"Stimuli-Responsive Polymers: The Key to Revolutionary Developments in Chemical Sensing "

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National Centre for Sensor Research

Dublin City University

presented at the International Conference

ICFPAM 2013

12th International Conference on Frontiers of Polymers and Advanced Materials

Auckland, New Zealand

13th December 2013.

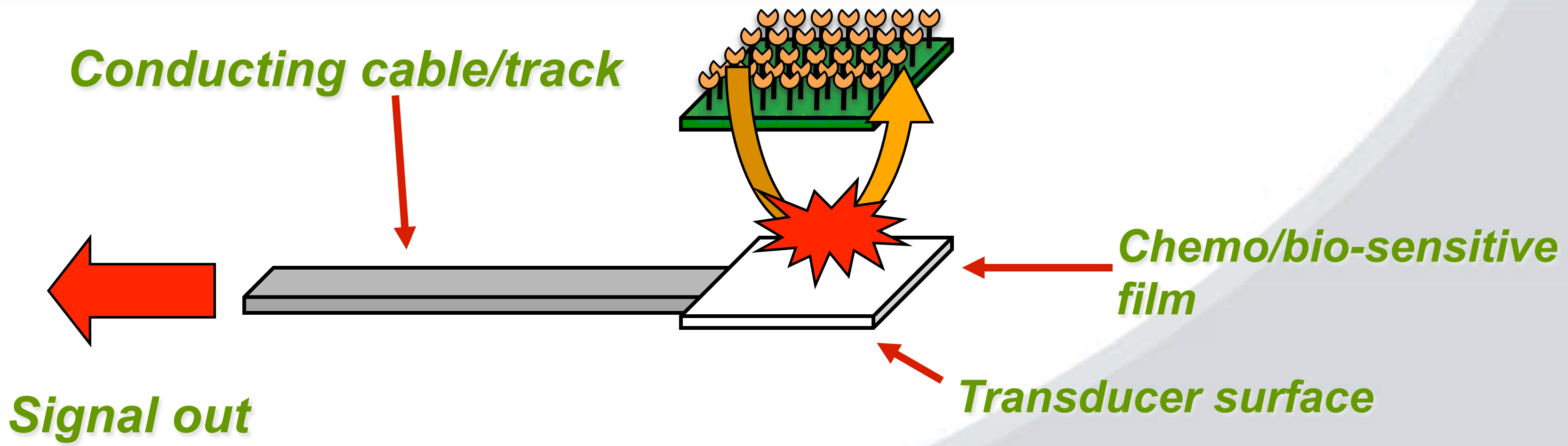
INSIGHT

INSIGHT
2013-2019
>300 researchers

- €45 million SFI + ca. €30 million industry
- July 2013-June 2019; >200 researchers
- Focused on ‘Big Data’; Sensor Networks; Cloud based data
- Clinical/Personal Health and Environmental Applications
- Big emphasis on ‘citizen scientist’ (quadruple helix of research’)

What is a Chemo/Bio-Sensor?

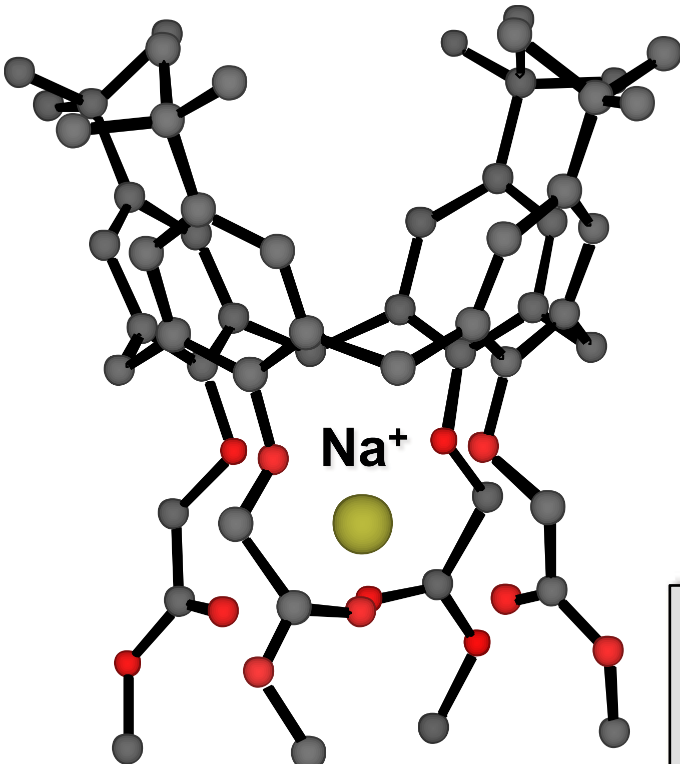
'a device, consisting of a transducer and a chemo/bio-sensitive film/membrane, that generates a signal related to the concentration of particular target analyte in a given sample'

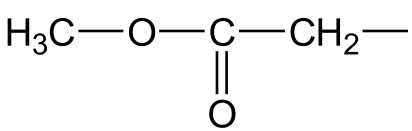


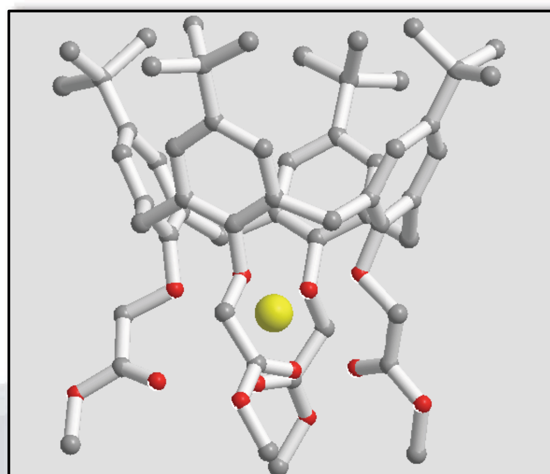
Chemo/Bio-sensing involves selective **BINDING** & **TRANSDUCTION** on the device surface; this also implies the target analyte MUST meet the device surface (**LOCATION** & **MOVEMENT**). It provides a signal observable in the macroscopic world (**COMMUNICATION**)

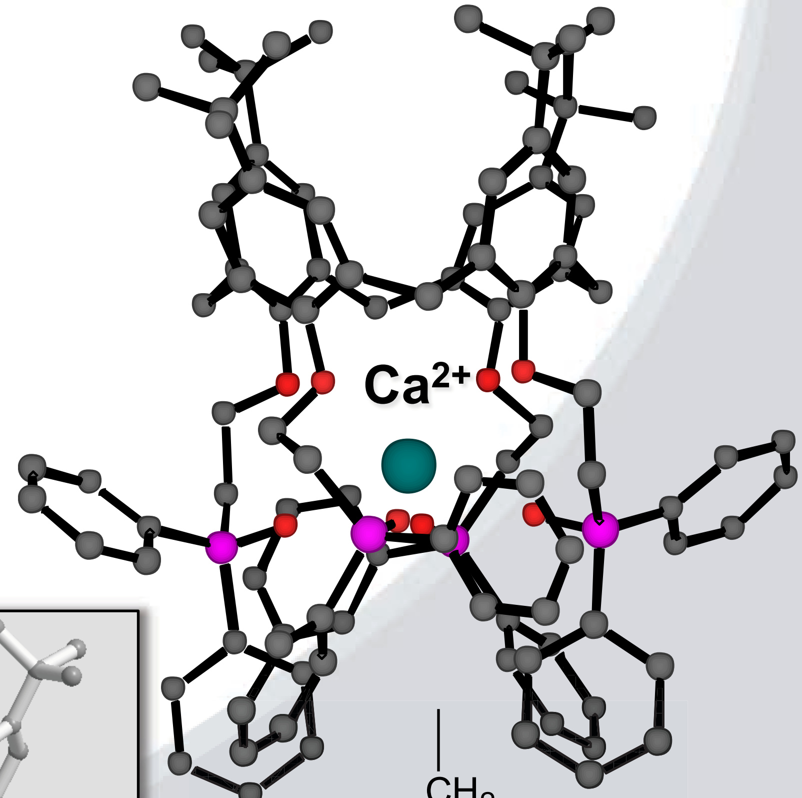
Calixarene Ionophores – controlling the selectivity

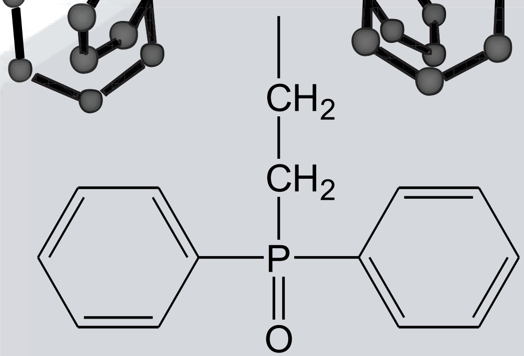
Neutral Carrier Based Ion-Selective Electrodes, D.Diamond, Anal. Chem. Symp. Ser., 25 (1986) 155.



