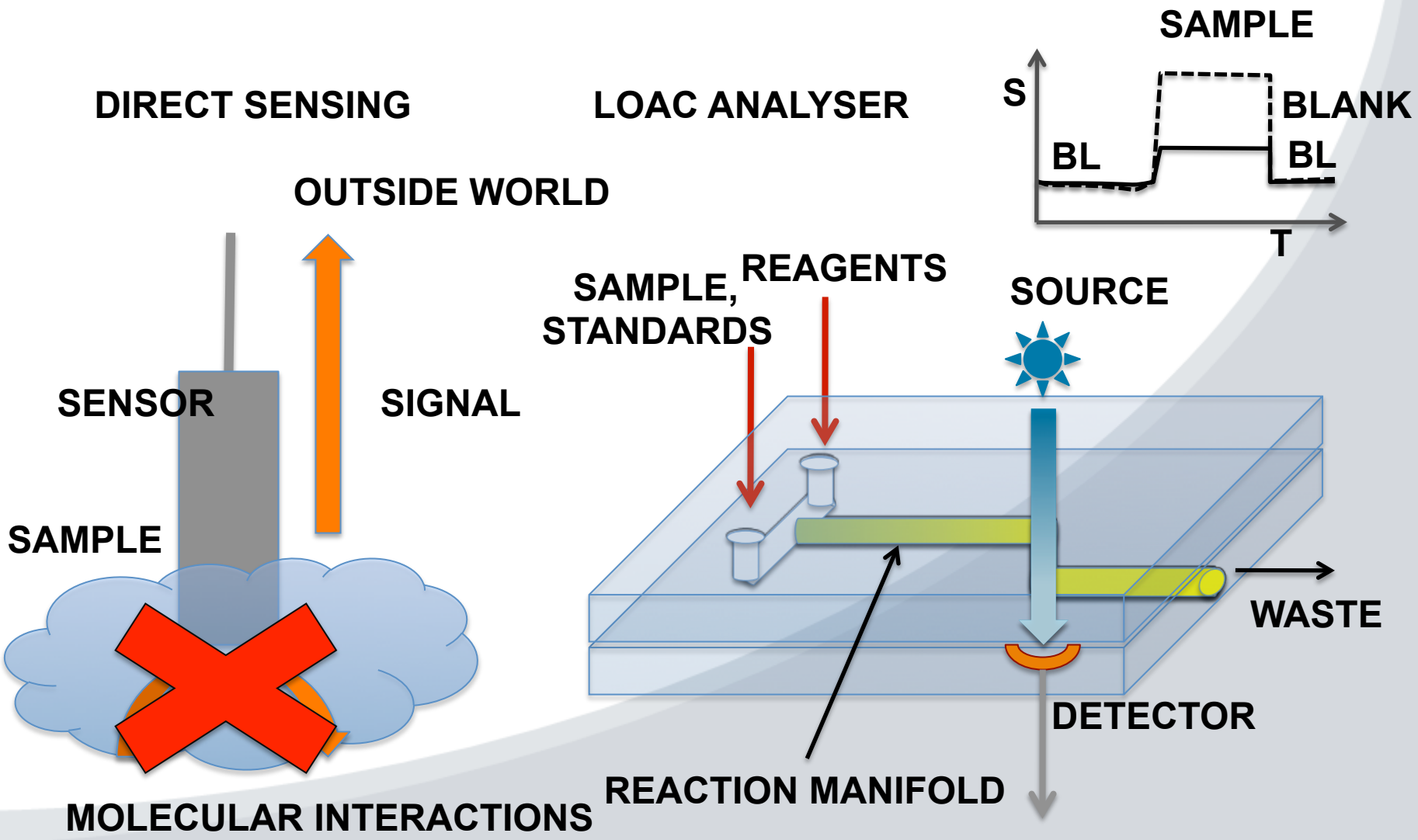
Fundamental Problem: Sensor surface will change with time!



SURFACES SUSCEPTIBLE TO BIOFOULING: THE SENSOR SAMPLES THE BIOFILM LAYER, NOT THE BULK SOLUTION!

=> DRIFT, LOSS OF SENSITIVITY/LOD/SELECTIVITY => REGULAR CALIBRATION (LIQUID HANDLING) => HIGH COST OF OWNERSHIP

Direct Sensing *vs.* Reagent Based LOAC



MANY PEOPLE, MYSELF INCLUDED, EXPECTED THAT THE ABILITY TO MANIPULATE FLUID STREAMS, IN MICROCHANNELS, EASILY, WOULD RESULT IN A PROLIFERATION OF COMMERCIAL LOAC SYSTEMS, AND THAT WE WOULD SEE APPLICATIONS OF THESE DEVICES PROLIFERATING THROUGHOUT SCIENCE. IN FACT, IT HAS NOT (YET) HAPPENED.

EDITORIAL 'SOLVING PROBLEMS', GEORGE WHITESIDES
LAB CHIP 10 (2010) 2317-2318

MICROFLUIDICS FOCUS:
SCIENCE & TECHNOLOGY
(scientific papers)

Use of microfluidics for the solution of problems??

PROBLEM ⇌ **MICROFLUIDIC TECHNOLOGY**

BETTER THAN EXSISTING TECHNOLOGY

MARKET

DEVELOPMENT!!!

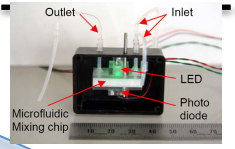
Achieving Scale-up

CLARITY
clarity-centre.org

CURRENT PLATFORMS

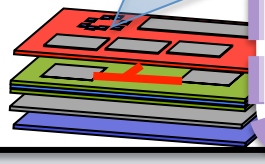
1

2. REVOLUTIONARY MATERIALS BREAKTHROUGHS; HIDDEN COMPLEXITY, BIOMIMETIC PLATFORMS, ALL FLUID HANDLING INTEGRATED ON CHIP, INDEFINITELY SELF-SUSTAINING



