Biomimetic Microfluidic Systems Incorporating Photoswitchable Building Blocks

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Reagent Based-Flow Analysis Evolution

- In contrast to HPLC, reagent based methods are relatively low pressure
- Emerged during 1960's (segmented flow) and 1970's (flow injection analysis)
- uTAS/Lab on a chip emerges late 1980's through 1990's
- Trend towards miniaturisation – attempts to move instrumentation to location of interest, rather than bring sample to centralised lab
- Despite this effort, successful examples are rare

MicroTAS/Lab on a Chip/Microfluidics

Many people, myself included, expected that the ability to manipulate fluid streams, in microchannels, easily, would result in a proliferation of commercial LoC systems, and that we would see applications of these devices proliferating throughout science. In fact, it has not (yet) happened.

Microfluidics, to date, has been largely focused on the development of science and technology, and on scientific papers, **rather than on the solution of problems**

Editorial 'Solving Problems', George Whitesides, Lab Chip 10 (2010) 2317-2318

Analyser (Continuous Monitoring) Platforms of the Future

- Must be able to function autonomously for years **OR**
- Have capability to self-assemble on demand, perform tasks for a limited time, and then degrade
- Must be able to cope with issues related to hostile deployment scenarios such as biofouling and physical damage
- Will be based on devices incorporating much more sophisticated flow regimes than current norm

2nd Generation Analyser: Design

Sampling port

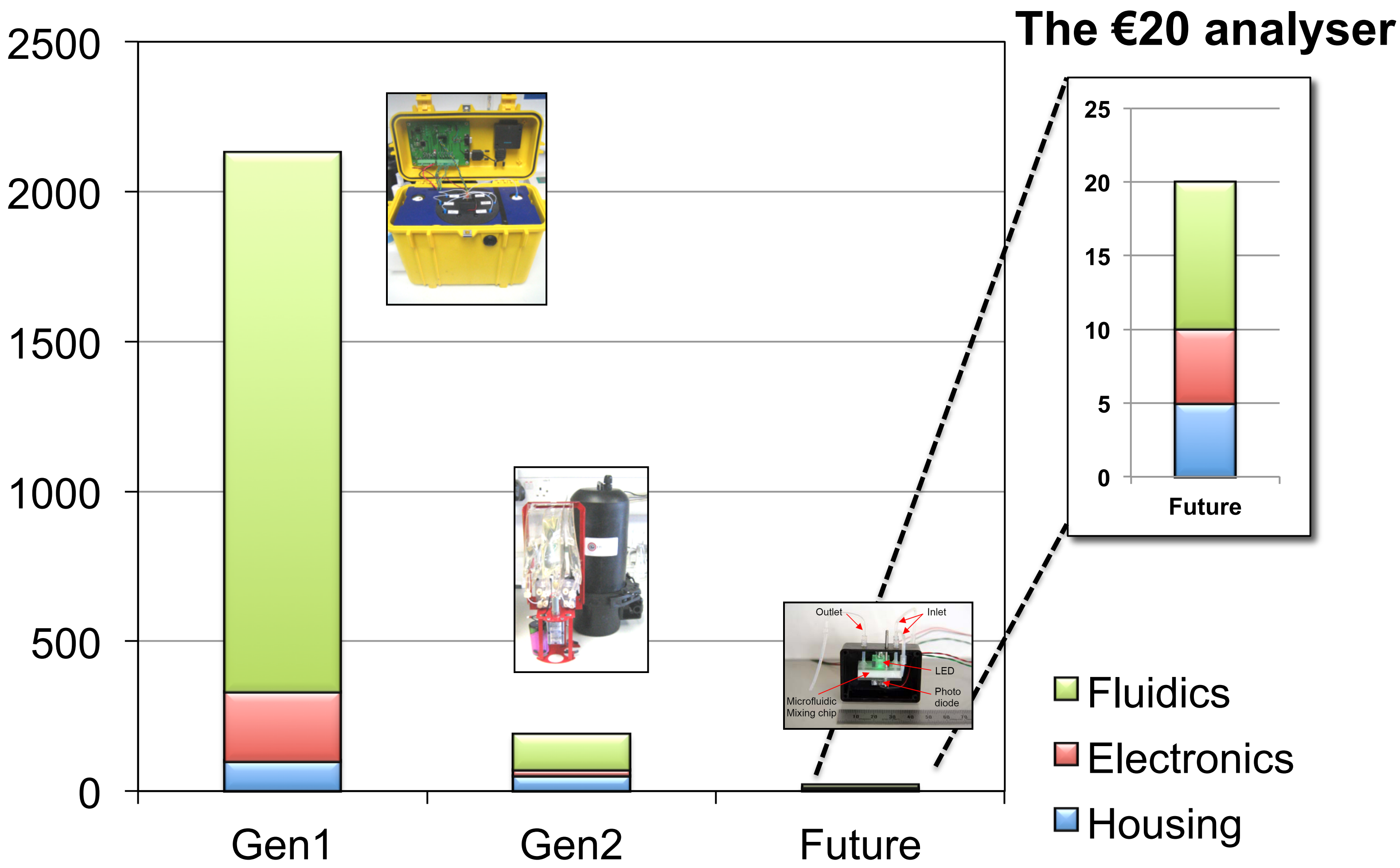
Deployment at Osberstown WWTP

- Phosphate monitoring unit deployed
- System is fully immersed in the treatment tank
- Wireless communications unit linked by cable
- Data transmitted to web

