Functional materials based on photo-responsive ionogels

Robert Byrne

National Centre for Sensor Research

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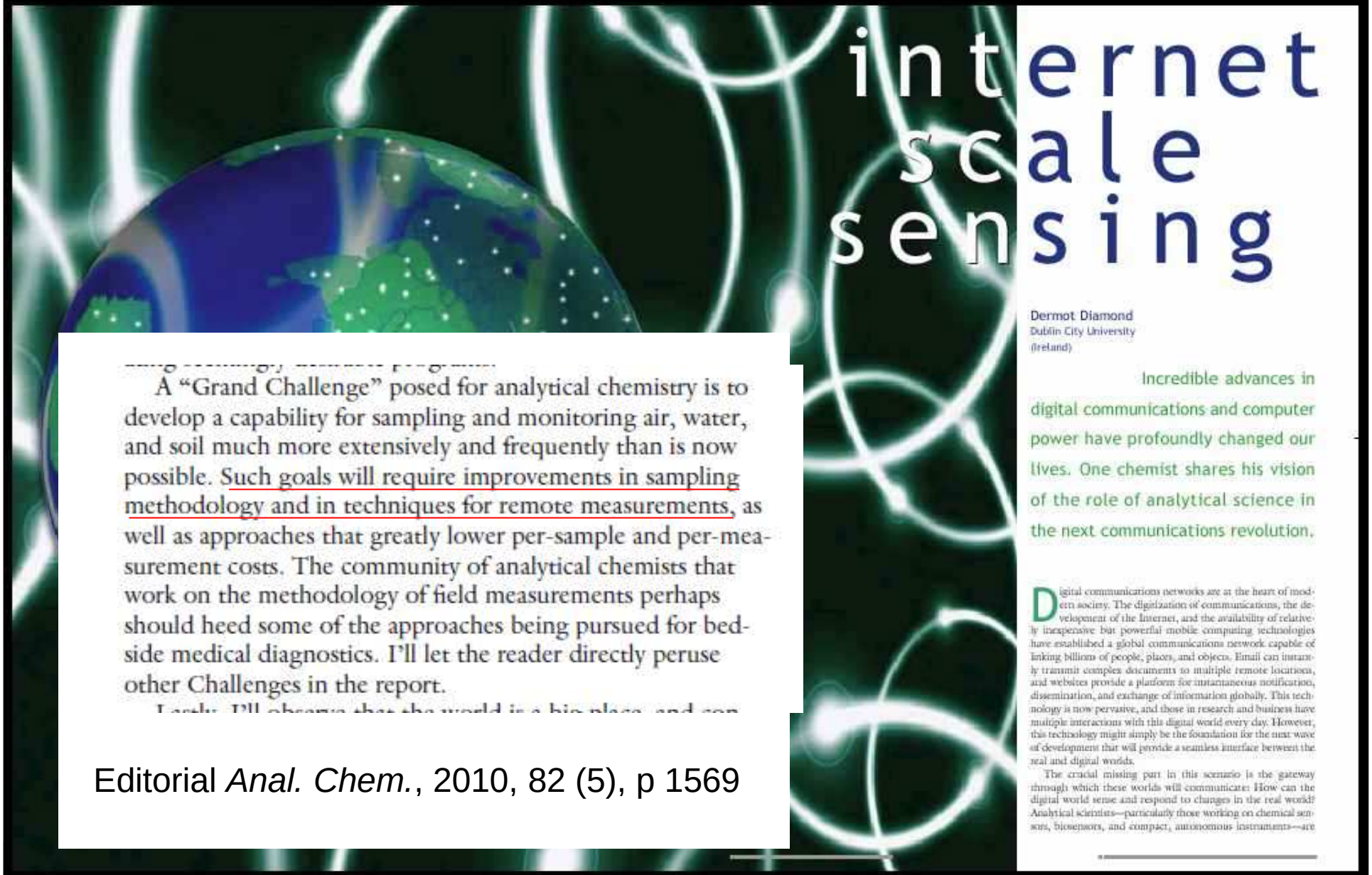
Keynote Article: August 2004, Analytical Chemistry (ACS)



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

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.

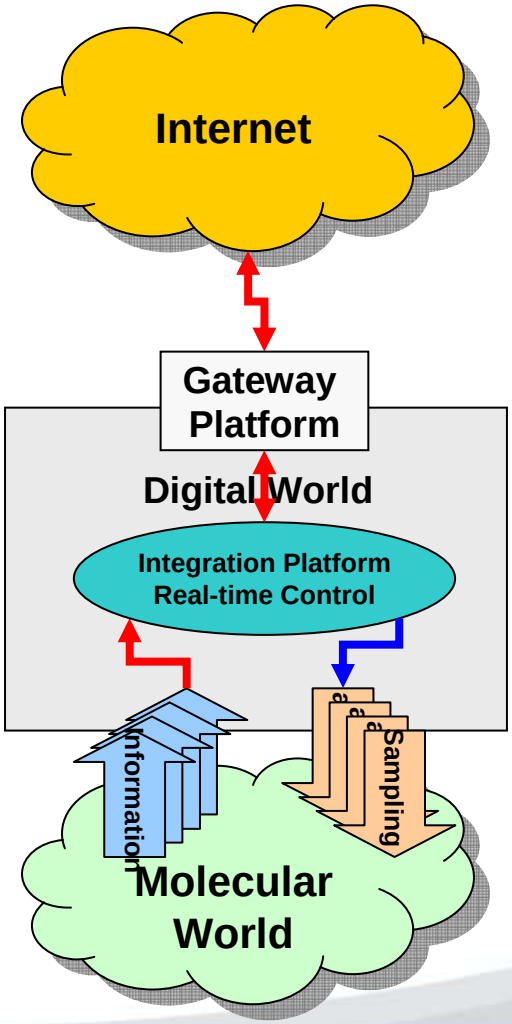
Digital communications networks are at the heart of modern society. The digitization of communications, the development of the Internet, and the availability of relatively inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions 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.

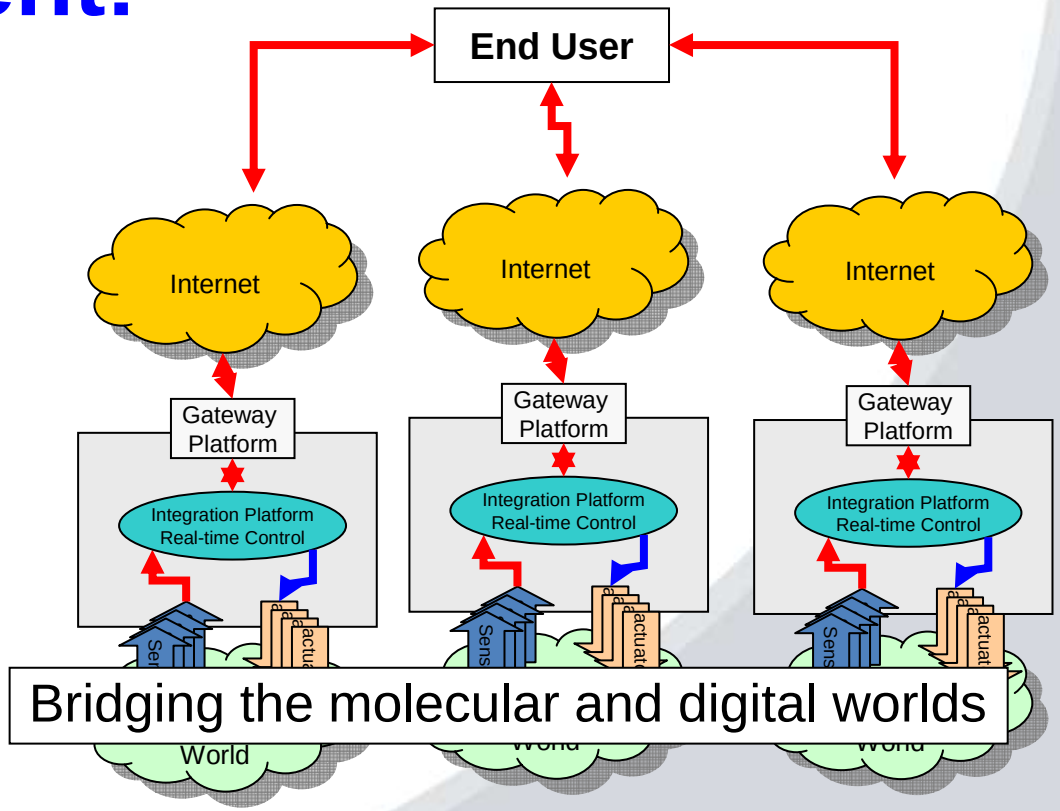
The crucial missing part in this scenario is the gateway through which these worlds will communicate: How can the digital world sense and respond to changes in the real world? Analytical scientists—particularly those working on chemical sensors, biosensors, and compact, autonomous instruments—are

