Realisation of Next Generation Lab-on-a-Chip Devices - Key Challenges in Fundamental Materials Science

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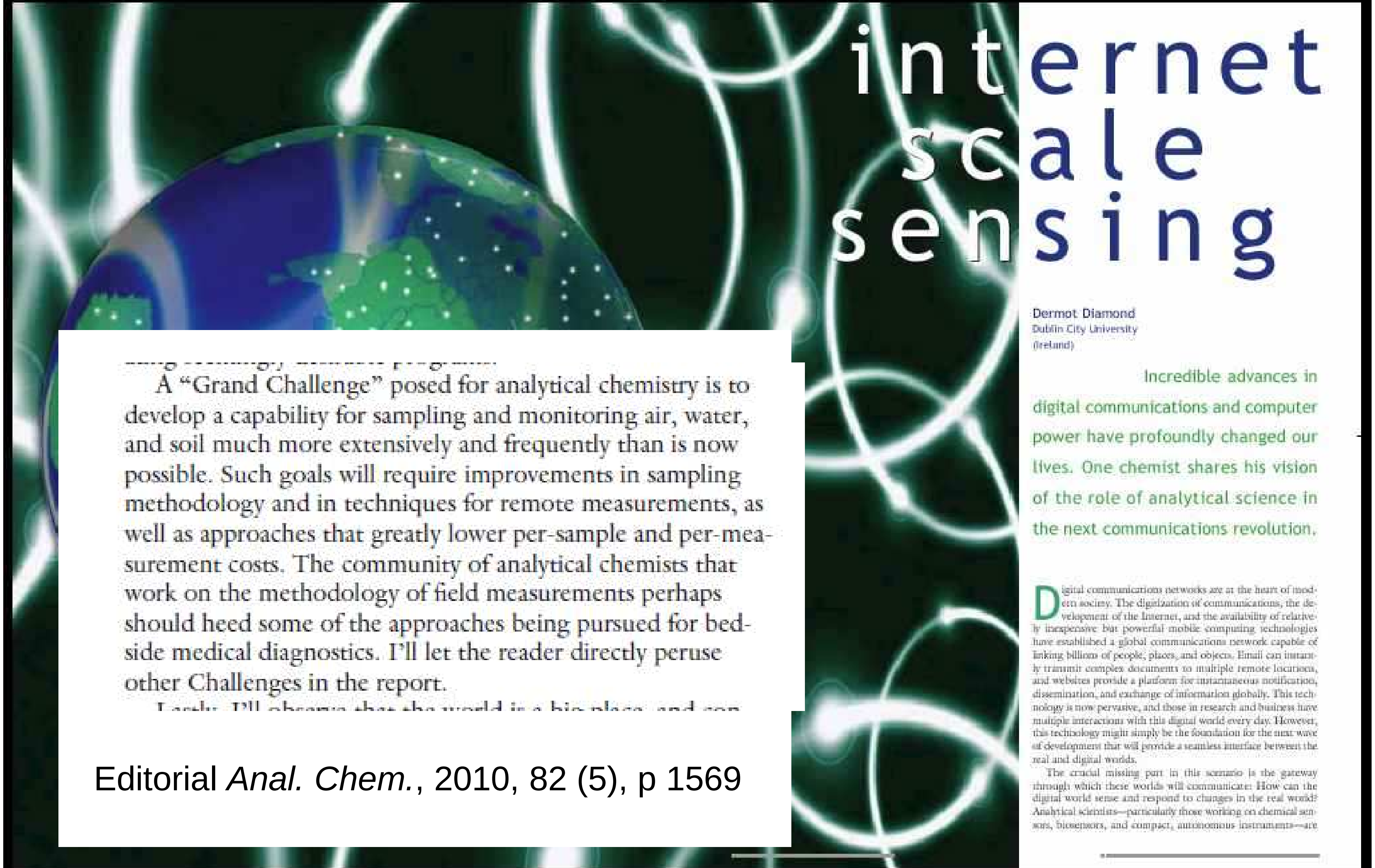
Keynote Article: August 2004, Analytical Chemistry (ACS)



internet scale sensing

Dermot Diamond
Dublin City University
(Ireland)

Incredible advances in digital communications and computer power have profoundly changed our lives. One chemist shares his vision of the role of analytical science in the next communications revolution.

Digital communications networks are at the heart of modern society. The digitization of communications, the development of the Internet, and the availability of relatively inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions of people, places, and objects. Email can instantly transmit complex documents to multiple remote locations, and websites provide a platform for instantaneous notification, dissemination, and exchange of information globally. This technology is now pervasive, and those in research and business have multiple interactions with this digital world every day. However, this technology might simply be the foundation for the next wave of development that will provide a seamless interface between the real and digital worlds.

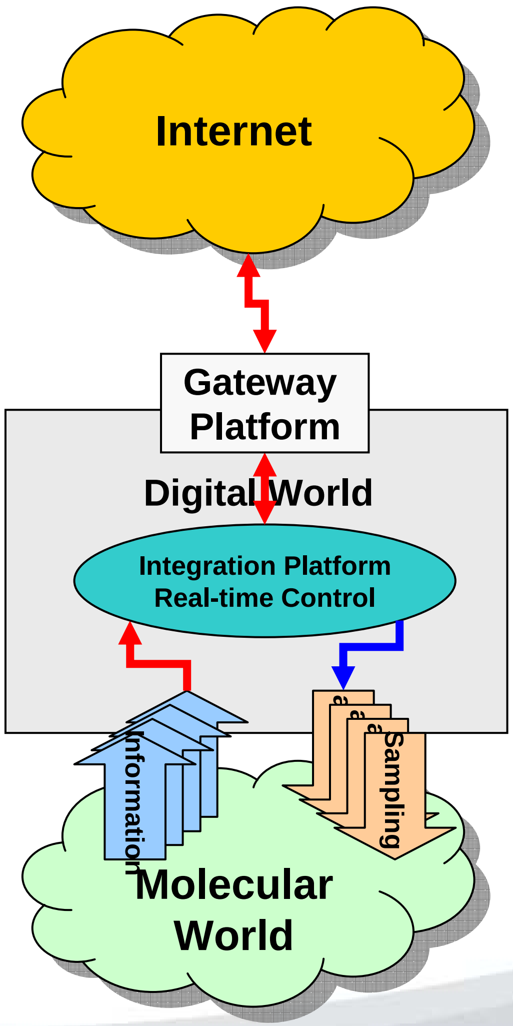
The crucial missing part in this scenario is the gateway through which these worlds will communicate: How can the digital world sense and respond to changes in the real world? Analytical scientists—particularly those working on chemical sensors, biosensors, and compact, autonomous instruments—are

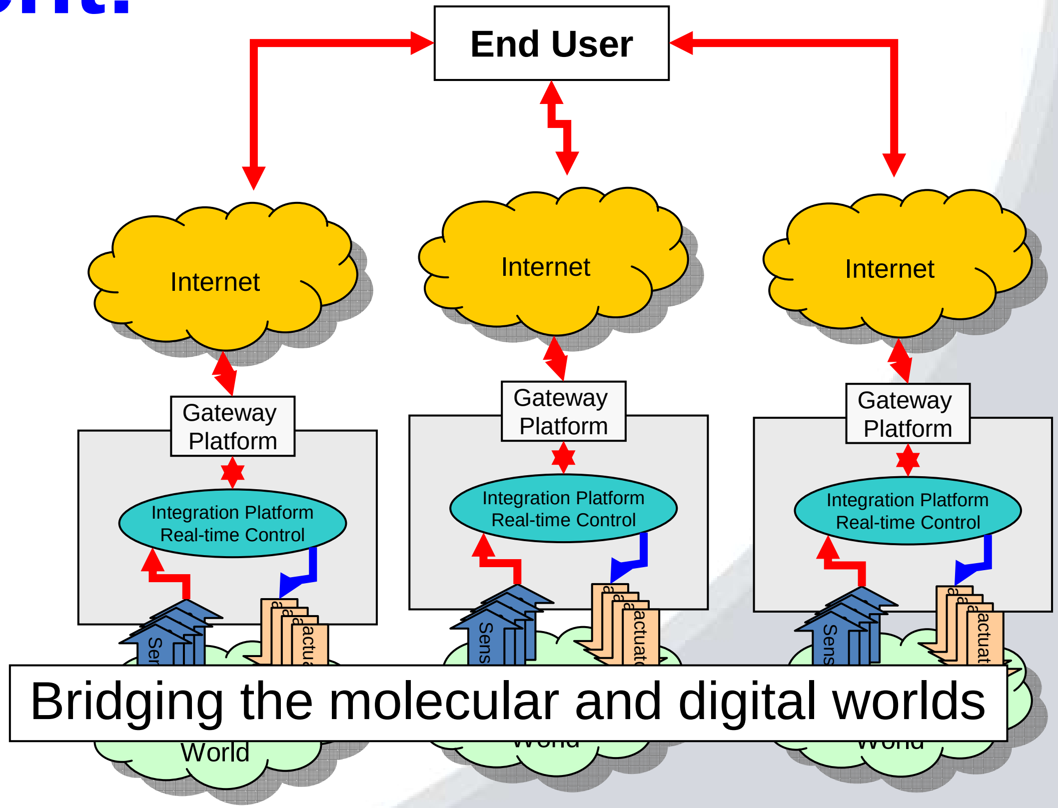
A "Grand Challenge" posed for analytical chemistry is to develop a capability for sampling and monitoring air, water, and soil much more extensively and frequently than is now possible. Such goals will require improvements in sampling methodology and in techniques for remote measurements, as well as approaches that greatly lower per-sample and per-measurement costs. The community of analytical chemists that work on the methodology of field measurements perhaps should heed some of the approaches being pursued for bedside medical diagnostics. I'll let the reader directly peruse other Challenges in the report.

Editorial *Anal. Chem.*, 2010, 82 (5), p 1569

Why? So events in the molecular world can be conveyed directly and instantly to the appropriate authorities. Prevent large scale contamination of environment.

Ubiquitous sensing: Internet-enable every measurement!





Environment
Chemical spills, Waste Management etc

Health
Homecare, e-Health
Elderly population

Security
Terrorist treats

This vision can only become a reality utilizing Lab on a Chip technology

Outline

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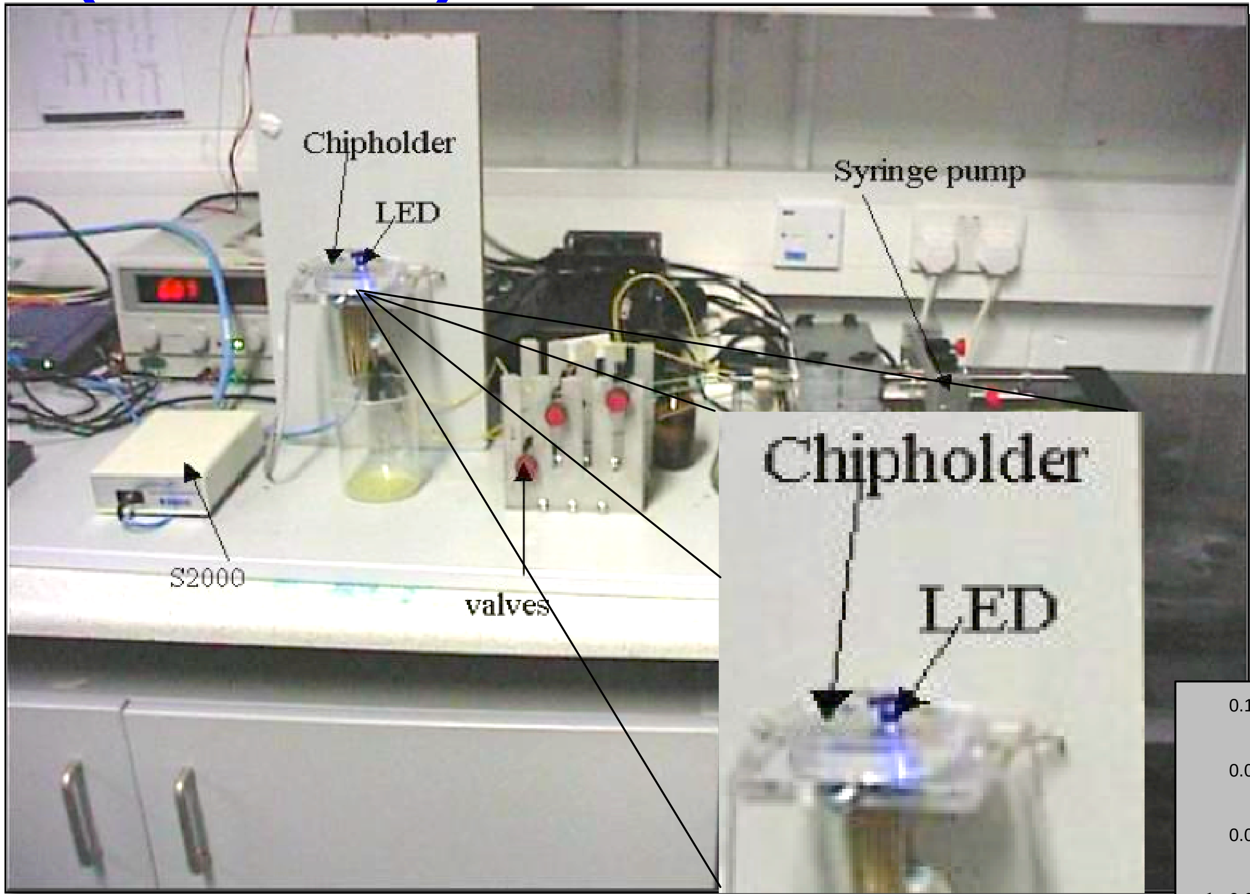
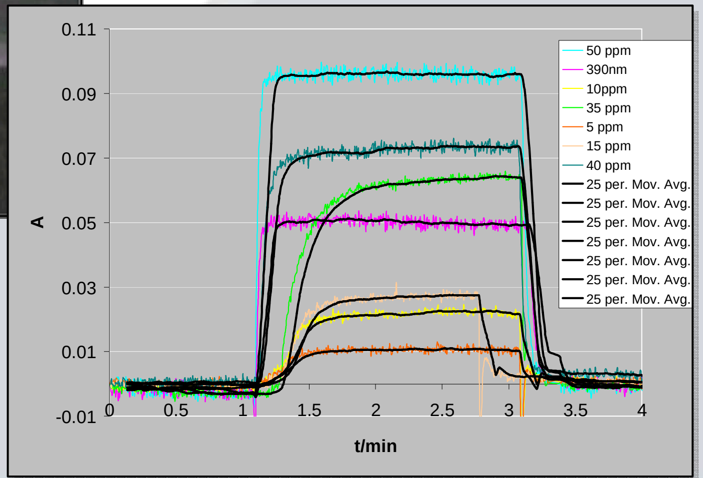
- **Group history of wireless environmental sensing**
- **Current issues of sensing systems**
  - Cost of ownership
  - Fluid handling using pumps and valves
- **Opportunity for Functional Materials**
  - Stimuli responsive materials
- **Outlook**