1. EVOLUTIONARY DEVELOPMENT, COST DRIVEN DOWN, RELIABLE, IMPROVED SCALABILITY

2



MASSIVELY SCALED DEPLOYMENTS OF THE FUTURE

COST/COMPLEXITY->

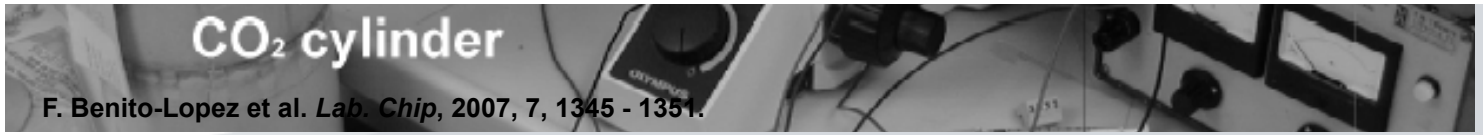
Scalability ->

Disadvantage of Microfluidics

NEW GENERATION OF MICROFLUIDIC DEVICES

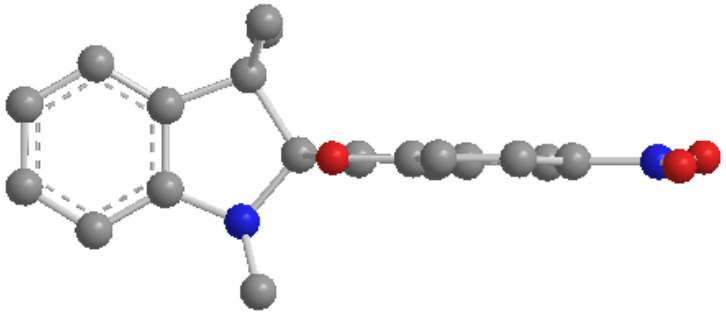
↓

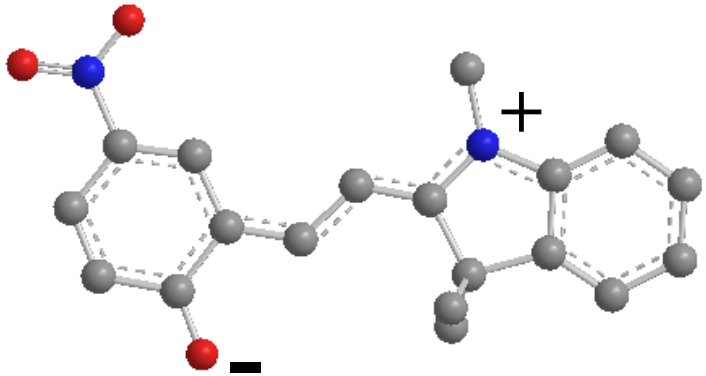
ADVANCES IN FUNDAMENTAL MATERIAL SCIENCE

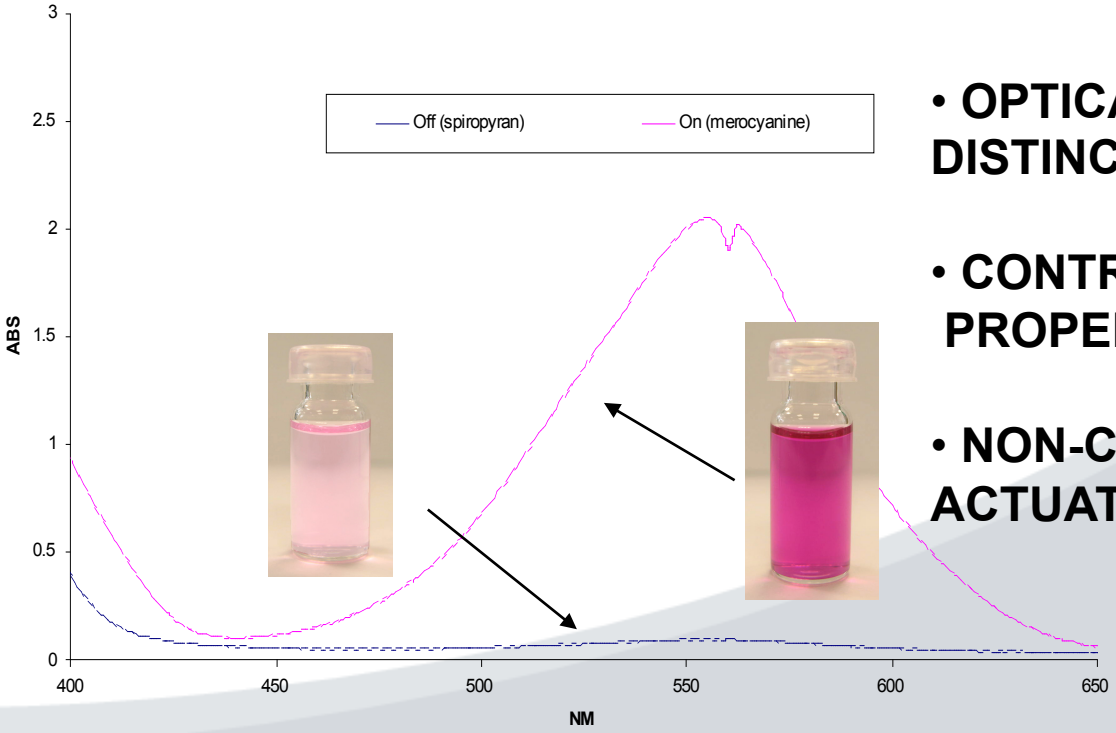


F. Benito-Lopez et al. *Lab. Chip*, 2007, 7, 1345 - 1351.

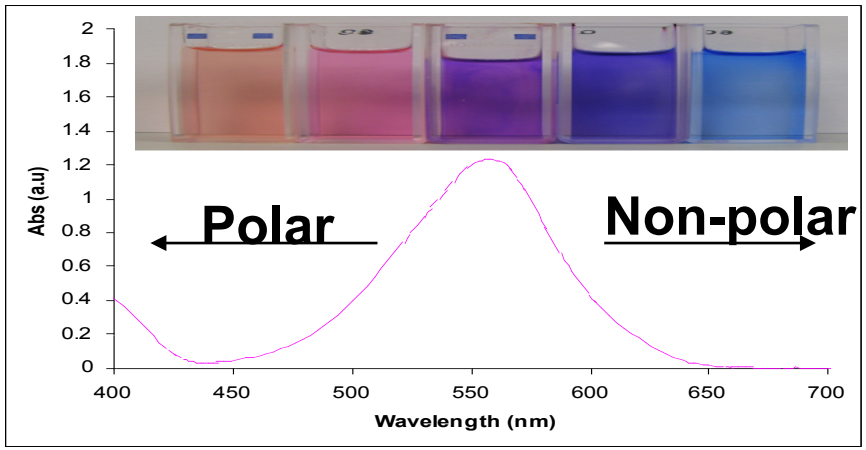
Photoswitchable Materials

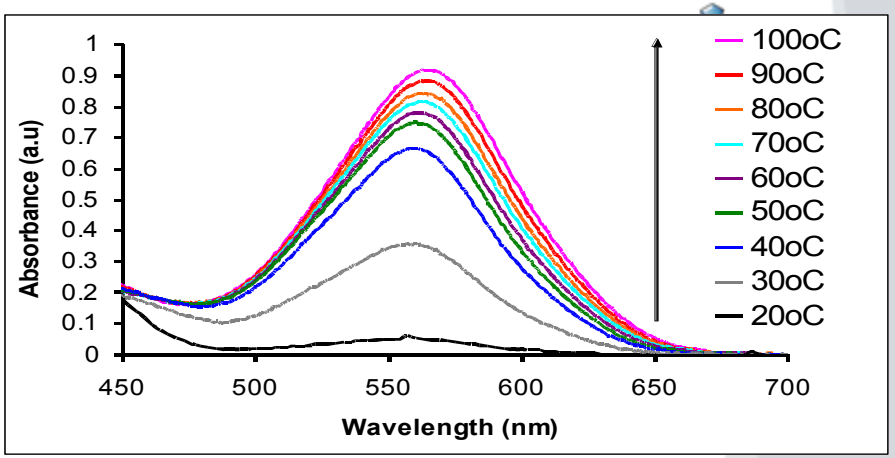




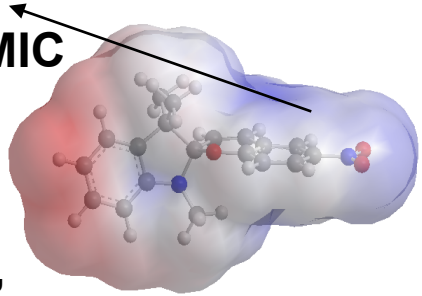


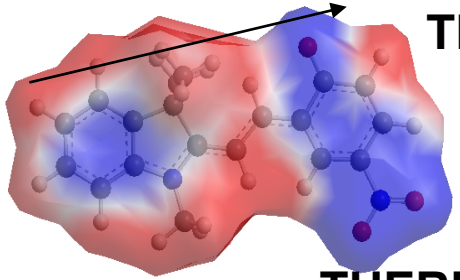
- **OPTICALLY ACTUATE BETWEEN TWO DISTINCT ISOMERS**
- **CONTROL PHYSICO-CHEMICAL PROPERTIES OF SYSTEM**
- **NON-CONTACT SPATIAL CONTROL OF ACTUATION**





SOLVATOCHROMIC

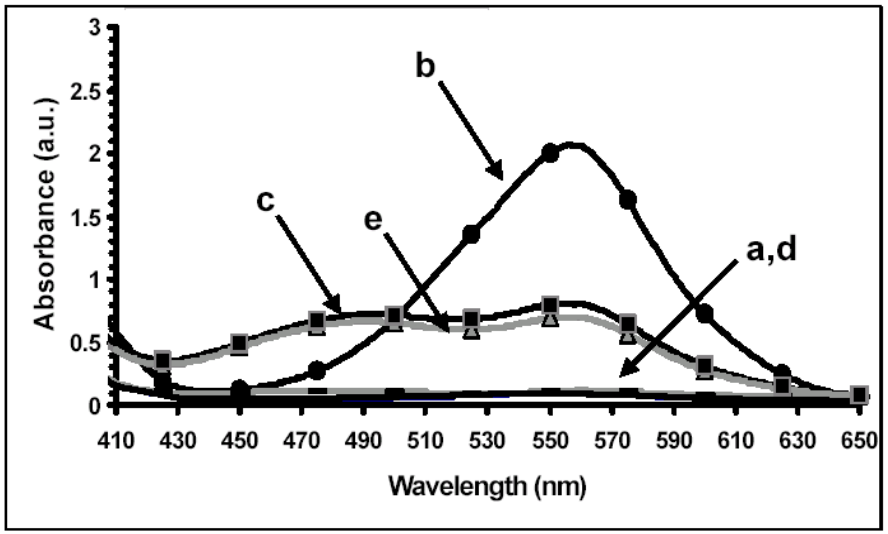




THERMOCHROMIC

METAL IONS, PROTON, PROTEIN AND DNA RECOGNITION SITE

THERMAL RELAXATION DEPENDENT ON ALL PROCESSES!



