Photo-responsive ionogels as functional materials in microfluidic systems

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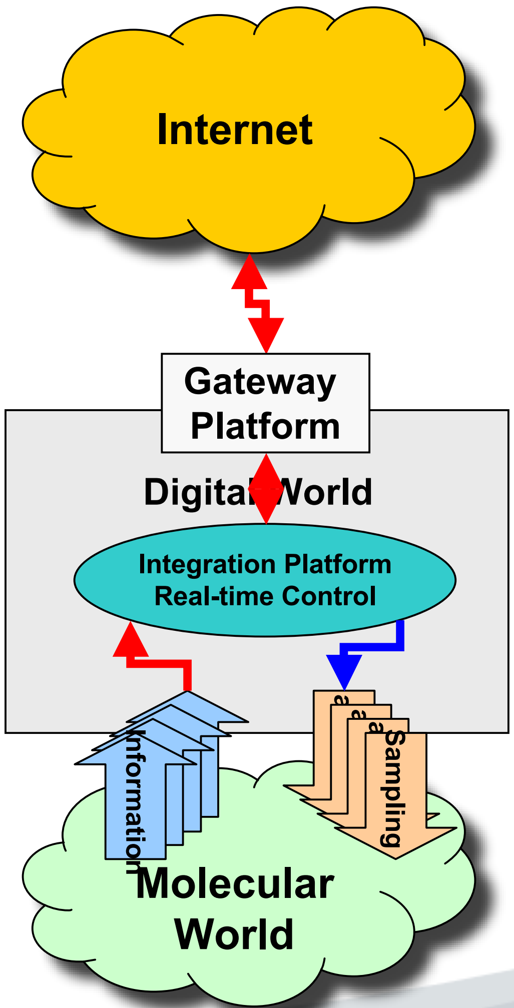
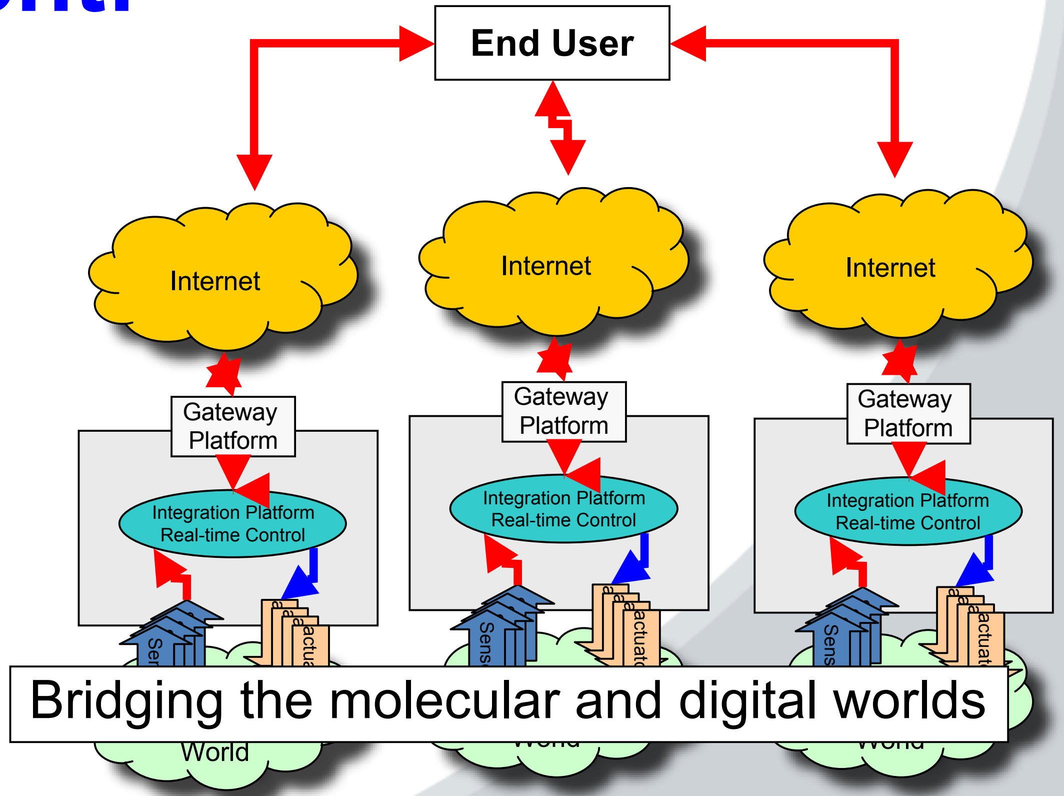
Outline

- **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**

Ubiquitous sensing: Internet-enable every measurement!





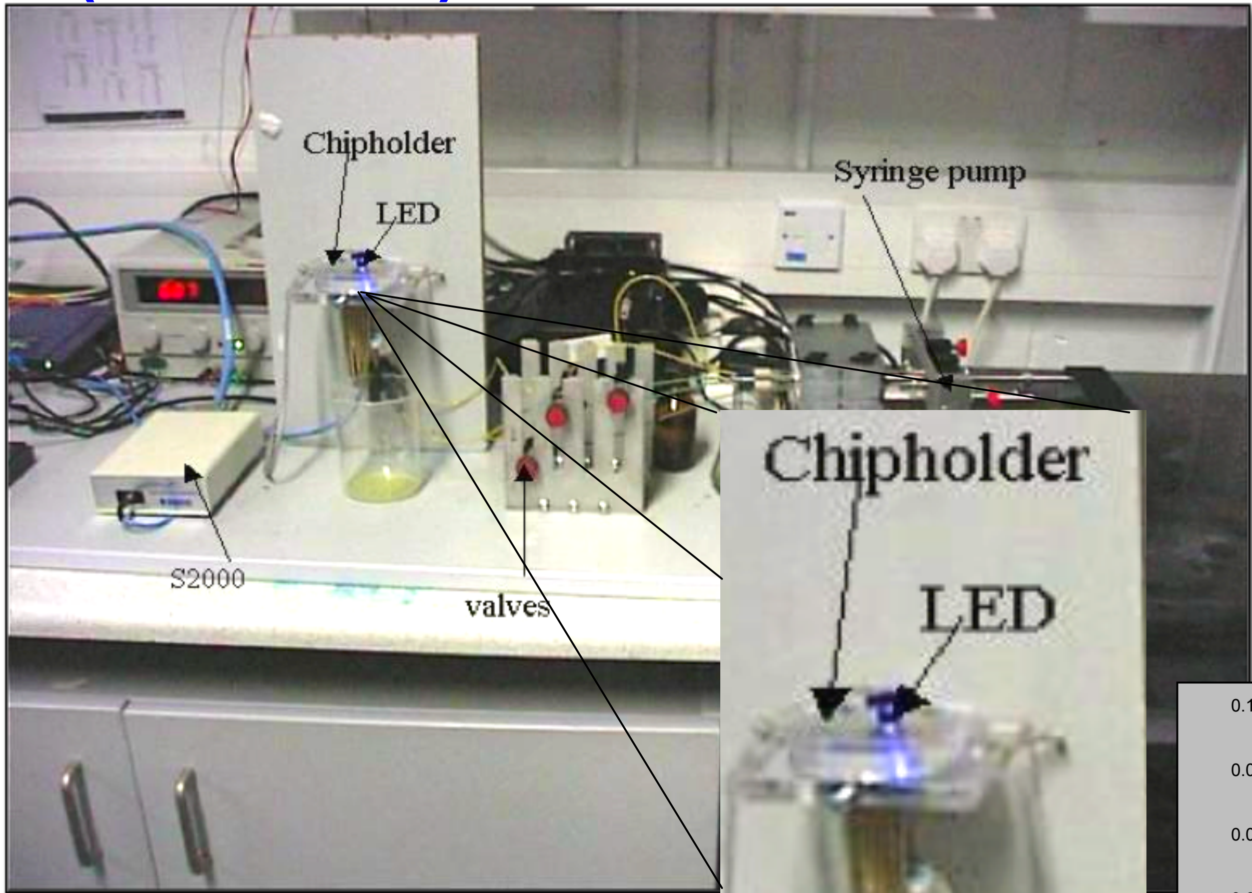
Environment
Chemical spills, Waste Management etc

Health
Homecare, e-Health
Elderly population

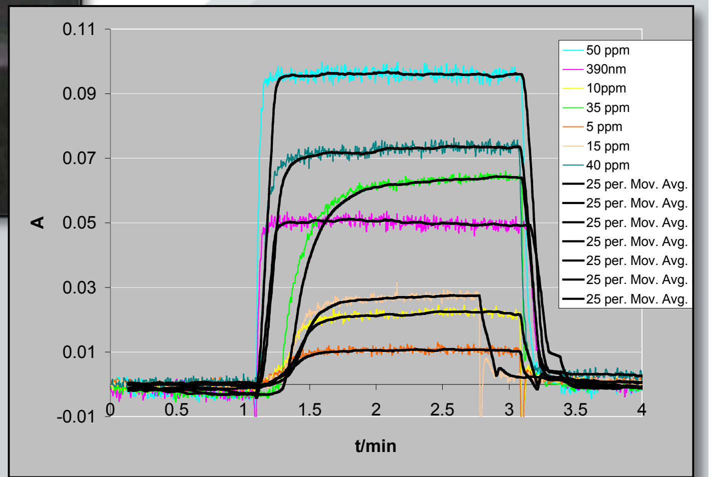
Security
Terrorist treats

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

Reagent based Nutrient Analyser (Ammonia)