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!

CLARITY
clarity-centre.org





Environment
Chemical spills, Waste Management etc

Health
Homecare, e-Health Elderly population

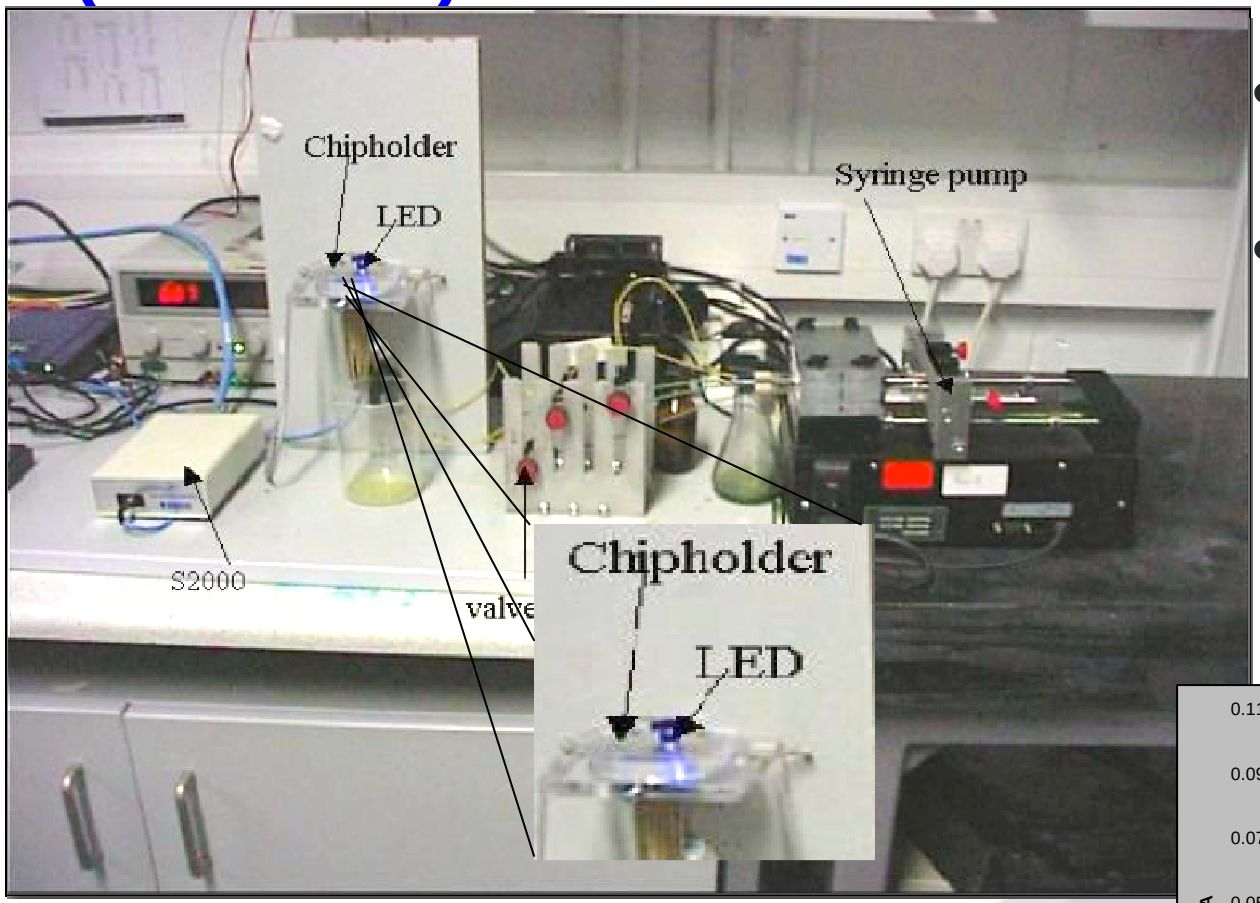
Security
Terrorist treats

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

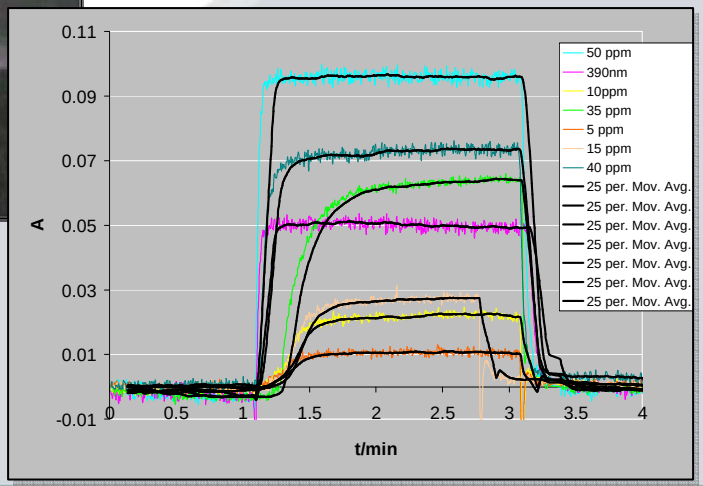
Outline

- **Current issues of sensing systems**
  - Cost of ownership
  - Fluid handling using pumps and valves
- **Opportunity for Functional Materials**
  - Stimuli responsive materials
  - Synthesis and characterisation
- **Integration of material into device for fluid handling**
- **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.