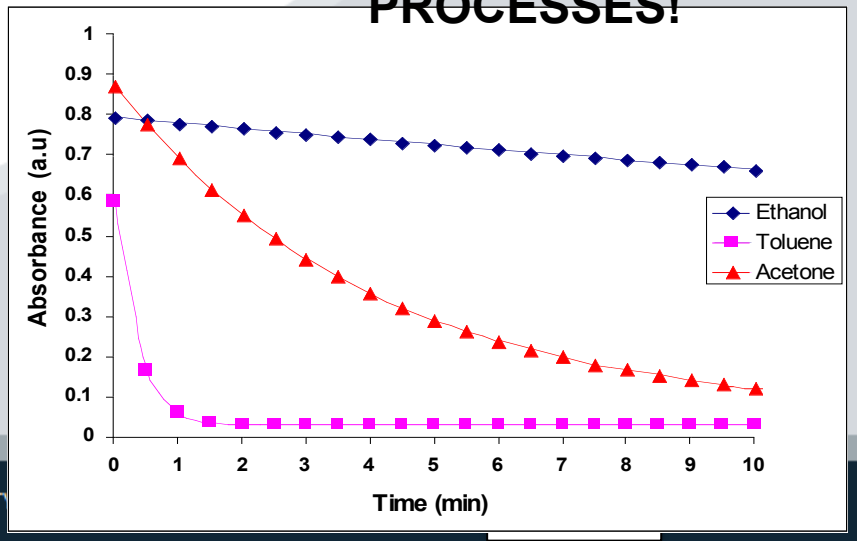


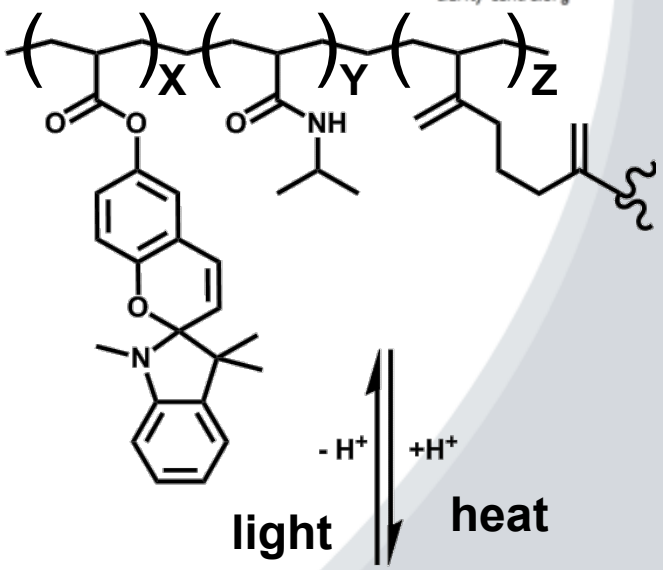
Photo-responsive polymer

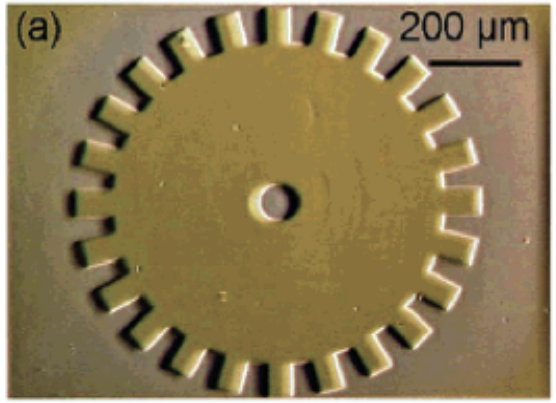
PROTONATED ISOMER INCORPORATED INTO CROSS LINKED THERMORESPONSIVE HYDROGEL

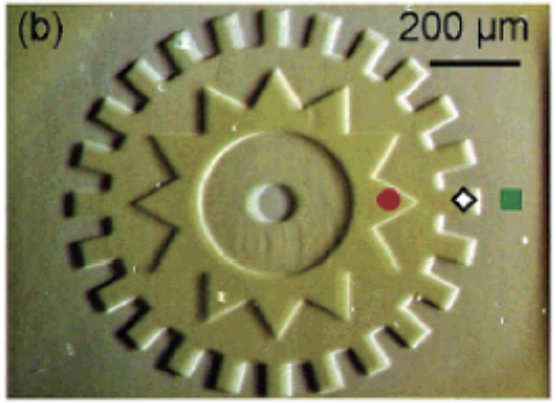
IRRADIATION OF BLUE LIGHT RESULTS IN CONTRACTION OF HYDROGEL

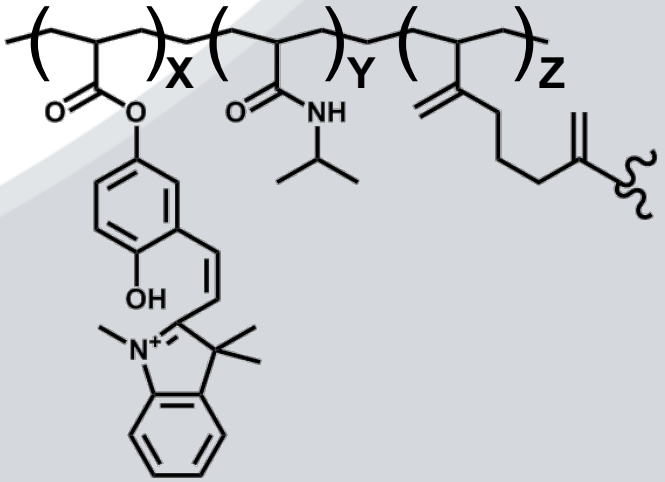
EXCELLENT SPATIAL RESOLUTION

TECHNICAL ISSUES INCLUDE EVAPORATION OF WATER FROM HYDROGEL









Sumaru *et al. Chem. Mater.,* 19 (11), 2730 -2732, 2007

Ionic Liquids- photoresponsive liquids

CLARITY
clarity-centre.org

CONSIST SOLELY OF IONS AND LIQUIDUS AT RT

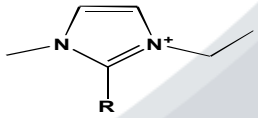
NEGLIGIBLE VAPOUR PRESSURE, NON-FLAMMABLE, THERMALLY STABLE AT HIGH TEMPERATURES

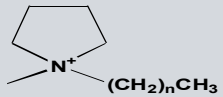
DESIGNER SOLVENTS (VISCOSITY, POLARITY, ACIDIC-BASIC, ELECTROCHEMICAL, ...)

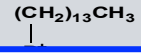
ABILITY TO TUNE ION COMPOSITION

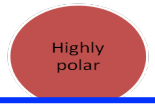
APPLICATIONS IN CATALYSIS, SEPARATIONS, POLYMERIZATIONS (IONIC LIQUIDS IN GELS, SOLID STATE ELECTROLYTES)

THE NUMBER OF PAPERS PUBLISHED IN 1995 WAS APPROXIMATELY 20 AND ROSE TO 2,500 IN 2006.

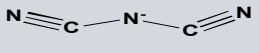


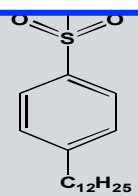


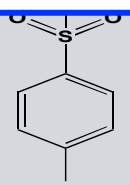




COMBINATION OF IONOGELS AND PHOTO-RESPONSIVE MATERIALS OFFERS MANY ADVANTAGES!!!!

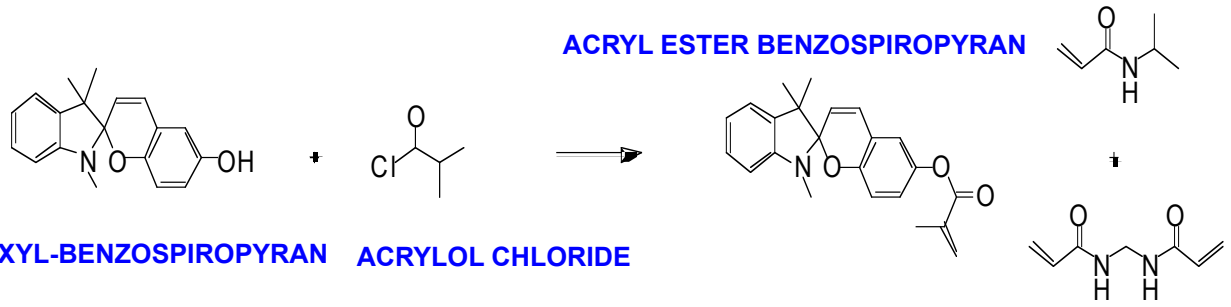


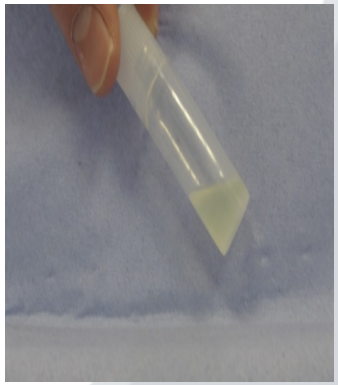


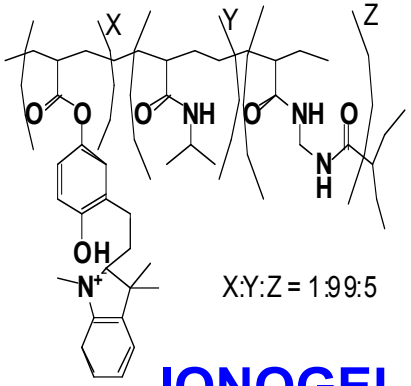


F. Benito-Lopez, et al., Mater. Today, 2010, 13, (7-8), July-August, 16-23.

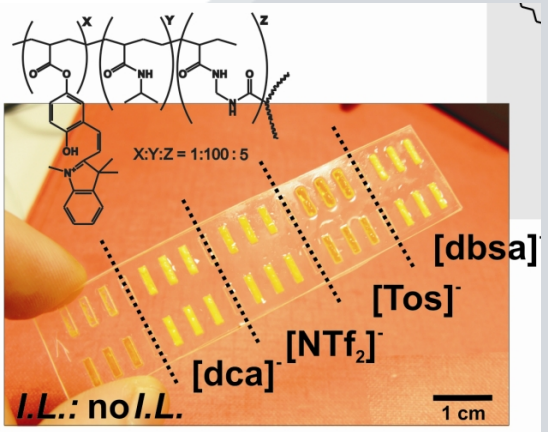
Preparation of photo-responsive ionogel







IONOGEL

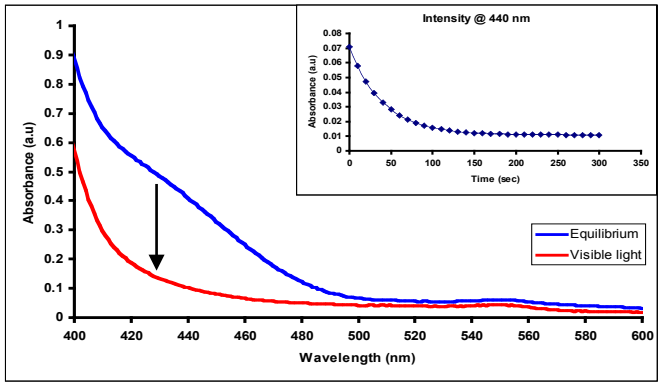


Byrne *et al.*, *Biosens & Bioelectron,* 26, 2010, 1392-1398

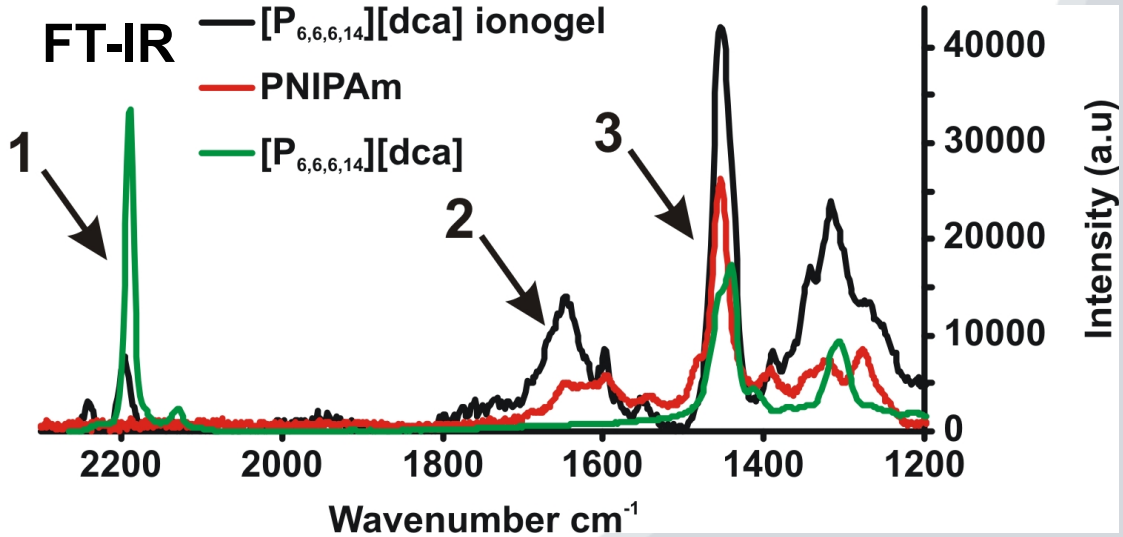
Photo-responsive ionogel properties

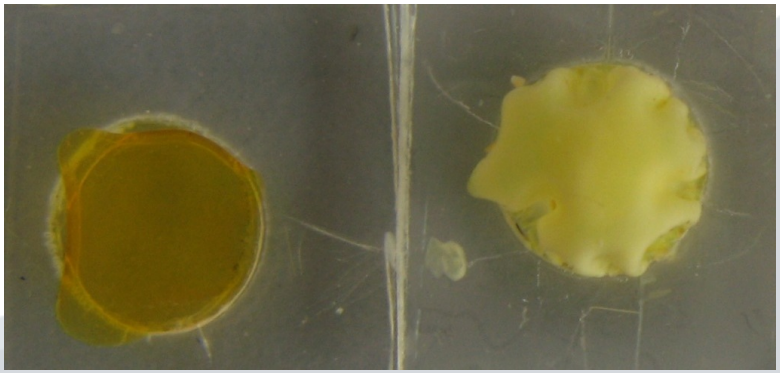
PHOTO-POLYMERISATION TAKES PLACE IN IONIC LIQUID MATRIX

IONOGELS HAVE DIFFERENT CHEMICAL AND PHOTO-PHYSICAL PROPERTIES DUE TO IONS WITH WITHIN THE GEL.