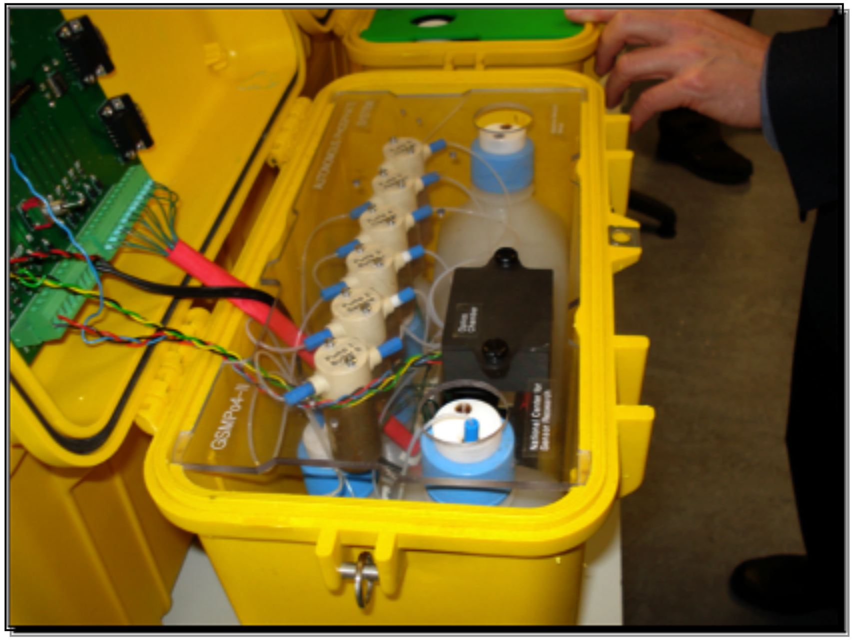


- **Setup ca. 1999**
- **Worked well but not an integrated system**



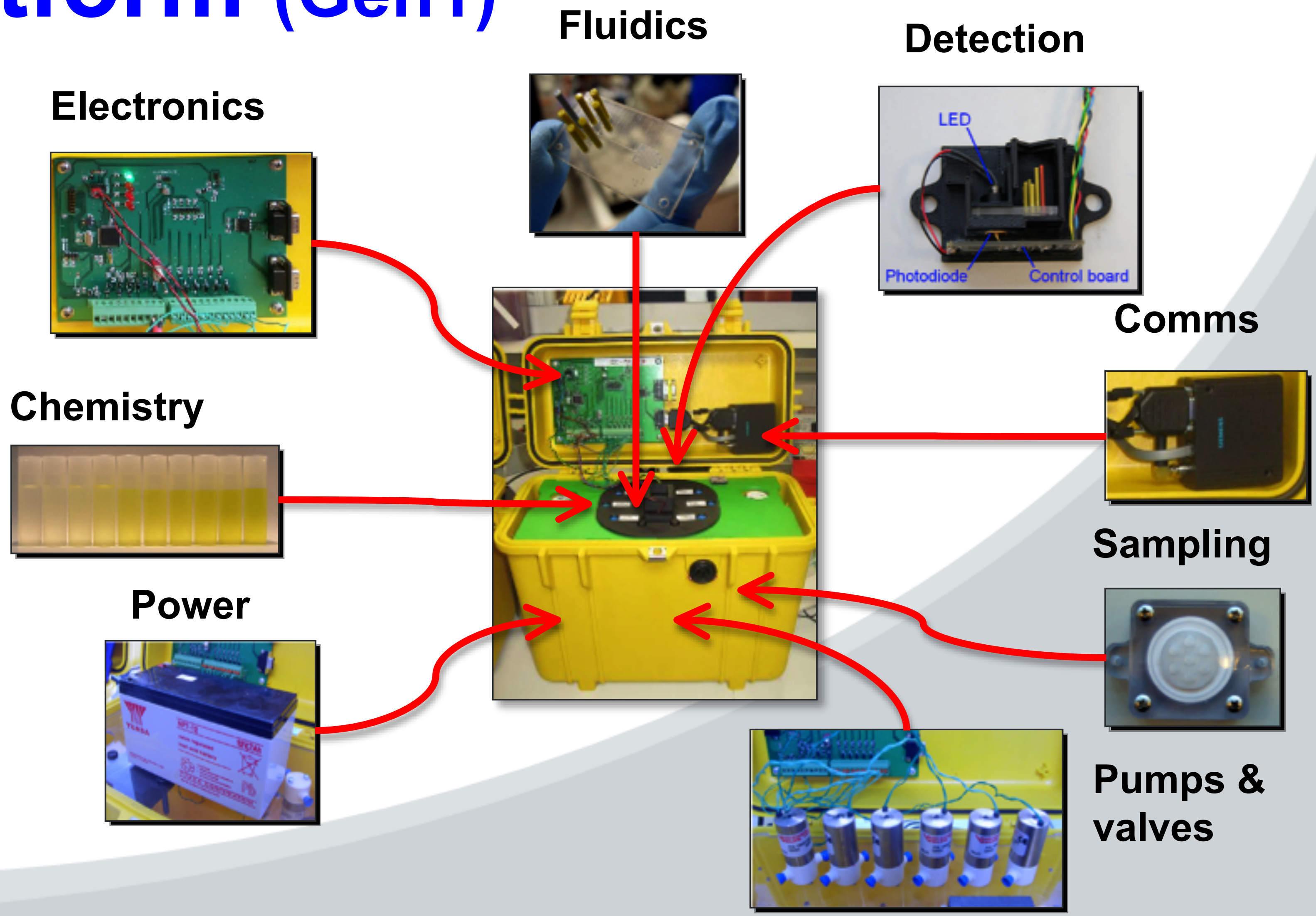
Chemical Sensing using an Integrated uFluidic System based on Colorimetrics: A Comparative Kinetic Study of the Bertholet Reaction for Ammonia Determination in Microfluidic and Spectrophotometric Systems, A Daridon, Sensors and Actuators B, 76/1-3, (2001) 235-243.

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



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

Phosphate Analyser Platform (Gen1)



Gen2 Detection System

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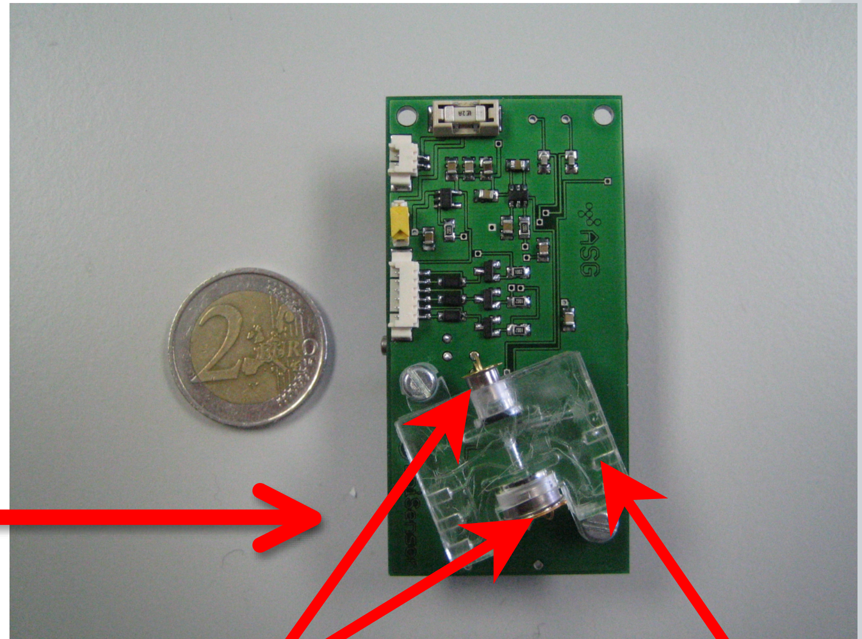
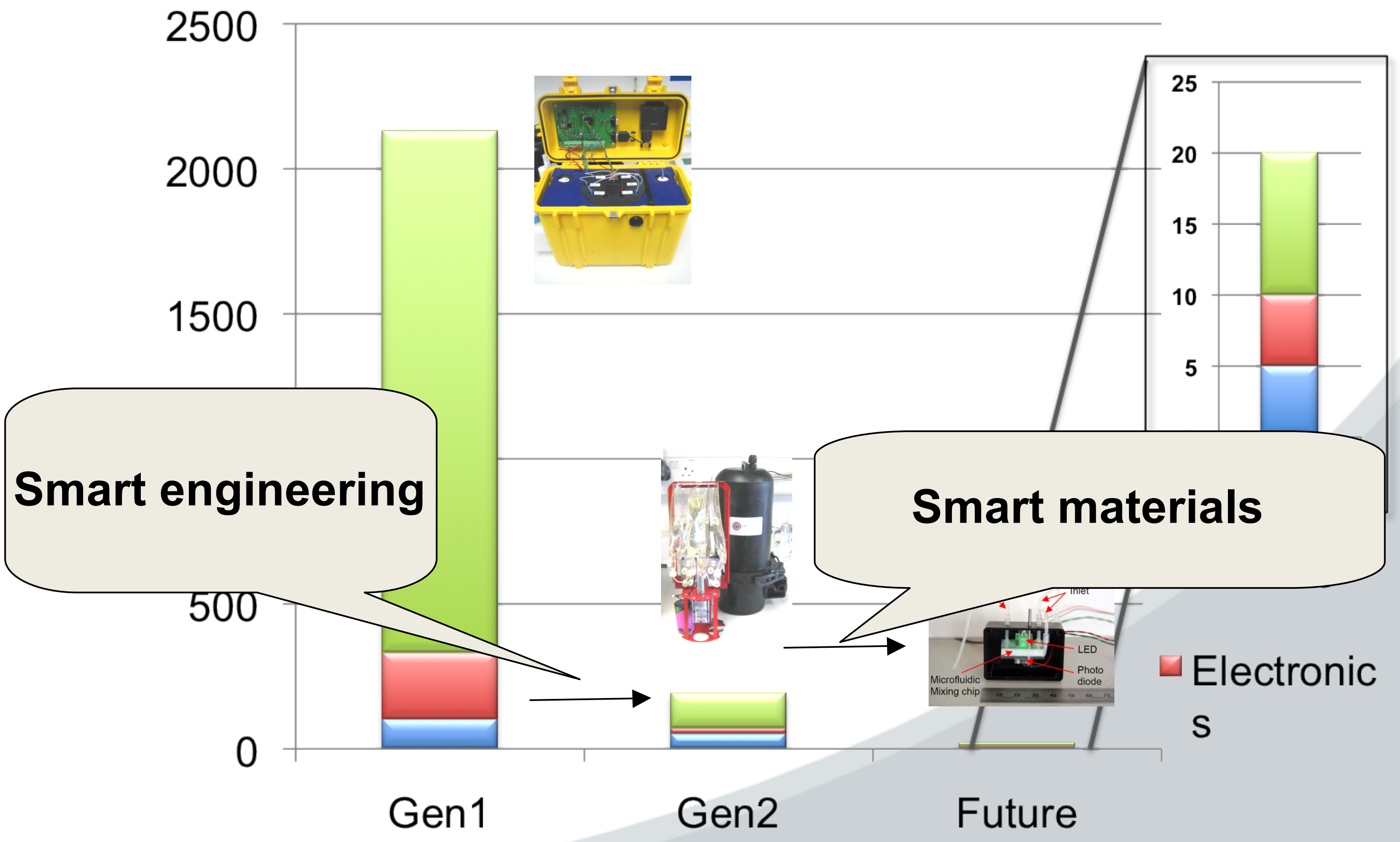
Microfluidic chip still the same as Generation 1 (ca. 1999)