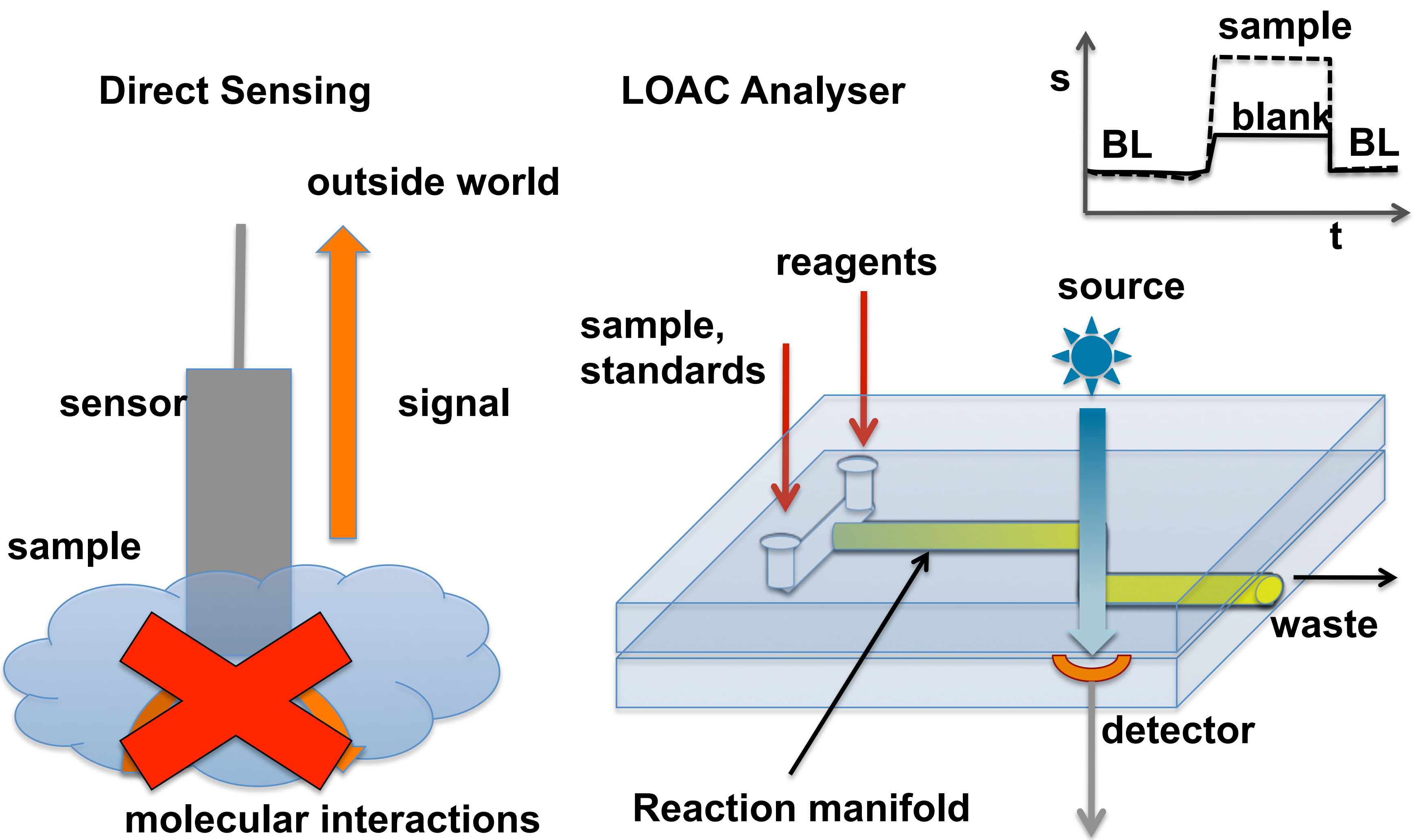
Osberstown – 3 week deployment

Biofouling of sensor surfaces is a major challenge for remote chemical sensing – both for the environment and for implantable sensors

Cost Comparison Analyser (€)



Direct Sensing vs. Reagent Based LOAC/ufluidics

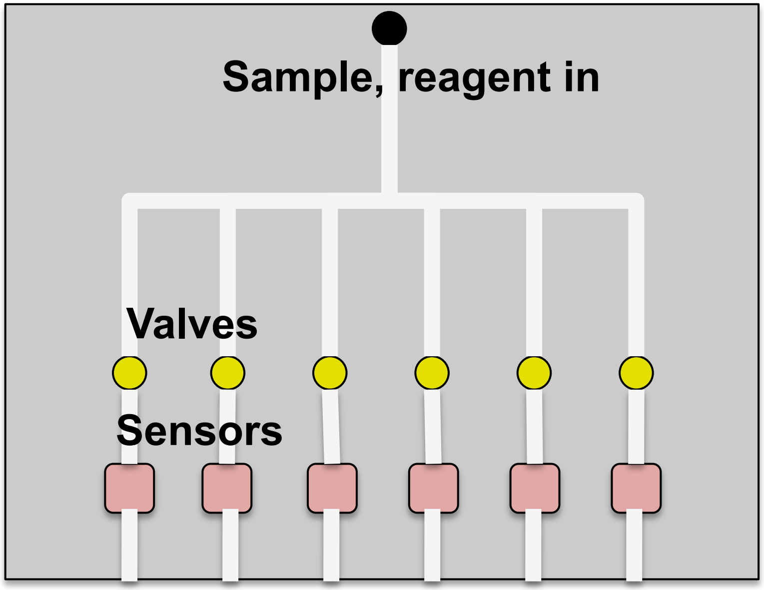


How to move things forward?

- The key is to make the circulation system much more sophisticated
- Current role is focused on transporting samples from sampling port, through the instrument, adding reagents, to the detector flow cell; cleaning and performing calibrations……
- In future devices, the fluidic circulation system will be much more sophisticated
  - Populated with micro/nano vessels with sensing, movement, communication functions
    - ➢ Spontaneous or directed movement through channels along chemical gradients
    - ➢ Autonomous detection of leak location; capable of repairing damage, removing blockages, opening alternative fluidic pathways, cleaning surfaces
    - ➢ Communicate status via colour/fluorescence at specific locations

Extend Period of Use via Arrays of Sensors….?

- If each sensor has an in-use lifetime of 1 week….
- And these sensors are very reproducible….
- And they are very stable in storage (up to several years)….

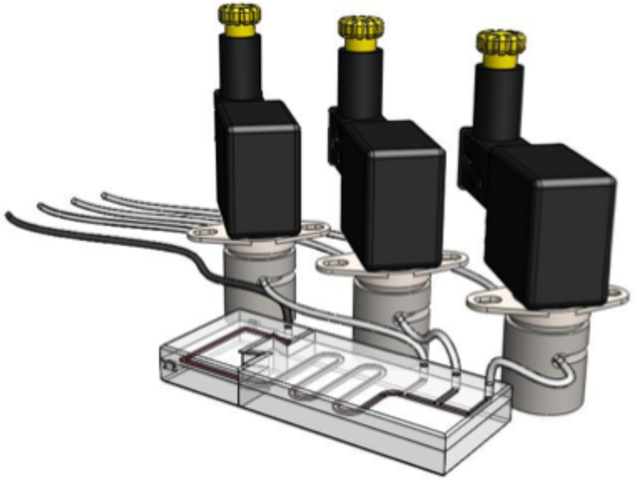


Then 50 sensors when used sequentially could provide an aggregated in-use lifetime of around 1 year

But now we need multiple valves integrated into a fluidic platform to select each sensor in turn