Phosphate Analyser Platform (Gen1)

CLARITY
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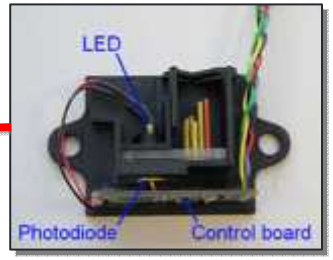
Fluidics

Detection



Electronics

Comms

Chemistry

Sampling

Power

Pumps & valves

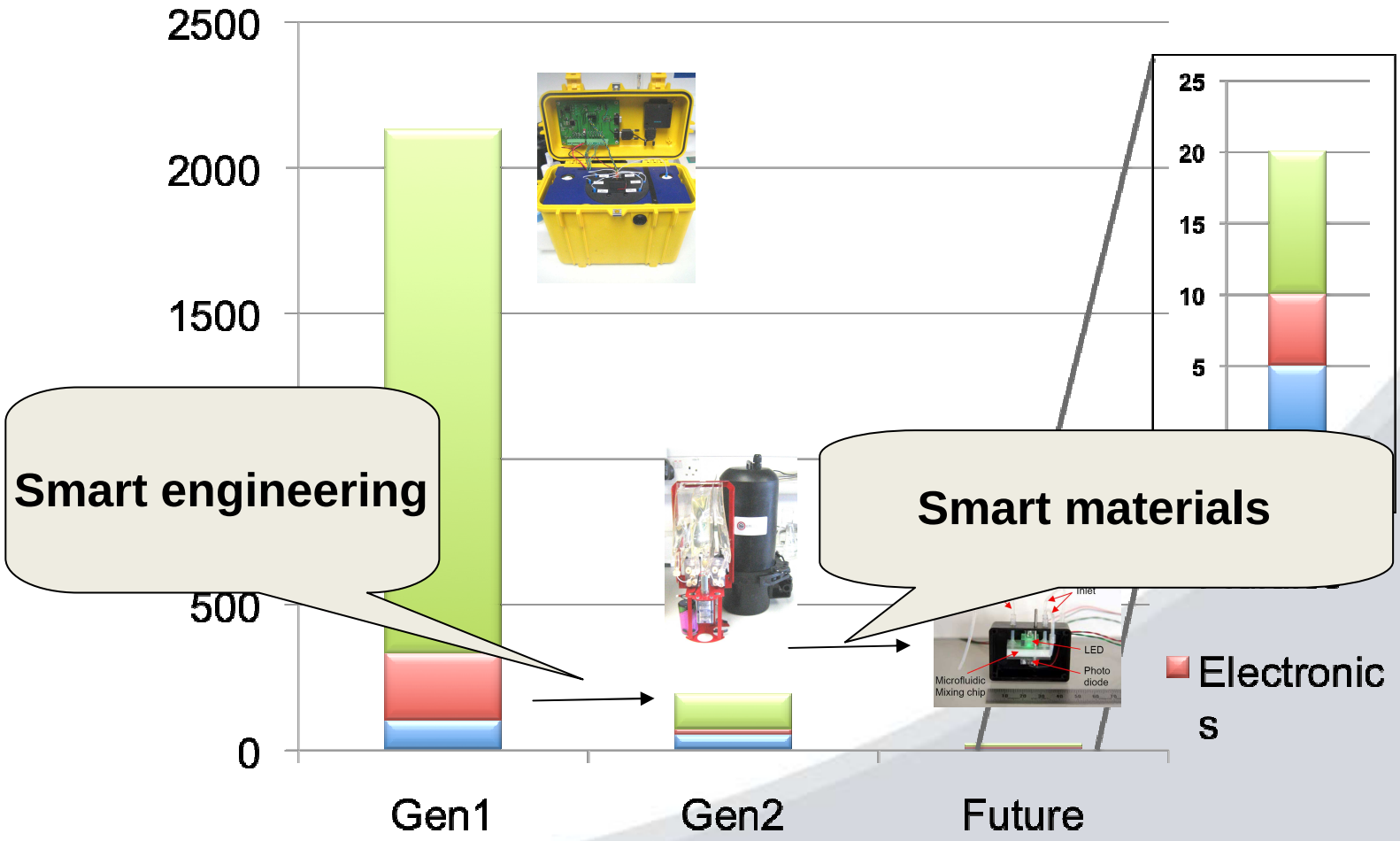
Next Generation device

- GEN2 developed; cost now ca. €250 per unit; launched at Environ 2010 (Feb)
- System still reliant

Gen1

Gen2

Cost Comparison of device (€)



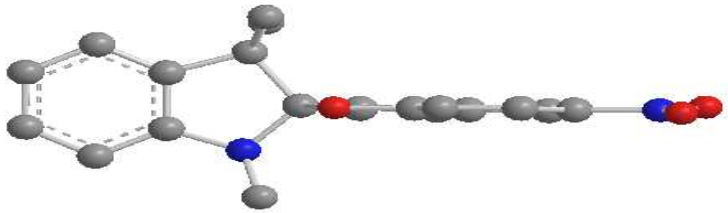
Generation 3 system

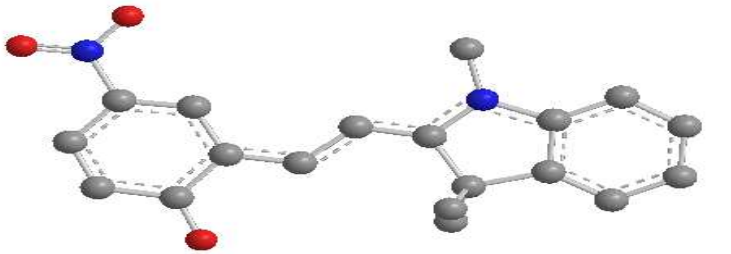
- Current fluid handling components not suitable to miniaturised microfluidic systems- solenoid and electric motors for valves, actuators, pumps etc.
- Existing systems require large amount of power, space and expense.
- 'Biomimetic' approach to sensing and liquid handling based on intelligent materials.
- Realisation of futuristic sensing systems (3G model) lies within materials science
- Stimuli responsive materials for fluid handling
  - Electrochemical
  - Magnetic
  - Chemical
  - **Optical**
- Properties that can reversibly change e.g. chemical binding behaviour, surface charge/polarity, porosity, permeability, dimensions,…..

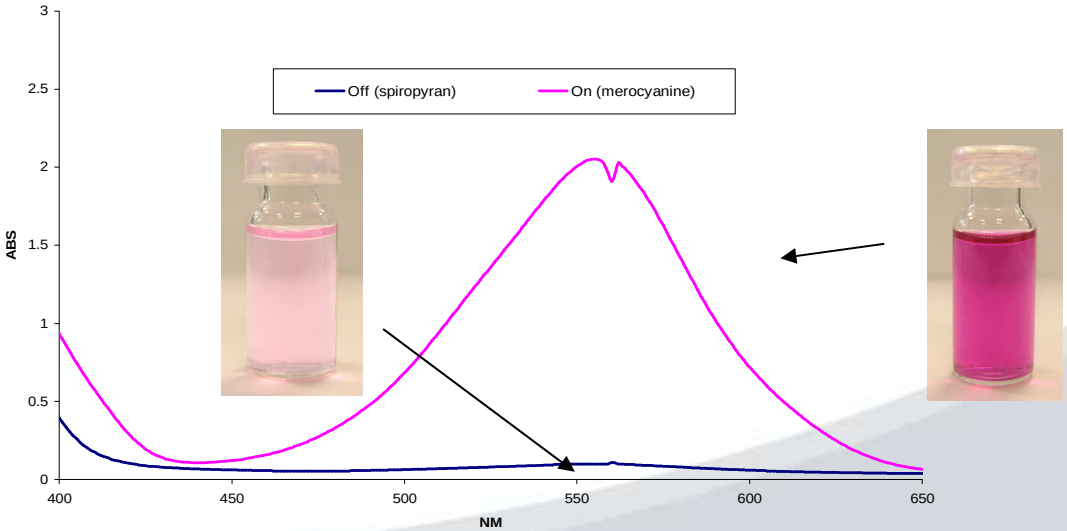
Photo-responsive materials based on spiropyran