LED and Photodiode Detector

Microfluidic Chip

Cost Comparison of device (€)



Stimuli-responsive materials

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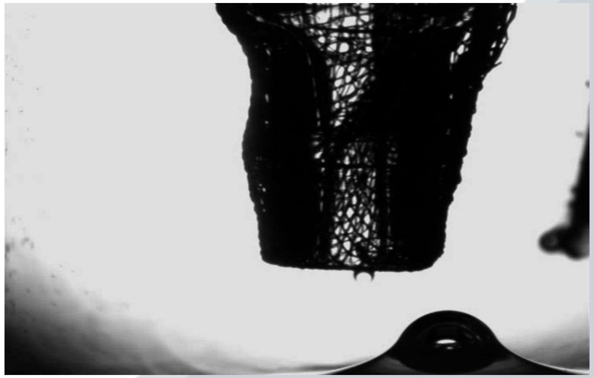
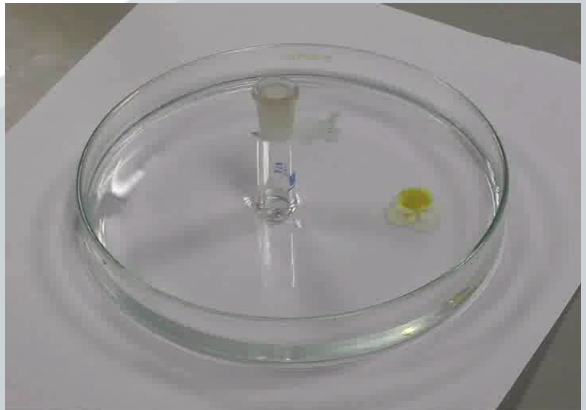
- **Realisation of futuristic sensing systems (3G model) lies within materials science**

- **Stimuli responsive materials for <u>fluid handling</u>**
  - Electrochemical
  - Optical
  - Magnetic
  - Chemical

- **Properties that can reversibly change e.g. chemical binding behaviour, surface charge/polarity, porosity, permeability, dimensions,…..**

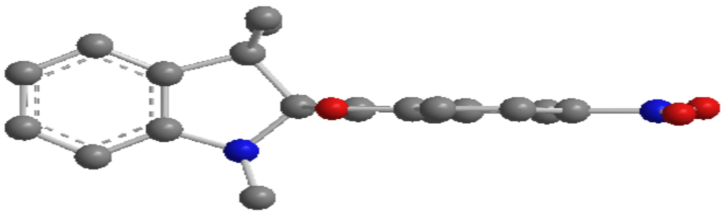


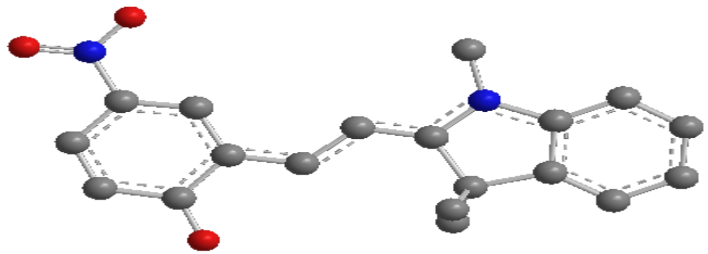


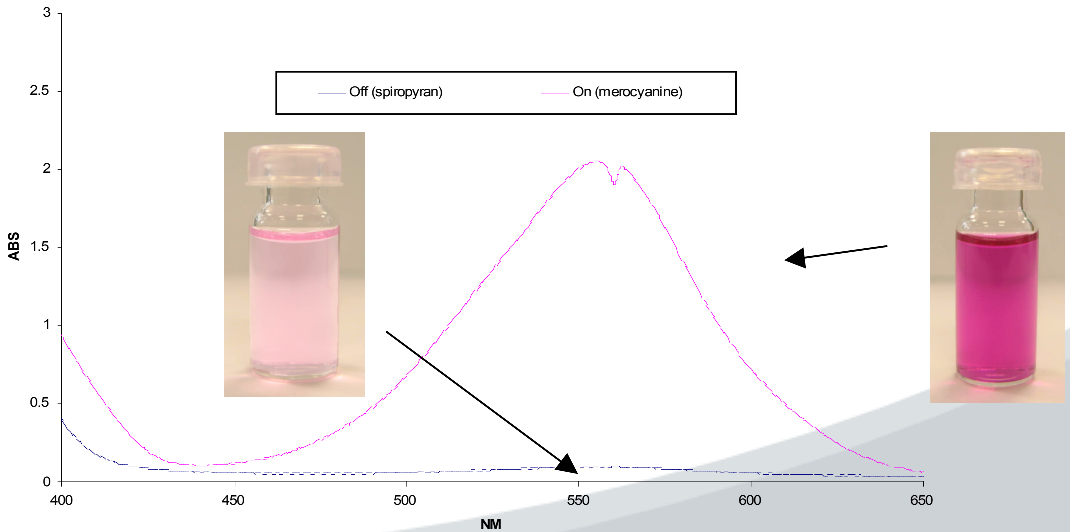
Byrne. R, Materials Today, 2010

Photo-responsive materials based on spiropyran

Spiropyran Merocyanine

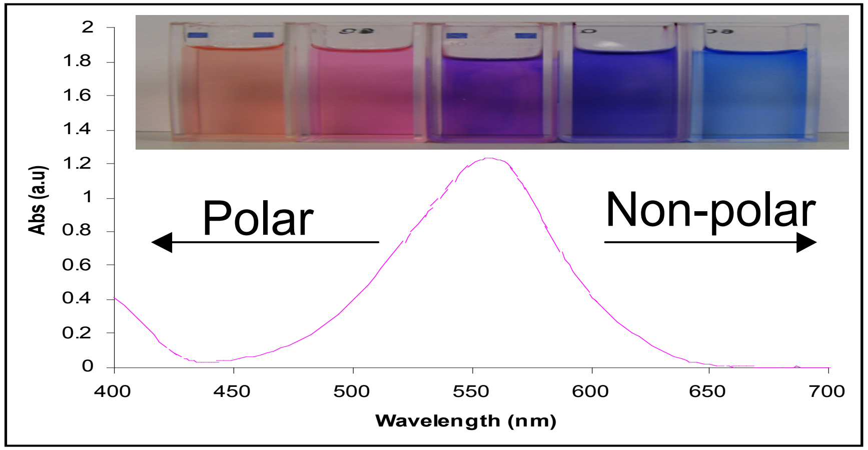


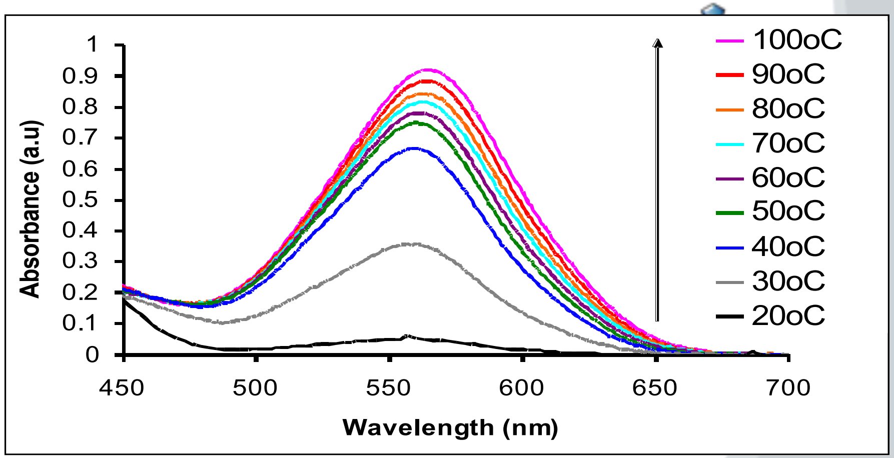




- Optically actuate between two distinct isomers
- Control physico-chemical properties of system
- Non-contact spatial control of actuation