Reagent based Nutrient Analyser (Ammonia)

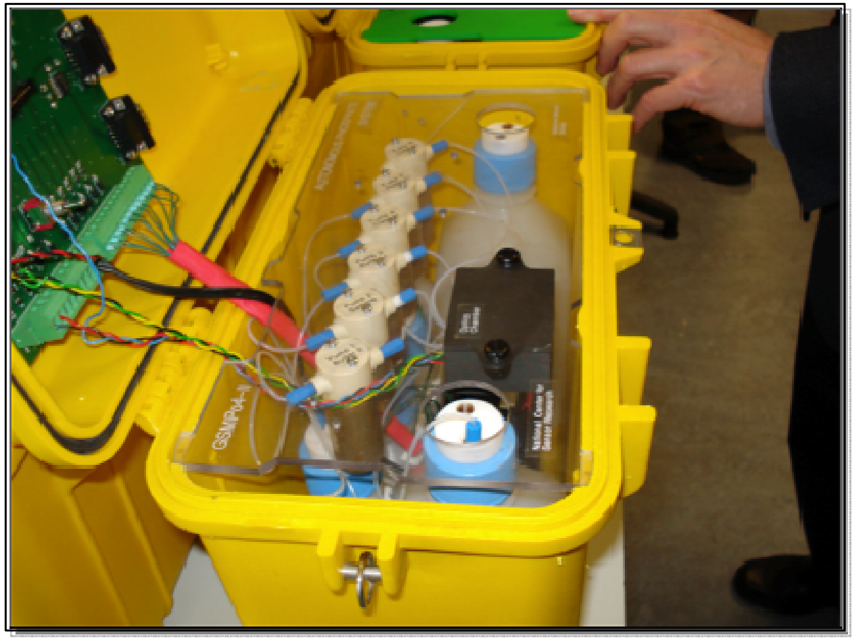


- **Setup ca. 1999**
- **Worked well but not an integrated system**



Chemical Sensing using an Integrated uFluidic System based on Colorimetrics: A Comparative Kinetic Study of the Bertholet Reaction for Ammonia Determination in Microfluidic and Spectrophotometric Systems, A Daridon, Sensors and Actuators B, 76/1-3, (2001) 235-243.

Autonomous Reagent-based Nutrient Phosphate Analyser (ca. 2008)



Complex system integrated into a robust platform: component cost ca. €2,000

Phosphate Analyser Platform (Gen1)

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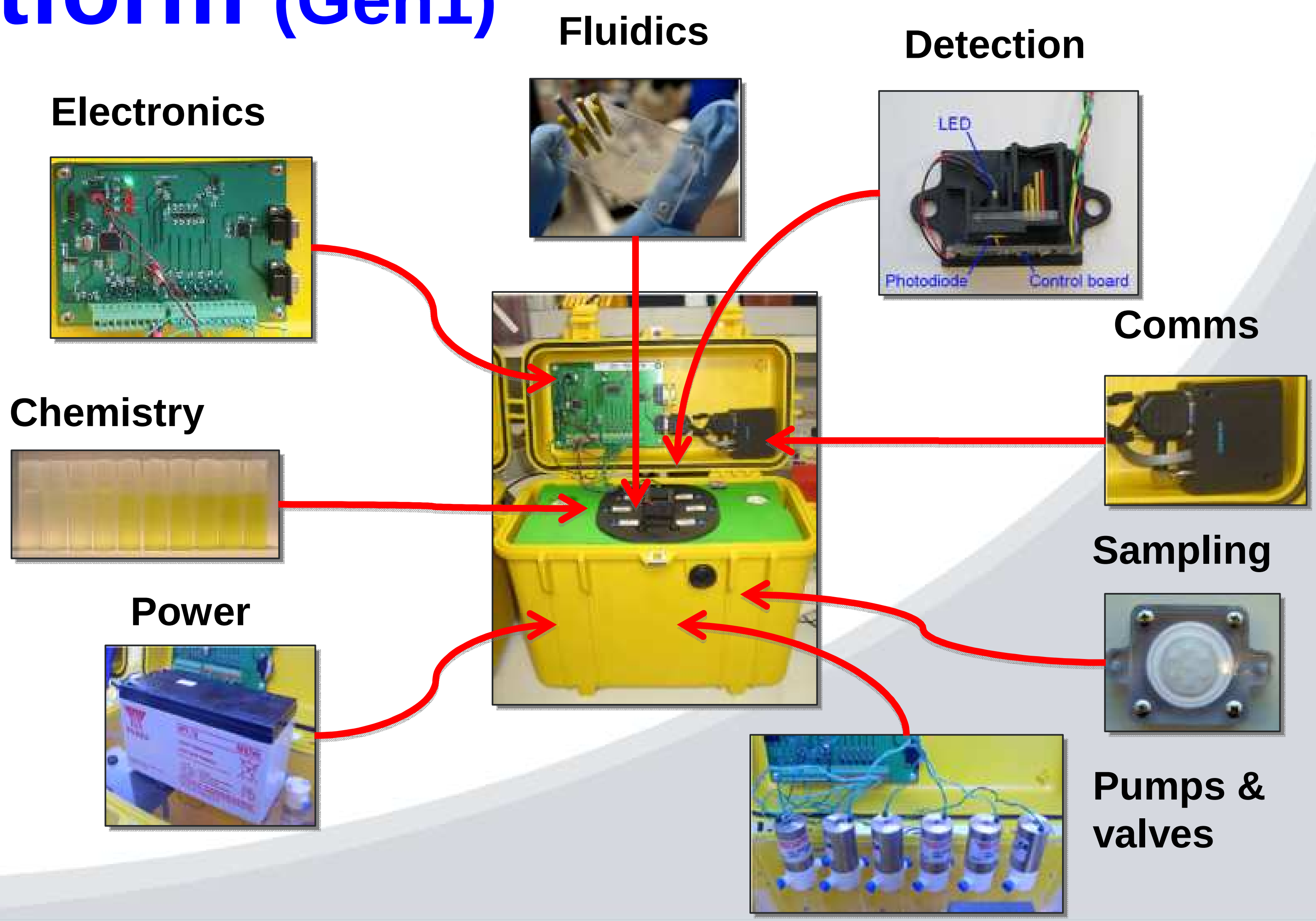
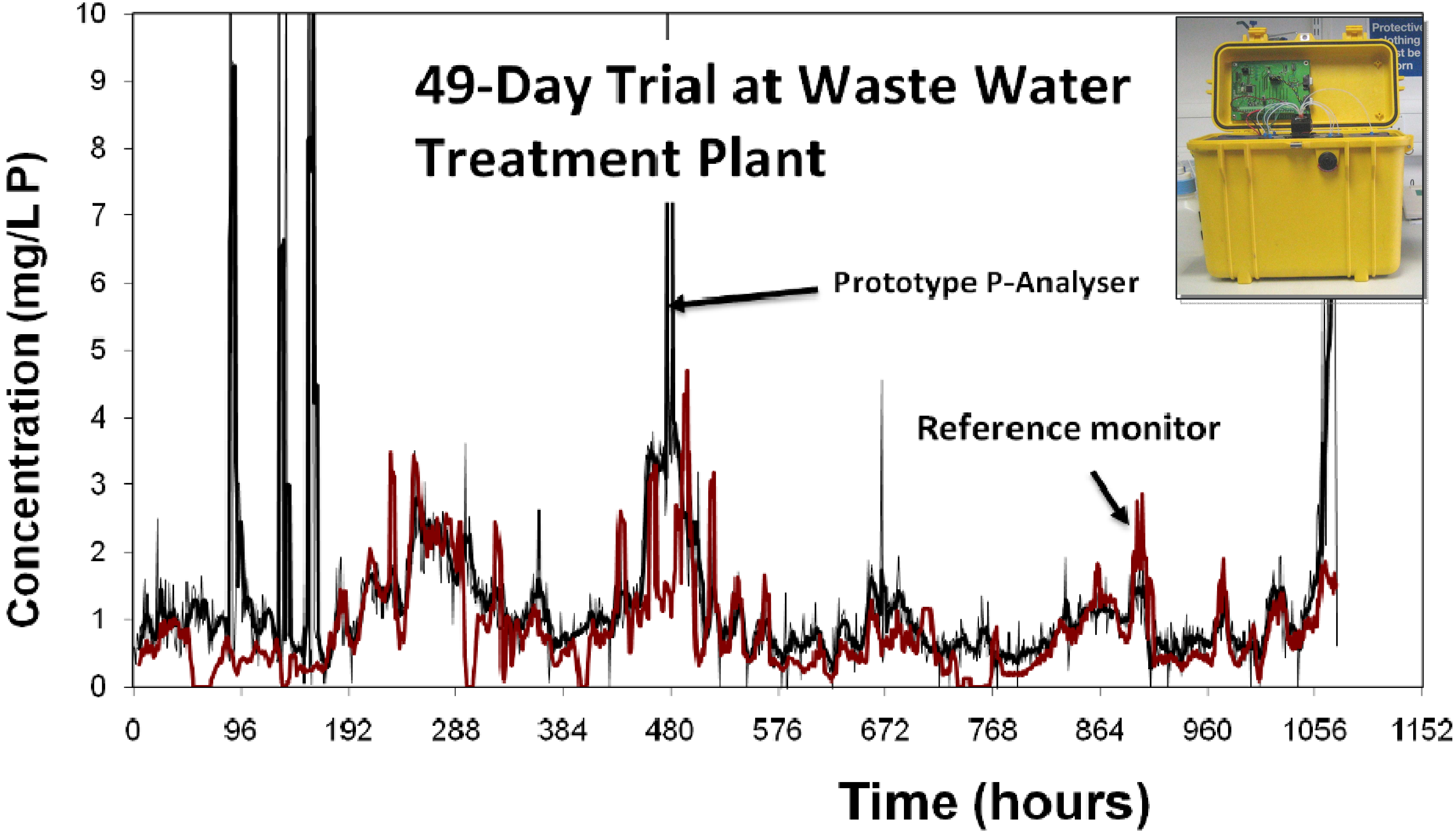


Autonomous Chemical Analyser



Next Generation device

- Episensor-CLARITY collaboration (EI Innovation Partnership) – GEN2 developed; cost now ca. €250 per unit; launched at Environ 2010 (Feb)