Spiropyran

Merocyanine

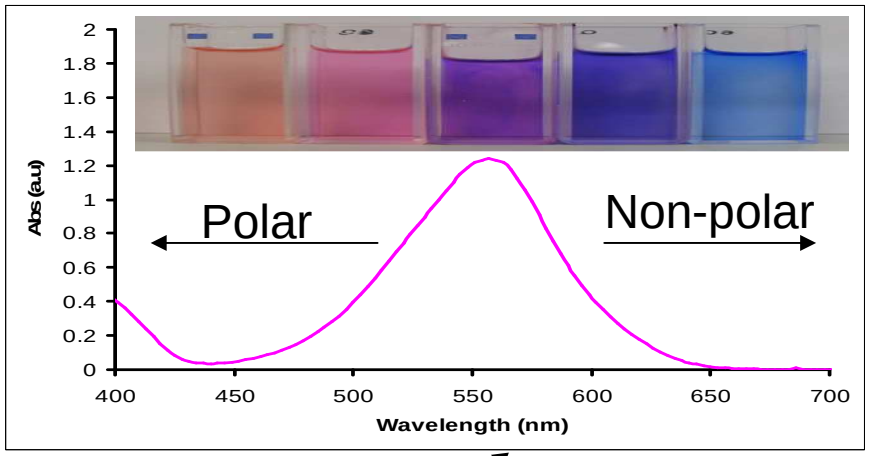


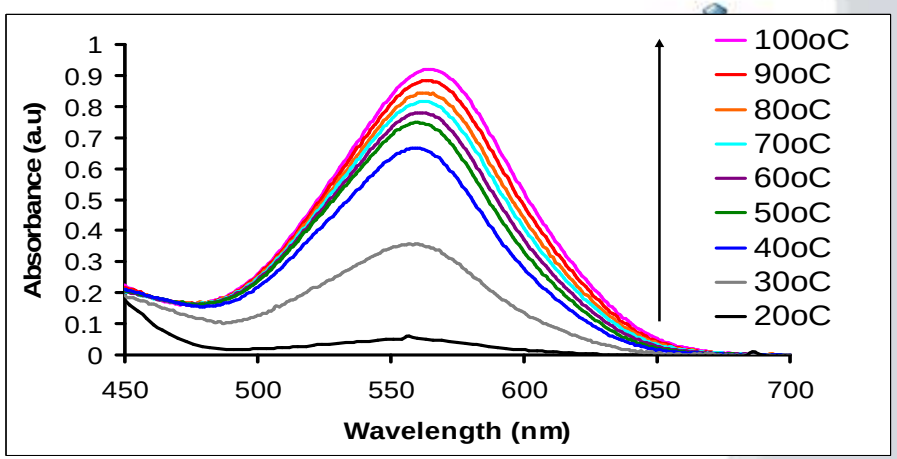




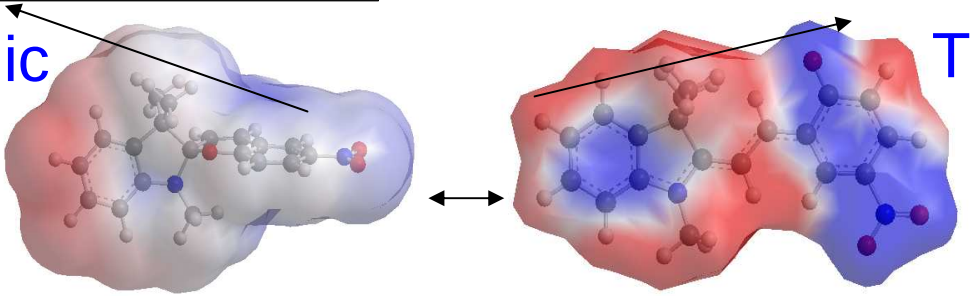
- **Optically actuate between two distinct isomers**
- **Control physico-chemical properties of system**
- **Non-contact spatial control of actuation**

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





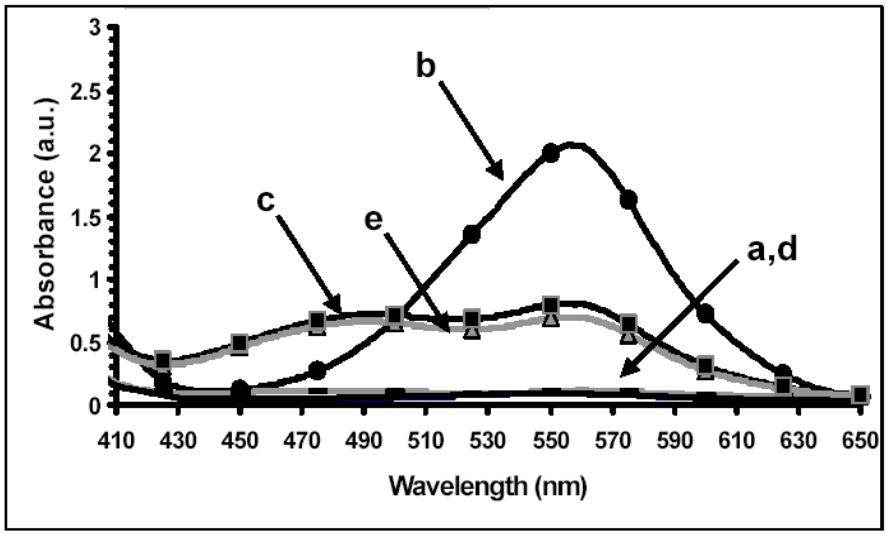
Solvatochromic

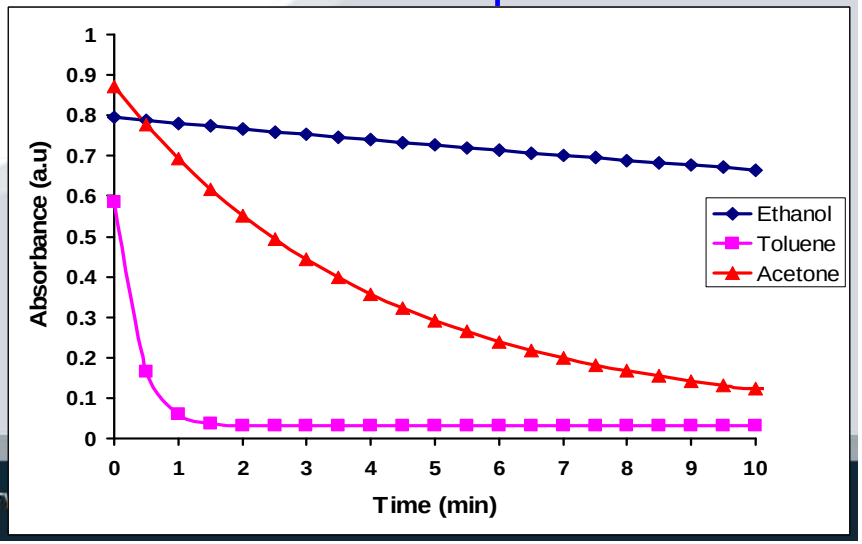


Thermochromic

Metal ions, Proton, Protein and DNA recognition site

Thermal relaxation dependent on all processes!