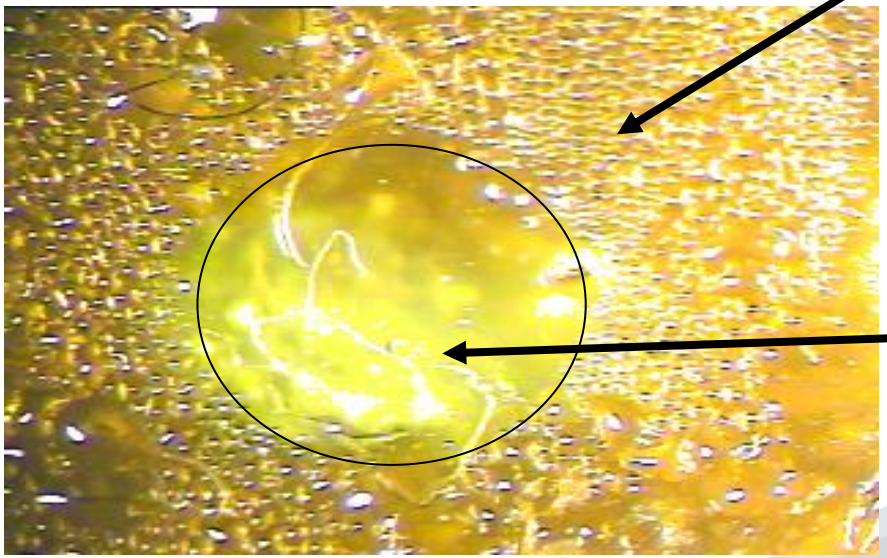
SPECTROSCOPIC ANALYSIS
RATE CONSTANT = 2.5 x10-2s^{-1}

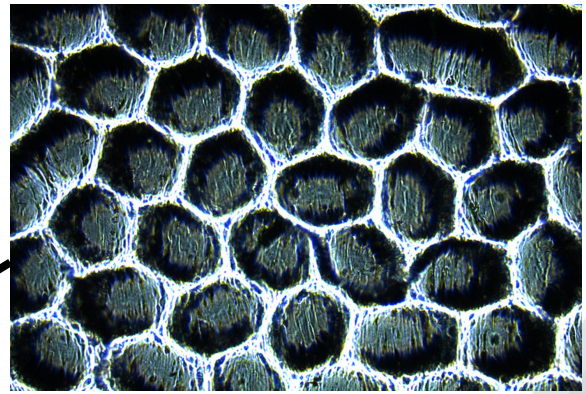




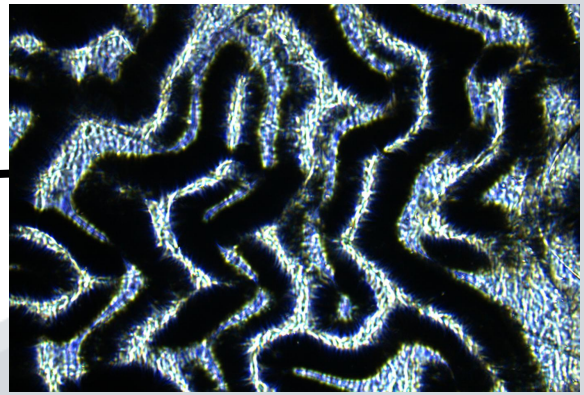
R. Byrne, Material Research Society, Adaptive materials, 2009, (NN) 1071.
F. Benito-Lopez, ECS transcations 2009, 19 (6) 199-210.

Photo-responsive ionogel properties



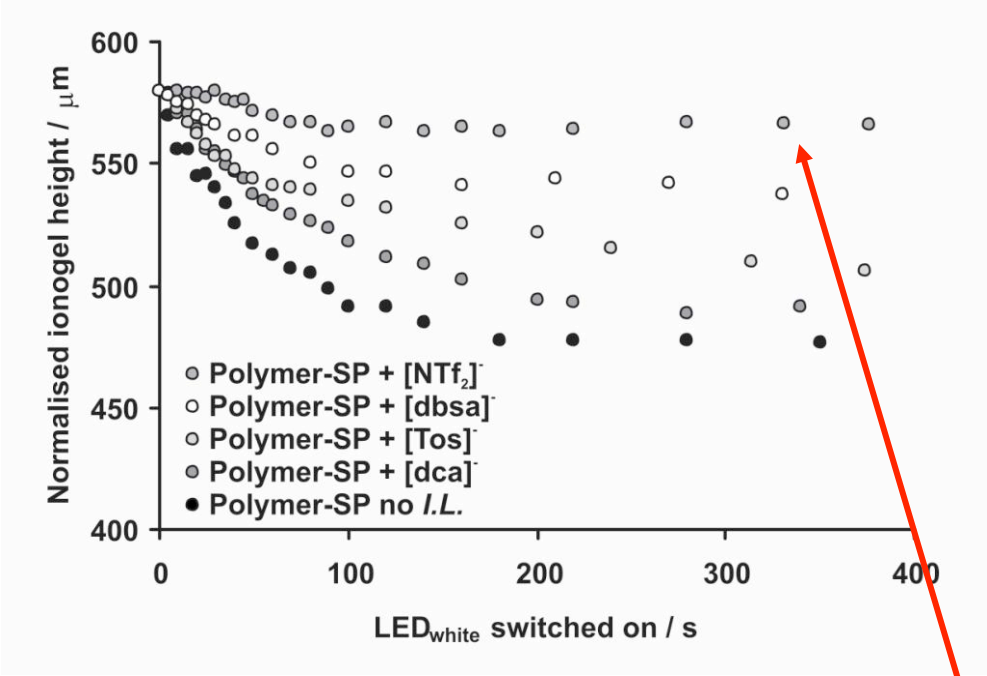


NO LIGHT



VISIBLE LIGHT

Physical characterisation of ionogel



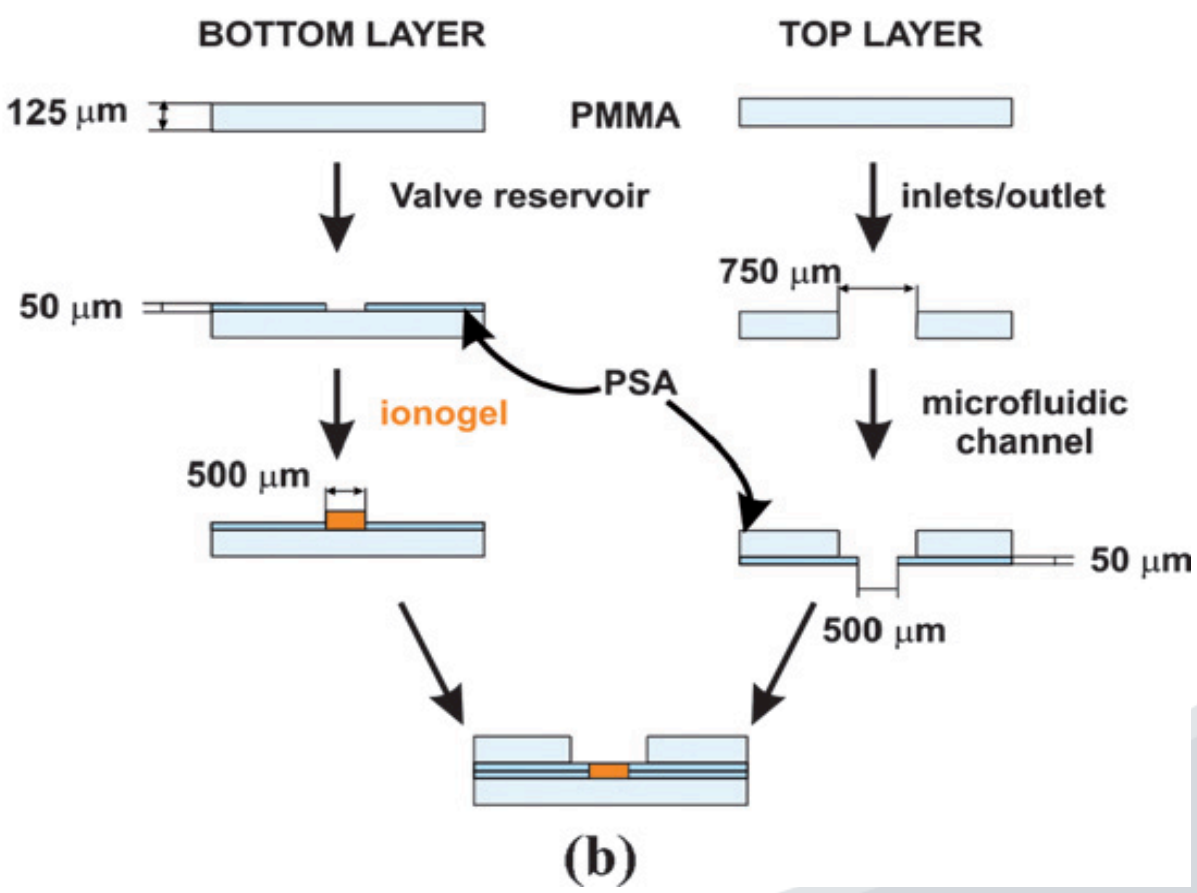
ALL MEASUREMENTS AT 25 °C

CORRELATION BETWEEN STIFFNESS AND ACTUATION BEHAVIOUR

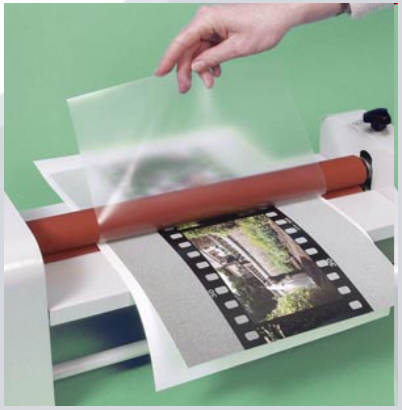
Table 1 Axial stiffness, ultimate tensile strength (UTS) and elongation at break values for the ionogels

Ionogel	Axial stiffness/N mm^{-1}	UTS/MPa	Elongation at break (%)
[dbsa]$^-$	0.1713	0.12	187.19
No I.L.	0.0493	0.08	65.910
[tos]$^-$	0.0187	0.02	545.48
[dca]$^-$	0.0149	0.02	131.53
[NTf$_2$]$^-$	2.9340	0.22	68.210