Gen1

Gen2

System Design

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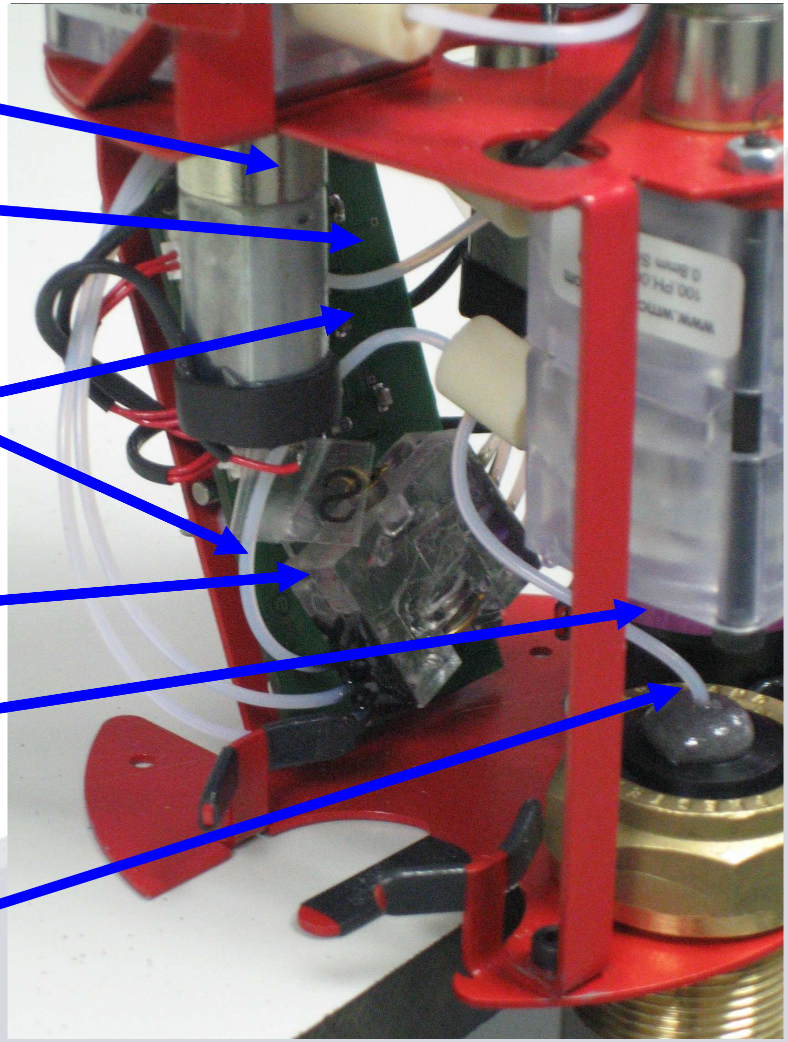
- Sheet Metal Frame
- Reagent & Standard Bags
- Dual Channel Pumps
- Control Board
- Detection System
- 3.6V Battery
- Sample Inlet(0.45um Filter)



Gen2 Detection System

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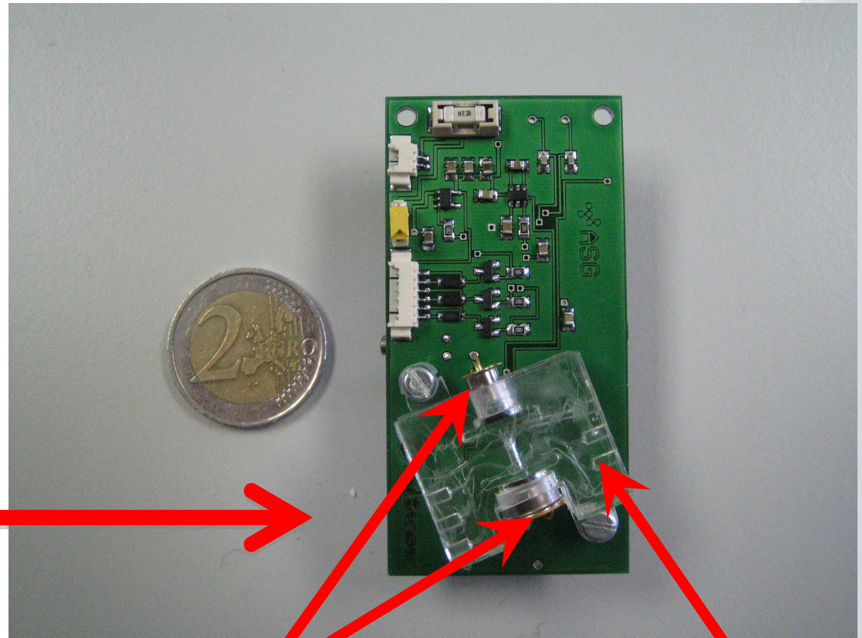

LED and Photodiode Detector

Microfluidic Chip

Evolutionary Improvements

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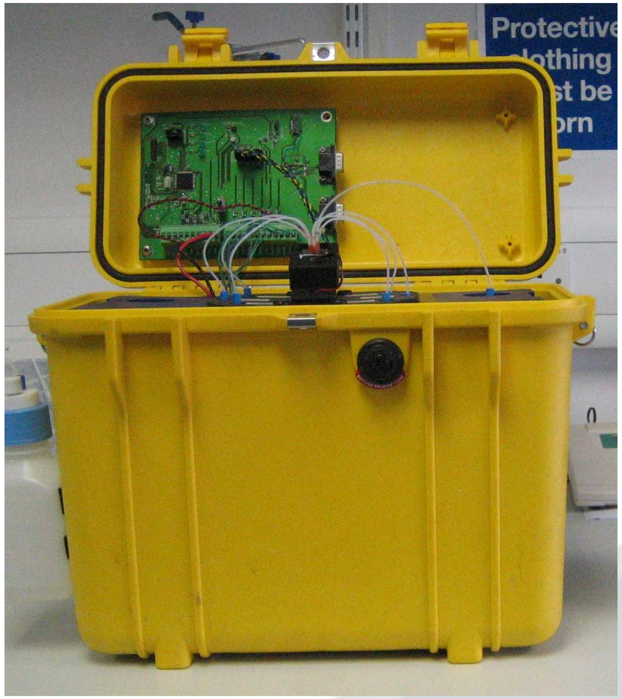
Microlab

>€20,000 per unit

1st Gen System (2008)



11 Deployments, almost 10,000 measurements over 282 days

2nd Gen System (now)

Handover of 10 systems to Episensor (March 2010); Deployments commencing

Cost Comparison Analyser (€)

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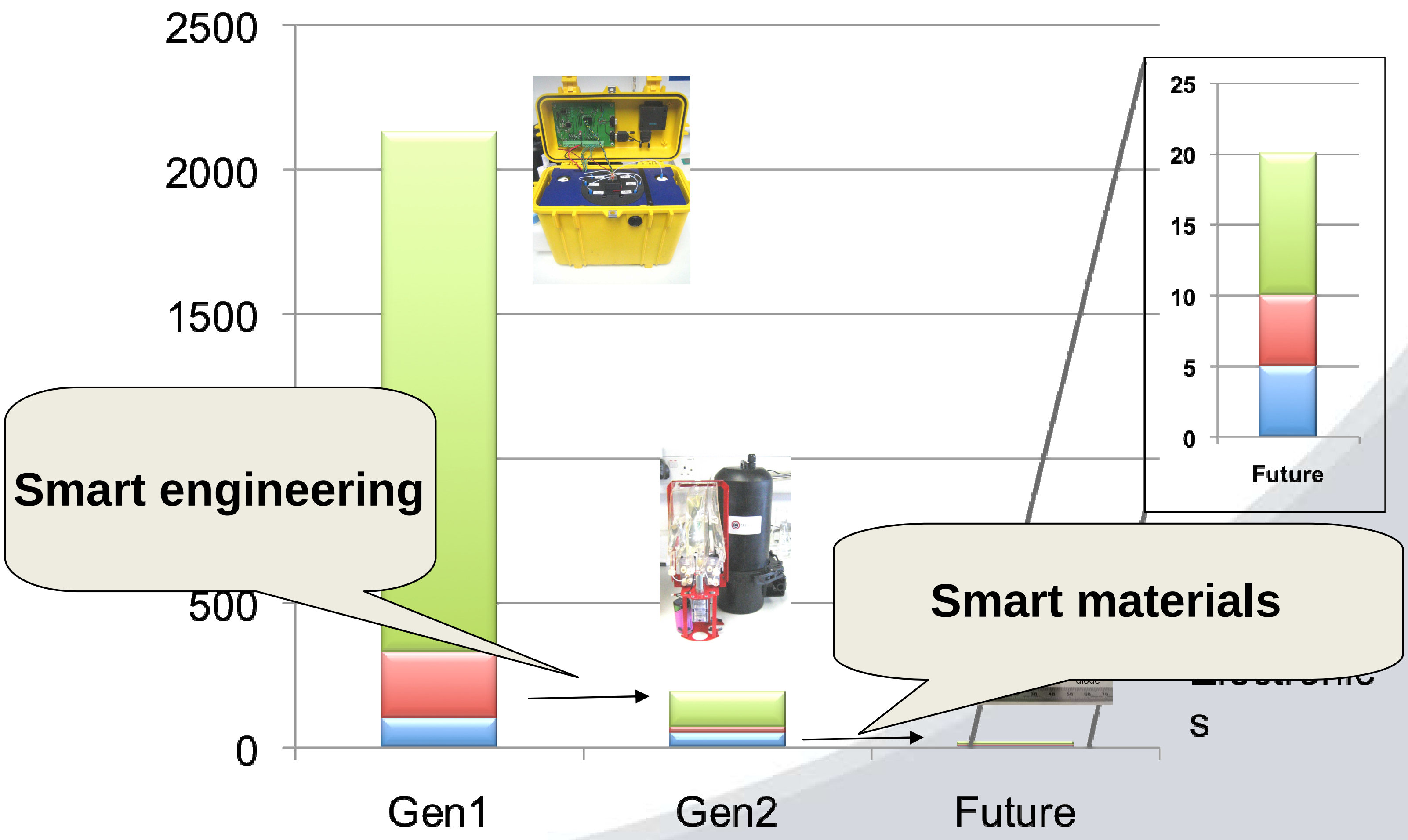

Generation 3 system

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- To realise the vision of chemical and biological sensor networks, we need low cost analytical devices for large scale distribution.
- Traditional chemical and biological sensing strategies not working due to biofouling, leaching, reagents, constant calibration etc.
- Current fluid handling components not suitable to miniaturised microfluidic systems- solenoid and electric motors for valves, actuators, pumps etc.
- Existing systems require large amount of power, space and expense.
- ‘Biomimetic’ approach to sensing and liquid handling based on intelligent materials.

Stimuli-responsive materials

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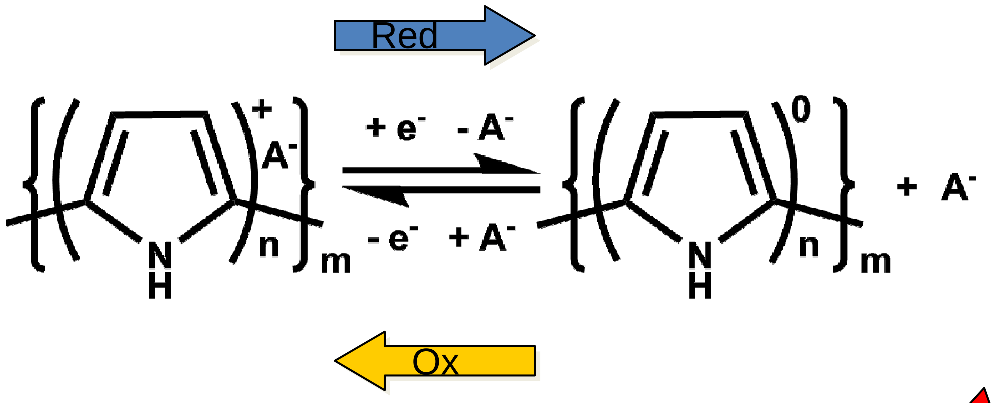
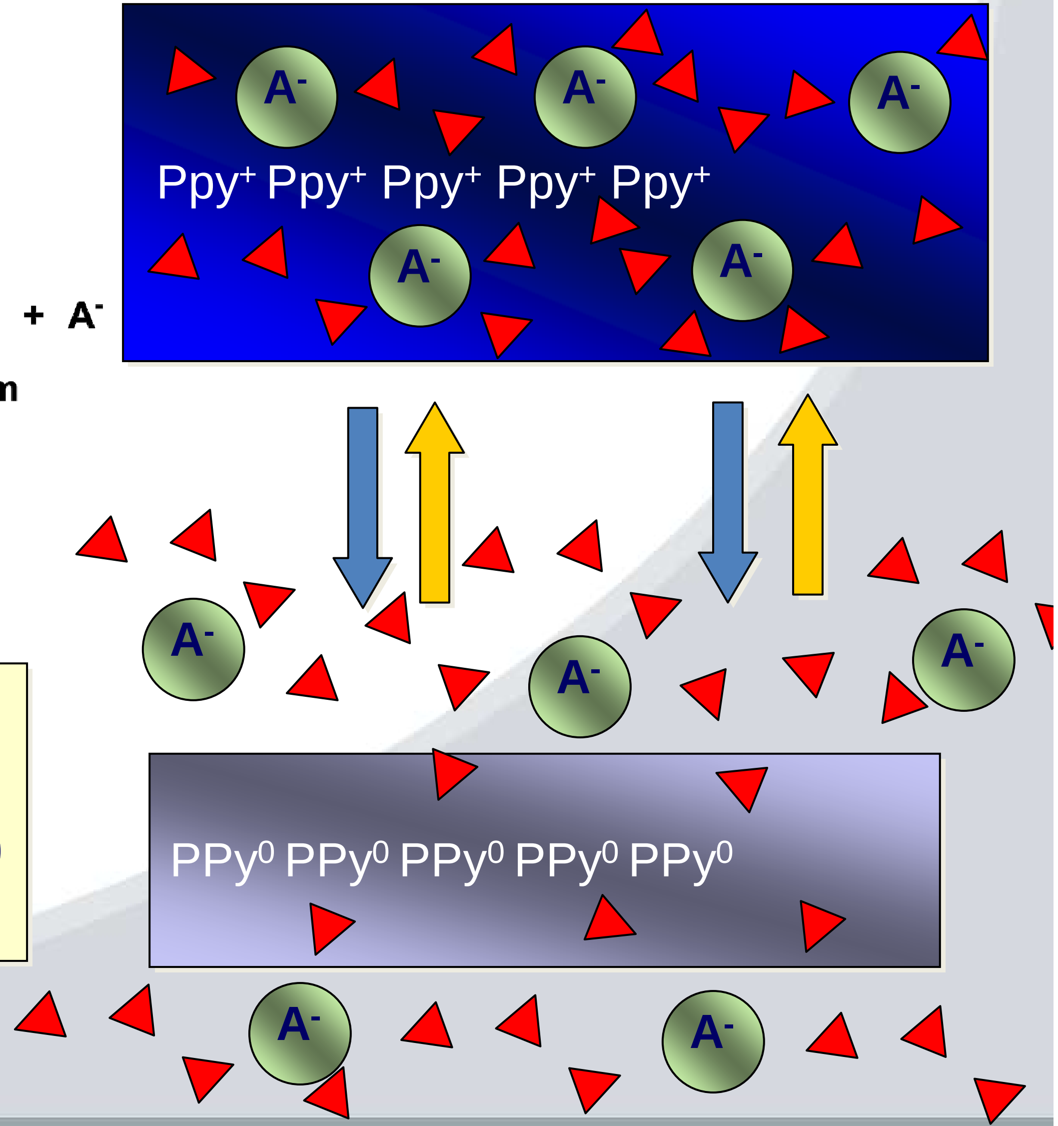
- **Realisation of futuristic sensing systems (3G model) lies within materials science**
- **Stimuli responsive materials for fluid handling**
  - Electrochemical
  - Optical
  - Magnetic
  - Chemical
- **Properties that can reversibly change e.g. chemical binding behaviour, surface charge/polarity, porosity, permeability, dimensions,…..**