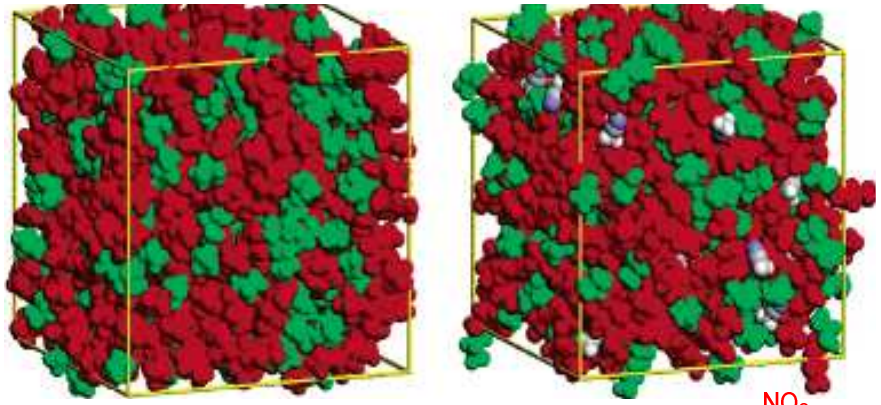


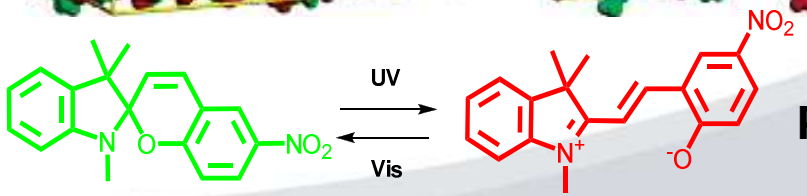


Ionic Liquids- photoresponsive liquids

- 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 (ionic liquids in gels, solid state electrolytes)

Nano-structured liquids (Lopes *et al* 2008)





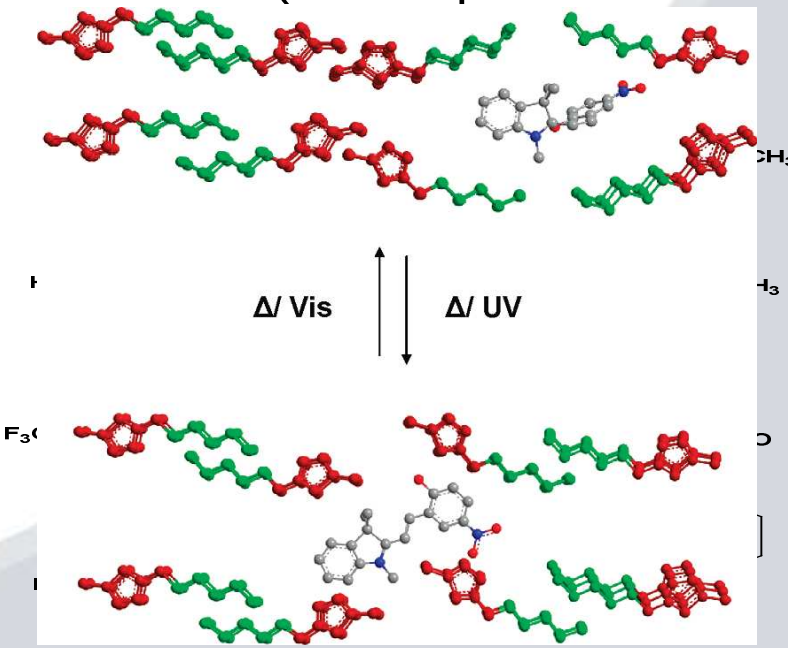
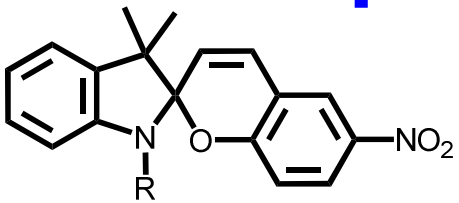


Photo-switching physicochemical interactions

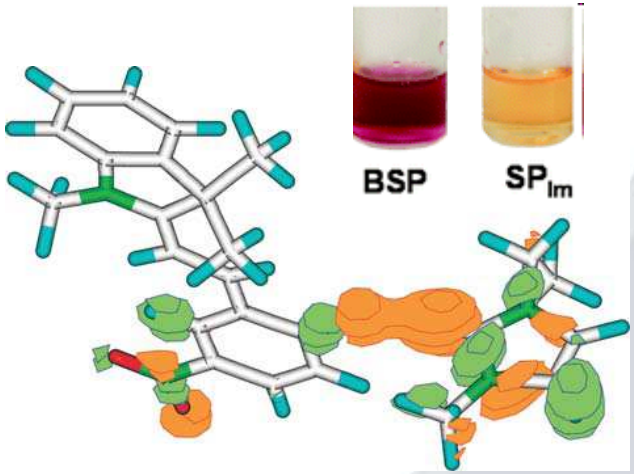
R. Byrne, *Phys. Chem. Chem. Phys.*,**2008**, 10, 5919–5924. S. Coleman, *Phys. Chem. Chem. Phys.*,**2009**, 11, 5608–5614

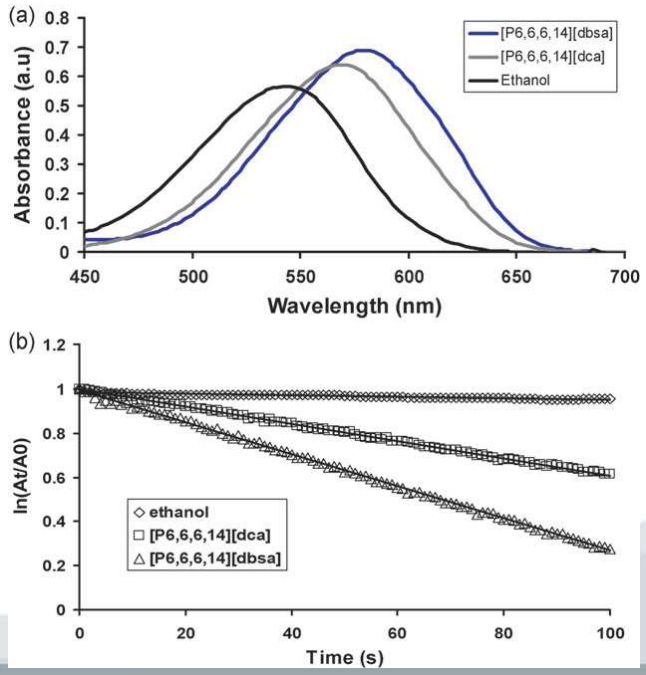
Designer photochromics in ionic liquids

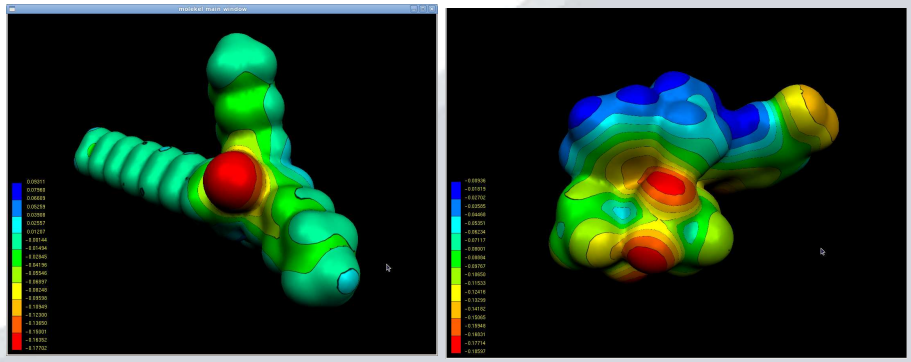


BSP 1 = R = $(CH_2)_2OH$
BSP 2 = R = $(CH_2)_3CO_2H$
BSP 3 = R = $(CH_2)_{13}CH_3$

Polar and non-polar appendages locate molecule into specific regions







Molecular modelling helps with design

R. Byrne, *Phys. Chem. Chem. Phys.* **2010**, *12*, 1895-1904.
R. Byrne, *Phys. Chem. Chem. Phys*., **2009**, 11, 7286–7291