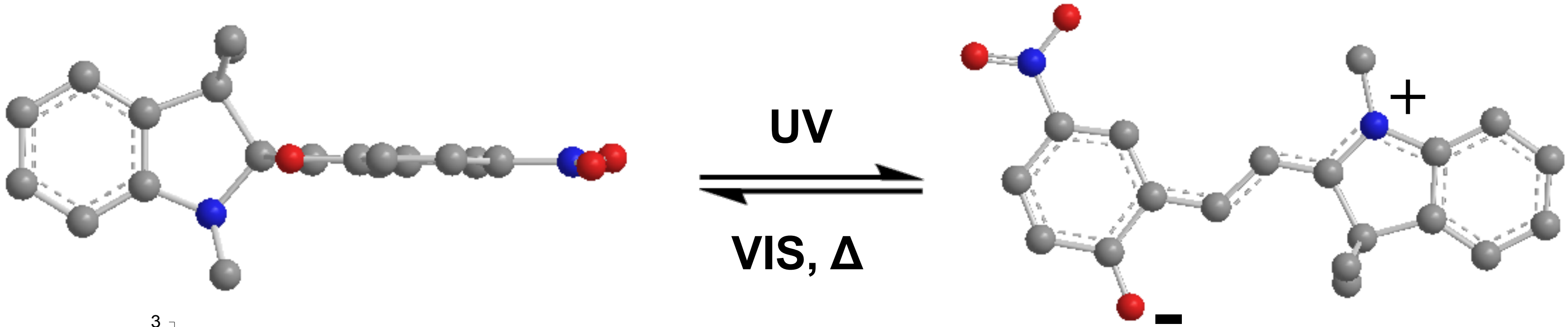
How to advance fluid handling in LOC platforms: re-invent valves (and pumps)!

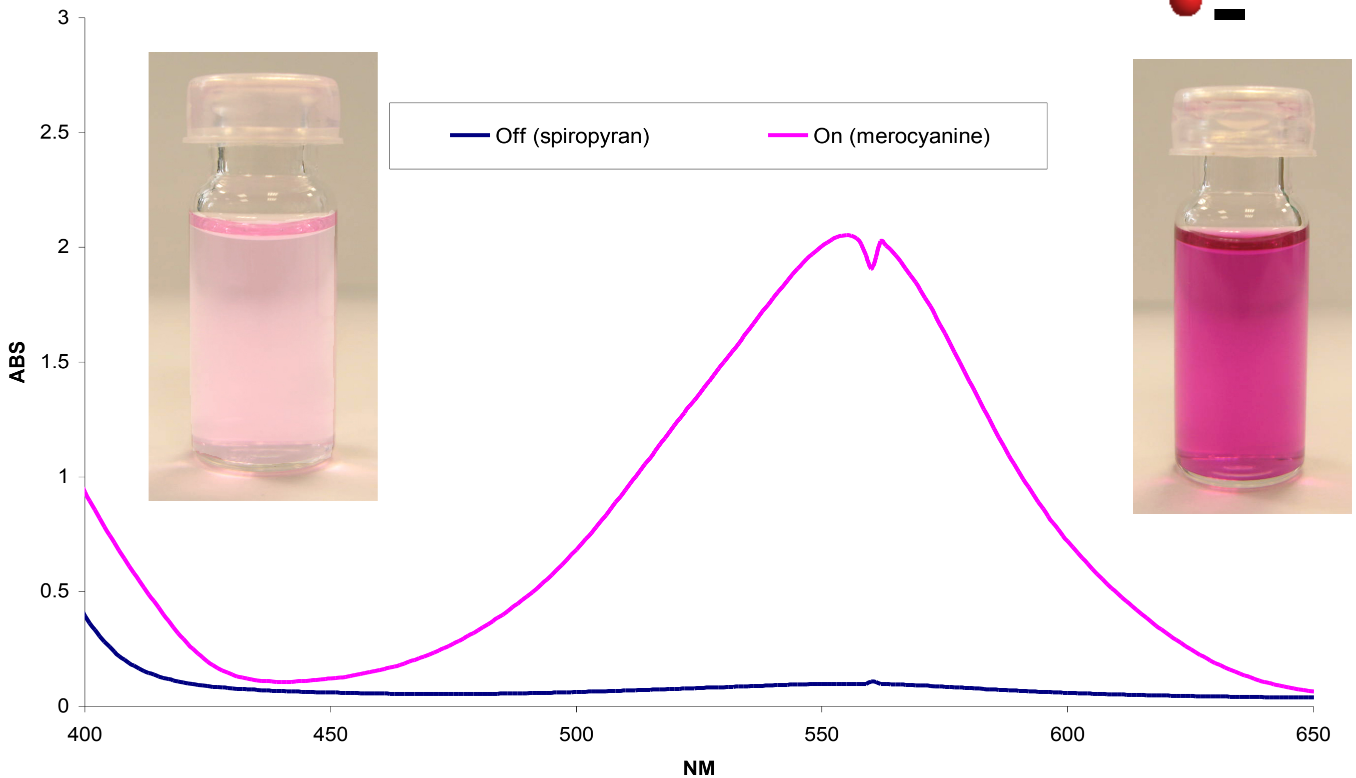
- **Conventional valves cannot be easily scaled down - Located off chip: fluidic interconnects required**
  - Complex fabrication
  - Increased dead volume
  - Mixing effects
- **Based on solenoid action**
  - Large power demand
  - Expensive



Solution: soft-polymer (biomimetic) valves fully integrated into the fluidic system

Photoswitchable Actuators

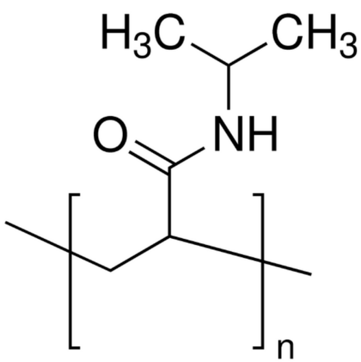


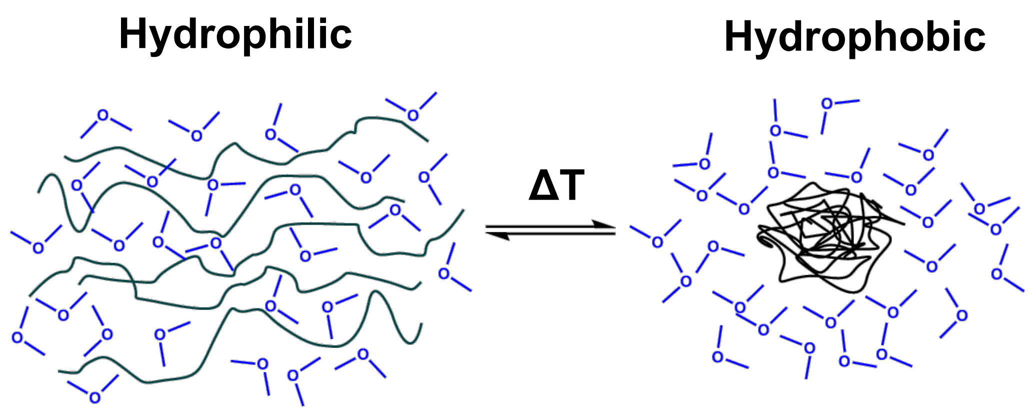


Poly(*N*-isopropylacrylamide)