Electrochemically responsive materials: Soft Polymer Actuators





Principle can be used to make soft polymer (biomimetic, artificial muscle) actuators

Electrochemically driven valves

Polypyrrole based conducting polymer coated on steel mesh

Pore size can be controlled electrochemically, completely reversible

Total Charge increasing

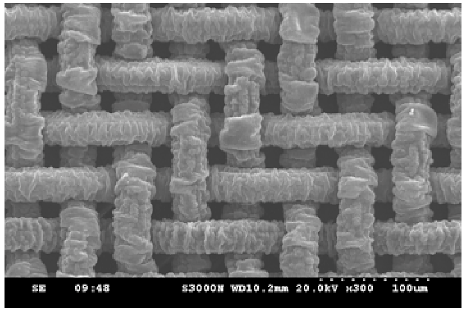
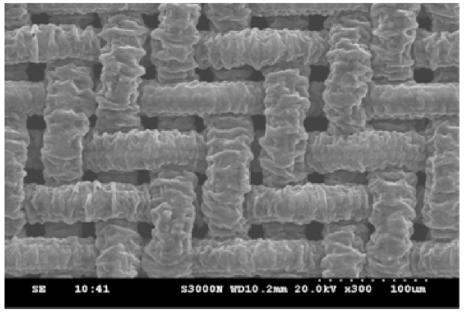
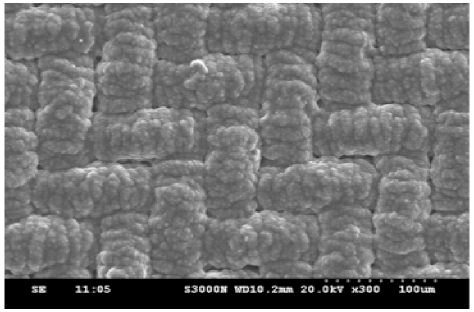
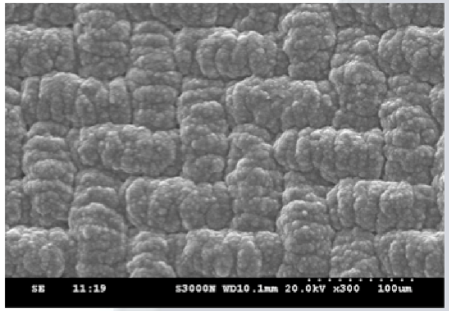
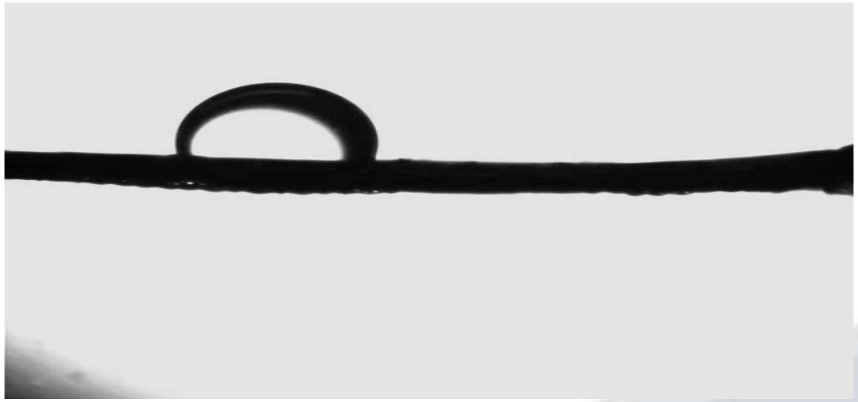


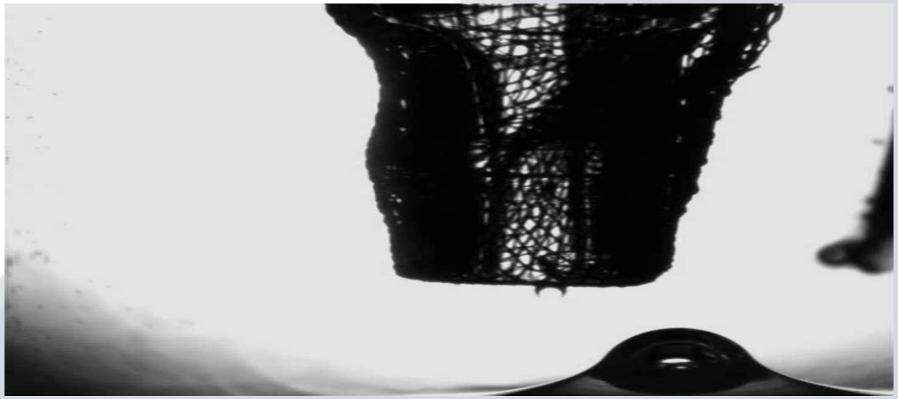
Figure 3.3.1 Ppy/ SS mesh at 1 mA/ cm² for 10 minutes (central image)







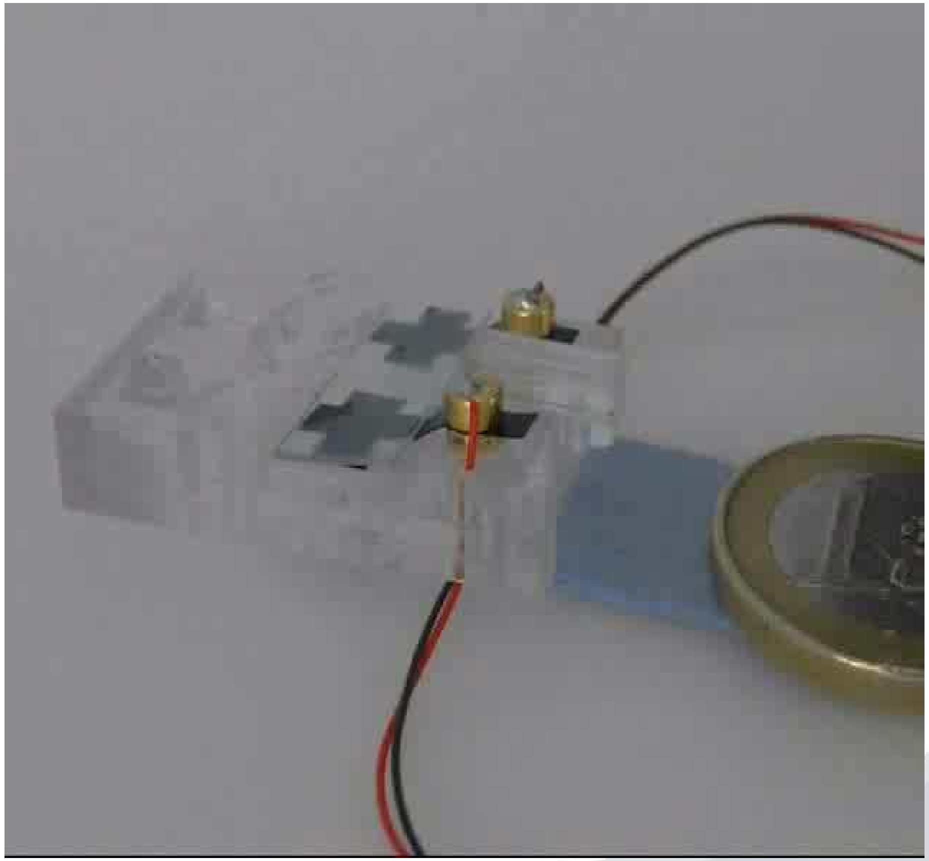




Collaboration with Prof. Gordon Wallace, University of Wollongong

Benitio-Lopez *et al ECS Transactions*, vol. 19, pp. 199-210, 2009.

Conducting Polymer Micropump



- Polypyrrole/PVDF based material
- Low power (±1.5V), low cost components are vital for realisation of next generation micro-dimensioned analytical platforms
- Soft polymer actuators more attractive for integrated ufluidics manifolds (52µL/min)
- 'lego' approach – detector block will slot in

Fully integrated optical sensing system

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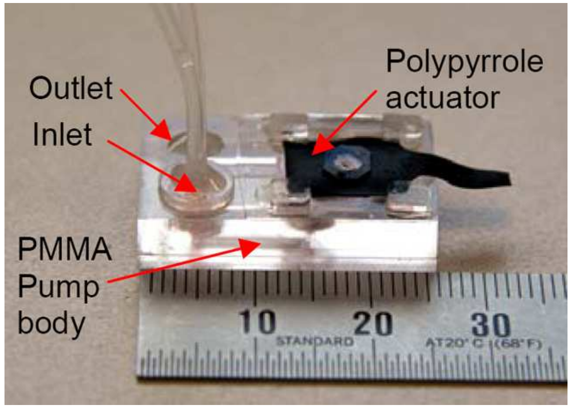
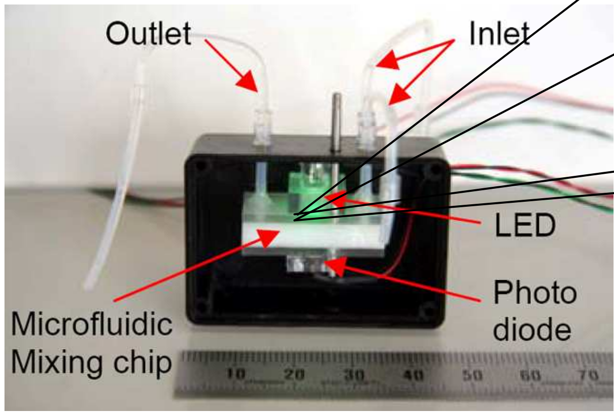
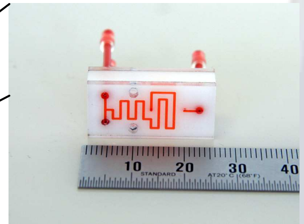
Pump