Encapsulation of ILs- Ionogels

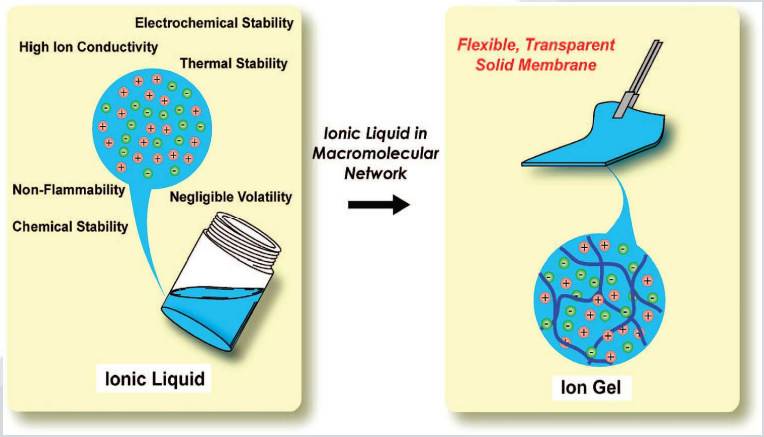
- Inorganic route **(Li et al, 2004)**
  - Oxides
  - Sol-gel
  - Applications in catalysis and photonics

Chem. Mater. **2006,** *18,* 3931−3936

Ionogels, New Materials Arising from the Confinement of Ionic Liquids within Silica-Derived Networks

Marie-Alexandra Néouze,† Jean Le Bideau,† Philippe Gaveau,‡ Séverine Bellayer,† and André Vioux*,†

- Organic route **(Watanabe, 2004)**
  - Polymers
  - Acrylamide gels
  - Applications in solid state electrolytes and separations

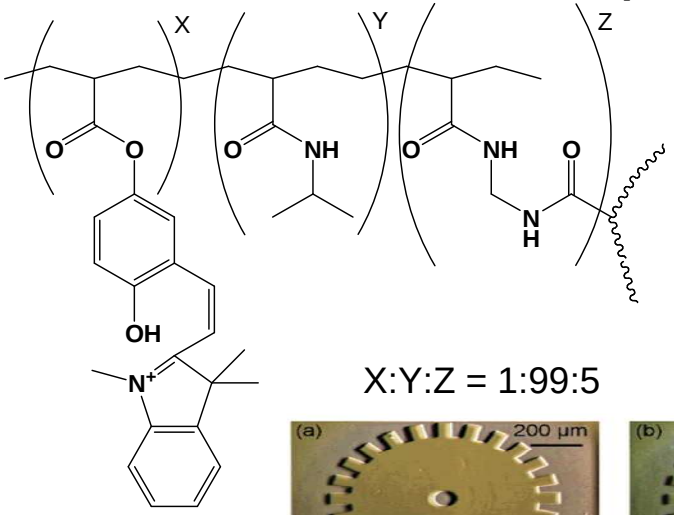


Watanabe *Macromolecules, Vol. 41, No. 11, 2008*

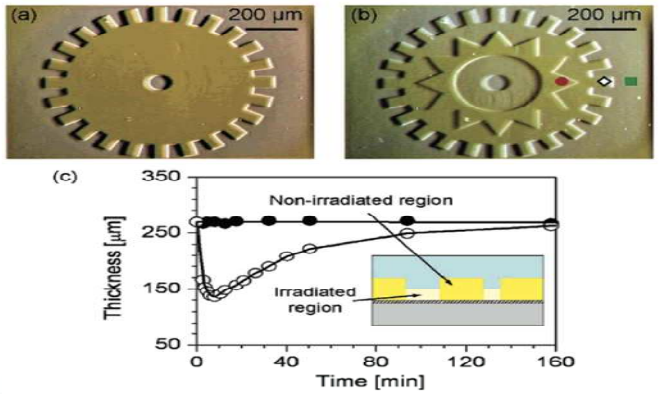
Combination of Ionogels and photo-responsive materials offers many advantages!!!!

Photo-responsive polymer

- 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 **<u>evaporation of water</u>** from hydrogel