Photo-responsive valve: Chip fabrication



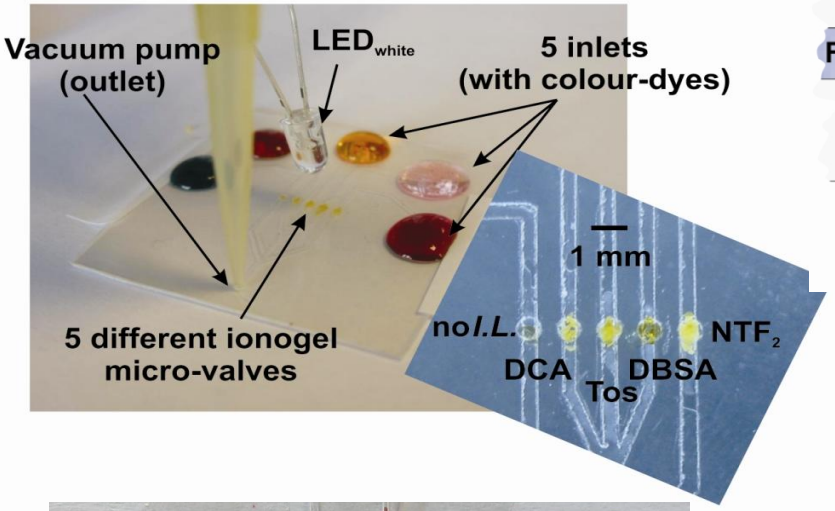
CO_2 laser

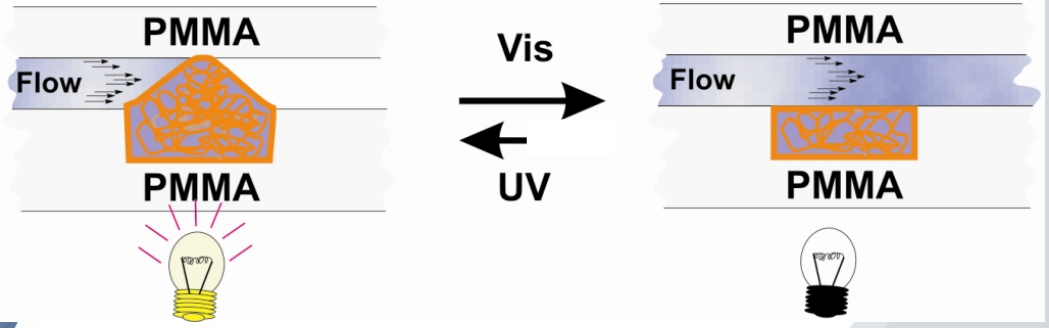


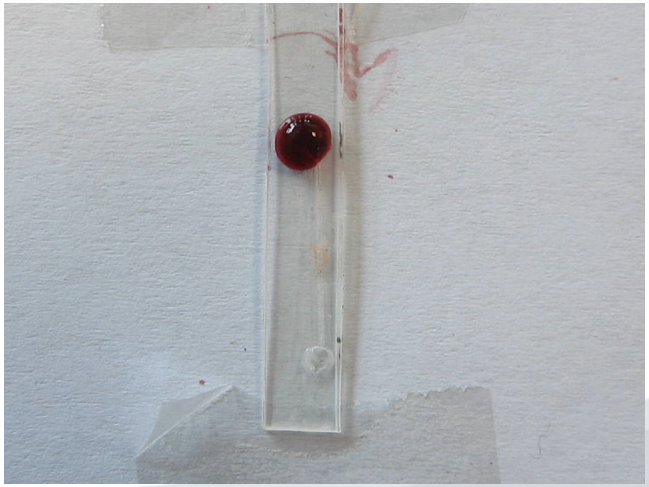
laminator

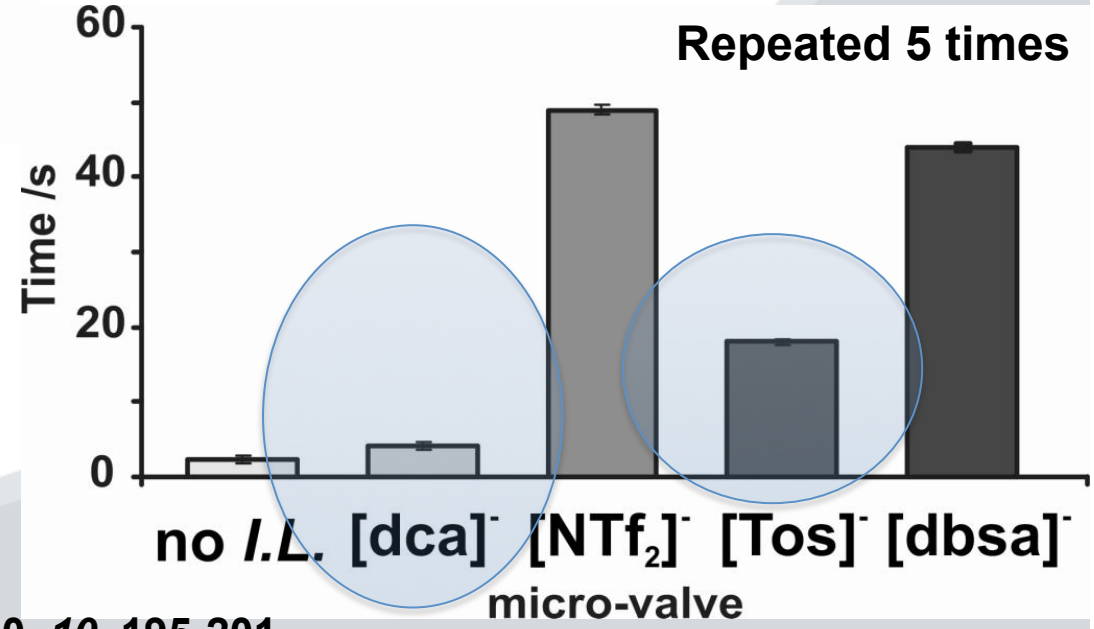
F. Benito-Lopez *et al.*, *Lab on a Chip* 2010, *10*, 195-201.

Multiple valves on one chip, using one actuation source!









F. Benito-Lopez *et al.*, *Lab on a Chip* 2010, *10*, 195-201.

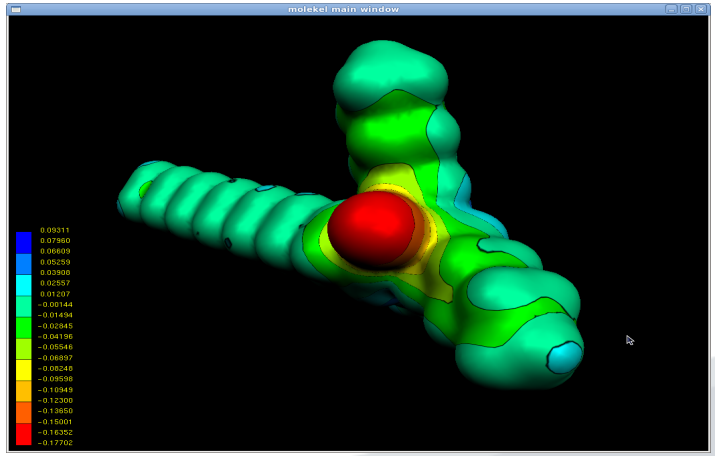
Magnetic control of hydrophobic liquids

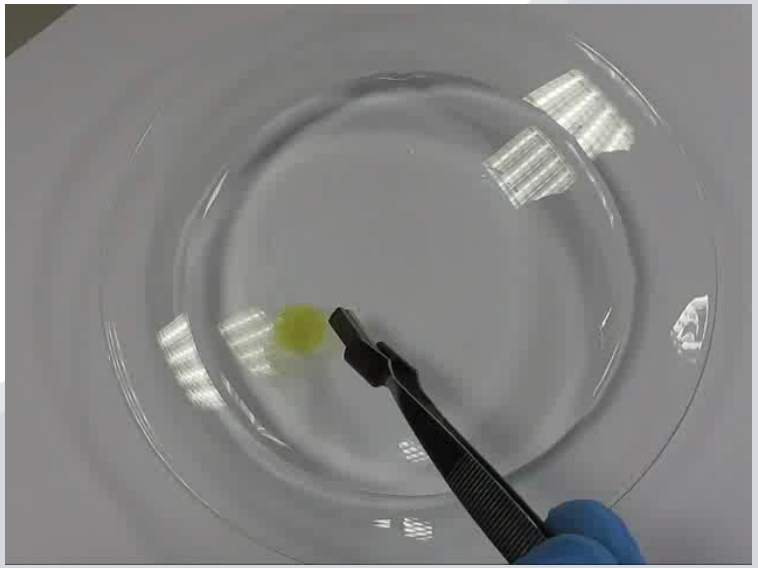
CLARITY
clarity-centre.org

Hydrophobic Ionic liquids (Phosphonium and Imidazolium based magnetic ionic liquids)

Prepared by salt metathesis with paramagnetic anions (Fe, Gd, Co, Mg)

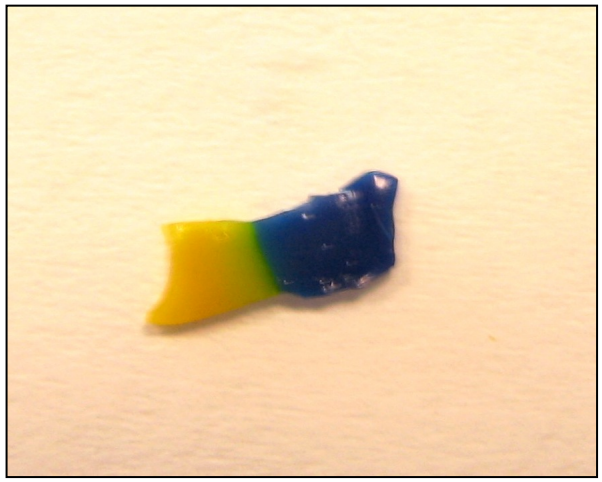
- **Non invasive control of $[P_{6,6,6,14}][FeCl_4]$ ionic liquid**
- **Disruption of laminar flow in micro fluidic channels**
- **Liquid tube stabilisation**