+

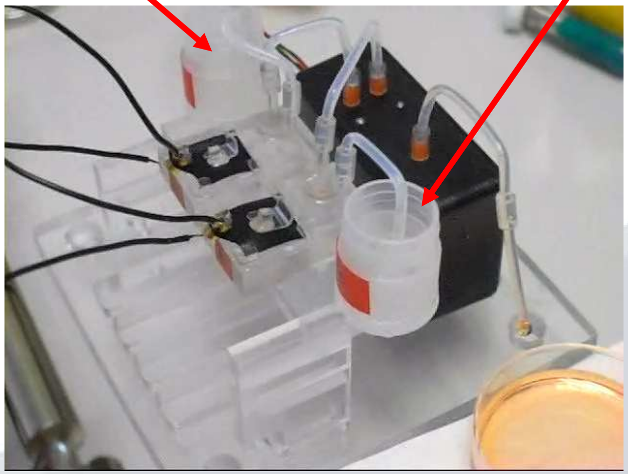
Reagent based detection of Fe2+

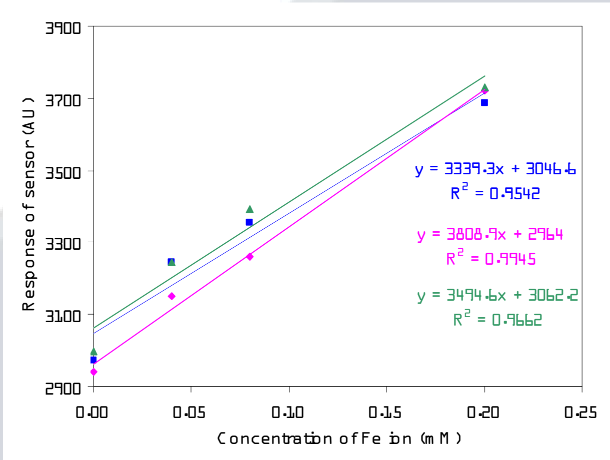




Aqueous Fe 2+ **Phenanthroline Chloride Monohydrate**

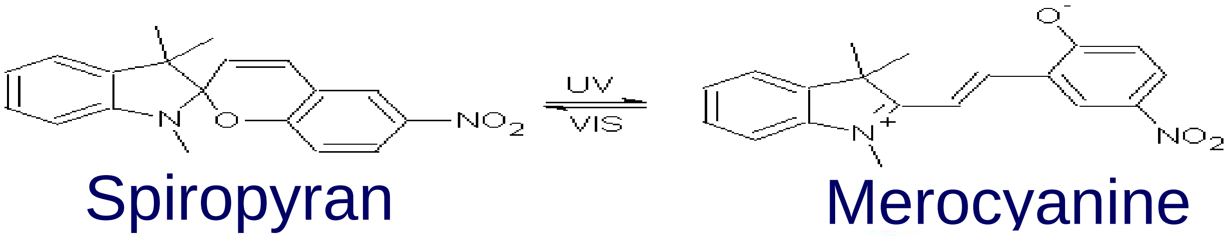
Low power, low cost FIA system microfluidic pump is developed for determination of low concentration of iron in aqueous samples

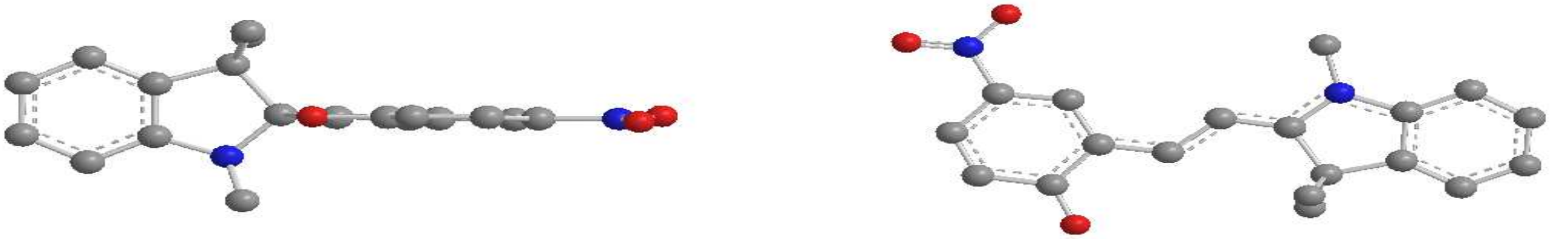


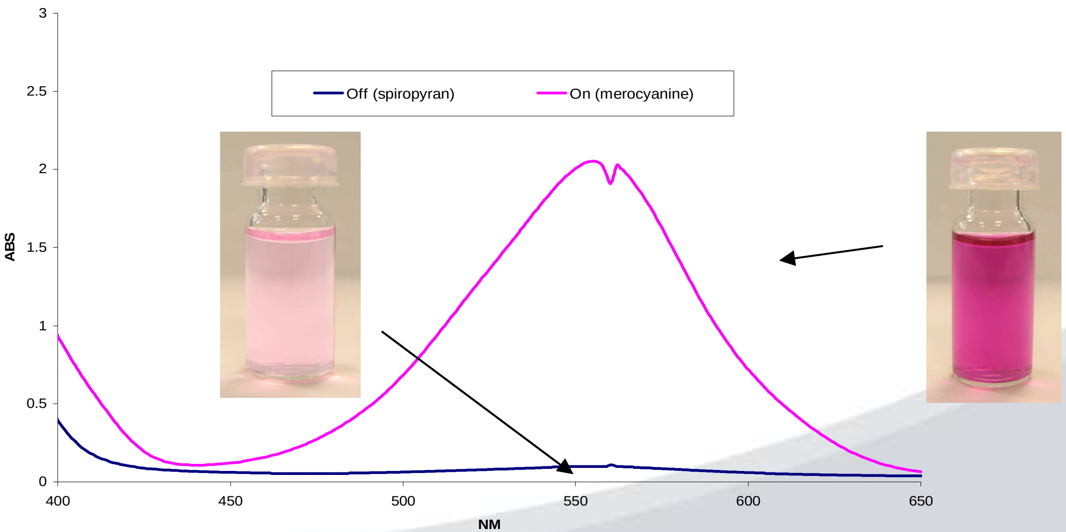


Linear range of detection: 0.04~0.20mM of Fe2+ ions

Photo-responsive materials based on spiropyran

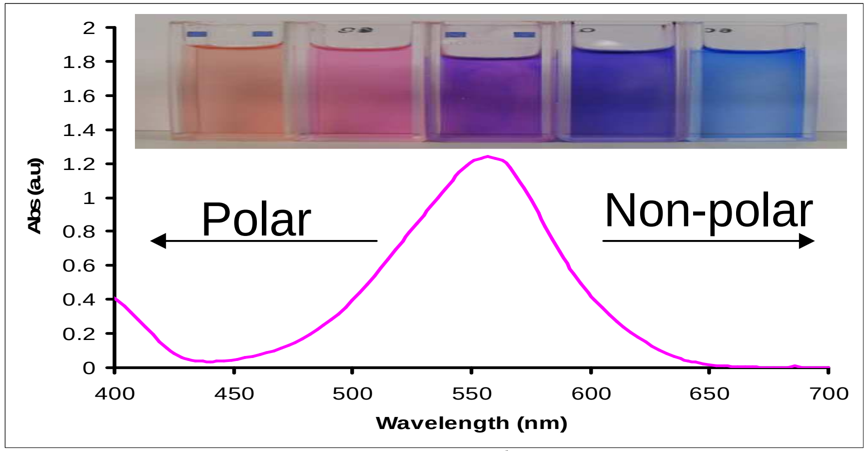




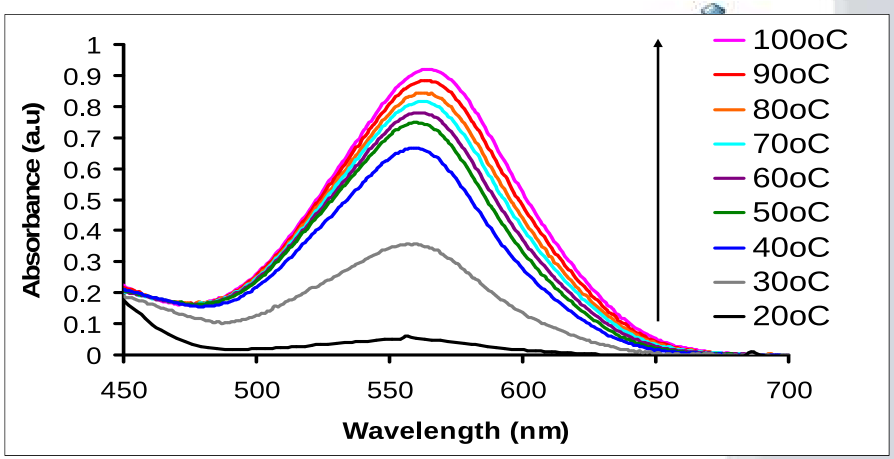


- **Optically actuate between two distinct isomers**
- **Control physico-chemical properties of system**
- **Non-contact spatial control of actuation**

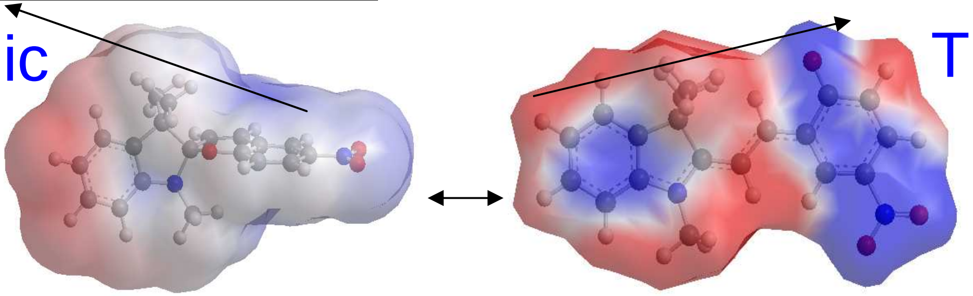
Byrne *et al*, *Nature Materials*, vol. 5, pp. 421-424, 2006.
Byrne *et al, Journal of Materials Chemistry*, vol. 16, pp. 1332-1337, 2006.



Solvatochromic

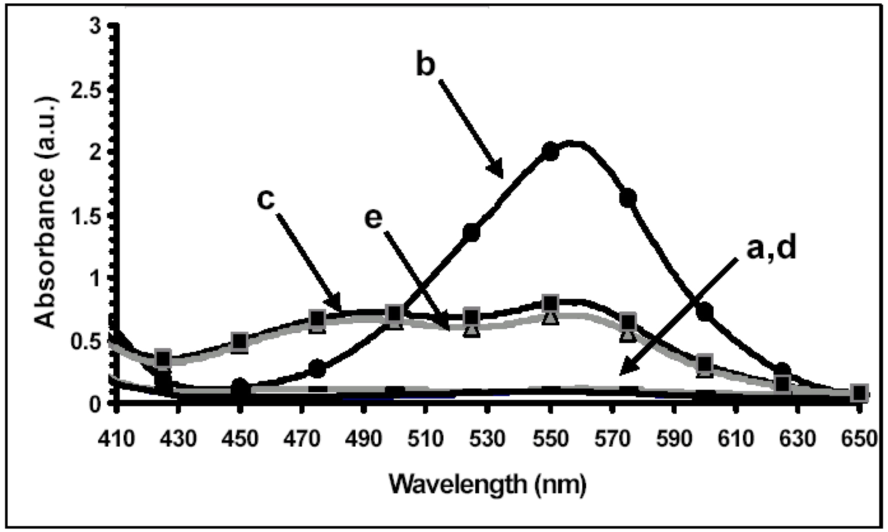


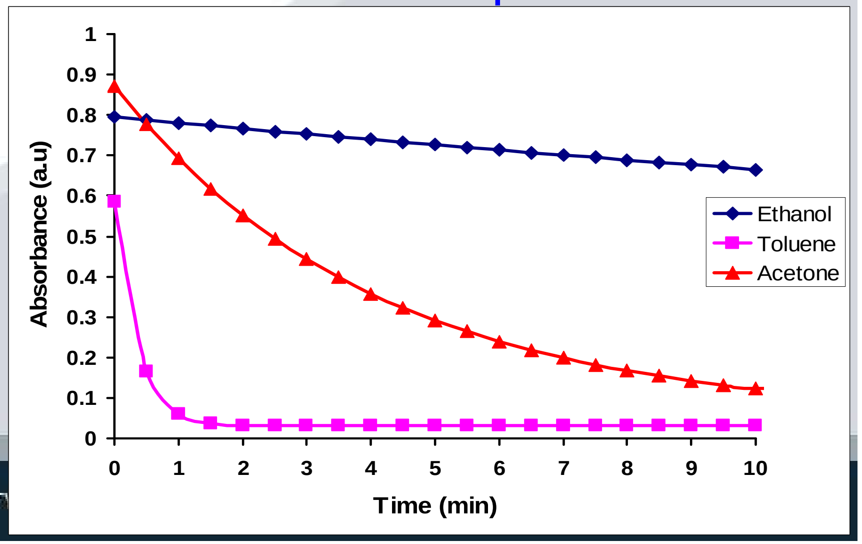
Thermochromic



Metal ions, Proton, Protein and DNA recognition site

Thermal relaxation dependent on all processes!