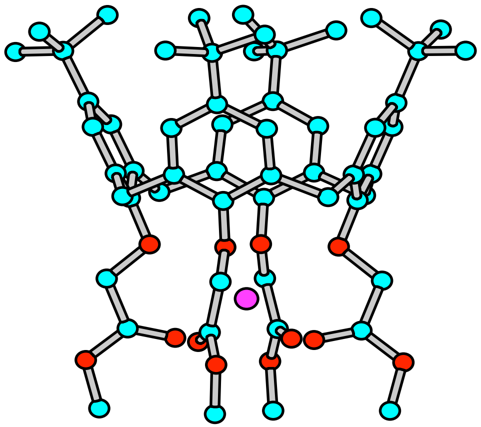


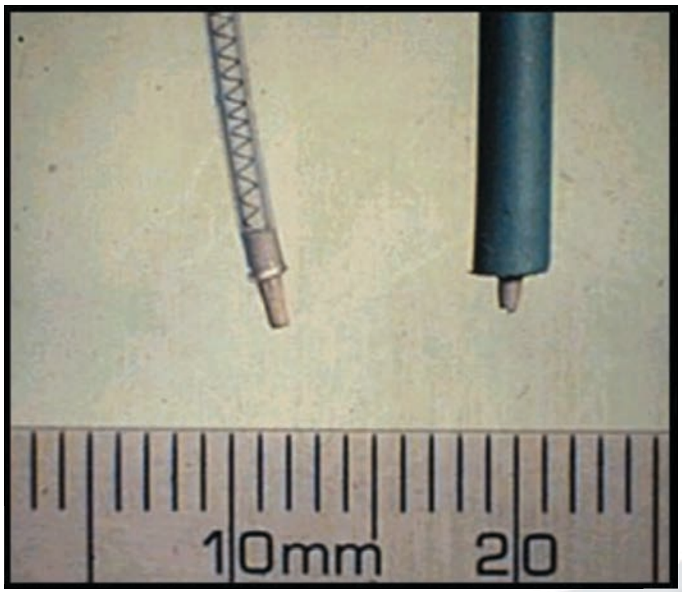






Blood Analysis; Implantible Sensors





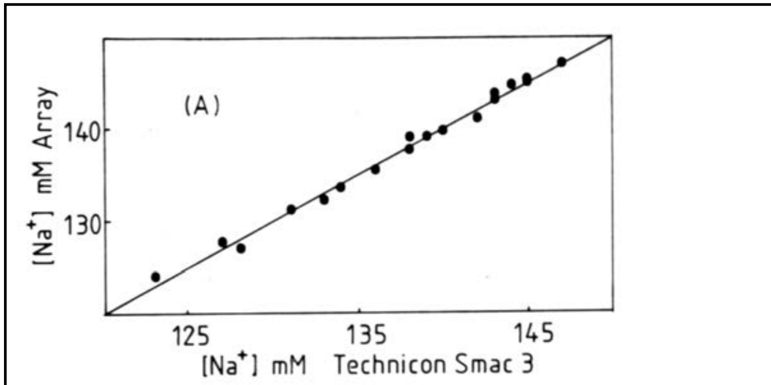
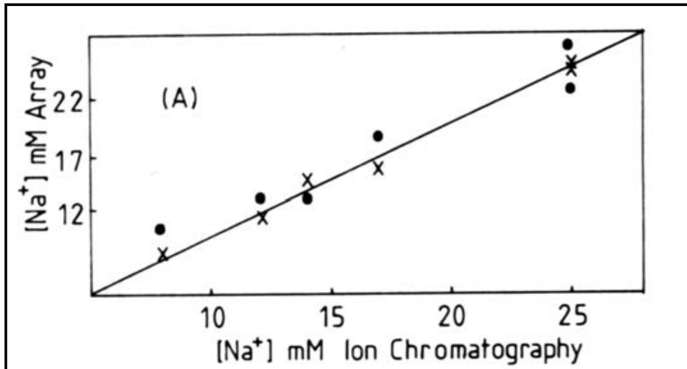


Fig. 3. Comparison of plasma sodium analysis using the array-FIA approach with a SMAC analyser. Good correlation without bias is obtained [5].

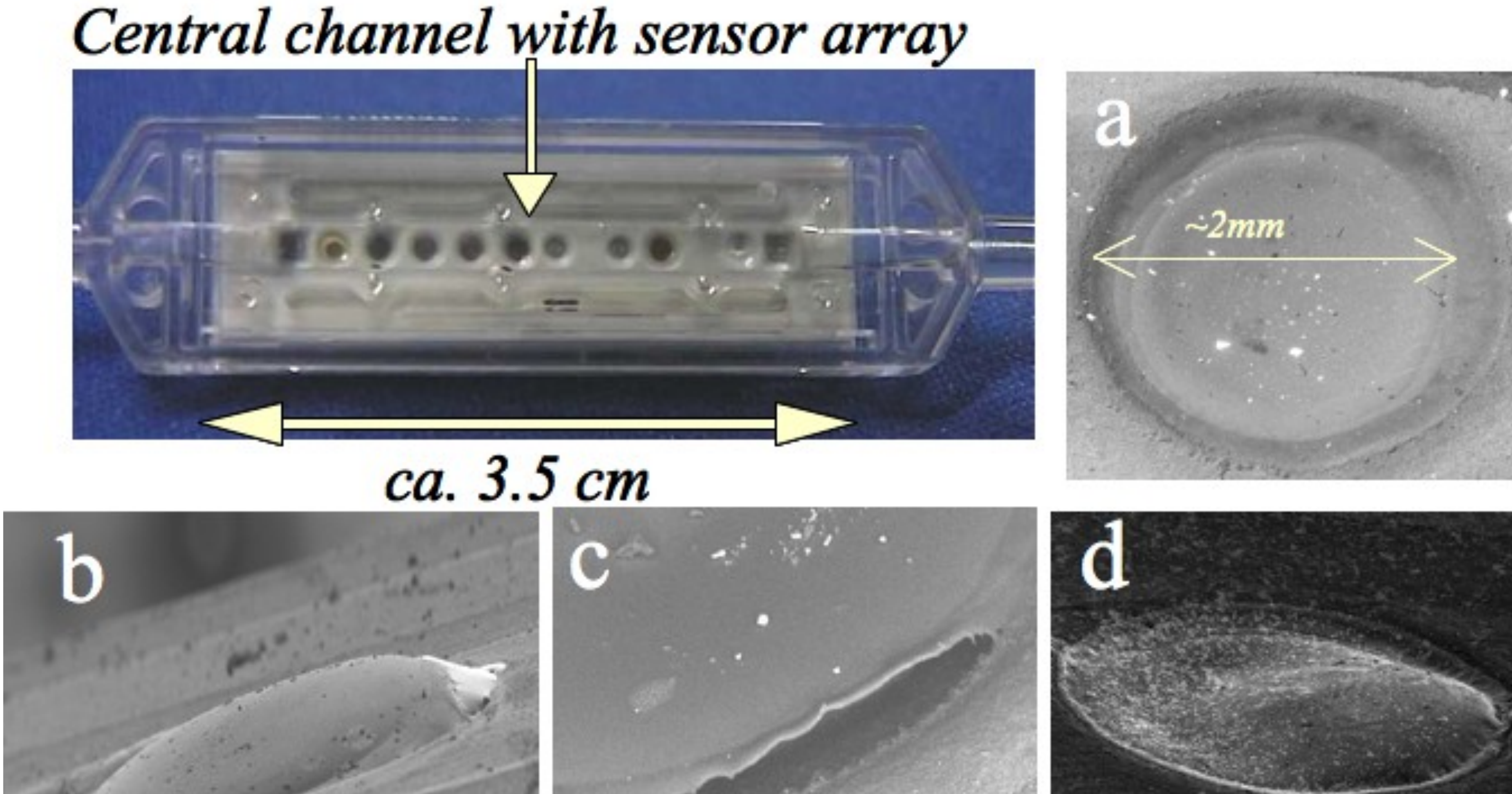


Anal. Chem., *64 (1992) 1721-1728.*

1985: Catheter Electrodes for intensive care – function for 24 hrs

Ligand (and variations of) used in many clinical analysers for blood Na^+ profiling