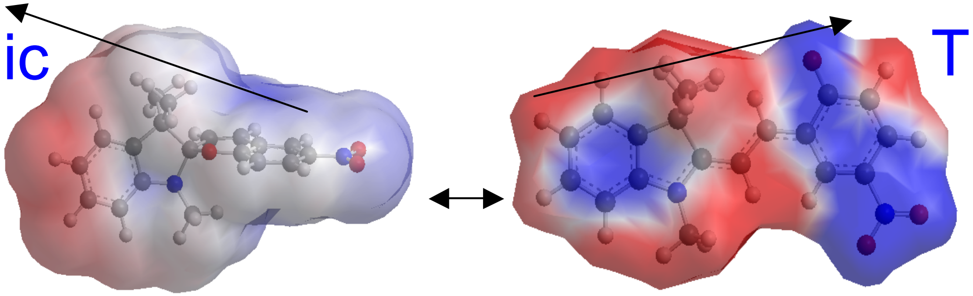
Byrne *et al*, *Nature Materials*, vol. 5, pp. 421-424, 2006.
Byrne *et al, Journal of Materials Chemistry*, vol. 16, pp. 1332-1337, 2006.





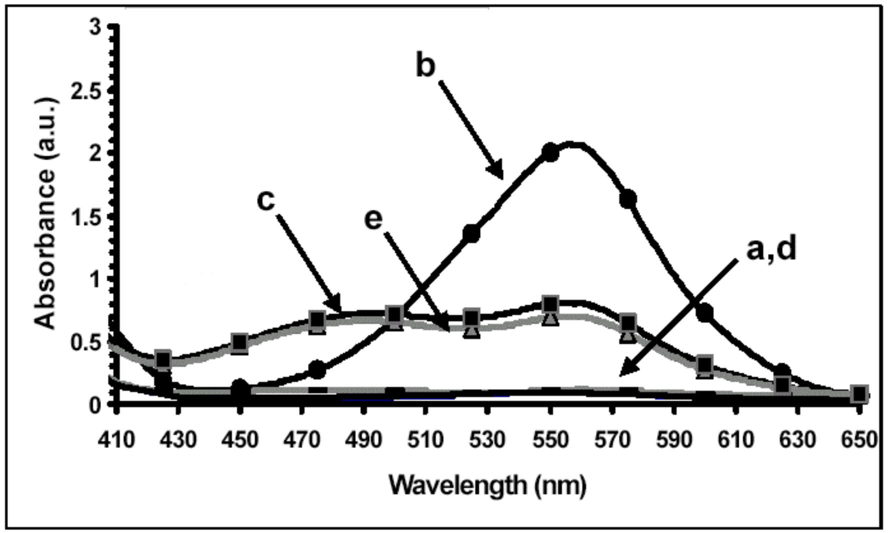
Solvatochromic

Thermochromic



Metal ions, Proton, Protein and DNA recognition site

Thermal relaxation dependent on all processes!



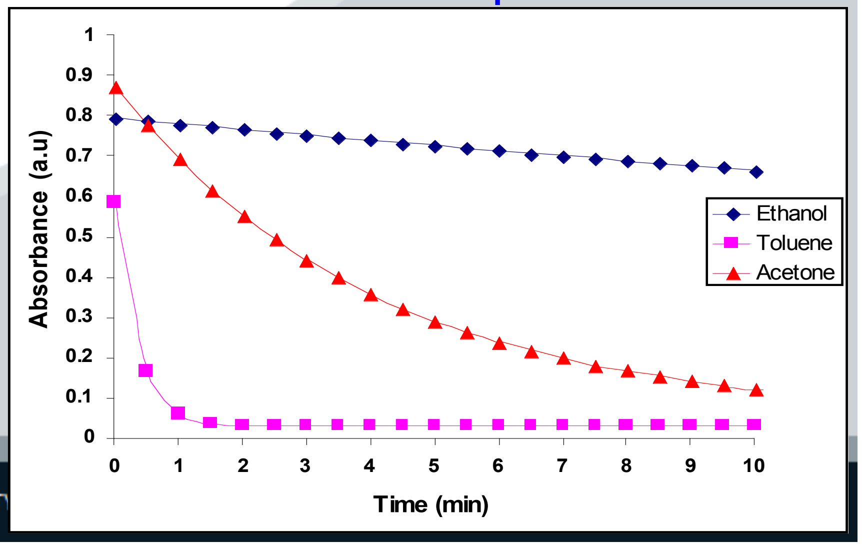
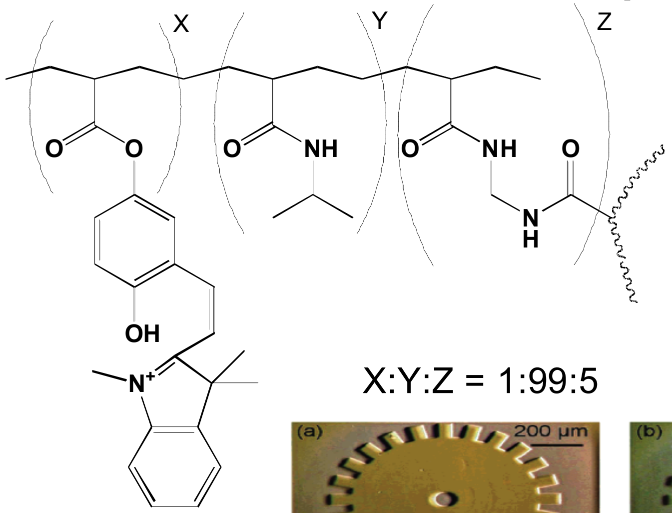


Photo-responsive polymer

- 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 **evaporation of water** from hydrogel



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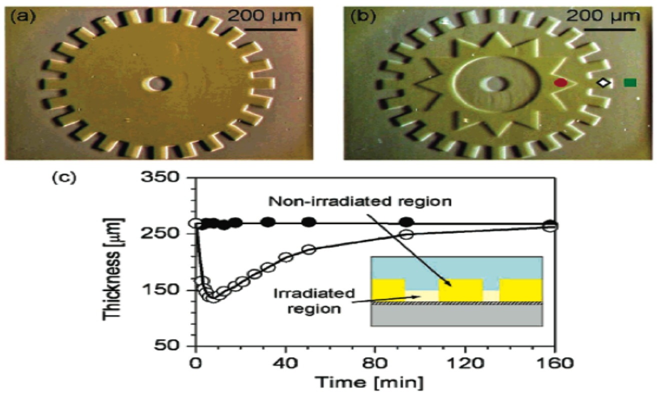
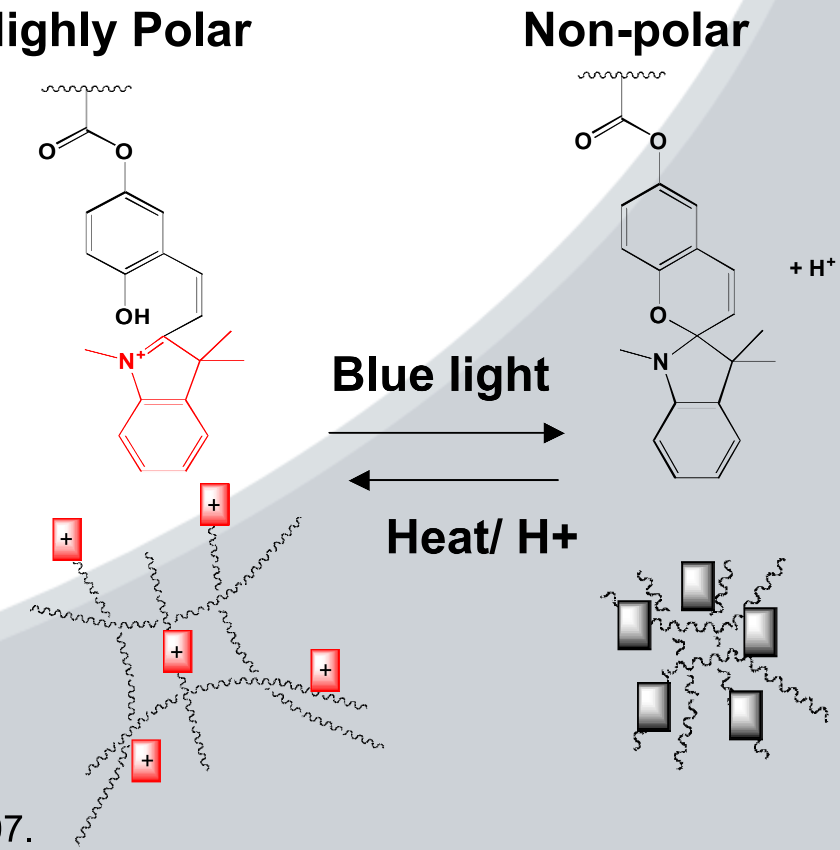