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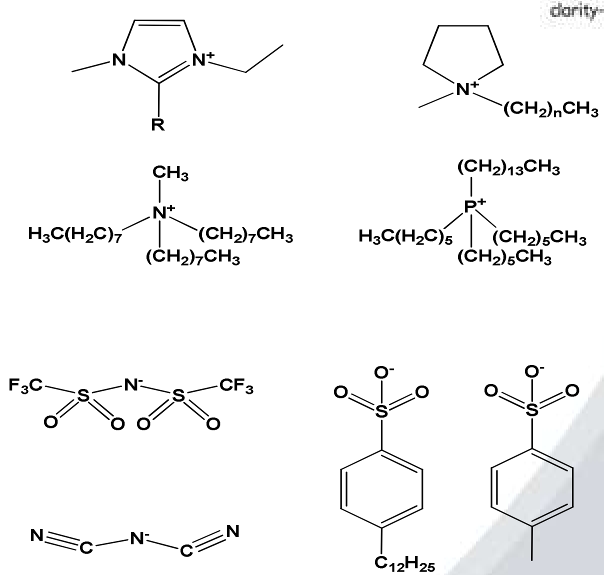
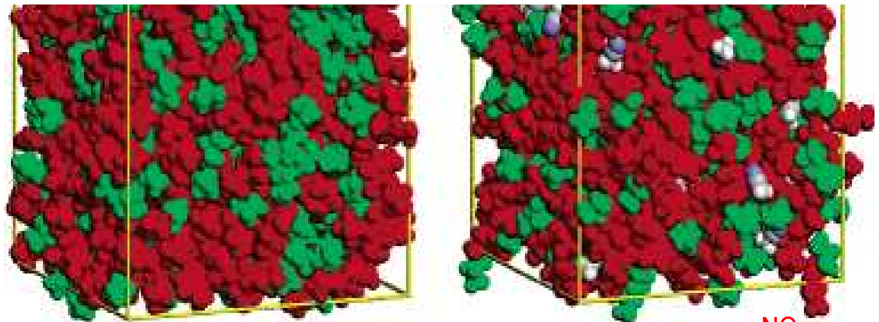
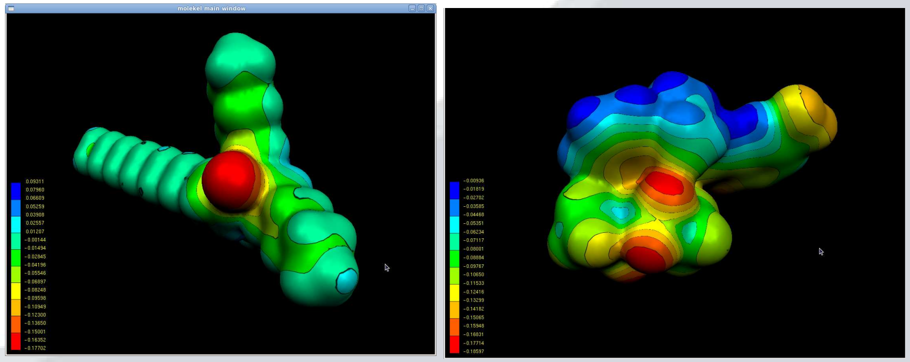
Ionic Liquids- photoresponsive liquids

- 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



Nano-structured liquids (Lopez et al 2008)





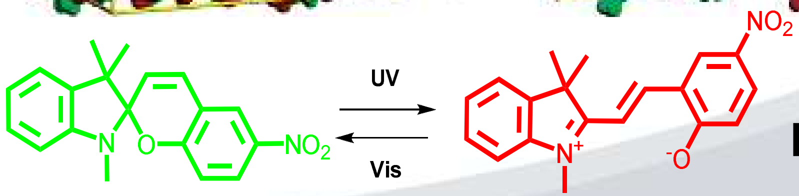


Photo-switching physicochemical interactions

R. Byrne, Phys. Chem. Chem. Phys.,**2008**, 10, 5919–5924. R. Byrne, Phys. Chem. Chem. Phys., **2009**, 11, 7286–7291
R. Byrne, *Phys. Chem. Chem. Phys.* **2010**, *12*, 1895-1904. S. Coleman, Phys. Chem. Chem. Phys.,**2009**, 11, 5608–5614

Photo-responsive polymer

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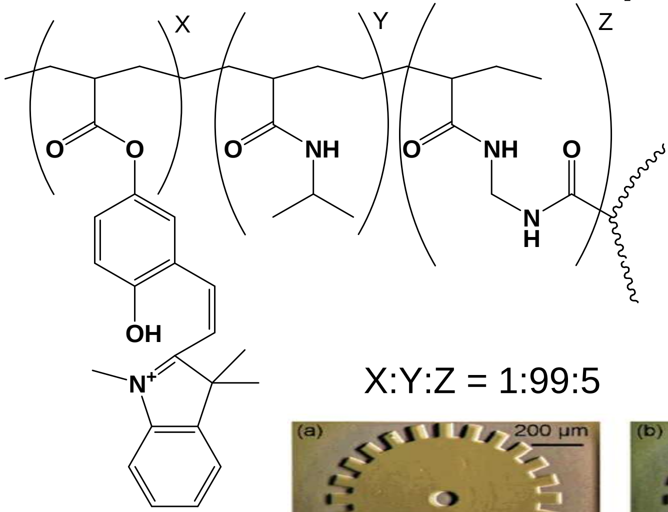
- Protonated isomer incorporated into cross linked thermoresponsive hydrogel
- Irradiation of blue light results in contraction of hydrogel
- Excellent spatial resolution demonstrated by micro-relief structures
- This offers the possibility of inducing dramatic changes to the bulk properties of a system by photonic irradiation.
- Technical issues include **evaporation of water** from hydrogel



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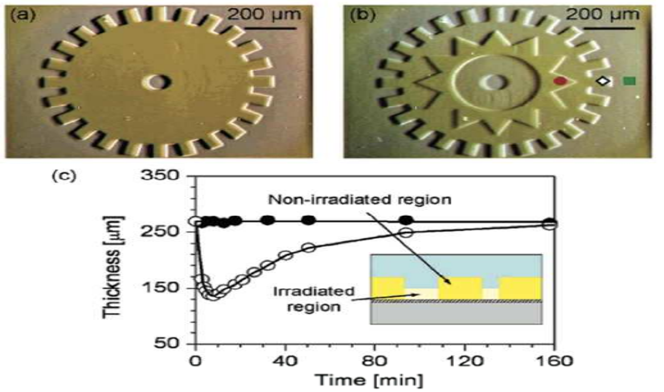
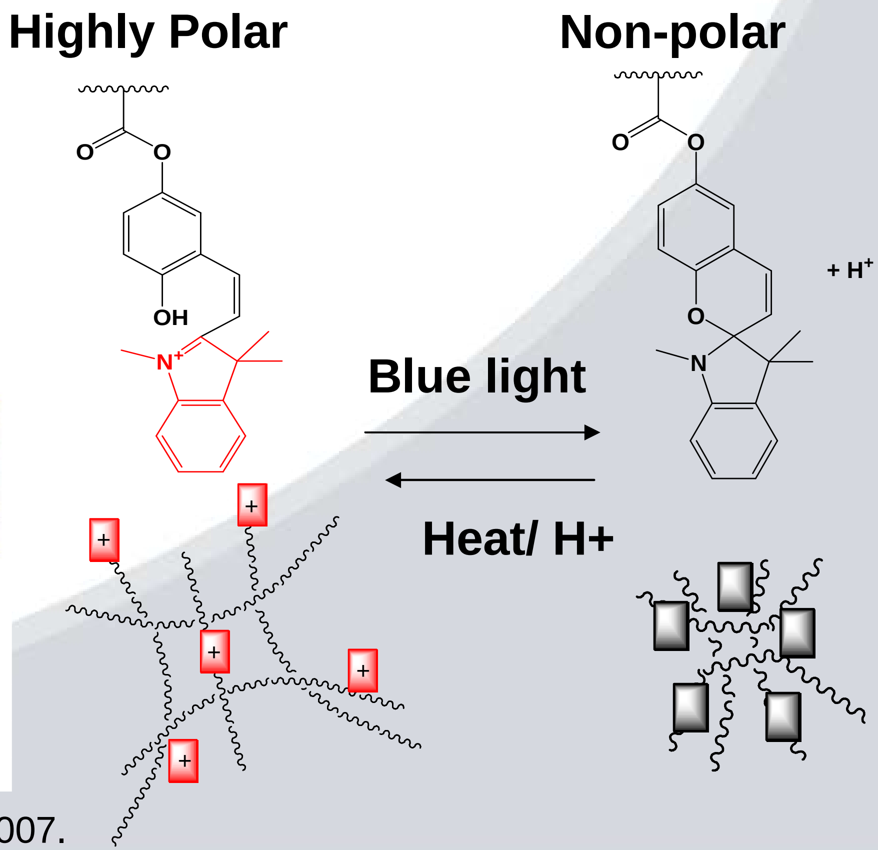
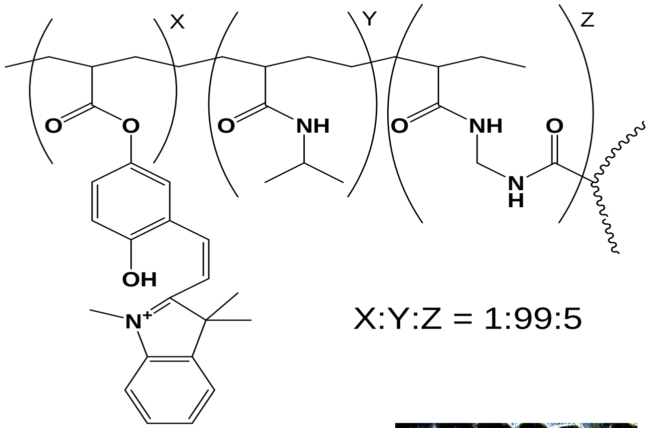




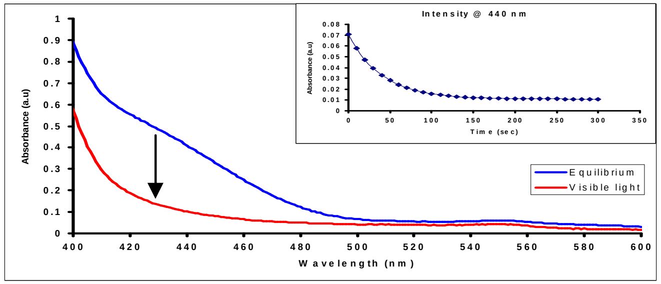
Sumaru et al *Chem. Mater.*, 19 (11), 2730 -2732, 2007.

Photoresponsive ionogel valves

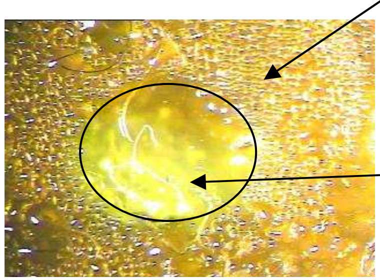
- •Photo-polymerization takes place in ionic liquid matrix.
- •Ionogels have different chemical and photo-physical properties due to ions with within the gel.