Planar ISE arrays for blood profiling: VP-SEM *(SenDx Corporation, Laguna, California ca. 2000)*



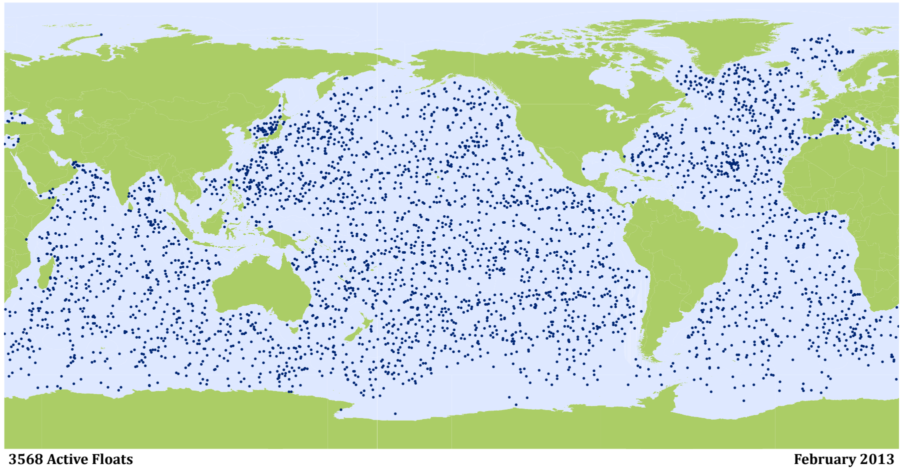
Use for up to 200 assays -> replace

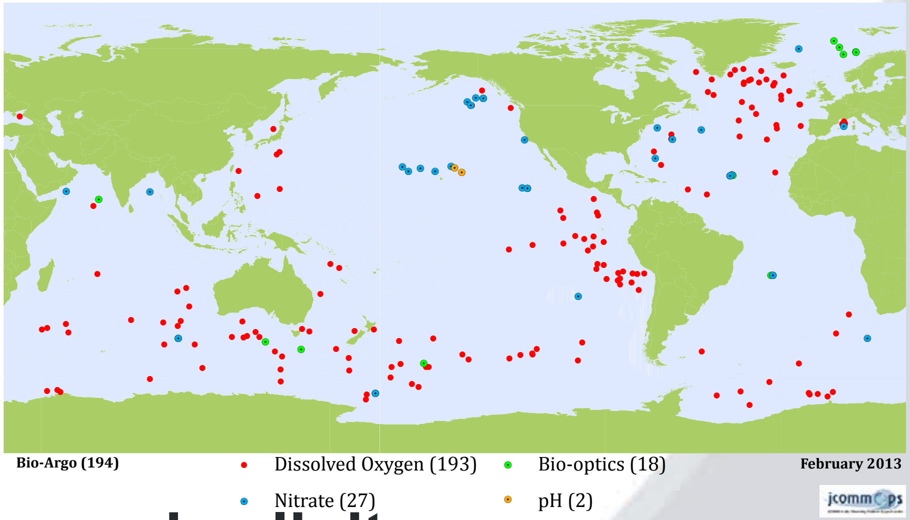
The dominant model for success (outside specialised laboratories) for clinical applications of chemical sensors and biosensors is primary based on short-term use, disposable devices.

Forget about long-term implants.

Lets try environmental monitoring…..

Argo Project (Feb 2013)





- **Ca. 3,600 floats: temperature and salinity**
- **Only 194 reporting chem/bio parameters (ca. 5%)**
- **Of these nitrate (27), DO (193), Bio-optics (18), pH (2)**

DO is by Clark Cell (Sea Bird Electronics) or Dynamic fluorescence quenching (Aanderaa)

'calibration of the DO measurements by the SBE sensor remains an important issue for the future', Argo report 'Processing Argo OXYGEN data at the DAC level', September 6, 2009, V. Thierry, D. Gilbert, T. Kobayashi

pH sensing – wasn't that solved by Nikolskii in 1935?

EVENT	DATE
Launch (San Francisco)	September 2013
PHASE 1: Innovation Phase	
Registration opens	January 1, 2014
Early-bird Registration deadline	March 2014
OA Solutions Fair and Kick-Off Event	March 2014

Overview

Competition Guidelines

Competition Schedule

Registration Process

OVERVIEW

The Challenge: Improve Our Understanding of Ocean Acidification

The Wendy Schmidt Ocean Health XPRIZE is a $2 million global competition that challenges teams of engineers, scientists and innovators from all over the world to create pH sensor technology that will affordably, accurately and efficiently measure ocean chemistry from its shallowest waters… to its deepest depths.

There are two prize purses available (teams may compete for, and win, both purses):

A. $1,000,000 Accuracy award – Performance focused ($750,000 First Place, $250,000 Second Place): To the teams that navigate the entire competition to produce the most accurate, stable and precise pH sensors under a variety of tests.

Wendy Schmidt Ocean Health XPRIZE

$2,000,000 up for grabs!
Task is to provide a way to do reliable measurements of pH in the ocean environment

The winner will almost certainly be a reagent based platform, not a conventional chemical sensor