- pNIPAAM exhibits inverse solubility upon heating
- This is referred to as the LCST (Lower Critical Solution Temperature)
- Typically this temperature lies between 30-35^{o}C, but the exact temperature is a function of the (macro)molecular microstructure
- Upon reaching the LCST the polymer undergoes a dramatic volume change, as the hydrated polymer chains collapse to a globular structure, expelling the bound water in the process

pNIPAAM

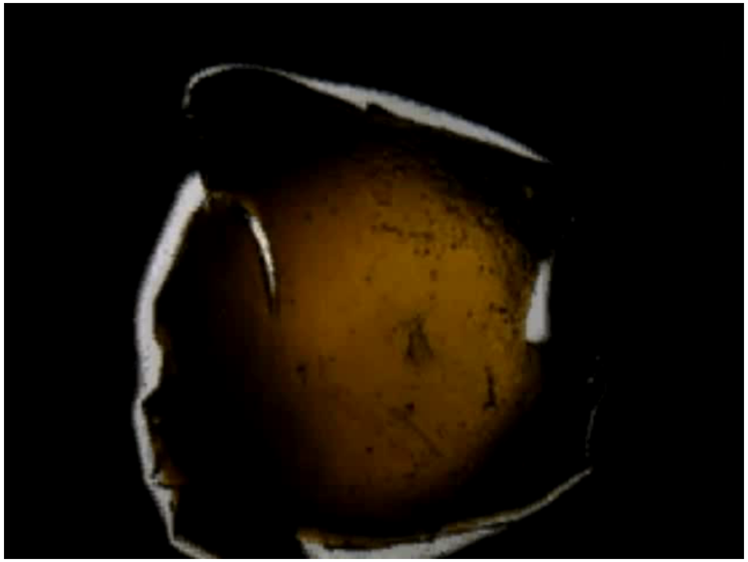


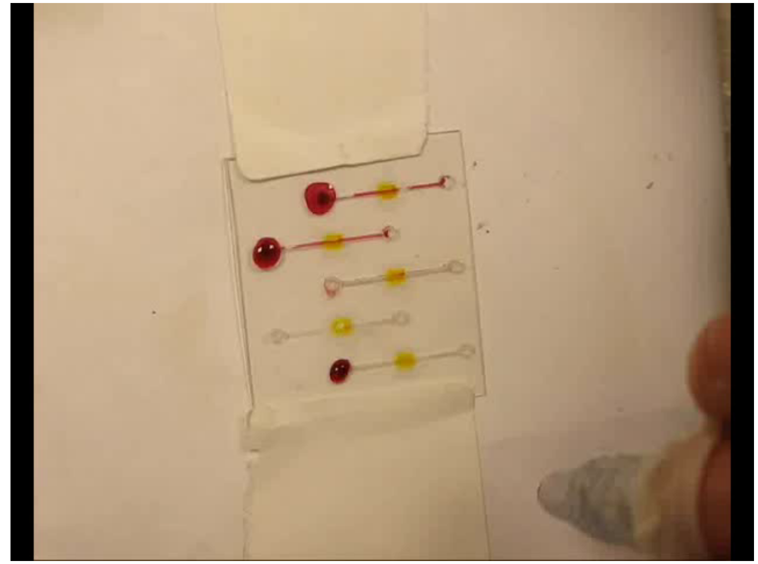


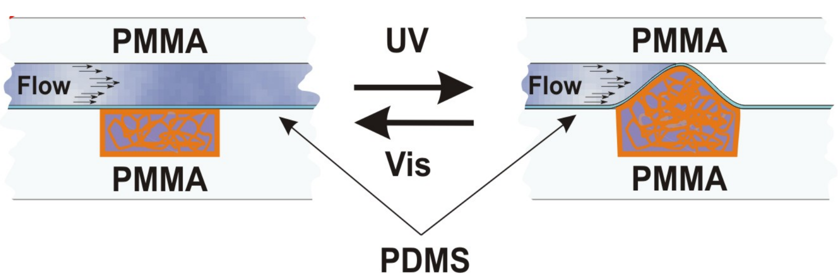
Hydrated Polymer Chains

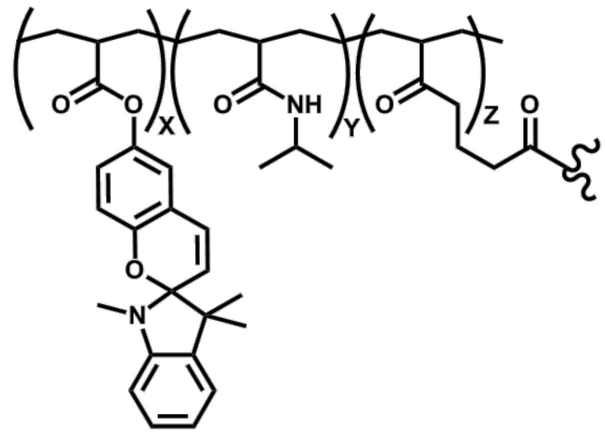
Loss of bound water -> polymer collapse

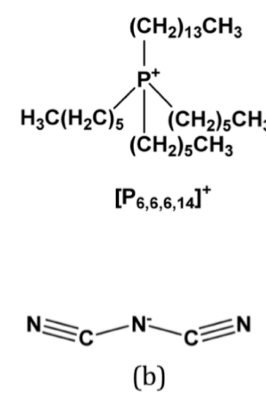
Photo-actuator polymers as microvalves in microfluidic systems