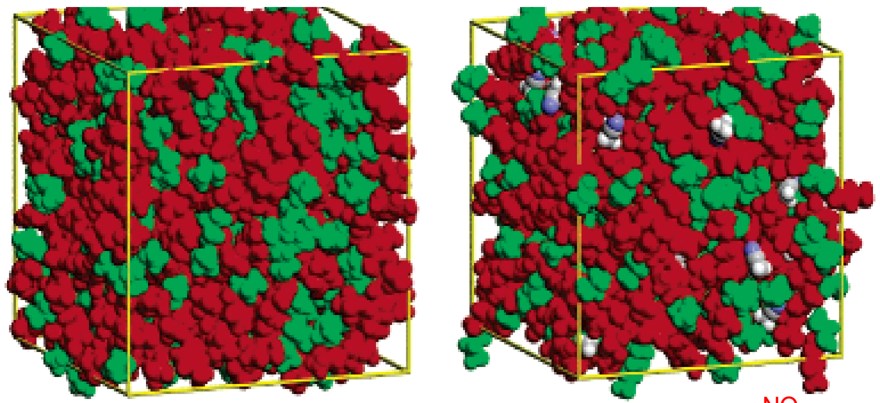


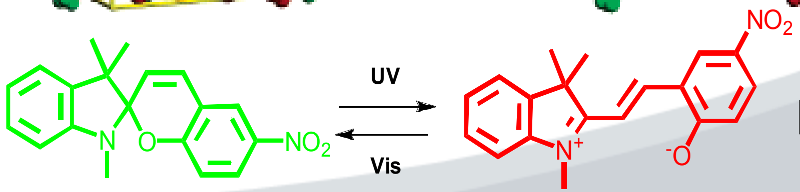
Sumaru et al *Chem. Mater.*, 19 (11), 2730 -2732, 2007.

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)





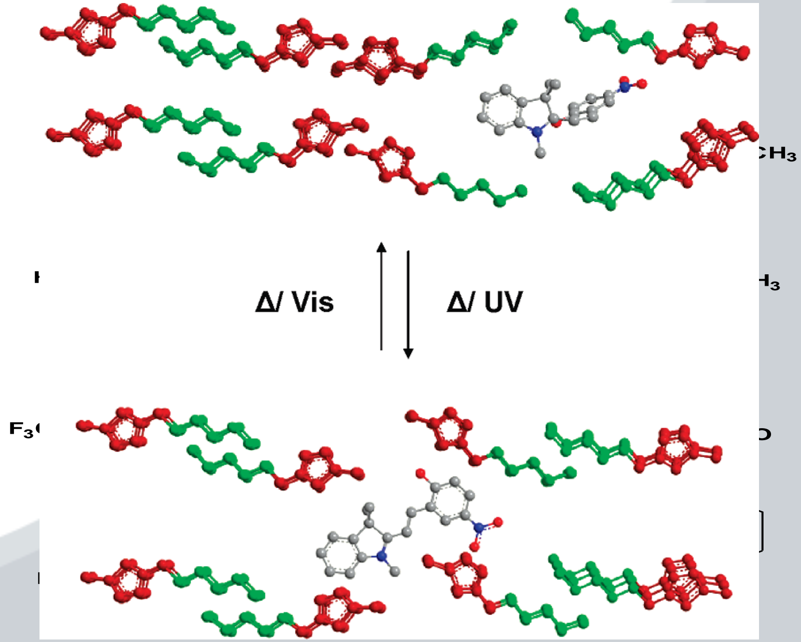
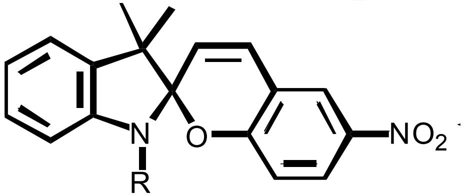


Photo-switching physicochemical interactions

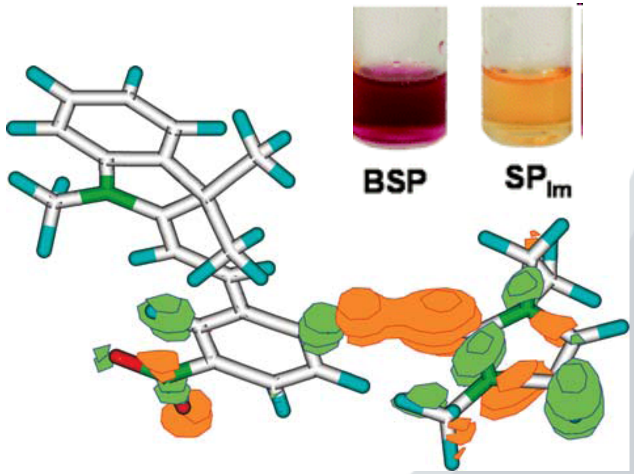
R. Byrne, *Phys. Chem. Chem. Phys.*,**2008**, 10, 5919–5924. S. Coleman, *Phys. Chem. Chem. Phys.*,**2009**, 11, 5608–5614
R. Byrne, *Phys. Chem. Chem. Phys.* **2010**, *12*, 1895-1904. R. Byrne, *Phys. Chem. Chem. Phys.*, **2009**, 11, 7286–7291

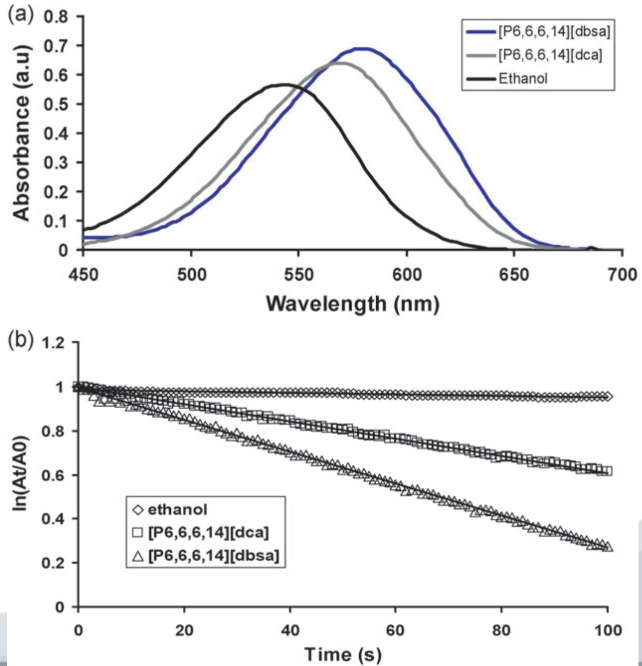
Designer photochromics in ionic liquids

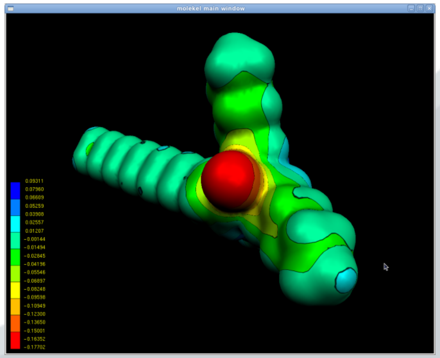


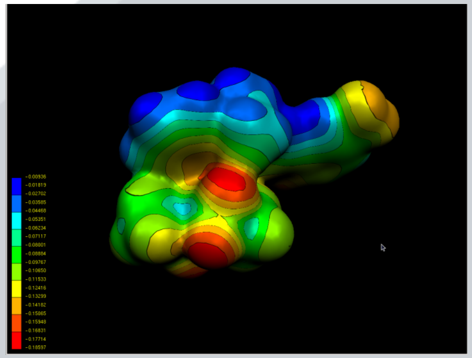
BSP 1 = R = $(CH_2)_2OH$
BSP 2 = R = $(CH_2)_3CO_2H$
BSP 3 = R = $(CH_2)_{13}CH_3$

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

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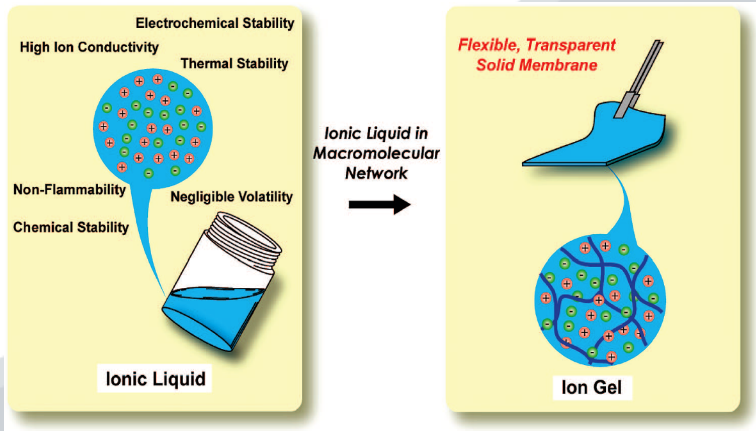
- Inorganic route **(Li et al, 2004)**
  - Oxides
  - Sol-gel
  - Applications in catalysis and photonics