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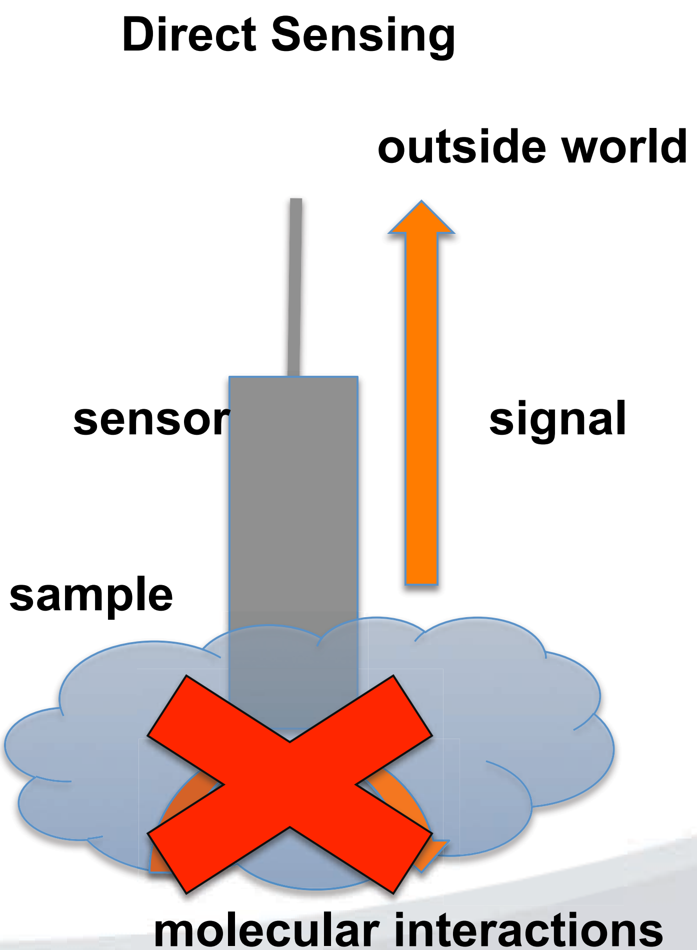
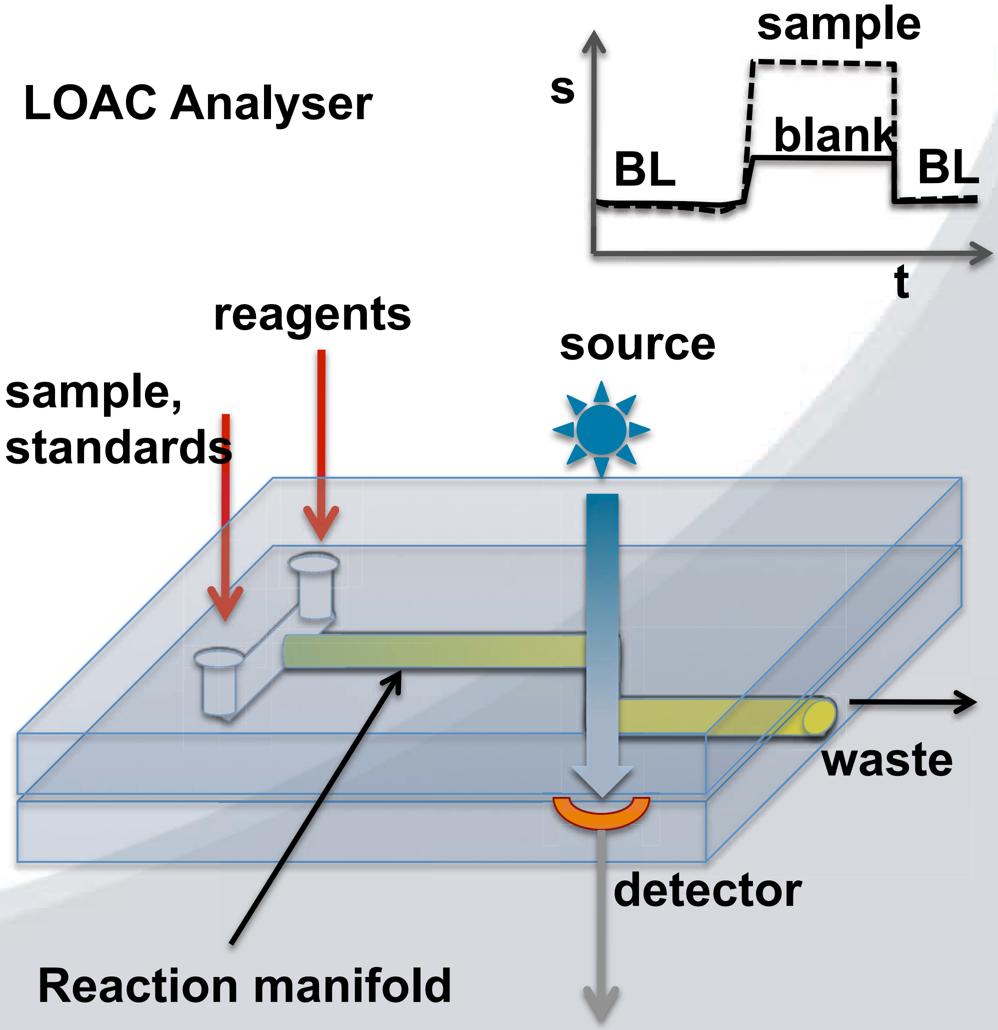
After decades of intensive research, our capacity to deliver successful long-term deployments of chemo/bio-sensors in remote locations (e.g. environmental, in-vivo clinical) is very limited

Direct Sensing vs. Reagent Based LOAC/ufluidics





MicroTAS/Lab on a Chip/Microfluidics

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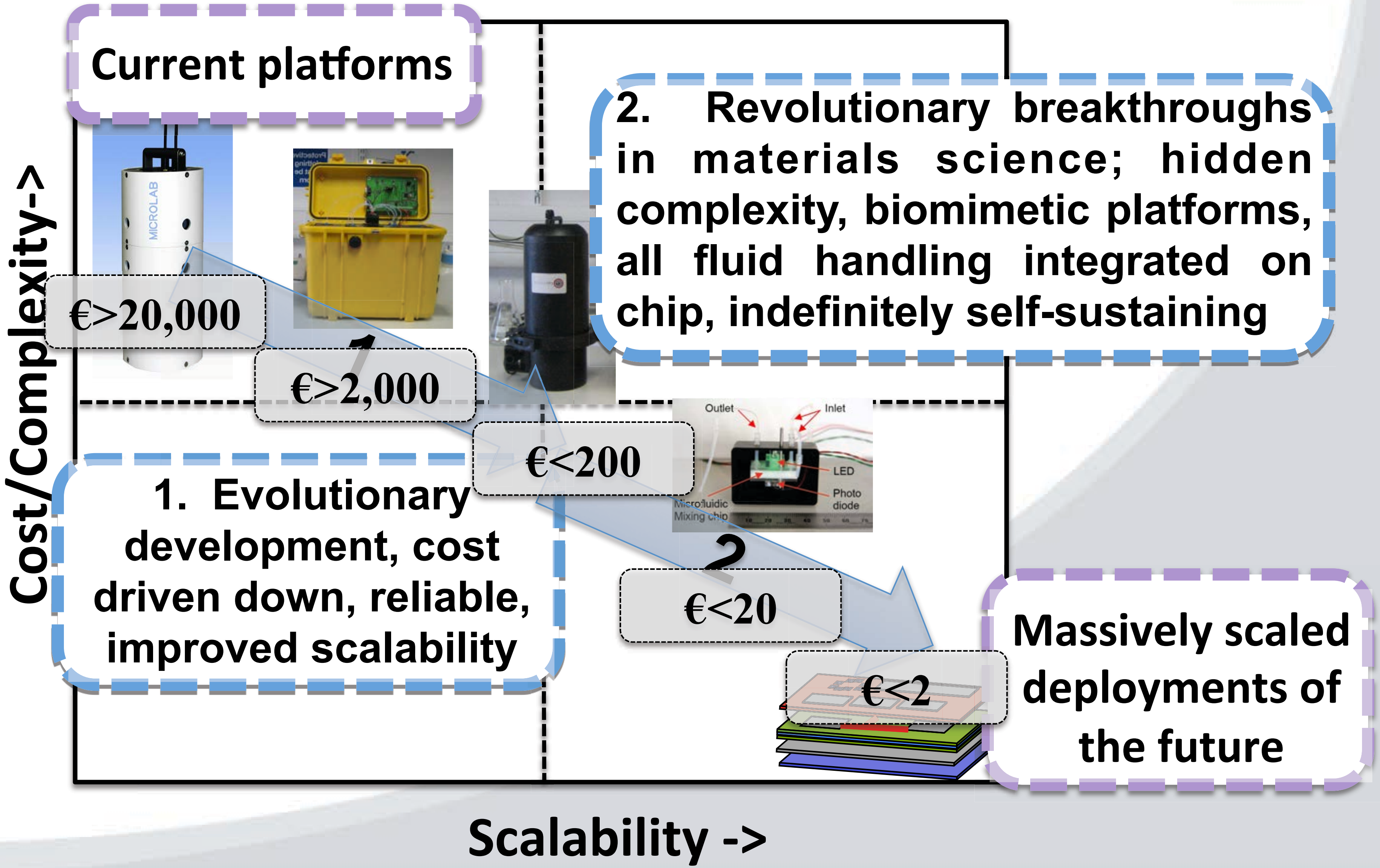
Many people, myself included, expected that the ability to manipulate fluid streams, in microchannels, easily, would result in a proliferation of commercial LoC systems, and that we would see applications of these devices proliferating throughout science. In fact, it has not (yet) happened.