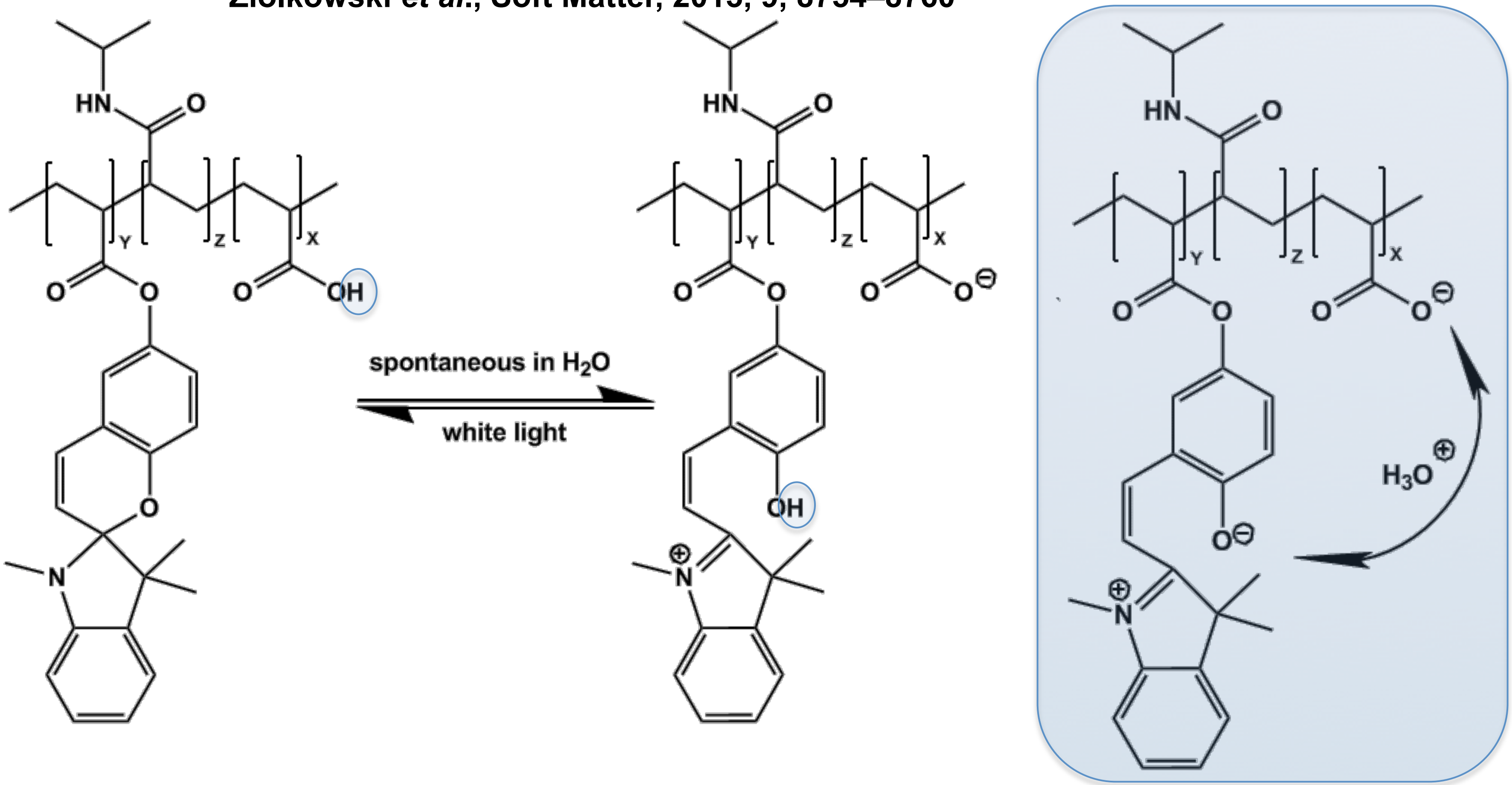


trihexyltetradecylphosphonium dicyanoamide $[P_{6,6,6,14}]^{+}[dca]^{-}$

Ionogel-based light-actuated valves for controlling liquid flow in micro-fluidic manifolds, Fernando Benito-Lopez, Robert Byrne, Ana Maria Raduta, Nihal Engin Vrana, Garrett McGuinness, Dermot Diamond, Lab Chip, 10 (2010) 195-201.

Self protonating photoresponsive gel

Ziolkowski *et al.*, Soft Matter, 2013, 9, 8754–8760



Previously proton source was external (acidic soln. required)
Protons, counter ions & solvent diffuse into/out of the gel

Now the proton exchange is 'internalised'
The proton population is essentially conserved

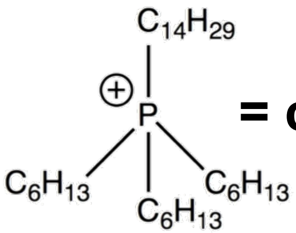
Why move the solvent at all?

[sample]/mol l^{-1}	Ratio H_2O/Sample
$1.0x10^{-6}$	$5.56x10^{7}$
$1.0x10^{-9}$	$5.56x10^{10}$
$1.0x10^{-12}$	$5.56x10^{13}$

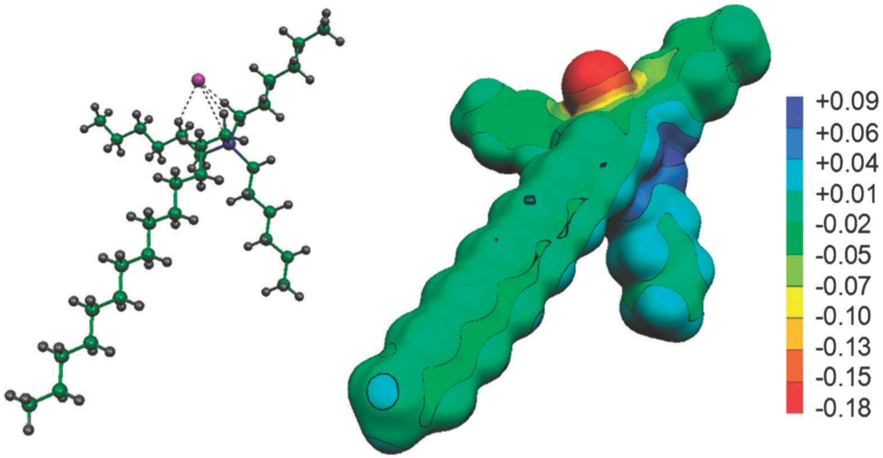
Strategy:
Move multifunctional micro/ nano-vehicles such as beads, vesicles, micelles, capsules, droplets through the sample to perform tasks……

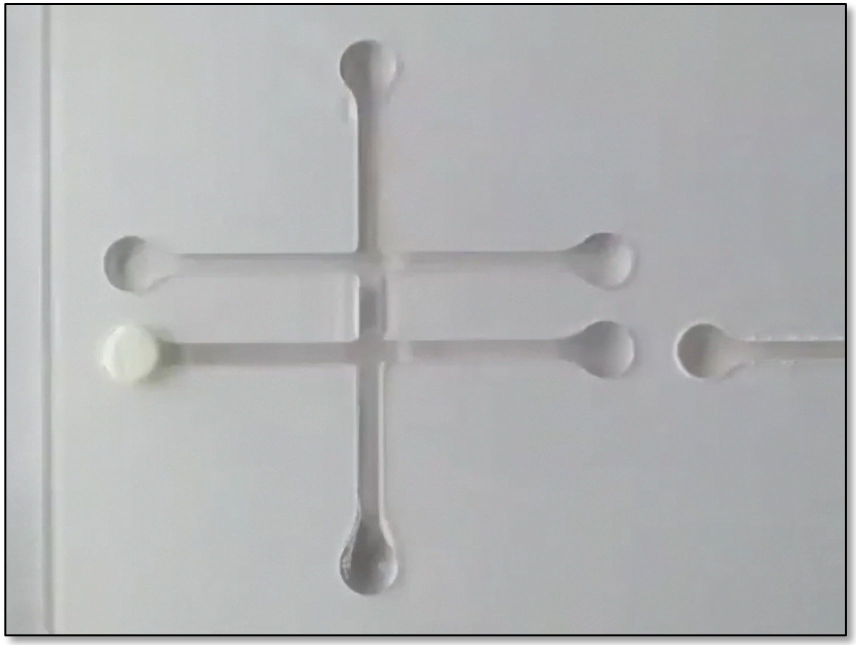
- **These vehicles should be able to;**
  - Spontaneously move under an external stimulus (e.g. chemical, thermal gradient) to preferred locations
  - Report selective binding of guest species
  - Release active payload to modify local environment