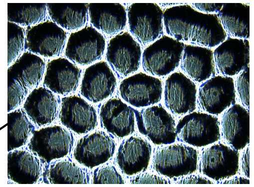


X:Y:Z = 1:99:5

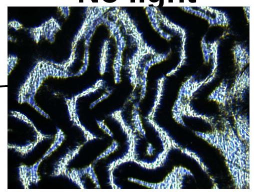


Spectroscopic analysis
Rate constant = 2.5 x10-2s-1

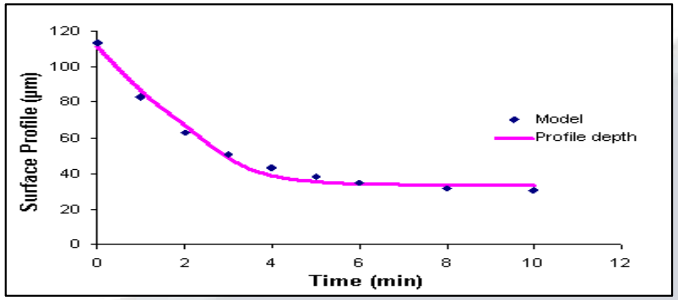




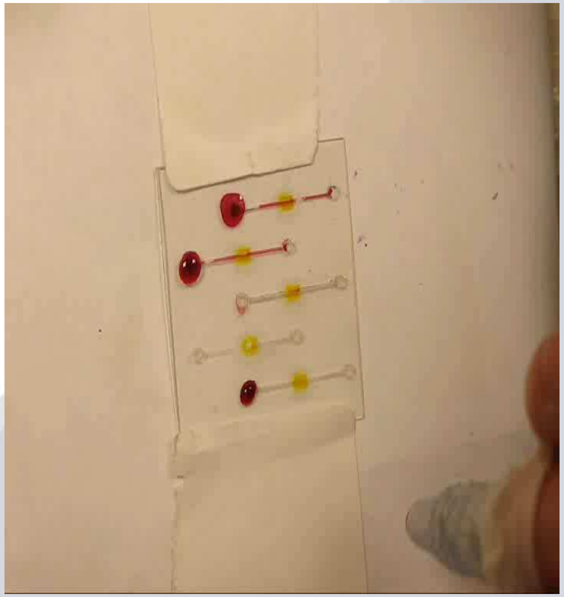
No light



Visible light

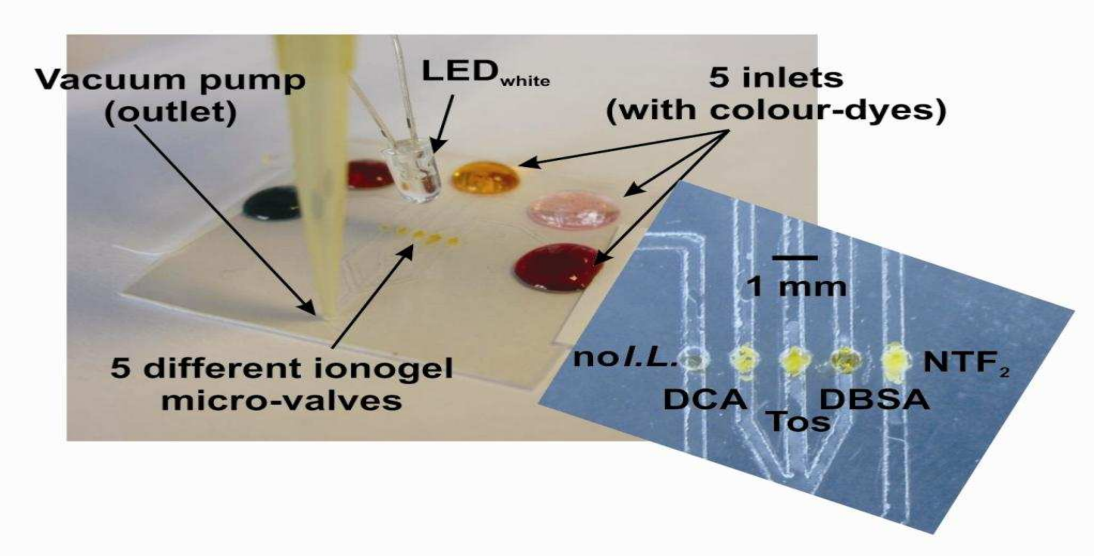


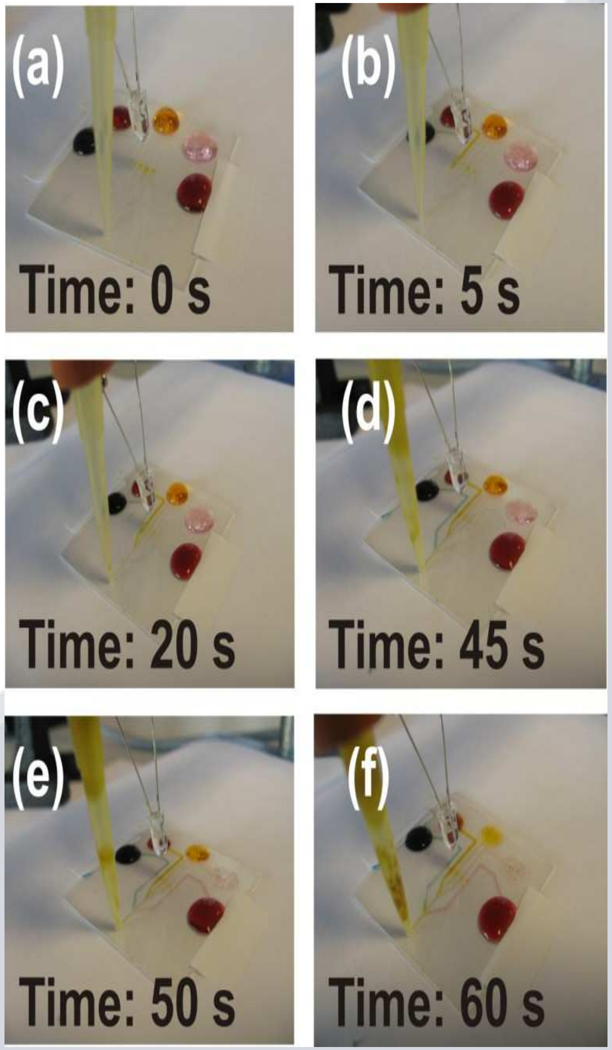
Physical profile analysis
Rate constant = 0.457 s-1.

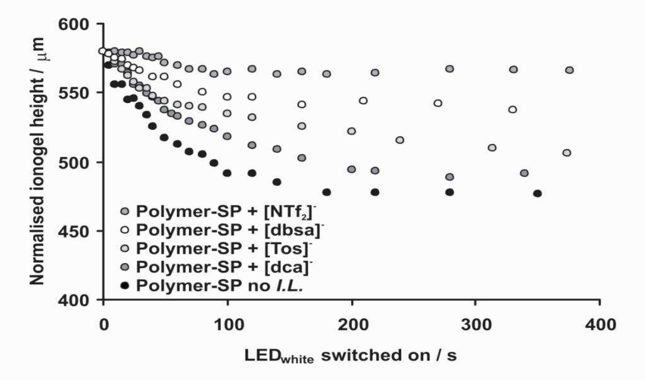


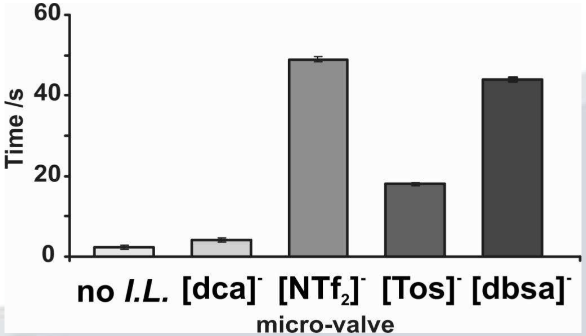
R. Byrne, Material Research Society, Adaptive materials, **2009**, (NN) 1071.
F. Benito-Lopez, ECS transcations **2009**, 19 (6) 199-210.

Multiple valves on one chip, using one actuation source!









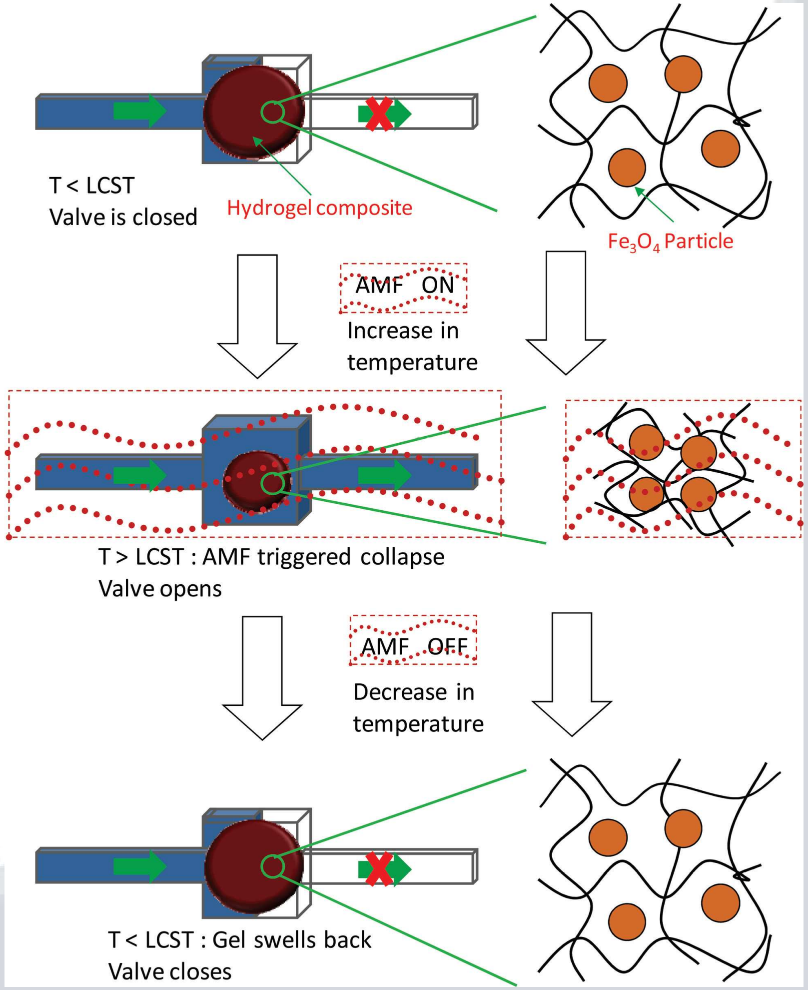
F. Benito-Lopez, *Lab on a Chip* **2010**, *10*, 195-201.

Magnetic materials for fluid handling

•Non-contact fluid manipulation in microchannels

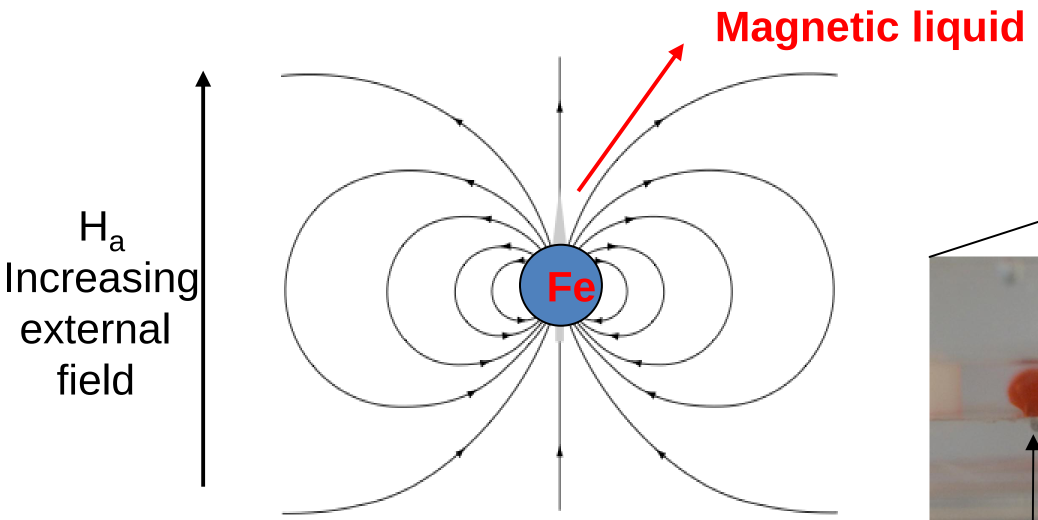
• Magnetic nanoparticles (Fe_3O_4) coupled with thermoresponsive polymers used as valves in microchannels

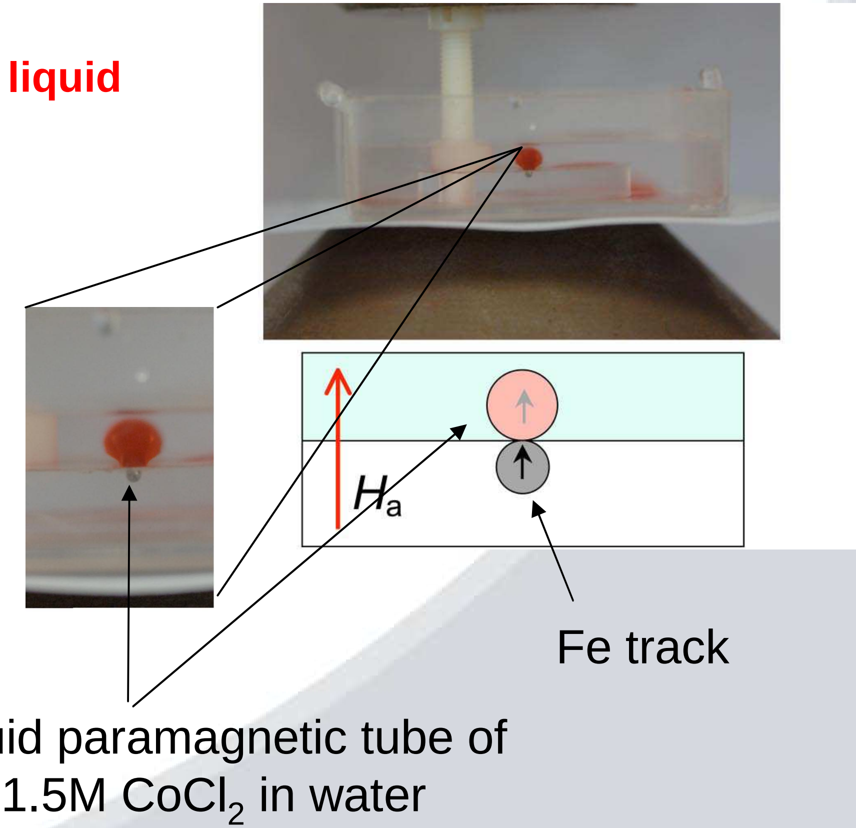
•Applying alternating magnetic field induces localised heat causing polymer to contract



Satarkar *et al*, *Lab on a Chip* **2009**, *9*, 1773-1779

Magnetic liquids in microfluidics



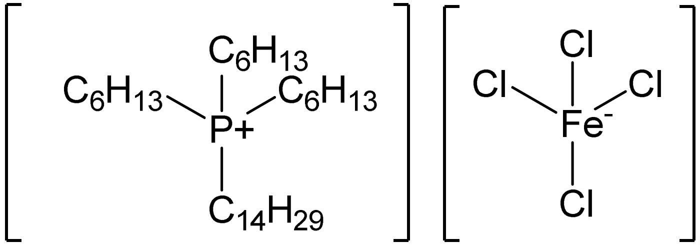


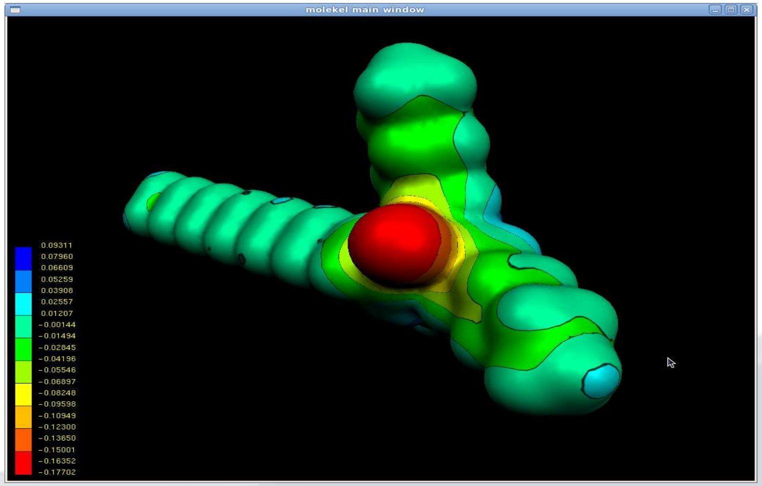
Disruption of laminar flow in microfluidic channels
Liquid tube is unstable after short period of time due to diffusion of water.