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

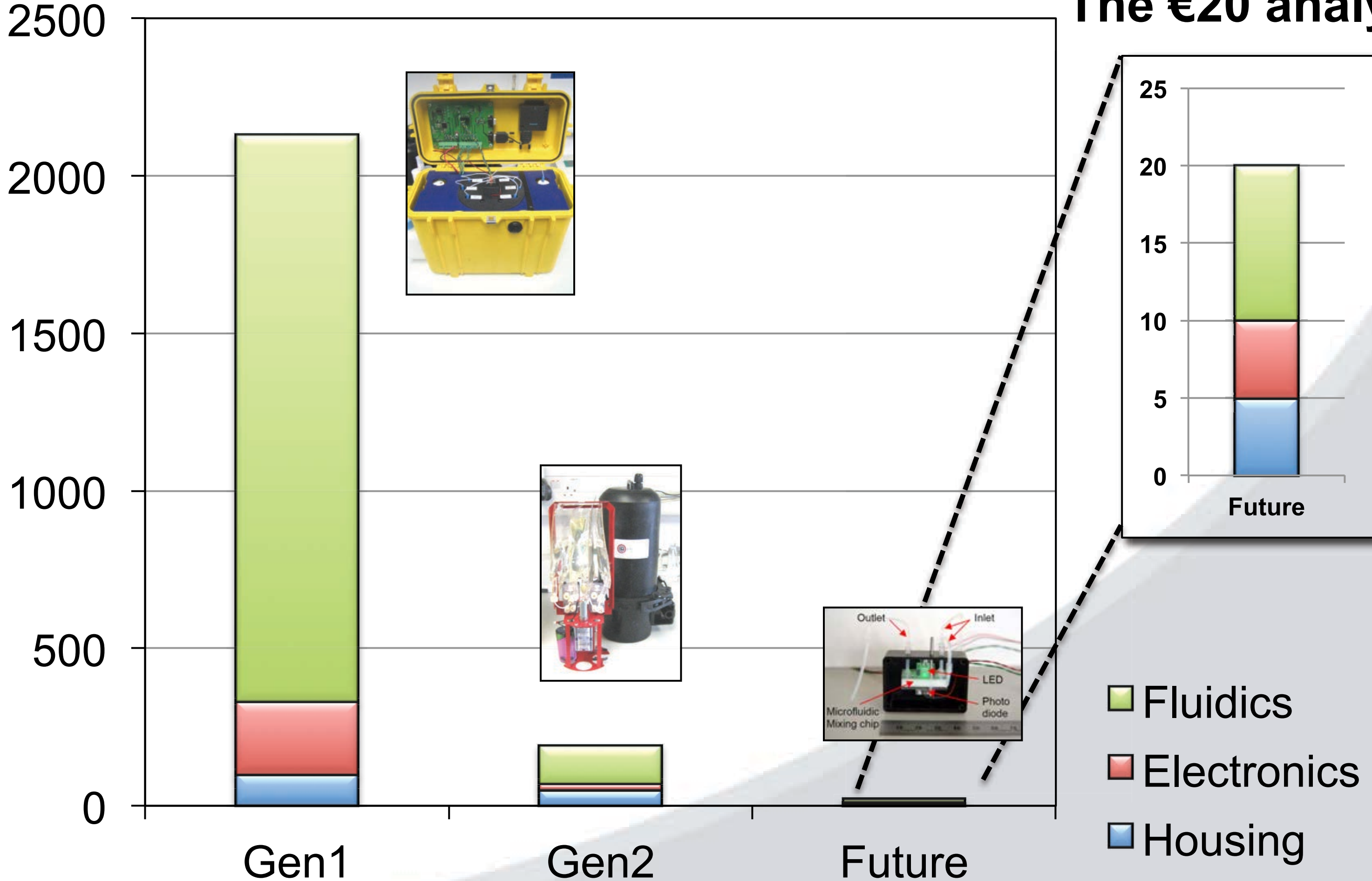
Editorial 'Solving Problems', George Whitesides, Lab Chip 10 (2010) 2317-2318

Achieving Scale-up



Cost Comparison Analyser (€)

The €20 analyser



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

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- **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 Materials

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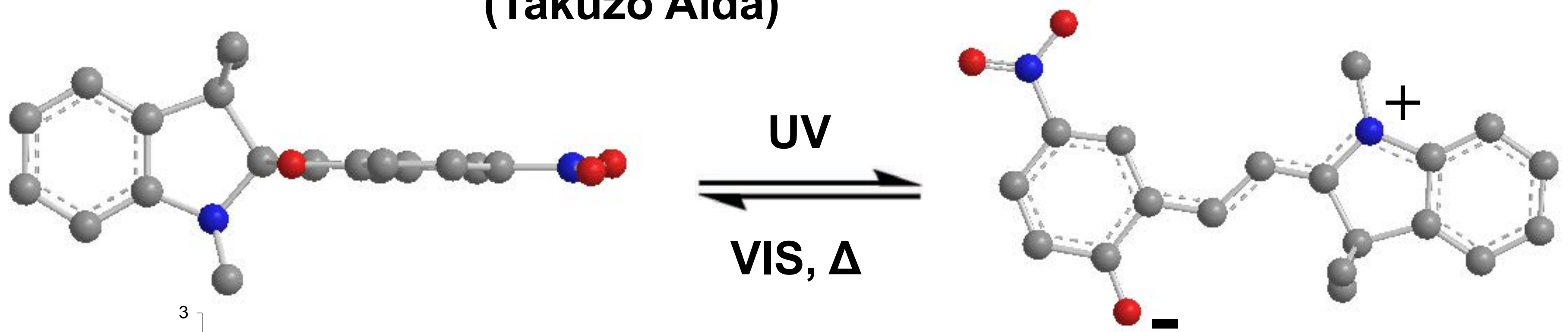
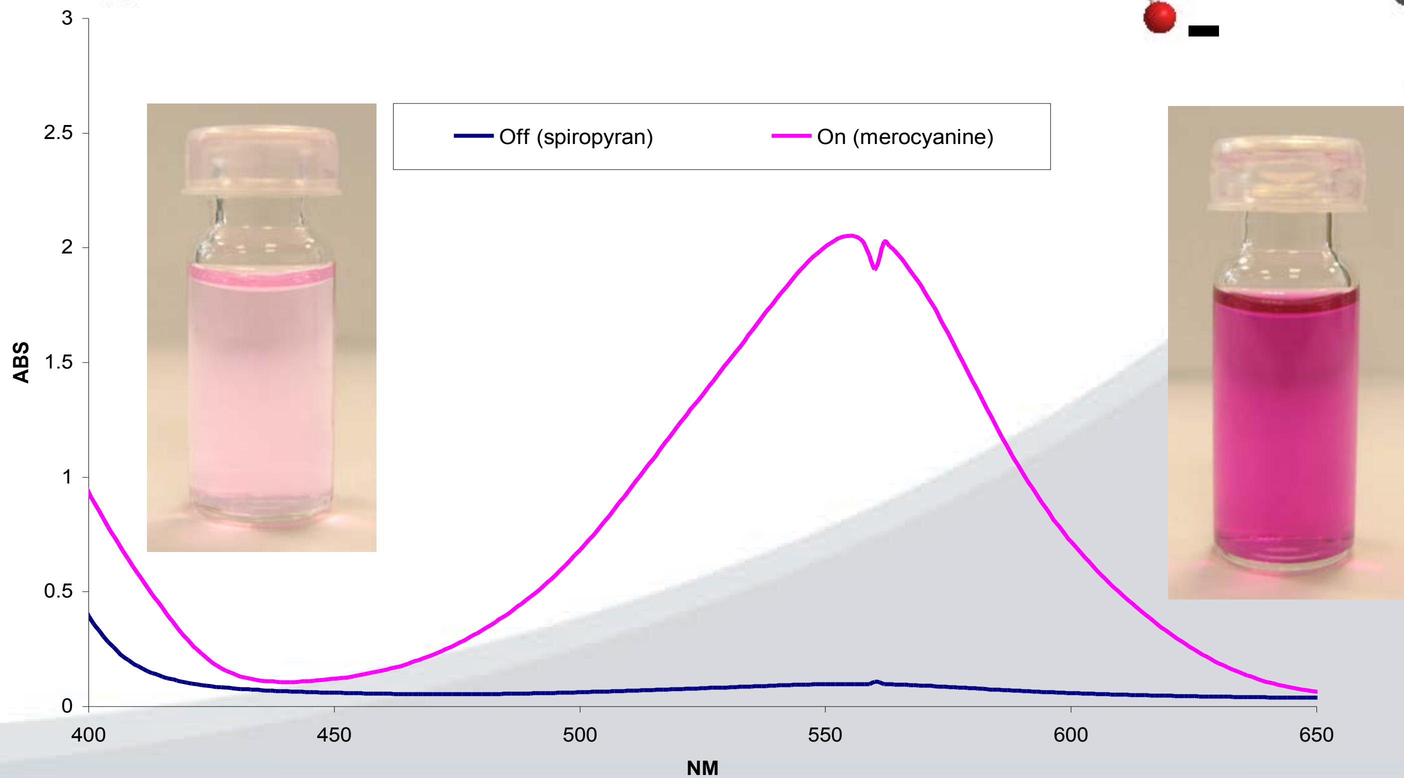
(Takuzo Aida)