We can do the same with IL Droplets



= cationic surfactant

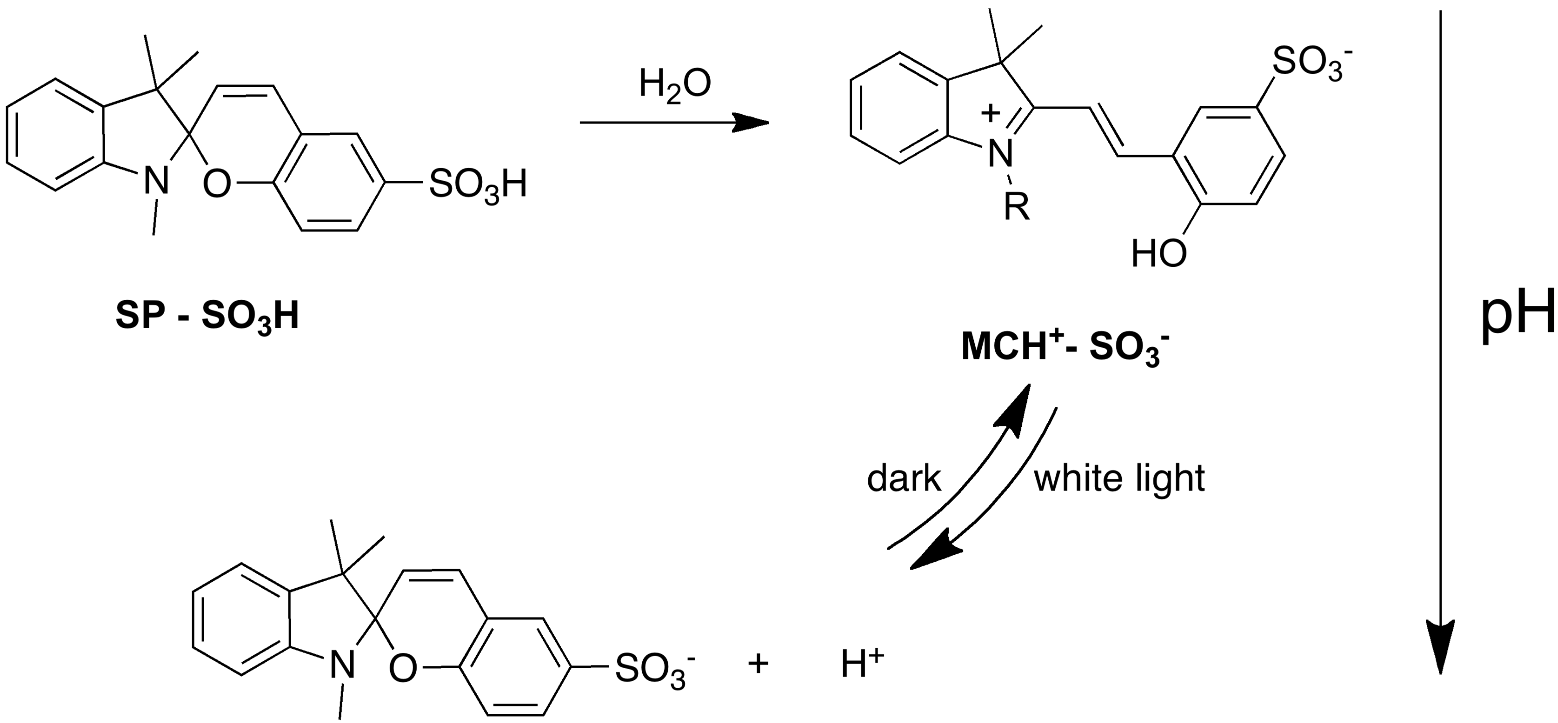




Trihexyl(tetradecyl)phosphonium chloride ([$P_{6,6,6,14}$][Cl]) droplets with a small amount of 1-(methylamino)anthraquinone red dye for visualization. The droplets spontaneously follow the gradient of the Cl^- ion which is created using a polyacrylamide gel pad soaked in 10^{-2} M HCl; A small amount of NaCl crystals can also be used to drive droplet movement.

Electronic structure calculations and physicochemical experiments quantify the competitive liquid ion association and probe stabilisation effects for nitrobenzospiropyran in phosphonium-based ionic liquids, D. Thompson et al., *Physical Chemistry Chemical Physics*, 2011, 13, 6156-6168.