50ul of $[P_{6,6,6,14}][FeCl_4]$ in water

Chemical Sensor



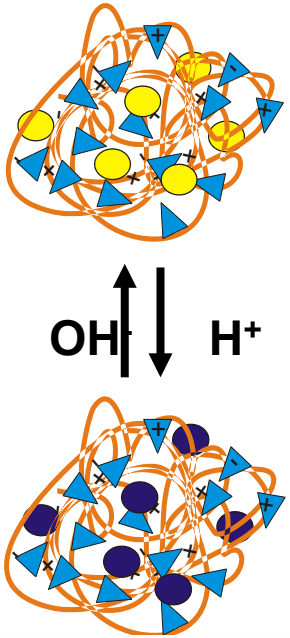
Stable after 20 cycles

BASE

ACID

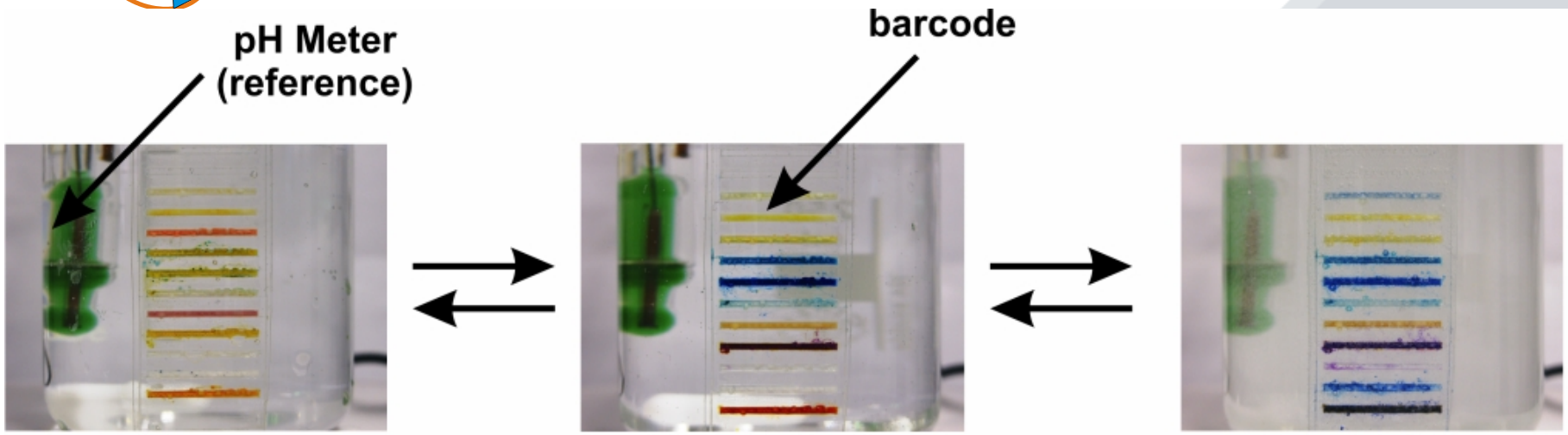
F. Benito-Lopez, et al. Pittcon Conference-2010, Orlando, Florida, USA, 28 March - 5 March, 2010. 610-3P.

Chemical Sensor



CHEAP
EASY TO FABRICATE
NO CHEMICAL MODIFICATION
NO LEACHING

UNIVERSAL
REUSABLE
LONG TERM DURATION
MASS PRODUCTION



Introduction

CLARITY
clarity-centre.org

SWEAT, WHY IS IMPORTANT?

Sweat is naturally generated during exercise.

Monitoring its contents provides very rich information about the physiological condition of the individual.

Rehydration and re-mineralisation

↓

Improve performance and general health

Sweat analysis: identify pathological disorders

* **cystic fibrosis***
* **information on dehydration**
• **changes in the concentration of biomolecules and ions.** **hyponatremia (low sodium concentration)**

*Common hereditary disease which affects the entire body, causing progressive disability and often early death.

Introduction

LIFESHIRT®

PHYSIOLOGICAL SENSORS

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

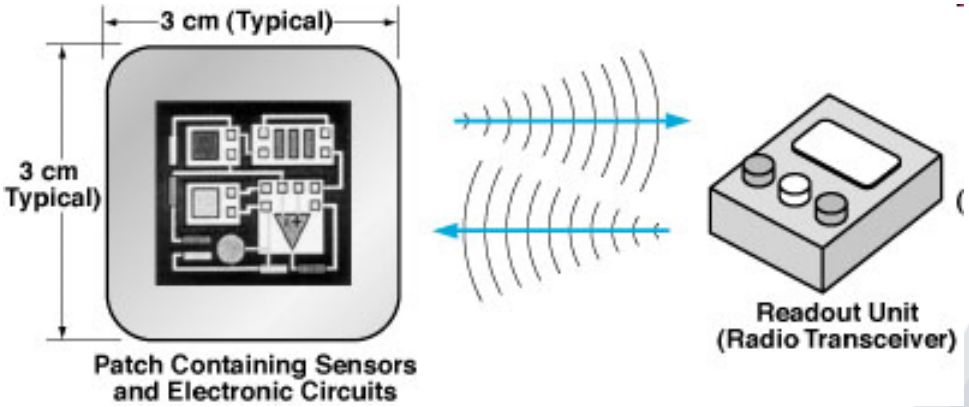
TRAINTRAK™

NIKE-APPLE IPOD SPORTS KIT

Introduction

CLARITY
clarity-centre.org

CHEMICAL SENSORS



NASA: WEARABLE SENSOR PATCHES

GLUCOWATCH

SWEAT COLLECTION PATCHES

Introduction

Current Ways of Sweat Collection and analysis

S. M. Shirreffs and R. J. Maughan, J Appl Physiol 82: 336-341, 1997

Introduction

PROBLEMS TO OVERCOME WITH CHEMICAL SENSOR?

SAMPLE GENERATION

COLLECTION

DELIVERY

SENSOR CALIBRATION

WEARABILITY

SAFETY ISSUES

SWEAT RATE AND FLUID LOSSES VARY FOR INDIVIDUALS AND ARE GENERALLY DEPENDENT ON BODY SIZE, GENDER, EXERCISE INTENSITY, ENVIRONMENTAL CONDITIONS AND INDIVIDUAL METABOLISM.

Introduction

WHAT DO WE NEED????

DEVICE:

WEARABLE

ROBUST

FLEXIBLE / ADAPTABLE

REUSABLE/ DISPOSABLE → **CHEAP**

CONTINUOUS REAL TIME ANALYSIS → **IMMEDIATE FEEDBACK**

MICRODEVICES!!

Introduction

DETECTION:

NOT INVASIVE

WIRELESS

FREEDOM FROM ELECTRICAL NOISE

MINIATURIZATION

NOT PHYSICAL CONTACT

FLEXIBILITY IN INTERROGATION APPROACHES
(HUMAN EYE, LED-SENSORS, CAMERAS, SPECTROMETERS, …)

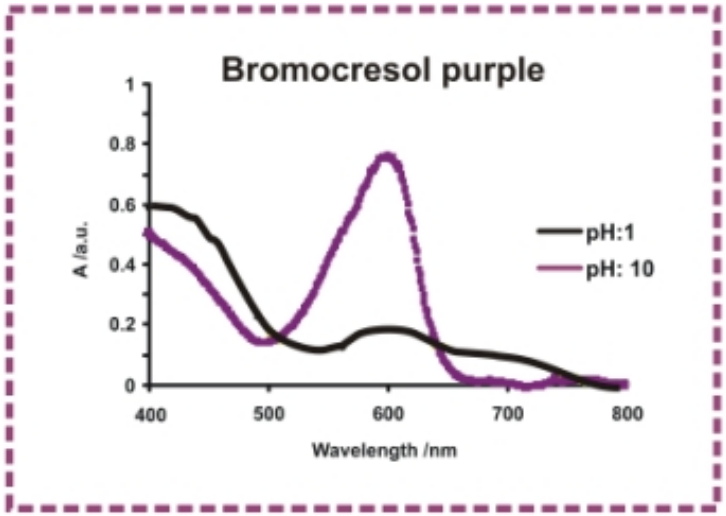
OPTICAL SENSORS!!

Ionogel pH sensor

DOPE THE IONOGEL WITH A pH-DYE

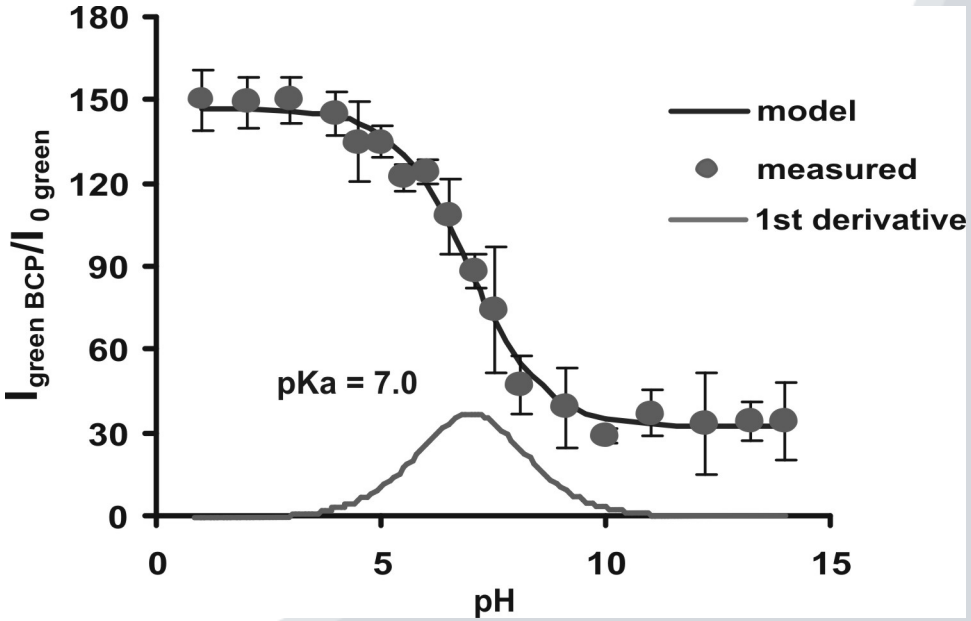
Sweat pH: 4.5-7.5

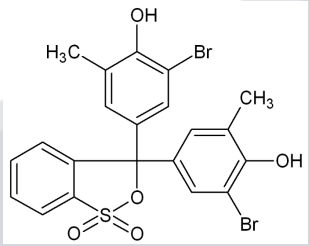
	pH
1- METHYL RED	4.4 - 6.2
2- BROMOCRESOL GREEN	3.8 - 5.4
3- BROMOCRESOL PURPLE	5.2 - 6.8
4- BROMOTHYMOL BLUE	6.0 - 7.6