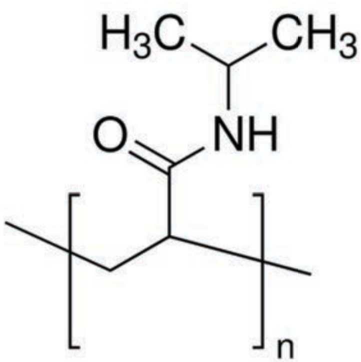




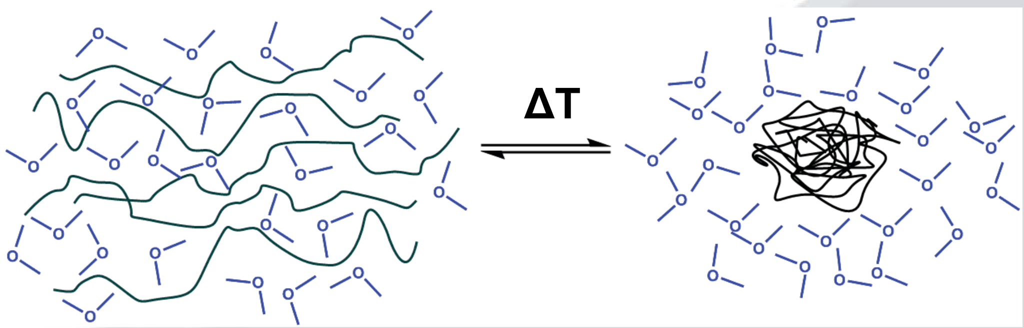
Poly(*N*-isopropylacrylamide)

- **PNIPAAm exhibits inverse solubility upon heating**
- **This is referred to as the LCST (Lower Critical Solution Temperature)**
- **Typically this temperature lies between 30-35°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



Hydrophilic **Hydrophobic**



Hydrated Polymer Chains

Loss of bound water -> polymer collapse

Controlling gel properties using Ionic Liquids (phosphonium $[P_{6,6,6,14}]$ based)

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

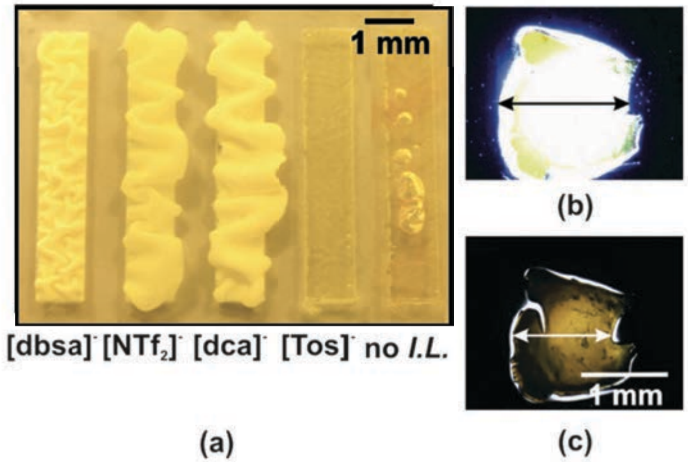


Fig. 3 (a) Photo-responsive polymer gels after immersion of the mould in a 1 mM HCl solution for 2 h. Right: $[dca]^-$ ionogel shrinking process; (b) ionogel before illumination and (c) the same sample after 2 s illumination with a white light LED, size decrease is *ca.* 30% by volume.

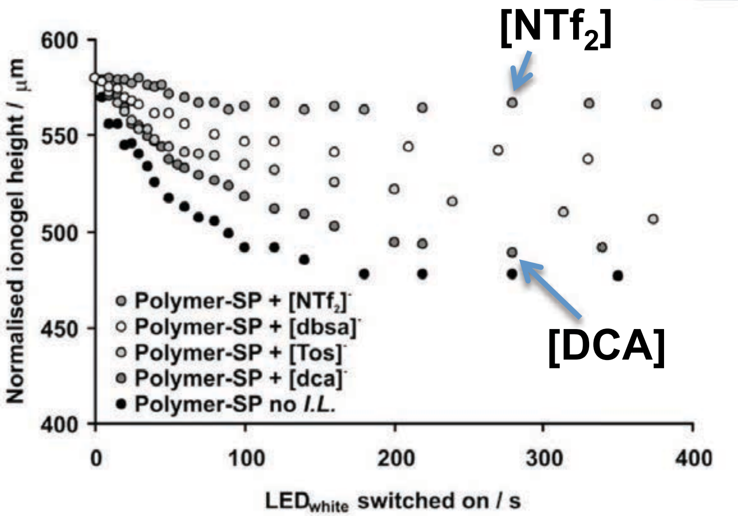
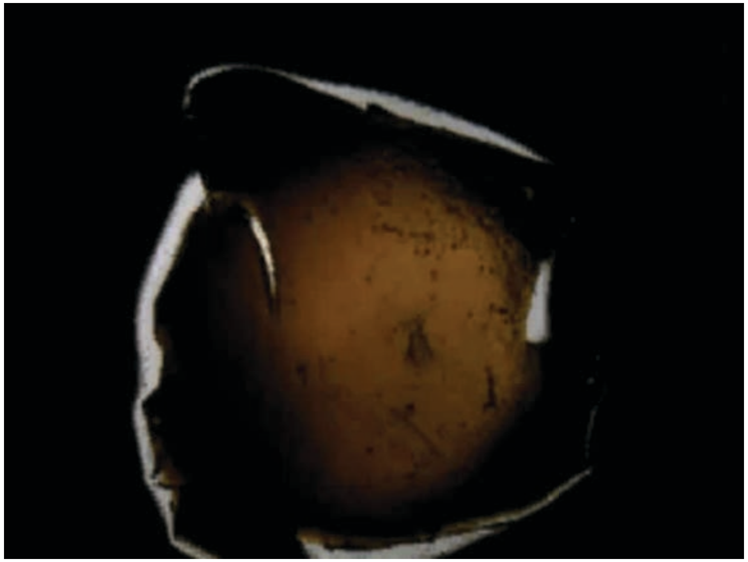
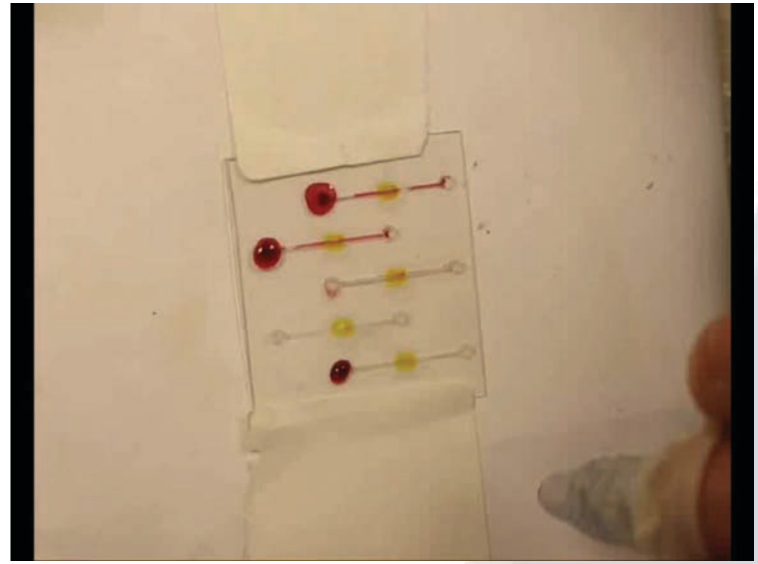
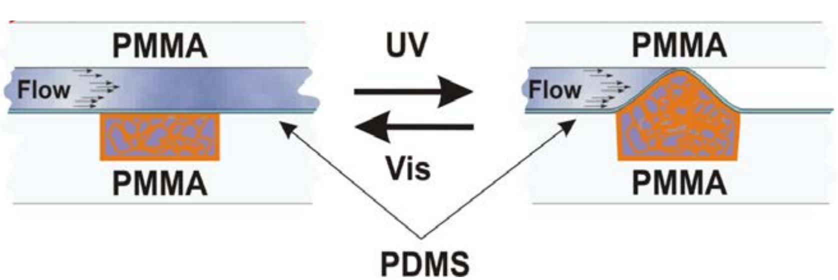