Photo-modulation of pH



SP - SO_3H

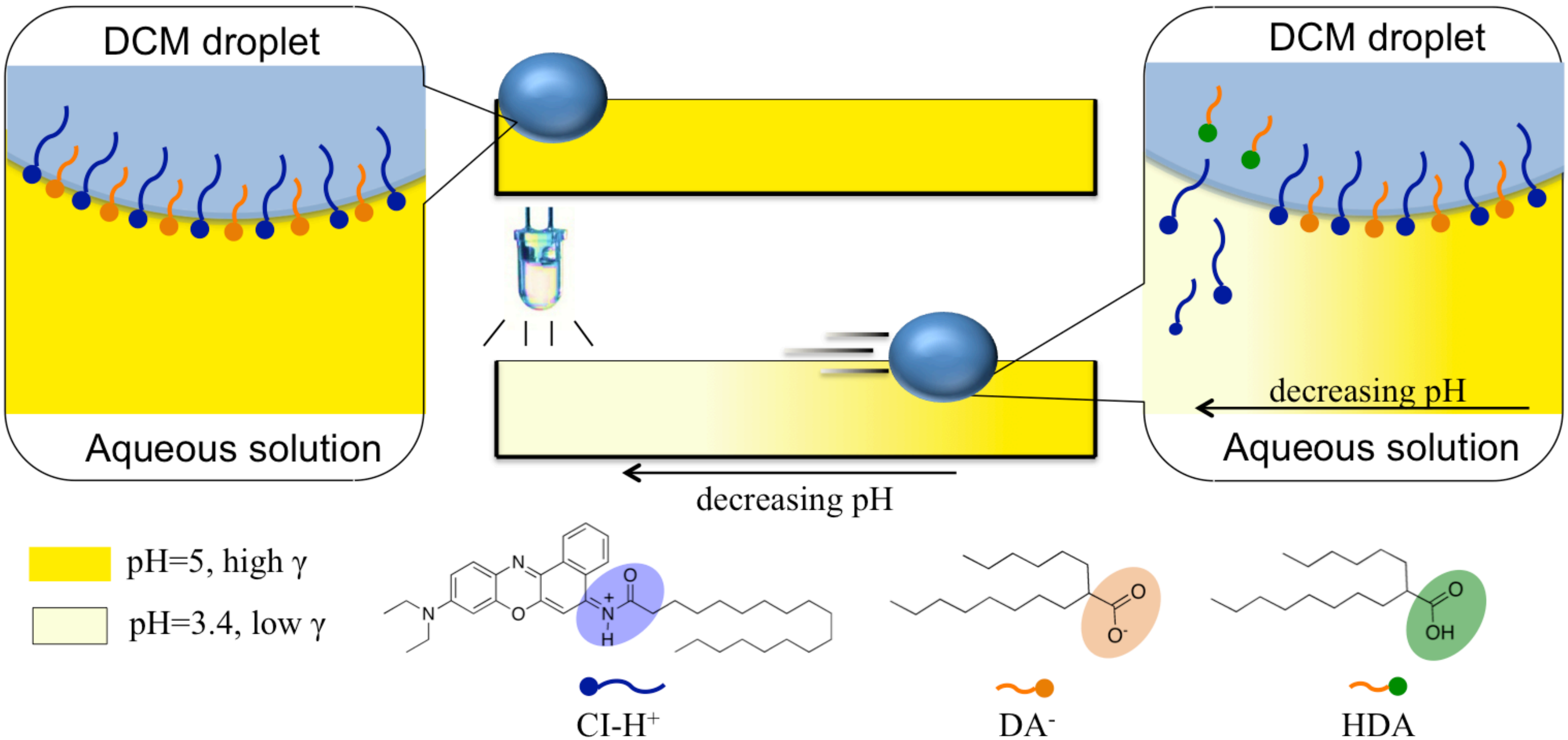
MCH^+- SO_3^-

SP - SO_3^-

	pH
H_2O	6.5
MCH^+-SO_3^-	4.8
SP-SO_3^-	3.4

Channel Solution: Spiropyran Sulfonic Acid 10^{-3}M (H_2O)

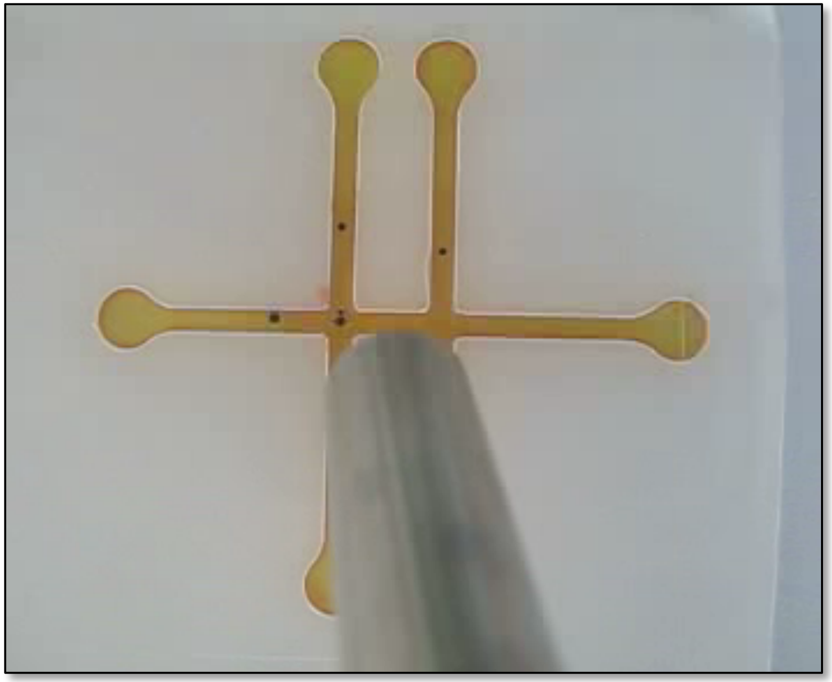
Mechanism of Photo-Stimulated Droplet Movement (with David Officer, UOW)

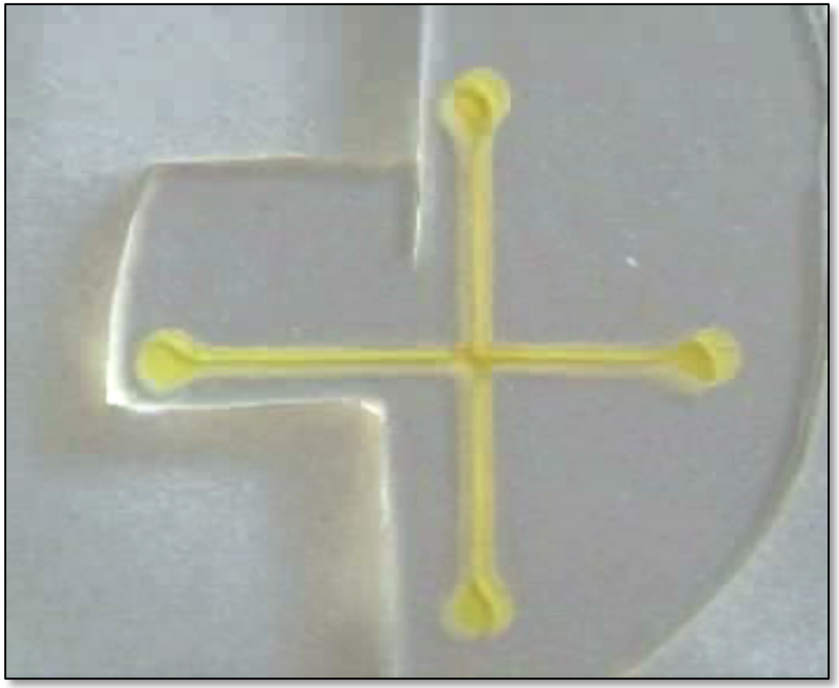


N-OCTADECANOYL-NILE BLUE

Photo-Chemopropulsion – Light-Stimulated Movement of Microdroplets, *Larisa Florea, Klaudia Wagner, Pawel Wagner, Gordon G. Wallace, Fernando Benito-Lopez, David L. Officer, and Dermot Diamond, Adv. Mater. 2014, DOI: 10.1002/adma.201403007*