DYE DO NOT LEACH OUT

DIGITAL CAMERA PHOTO RGB-MATLAB



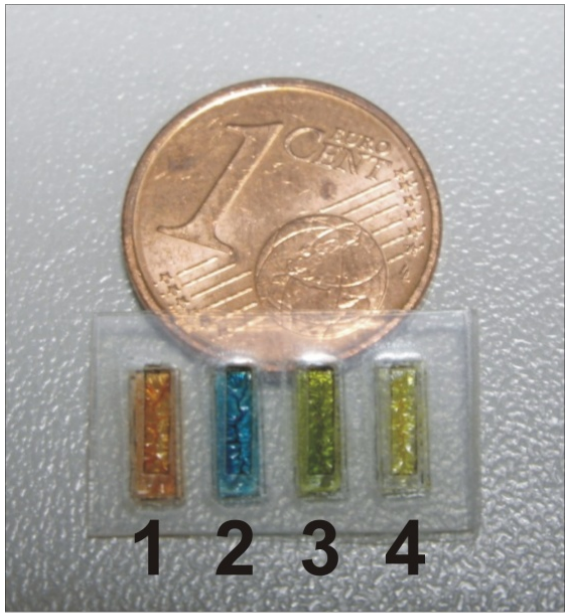


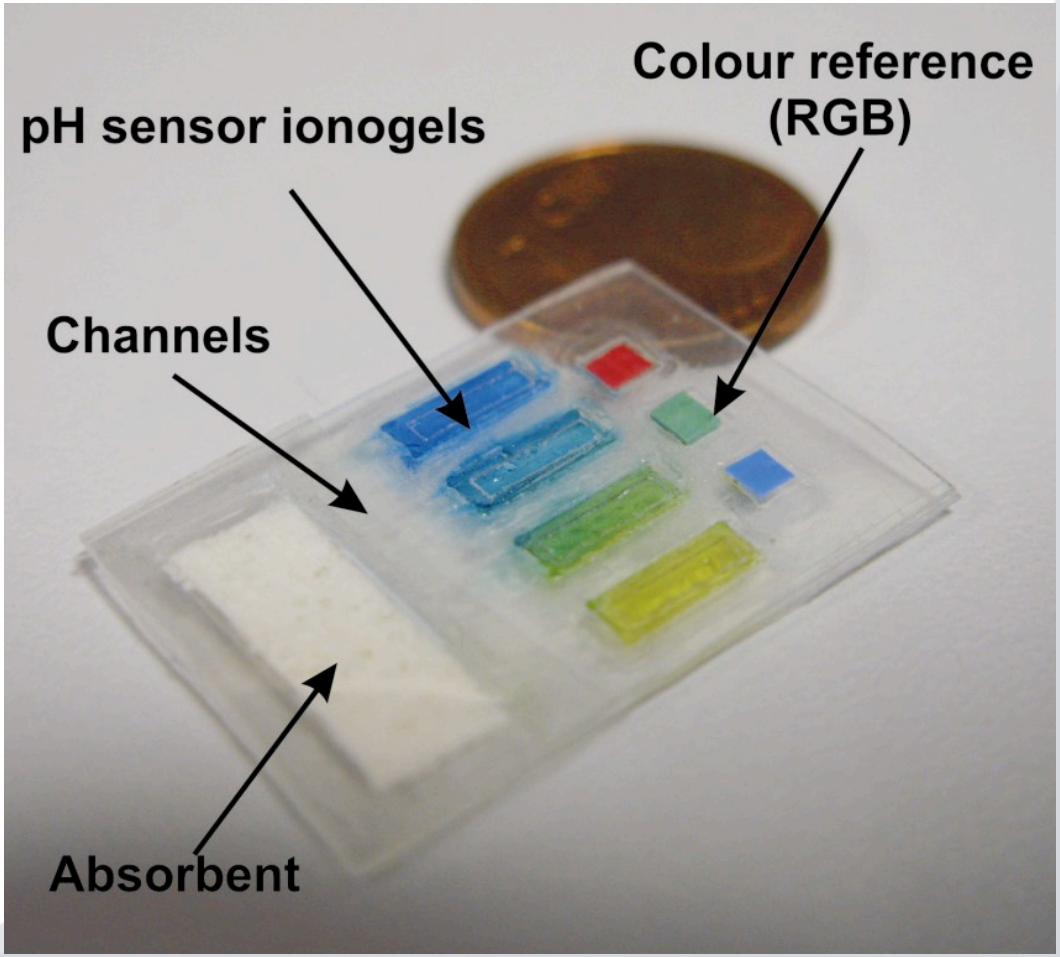
$pKa_{lit.}$ = 7.1

OPTICAL DETECTION

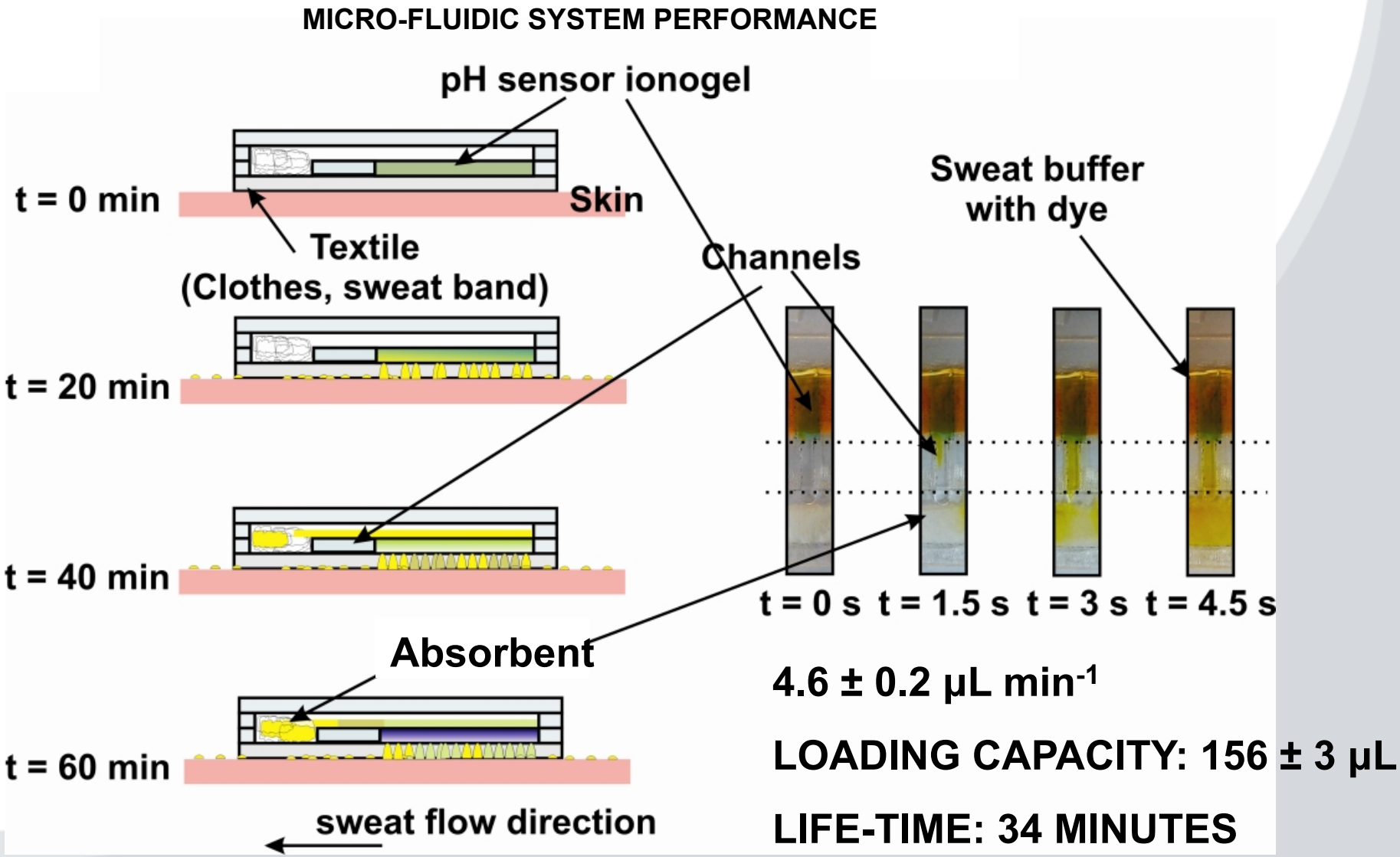
F. Benito-Lopez, R. Byrne, D. Diamond, Dublin City University, 2009, Patent Application No: GB 0904627-7.

Barcode & Micro-fluidic





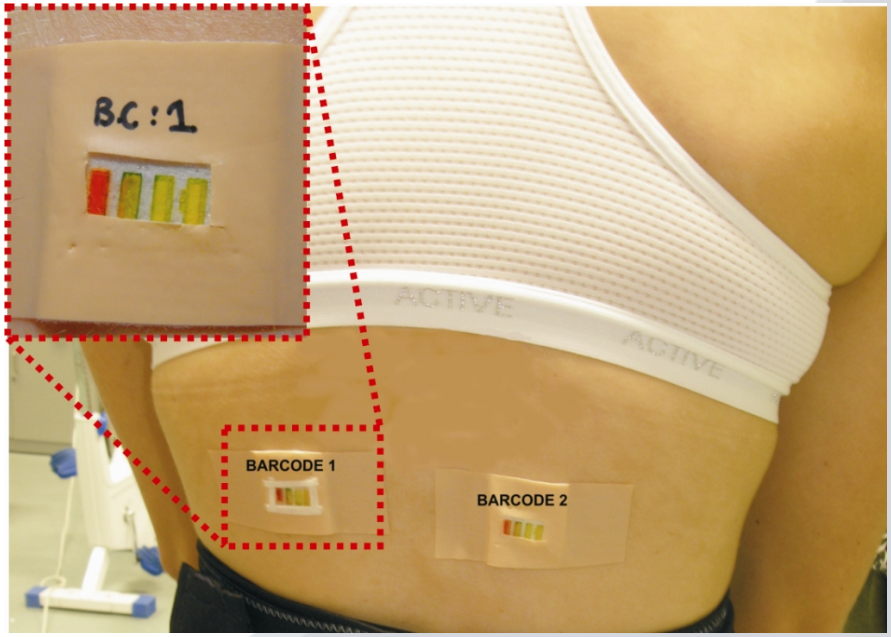
Characterisation



Results

Colour profile of each of the indicators at different pH's (pH range: 1-14)