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*,†

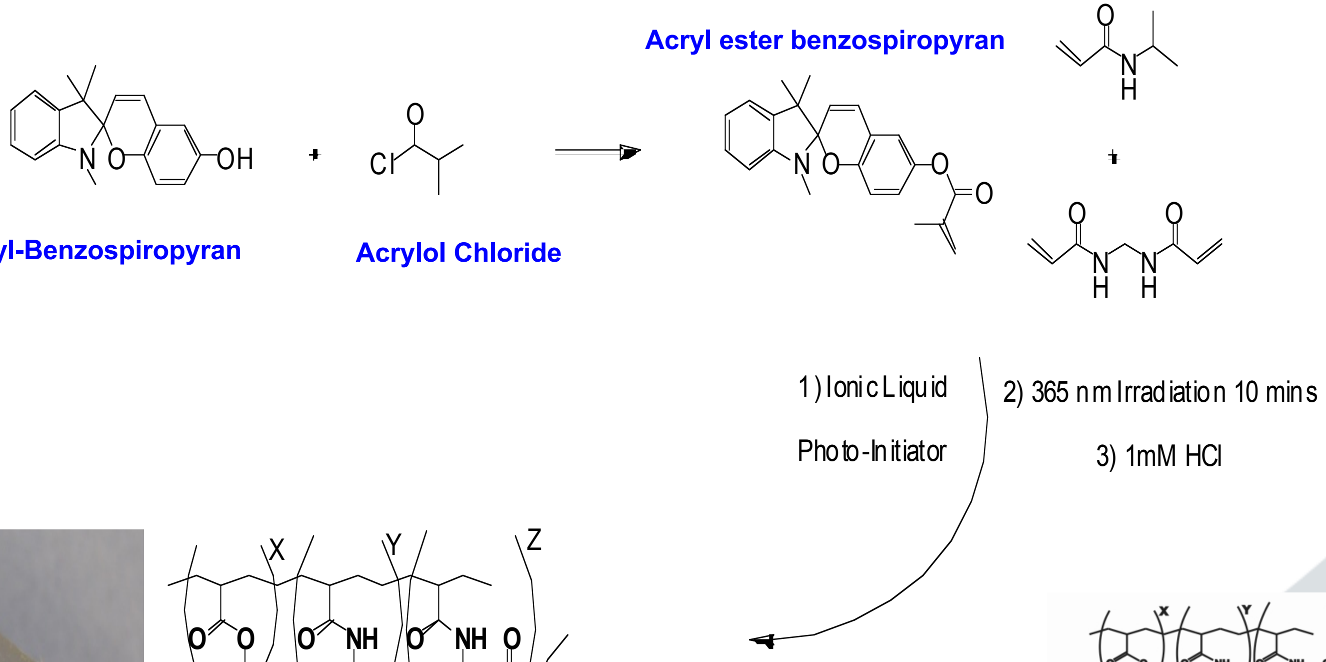
- Organic route **(Watanabe, 2004)**
  - Polymers
  - Acrylamide gels
  - Applications in solid state electrolytes and separations

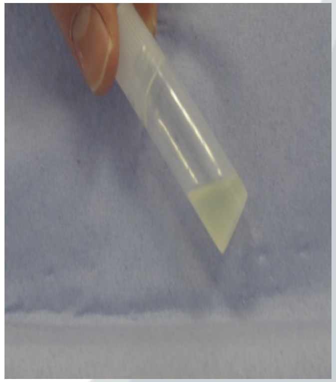


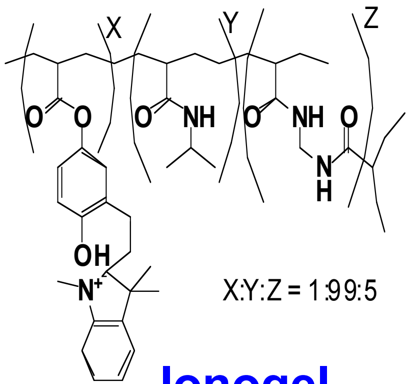
Watanabe *Macromolecules, Vol. 41, No. 11, 2008*

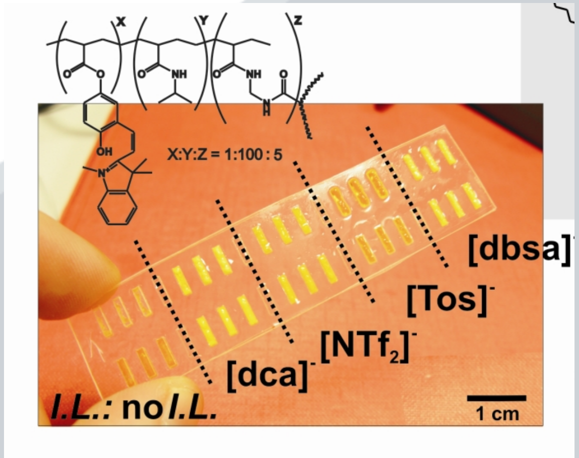
Combination of Ionogels and photo-responsive materials offers many advantages!!!!

Preparation of photo-responsive ionogel





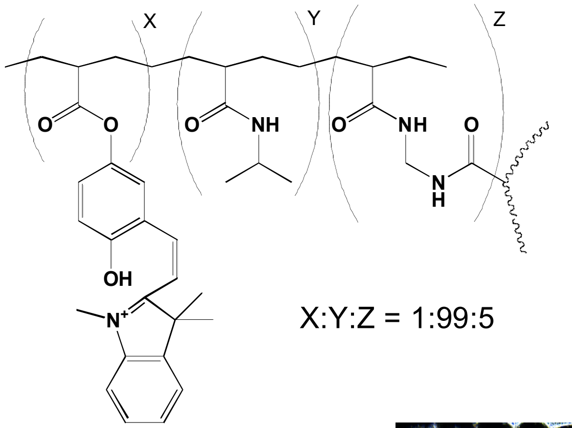




Byrne, *Biosens & Bioelec,* 2010 (accepted)

Photo-responsive ionogel properties

•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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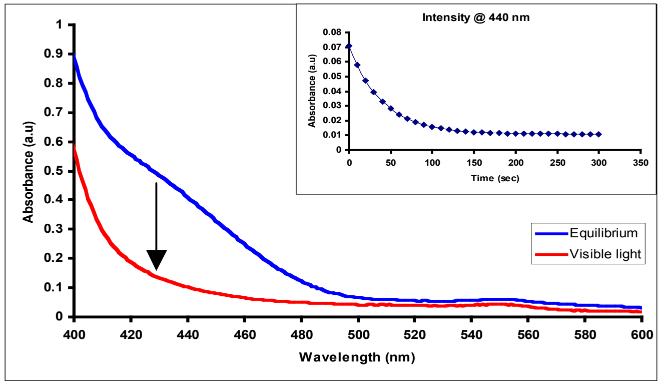
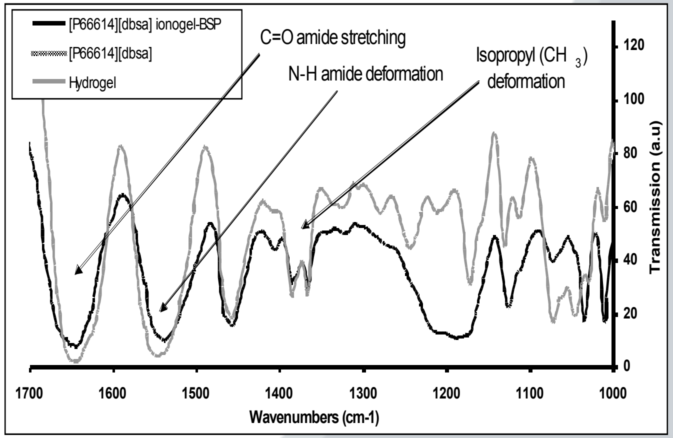
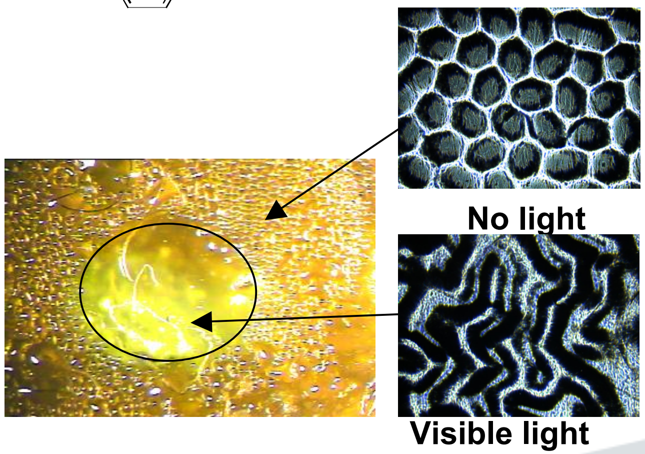
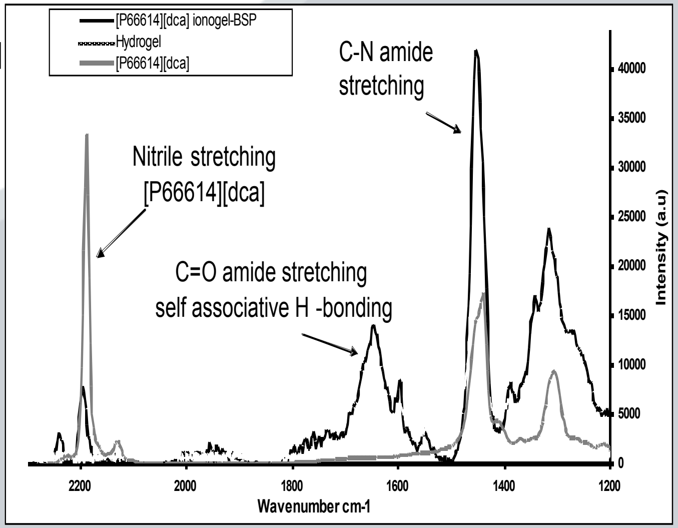