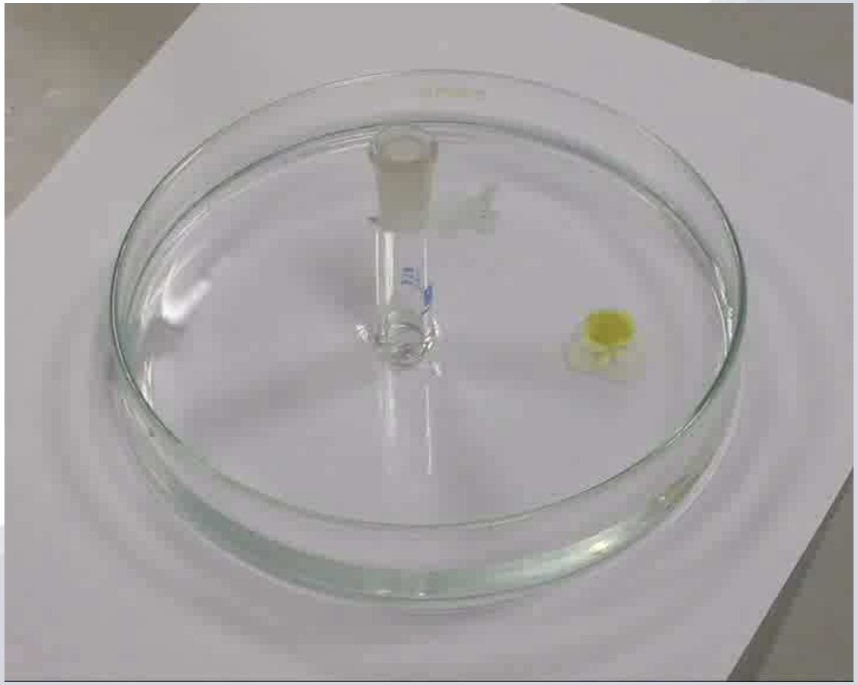
Coey *et al*, PNAS, 2009, 106, 22, 8811–8817.

Magnetic control of hydrophobic liquids

- **Phosphonium and Imidazolium based magnetic hydrophobic 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**



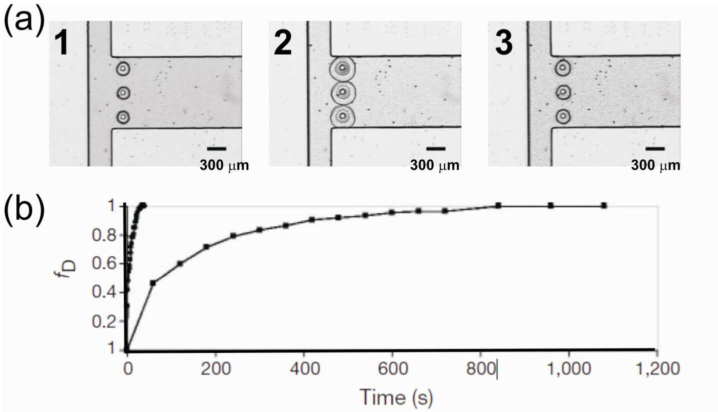




50ul of $[P_{6,6,6,14}][FeCl_4]$ in water

Chemically responsive materials

- **Convert chemical energy into mechanical**
- **When acidic solution flows through the channel, the hydrogel contracts, and when basic solution flows through, the hydrogel expands to occlude the channel by increasing the resistance of fluid flow**
- **The stimulus to trigger the valve is isolated from the regulated stream by an impermeable PDMS membrane. No need for power or external connections**

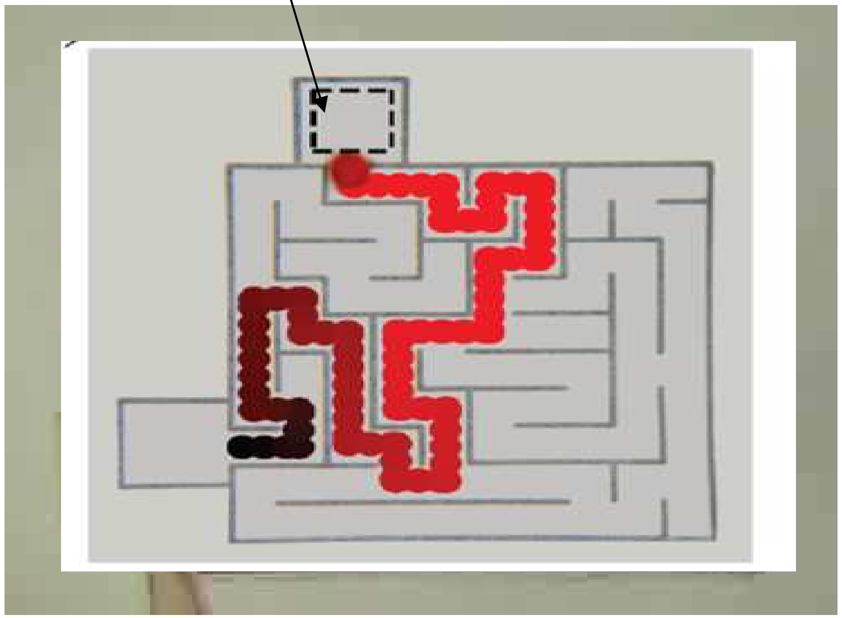


The improvement in time response of the hydrogel design (circles) versus an alternative design that uses a single larger cylindrical structure in the same size channel (squares). *fD* is the fractional change in diameter.

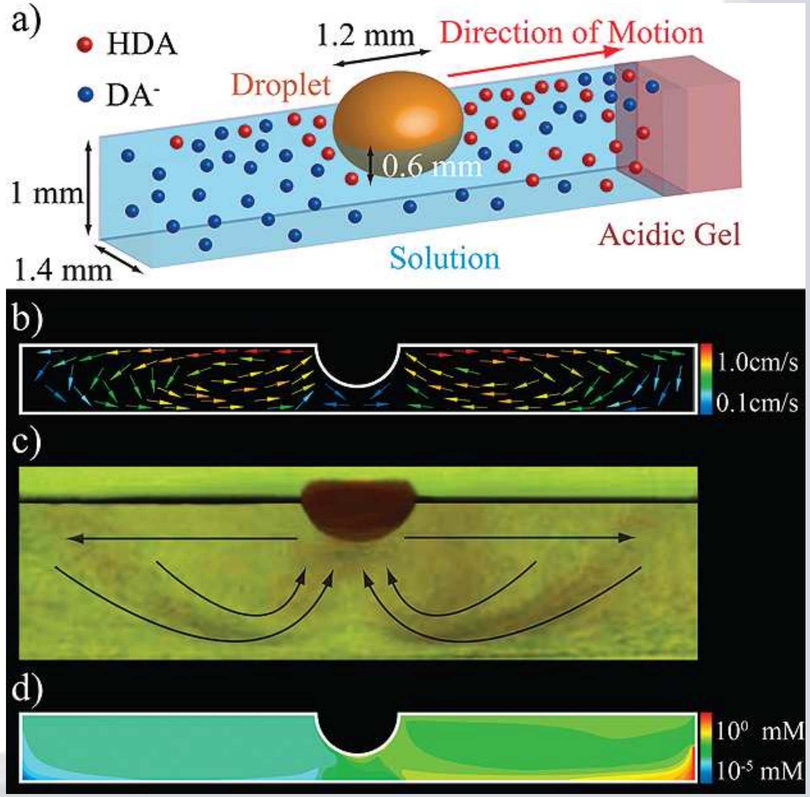
Beebe and Eddington,*Nature* **2000**, *404*, 588.

Molecular taxis

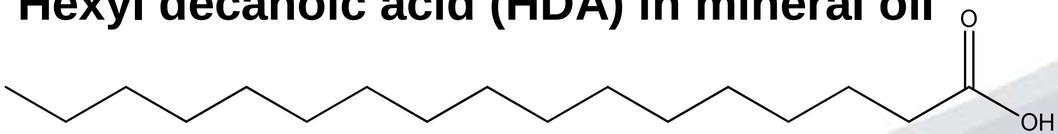
Agarose gel soaked in HCl (pH 1.2)



Maze filled with aqueous KOH (pH 12.3)



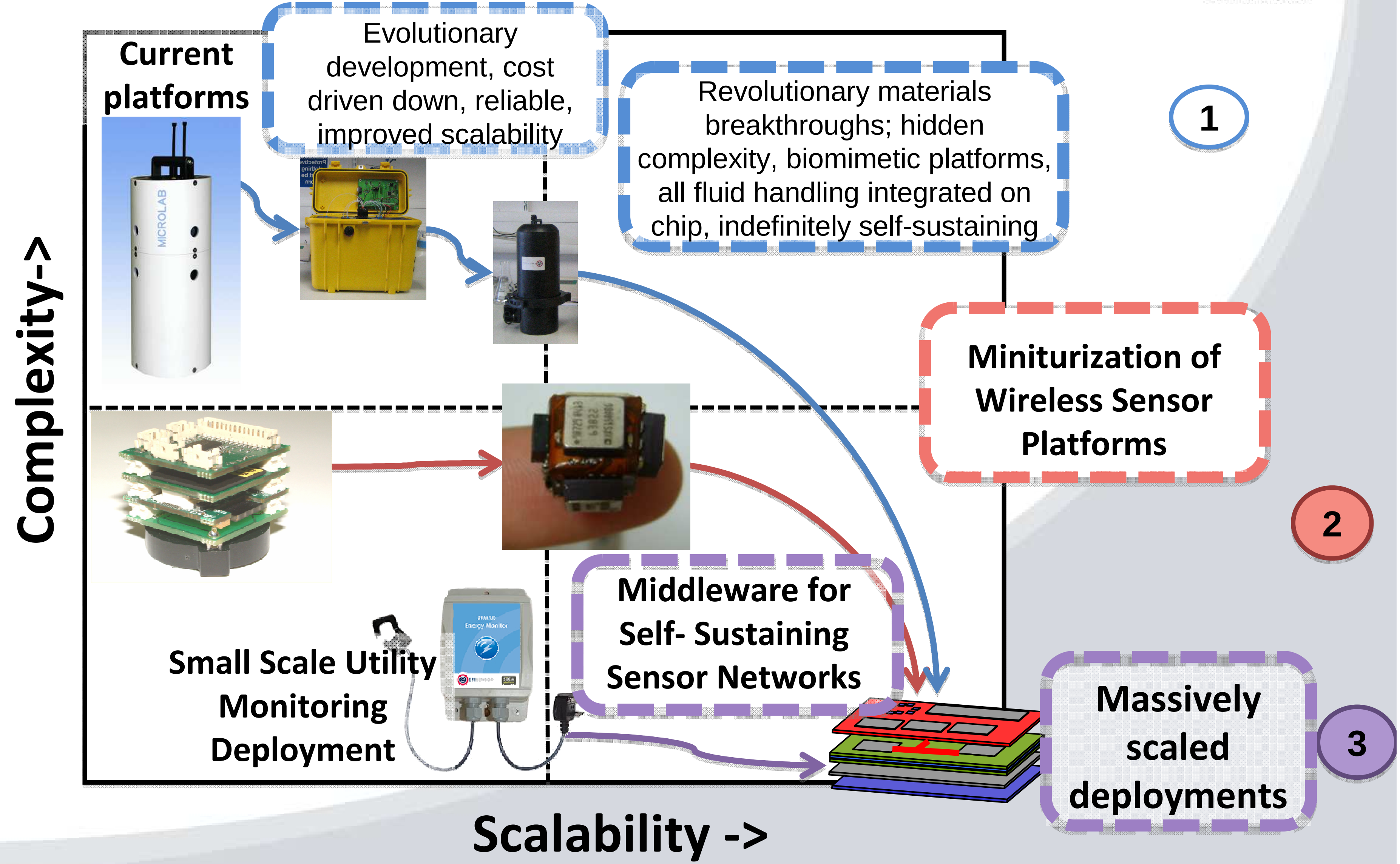
Hexyl decanoic acid (HDA) in mineral oil



More protonated HDA is found facing the source of acid, this results in a asymmetric distribution which gives rise to convective flows

Grzybowski *et al*, JACS 2009 *132*, 1198–1199

Outlook: Sensor Web Infrastructure



Conclusions

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- **Great potential for platforms capable of sophisticated multi-functional behaviour**
  - Pumping
  - Valving
- **Need for joint academic & industry research effort**
  - Establish better links between fundamental materials chemistry, emerging platform technologies, and the needs/markets to realise applications

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Thanks for listening!