ON-BODY TRIALS



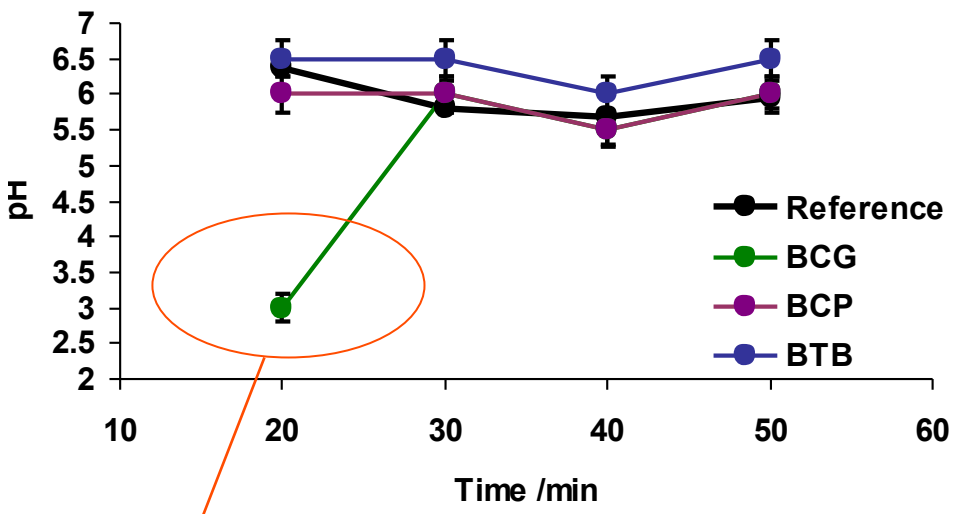
Back of a trainer with a chip (1) and barcode (2) systems (activated at pH 2)

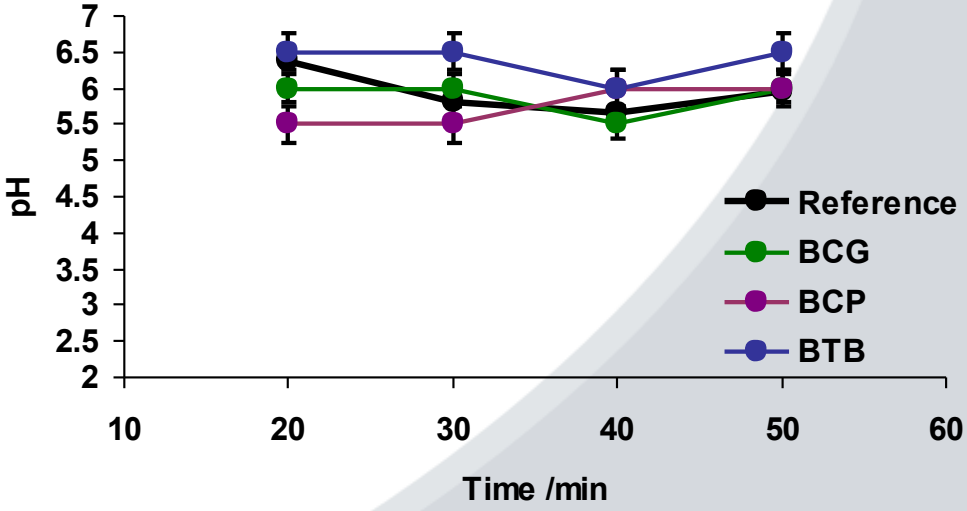
Results

CLARITY
clarity-centre.org

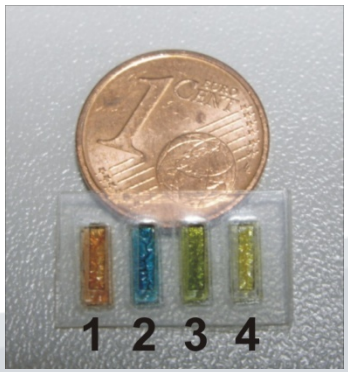
ON-BODY TRIALS

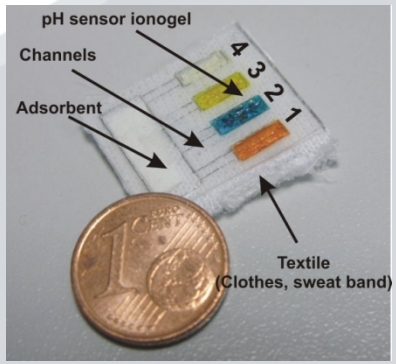
RESULTS: camera pictures and RGB colour analysis using a reference.



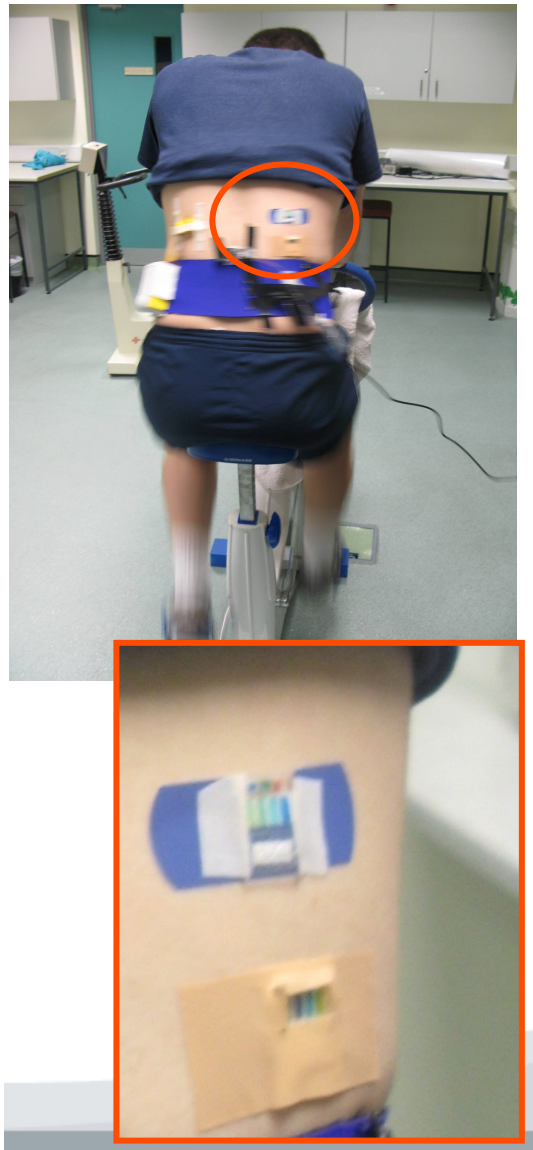


Activation pH

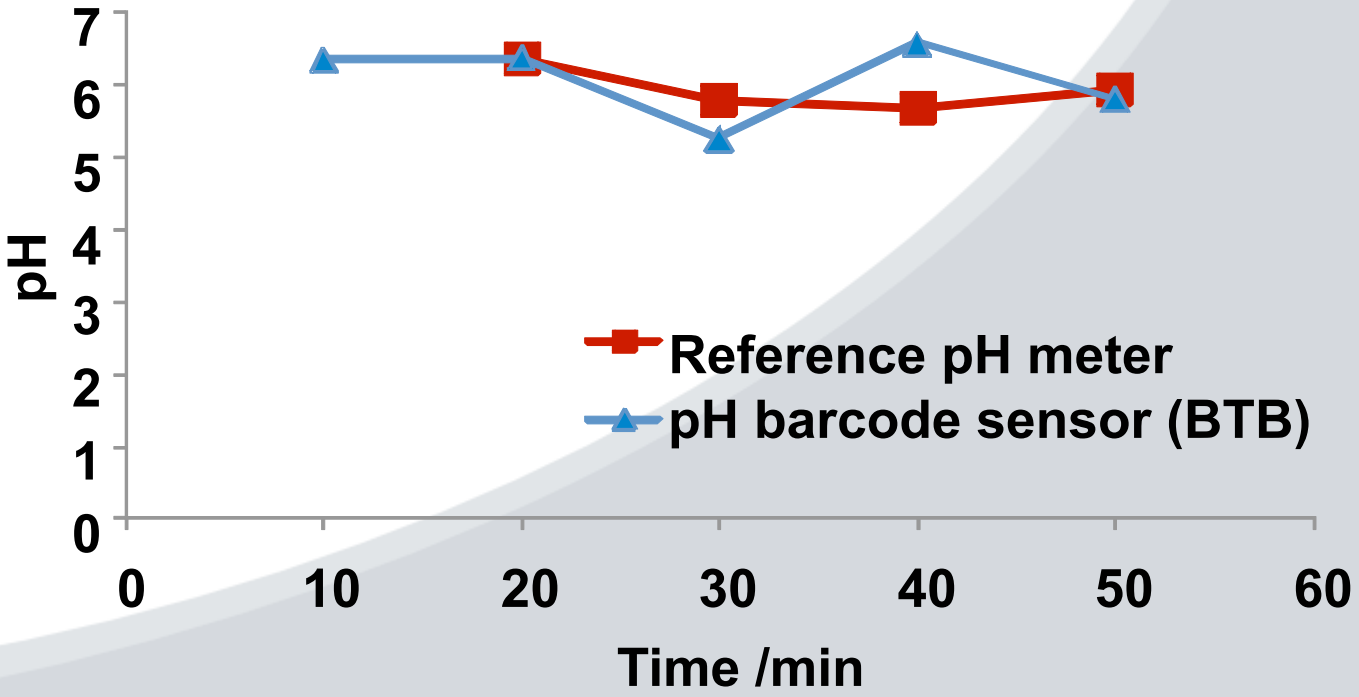




Results



Sweat pH determination using the barcode in an athlete during a 50 min training period



S. Coyle, T. Radu, F. Benito-Lopez, K.-T. Lau, D. Diamond, Res. J. Text. Apparel. 2010. *Accepted.*

Conclusions

- MICROFLUIDICS HAS ACHIEVED MUCH IN TERMS OF DELIVERING A BASIC UNDERSTANDING OF FLUID HANDLING AND ANALYTICAL MEASUREMENTS IN MICRO/NANO-CHANNELS.

- THE NEXT PHASE HAS TO DELIVER FULLY INTEGRATED AND FUNCTIONING 'MICRO-TOTAL ANALYSIS SYSTEMS' THAT CAN PROVIDE SOLUTIONS WITH REAL SOCIO-ECONOMIC IMPACT.

- VITAL TO COMBINE STRONG APPLIED EFFORT TO PRODUCE NEXT GENERATION PLATFORMS & PROTOTYPES (EVOLUTIONARY ADVANCES) WITH FUNDAMENTAL BREAKTHROUGHS IN MATERIALS SCIENCE (REVOLUTIONARY ADVANCES).

Thanks to…..

CLARITY
clarity-centre.org

QUESTIONS?