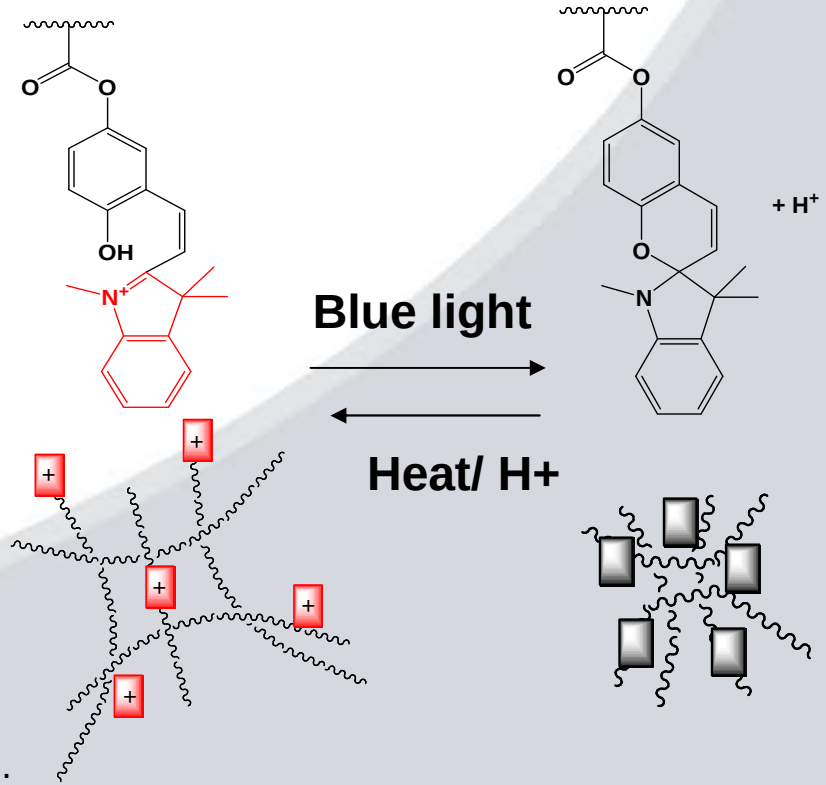


X:Y:Z = 1:99:5



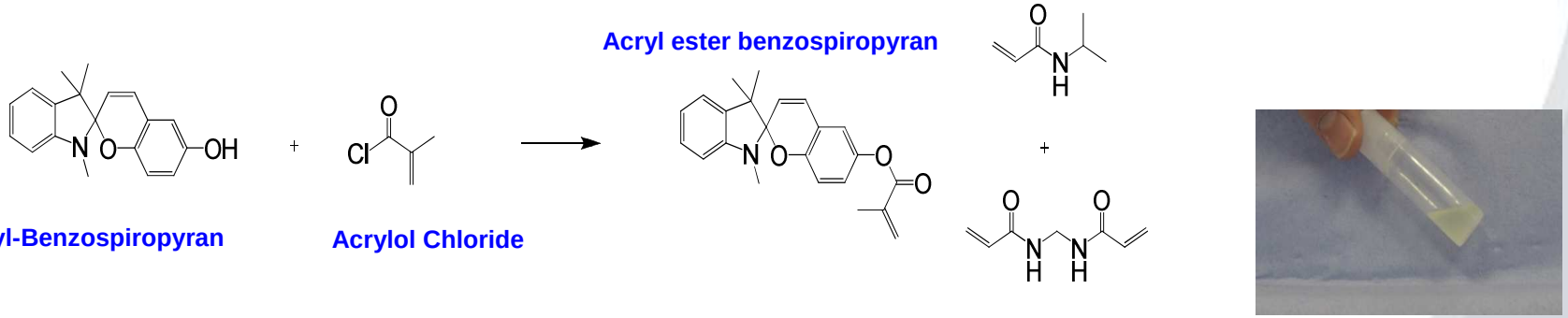
Highly Polar

Non-polar



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

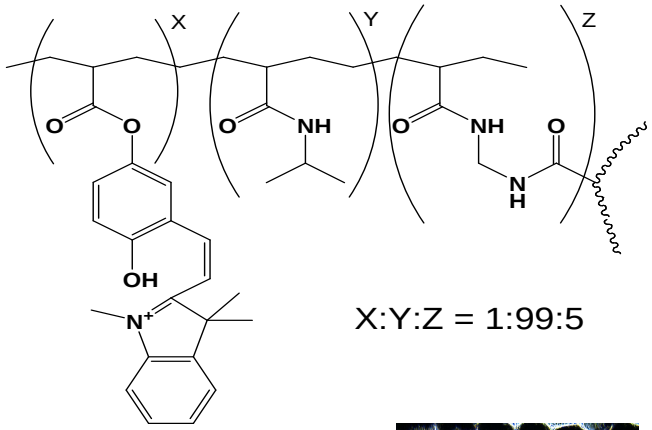
Preparation of photo-responsive ionogel



Byrne, *Biosens & Bioelec,* 2010 (accepted)

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.



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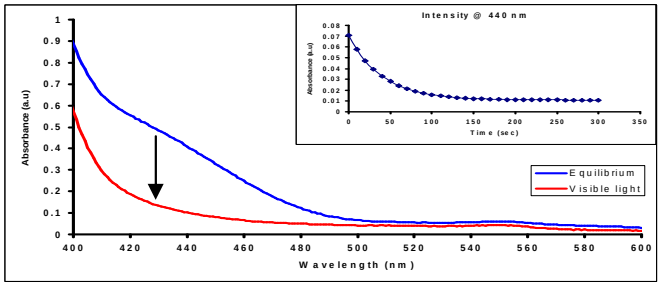
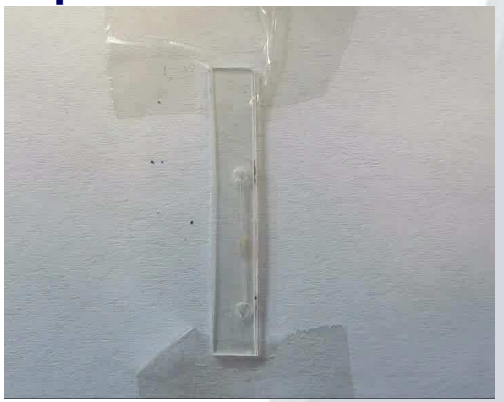
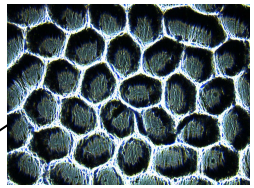
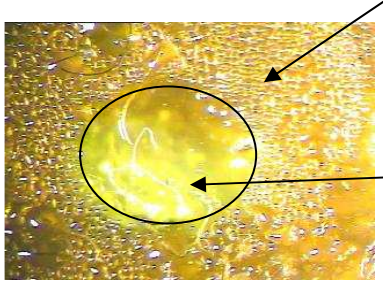