Movement of Droplets in Channels using Light





- We use light to create a localised pH gradient
- This disrupts an ion pair at the droplet interface
- Surfactant is expelled and movement of the droplet occurs
- Interested in exploring how to use droplets for sensing and for transport & release of active components

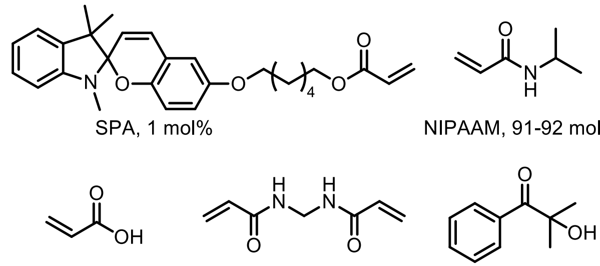
Photocontrol of Assembly and Subsequent Switching of Surface Features

ACS APPLIED MATERIALS & INTERFACES
Research Article
www.acsami.org

ACS applied materials & interfaces, 6 (2014) 7268-7274

Photoswitchable Ratchet Surface Topographies Based on Self-Protonating Spiropyran–NIPAAM Hydrogels

Jelle E. Stumpel,[†] Bartosz Ziółkowski,[‡] Larisa Florea,[‡] Dermot Diamond,[‡] Dirk J. Broer,[*,†,§] and Albertus P. H. J. Schenning[*,†,§]

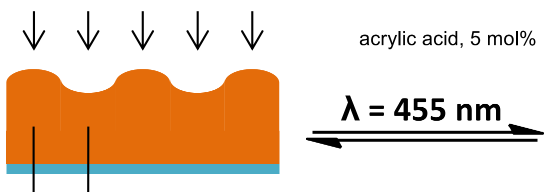


SPA, 1 mol% NIPAAM, 91-92 mol%

acrylic acid, 5 mol% MBIS, 1-2 mol% Darocur 1173, 1 mol%

a)

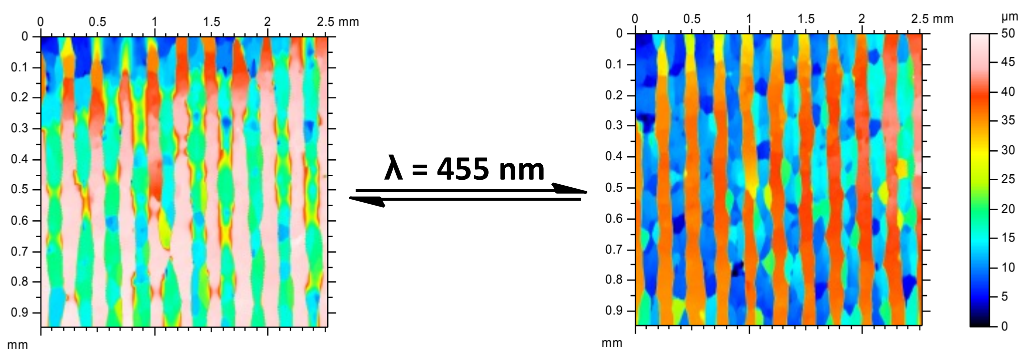
Light source

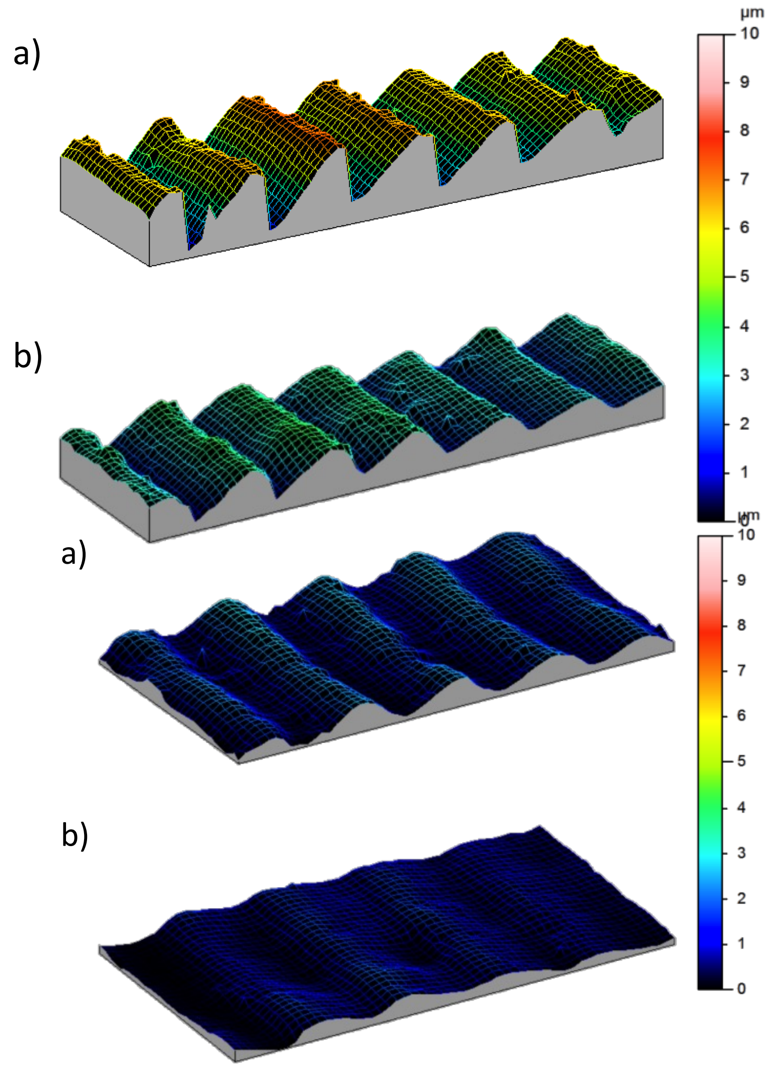


High crosslink density

Low crosslink density

b)





Time to re-think the game!!!

- New materials with exciting characteristics and unsurpassed potential…
- Combine with emerging technologies and techniques for exquisite control of 3D morphology
- And greatly improved methods for characterisation of structure and activity

We have the tools – now we need creativity!

Sensor Research Clustering: Steering Committee

Chairman: Michele Penza
Observer: Hans Hartmann Pedersen (EC)

Towards to a cluster on Characterization

Environmental sensors	D. Diamond
Indoor quality sensors	A. Schütze (O. Martimort)
Health monitoring sensors	P. Galvin (A. Prina Mello)
Monitoring of industrial processes	T. Mayr
Integration and commercialization	O. Martimort
Dissemination and Outreach	T. Simmons (Eurice)

Questions?

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http://www.dcu.ie/chemistry/asg/index.shtml

www.ncsr.ie