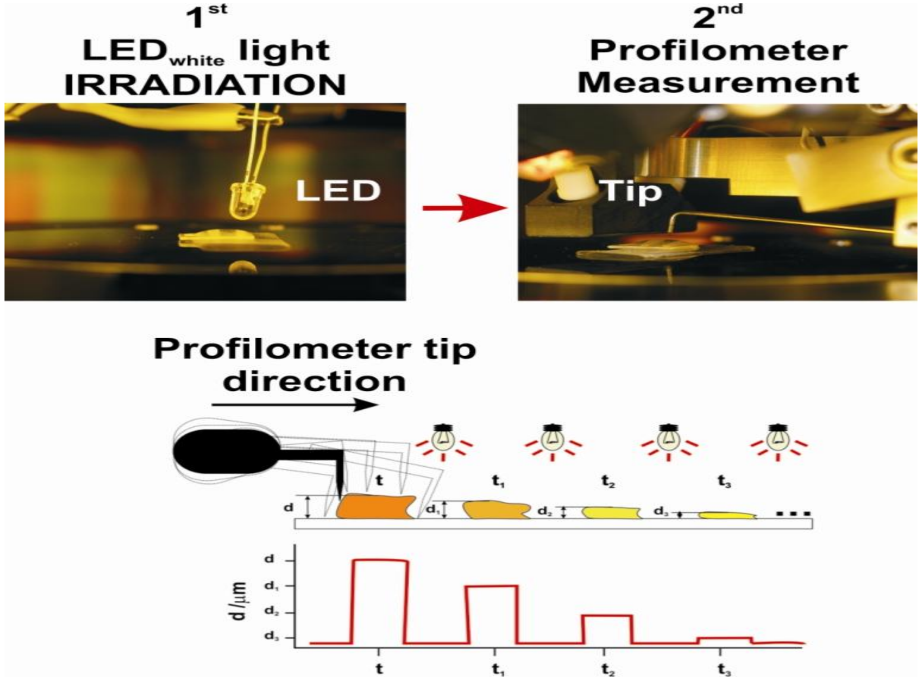


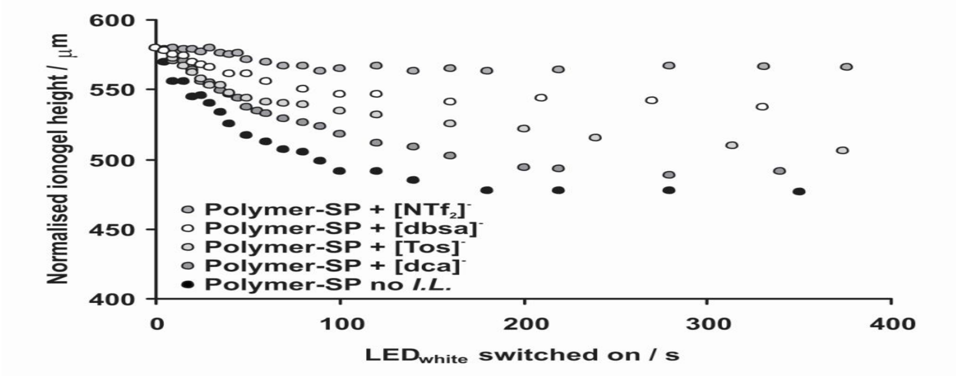
Spectroscopic analysis
Rate constant = 2.5 x10-2s-1



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

Physical characterisation of ionogel





All measurements at 25°C

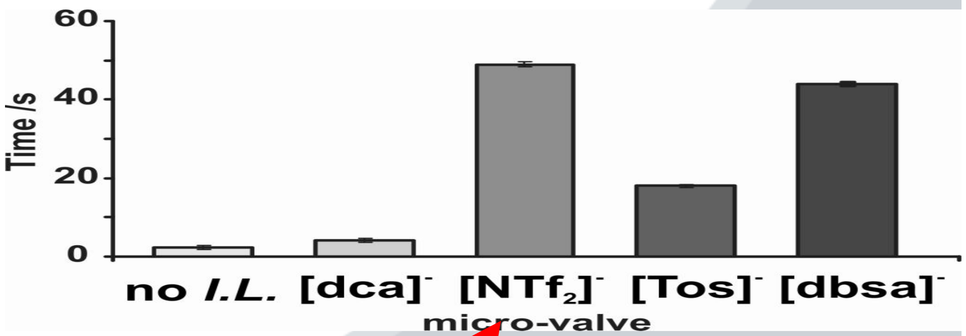
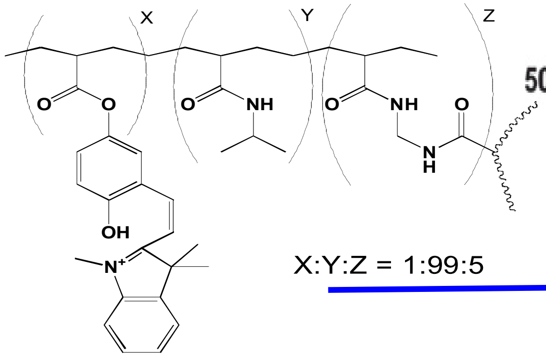


Table 1 Axial stiffness, ultimate tensile strength (UTS) and elongation at break values for the ionogels

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

Correlation between stiffness and actuation behaviour

Photo-responsive valve



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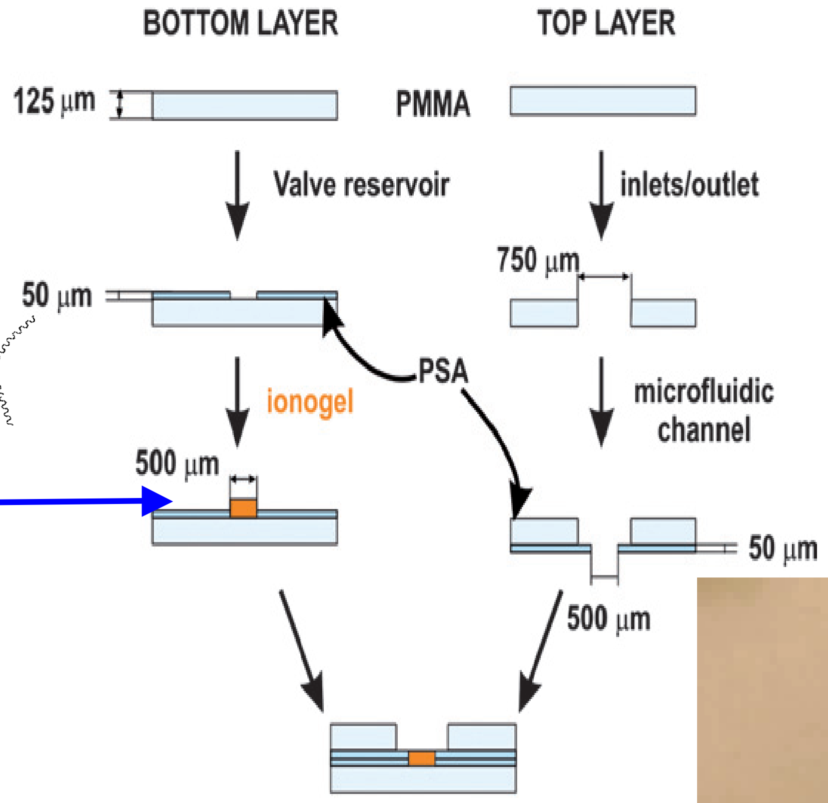
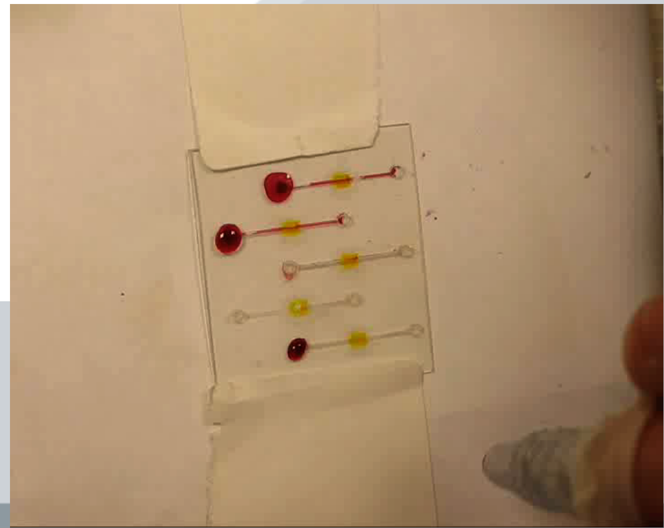
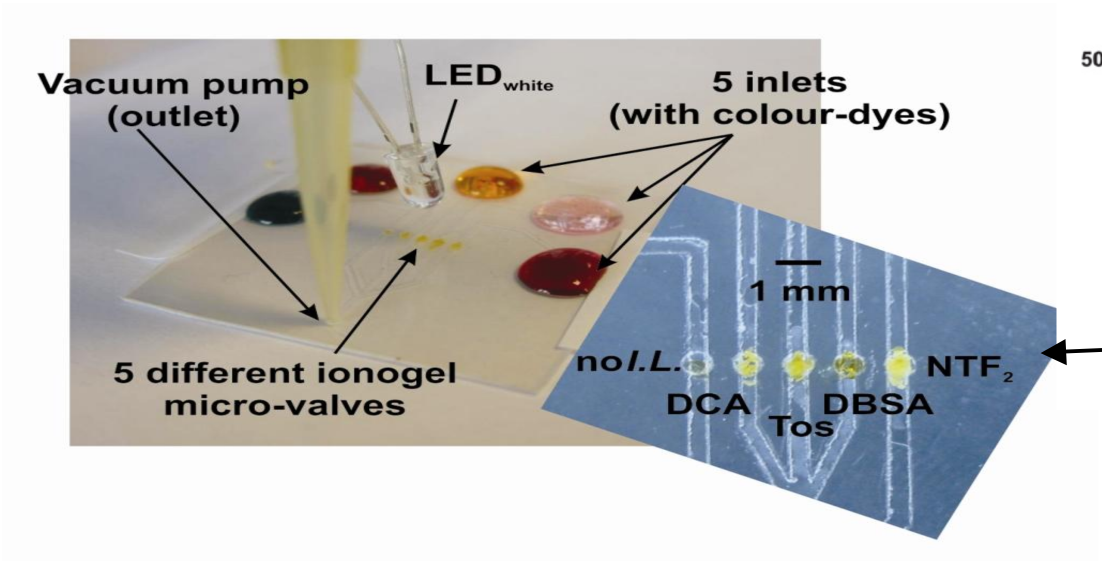