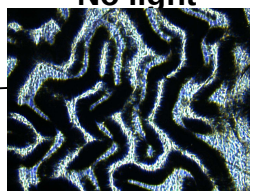


Spectroscopic analysis
Rate constant = 2.5 x10-2s-1

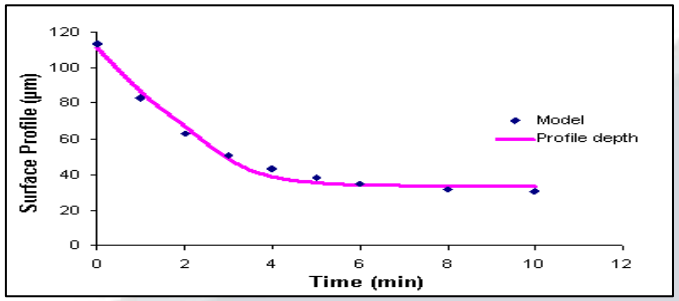


No light

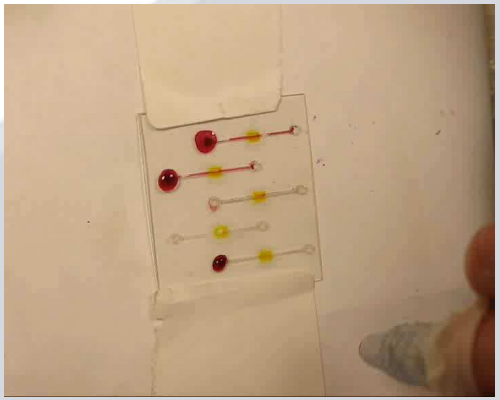




Visible light

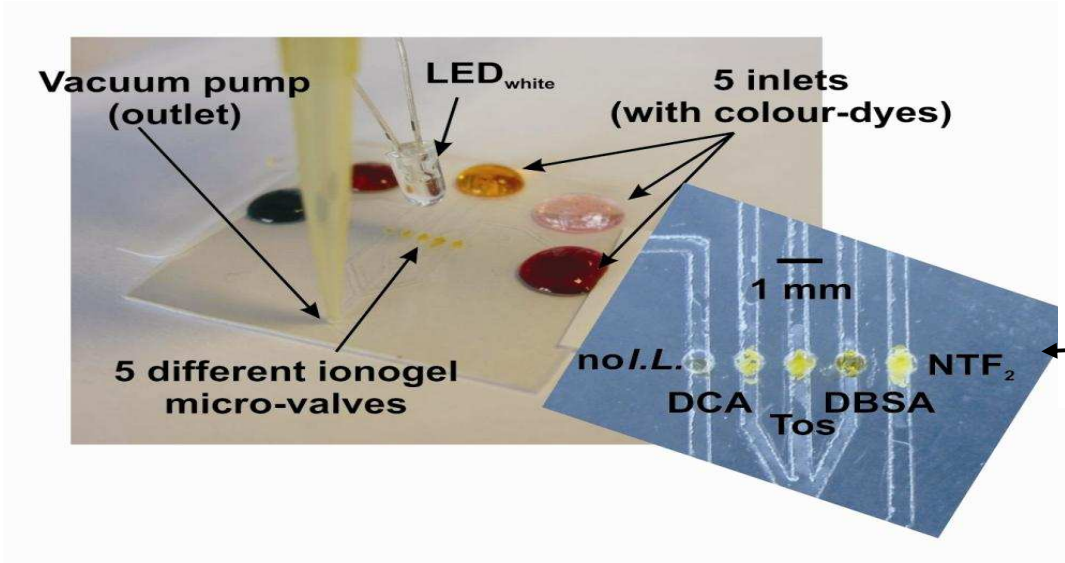


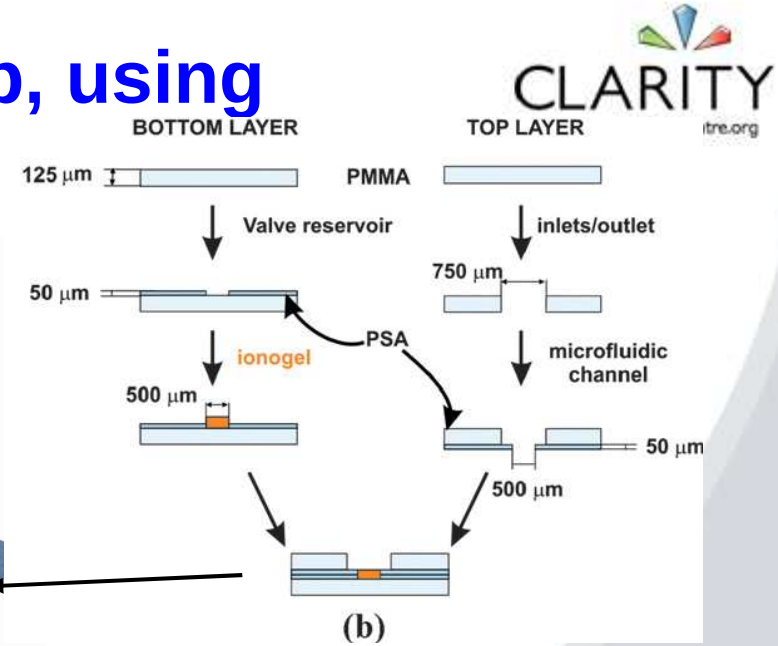
Physical profile analysis
Rate constant = 0.457 s-1.

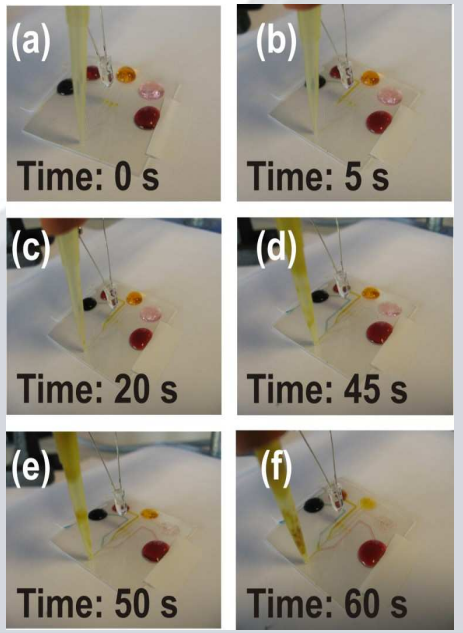


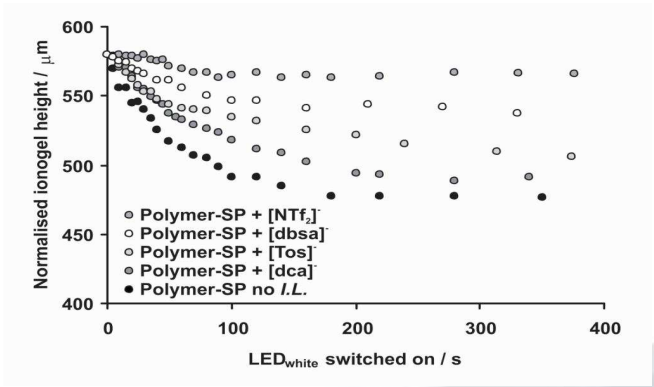
R. Byrne, Material Research Society, Adaptive materials, **2009**, (NN) 1071.
F. Benito-Lopez, ECS transcations **2009**, 19 (6) 199-210.

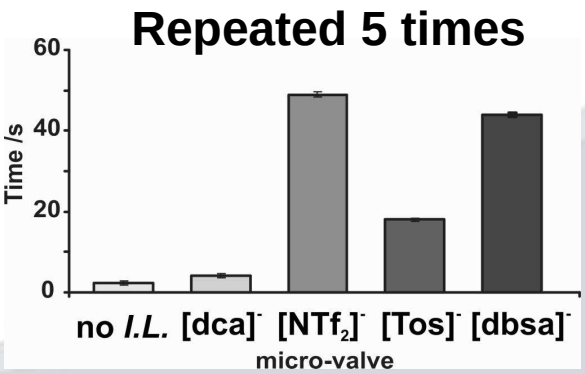
Multiple valves on one chip, using one actuation source!





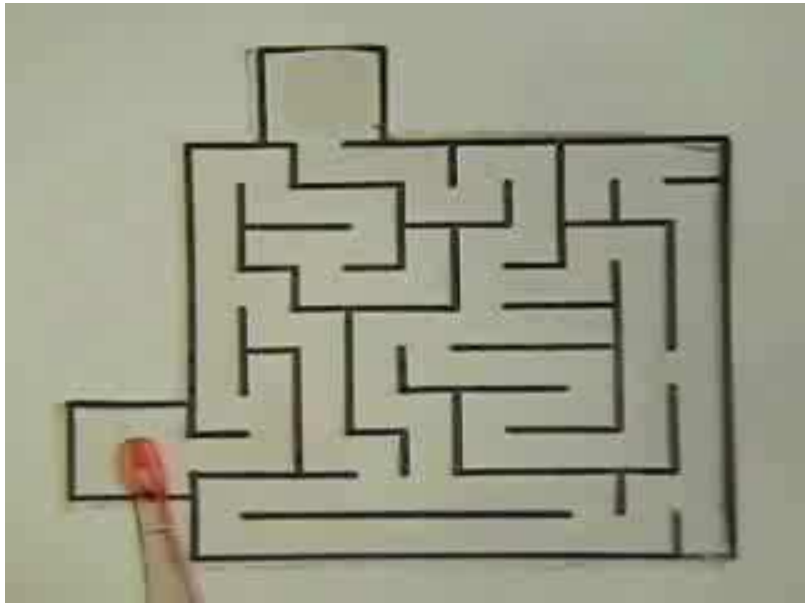






F. Benito-Lopez, *Lab on a Chip* **2010**, *10*, 195-201.

Let the chemistry do the work!!



Grzybowski *et al*, JACS 2009 *132*, 1198.

Benito-Lopez, F. *ECS Transactions* **2009**, *19*, 199.

Conclusions

- **Great potential for platforms capable of sophisticated multi-functional behaviour**
  - Pumping
  - Valving
  - Predetermined delivery functions
  - Ionogel Biosensors (Caroline Barry Thursday 11.40am Symposium B)
- **Materials must reliably perform functions comparable to conventional devices**

Acknowledgements

- **DCU**
  - Dermot Diamond
  - Fernando Benito Lopez
  - Simon Coleman
- **Monash University**
  - Doug MacFarlane
  - Kevin Fraser
- **Tyndall**
  - Damien Thompson
- **Cytec Industries**
  - Al Robertson
- **Lest we forget**


Thanks for listening!