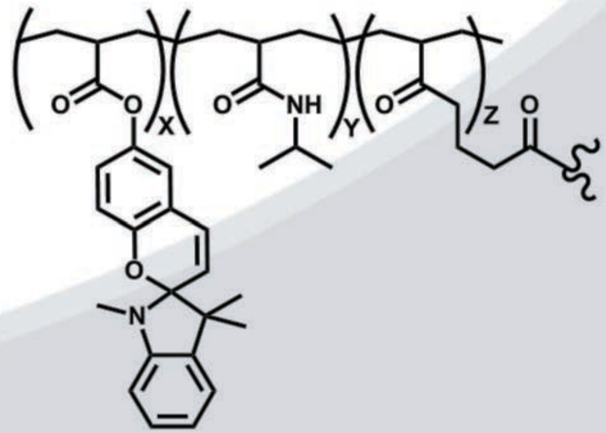
Fig. 6 Response kinetics of ionogels upon irradiation with white light (ionogel height error: ±5 µm).

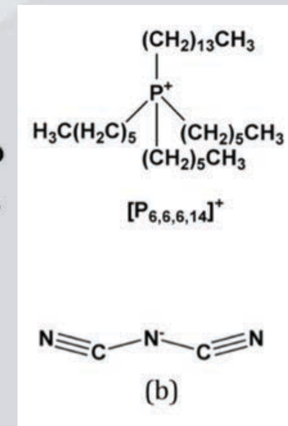
Photo-actuator polymers as microvalves in microfluidic systems









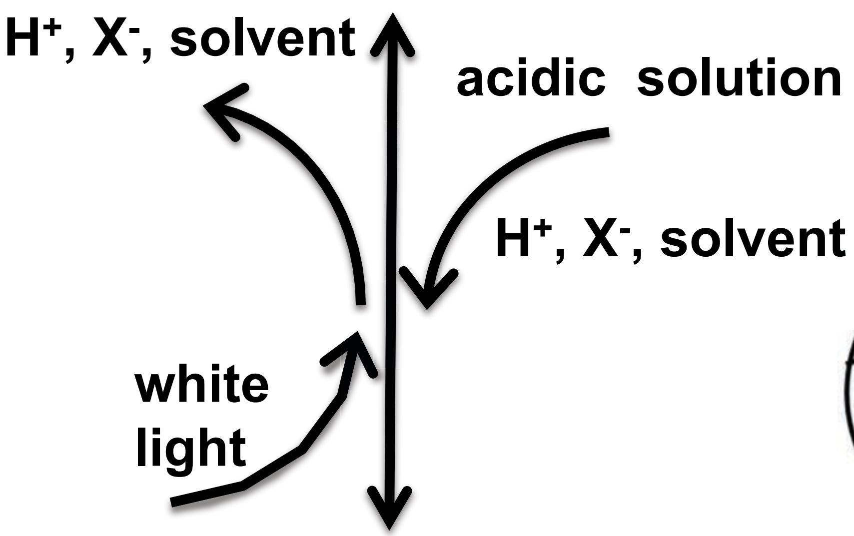


trihexyltetradecylphosphonium dicyanoamide $[P_{6,6,6,14}]^+[dca]^-$

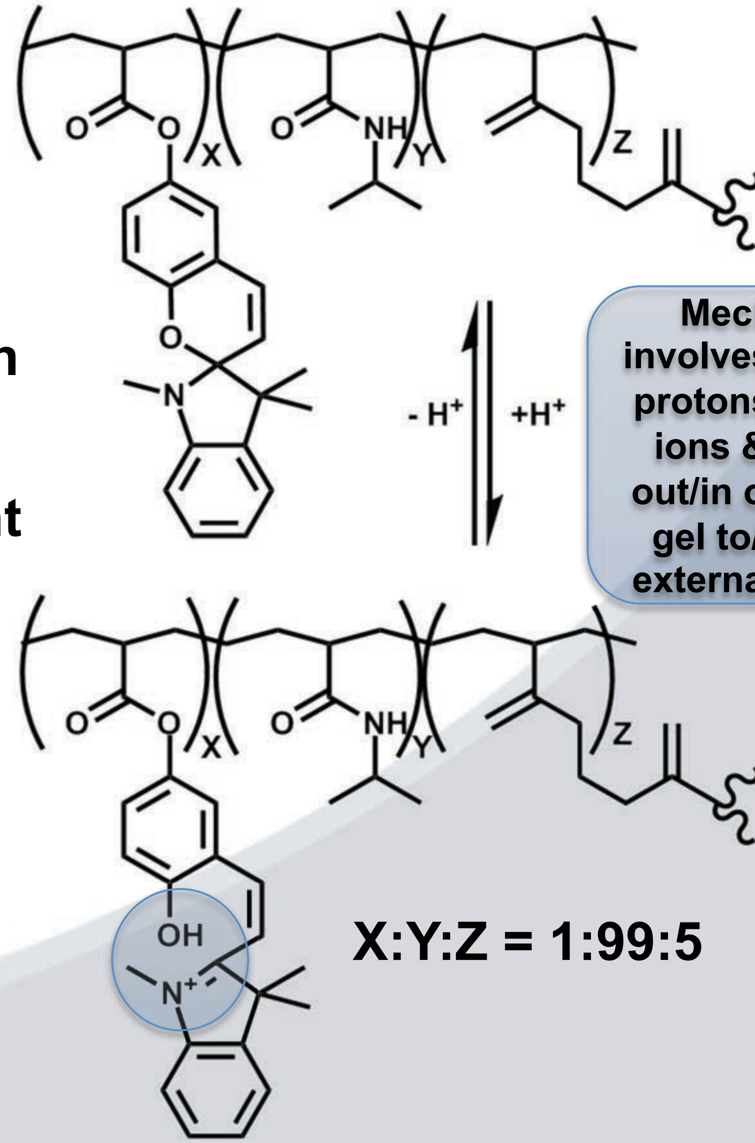
Ionogel-based light-actuated valves for controlling liquid flow in micro-fluidic manifolds, Fernando Benito-Lopez, Robert Byrne, Ana Maria Raduta, Nihal Engin Vrana, Garrett McGuinness, Dermot Diamond, Lab Chip, 10 (2010) 195-201.

Actuation Mechanism

SPIRO (contracted)



MERO-H+ (expanded)



Mechanism involves diffusion protons, counter ions & solvent out/in of the bulk gel to/from the external solution

X:Y:Z = 1:99:5

So far, so good: but what are the limitations?