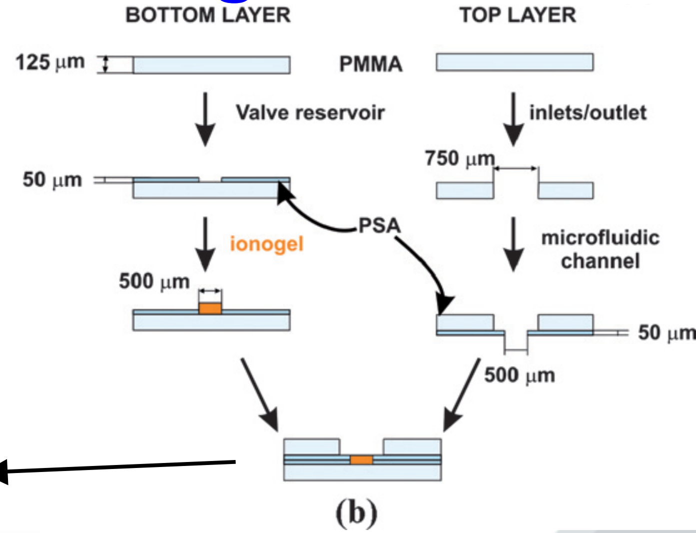
(b)

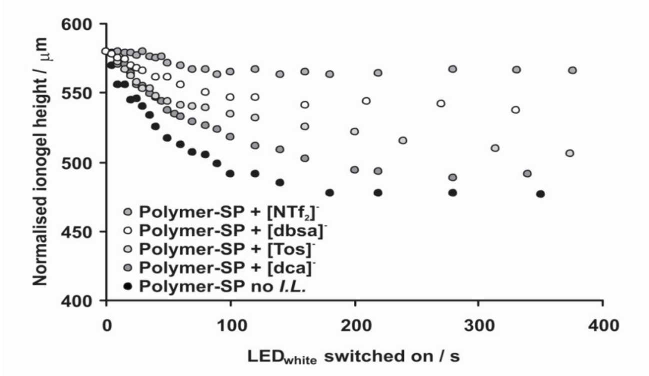


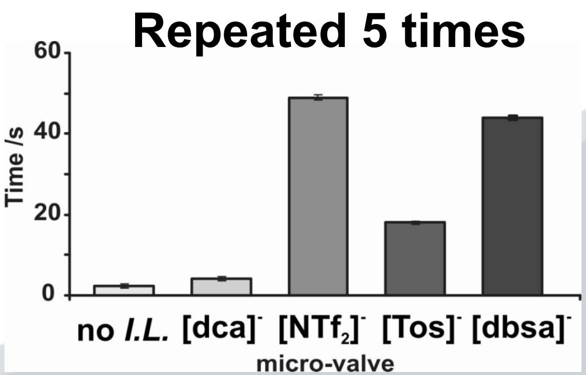
Benito-Lopez and Byrne, *Lab on a Chip* **2010**, *10*, 195-201.

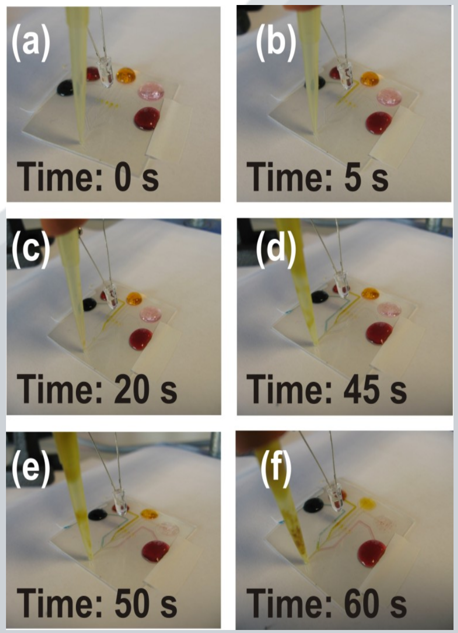
Multiple valves on one chip, using one actuation source!











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

Conclusions

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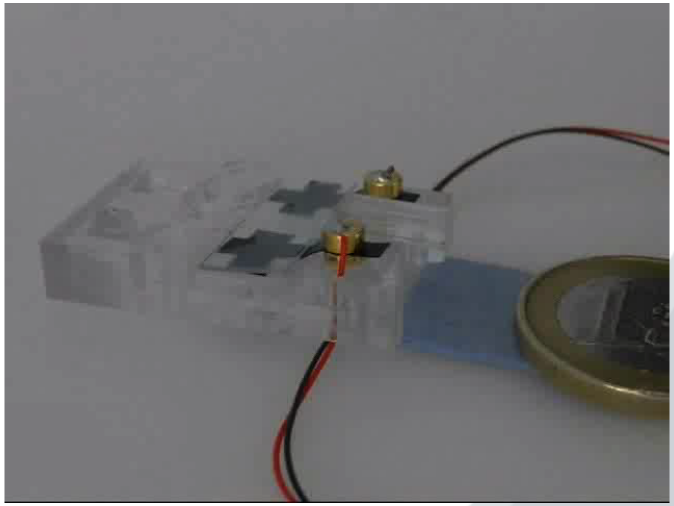
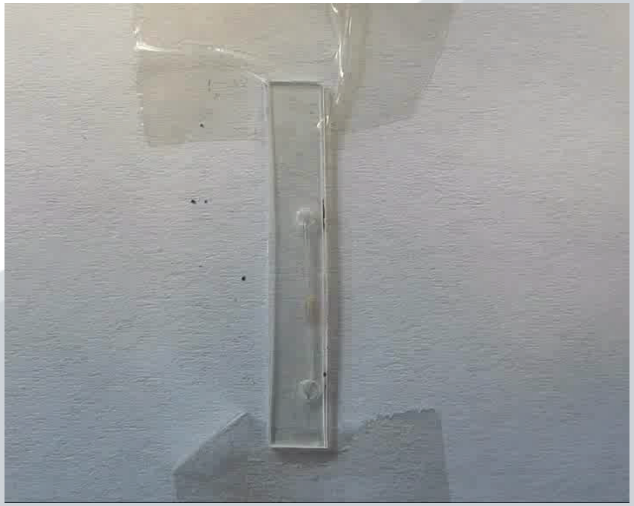
- **Great potential for platforms capable of sophisticated multi-functional behaviour**
  - Pumping
  - Valving
  - Predetermined delivery functions

- **Materials must reliably perform functions comparable to conventional devices**





Acknowledgements

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  - NCSR and CLARITY
- **Tyndall**
  - Damien Thompson
- **Cytec Industries**
  - Al Robertson


Thanks for listening!
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