- Response time for re-swelling is slow - 10’s of minutes due to diffusion mechanism
- Swelling requires protonation of the MC to $MC\text{-}H^+$ within the ionogel by the external bathing solution
- These issues more or less limit the applicability of the valves to single use

Self protonating photoresponsive gel

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

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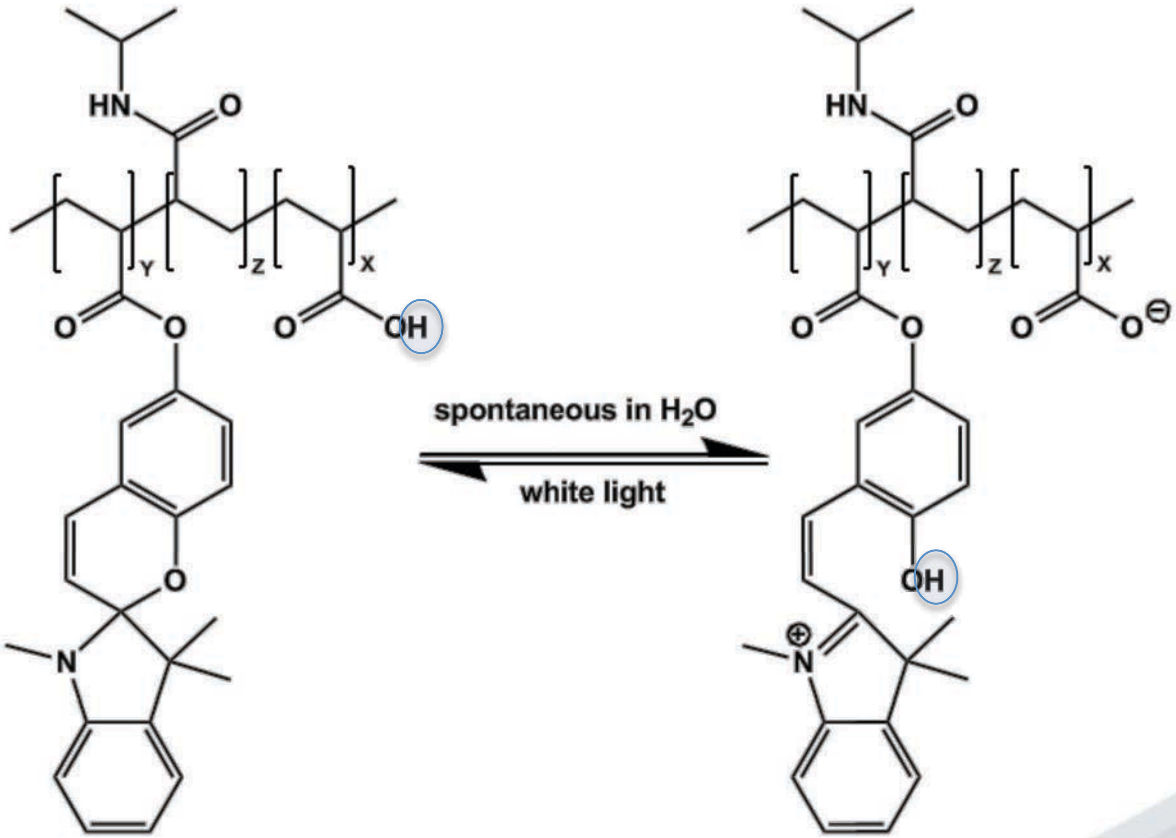
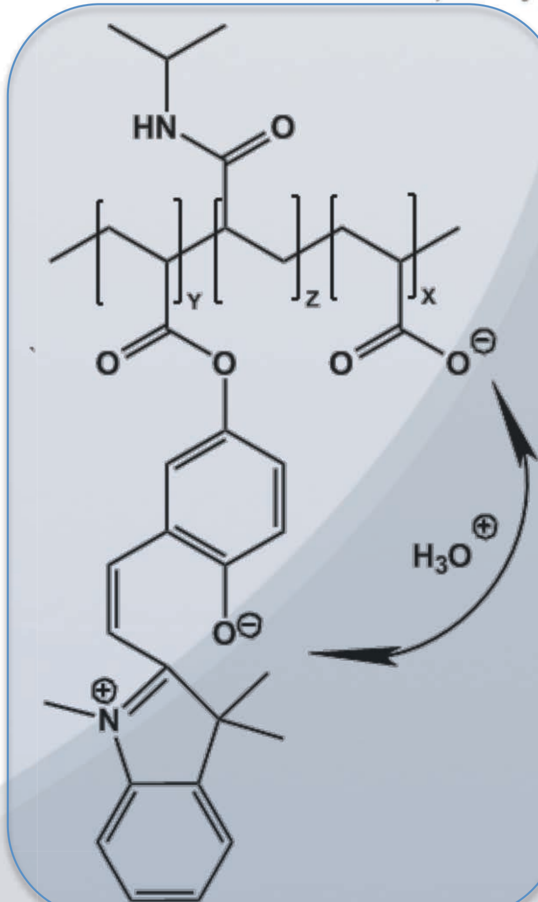
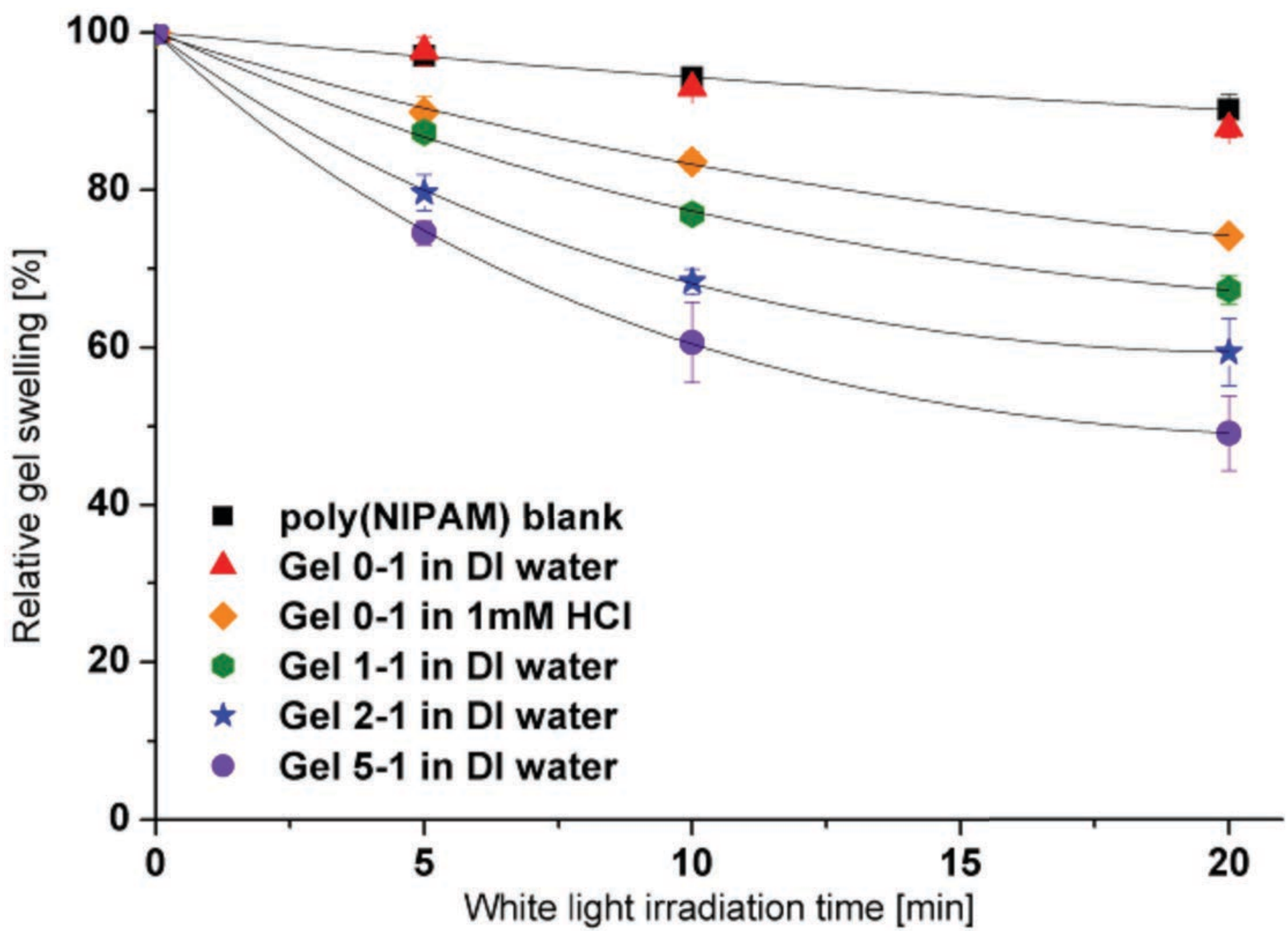




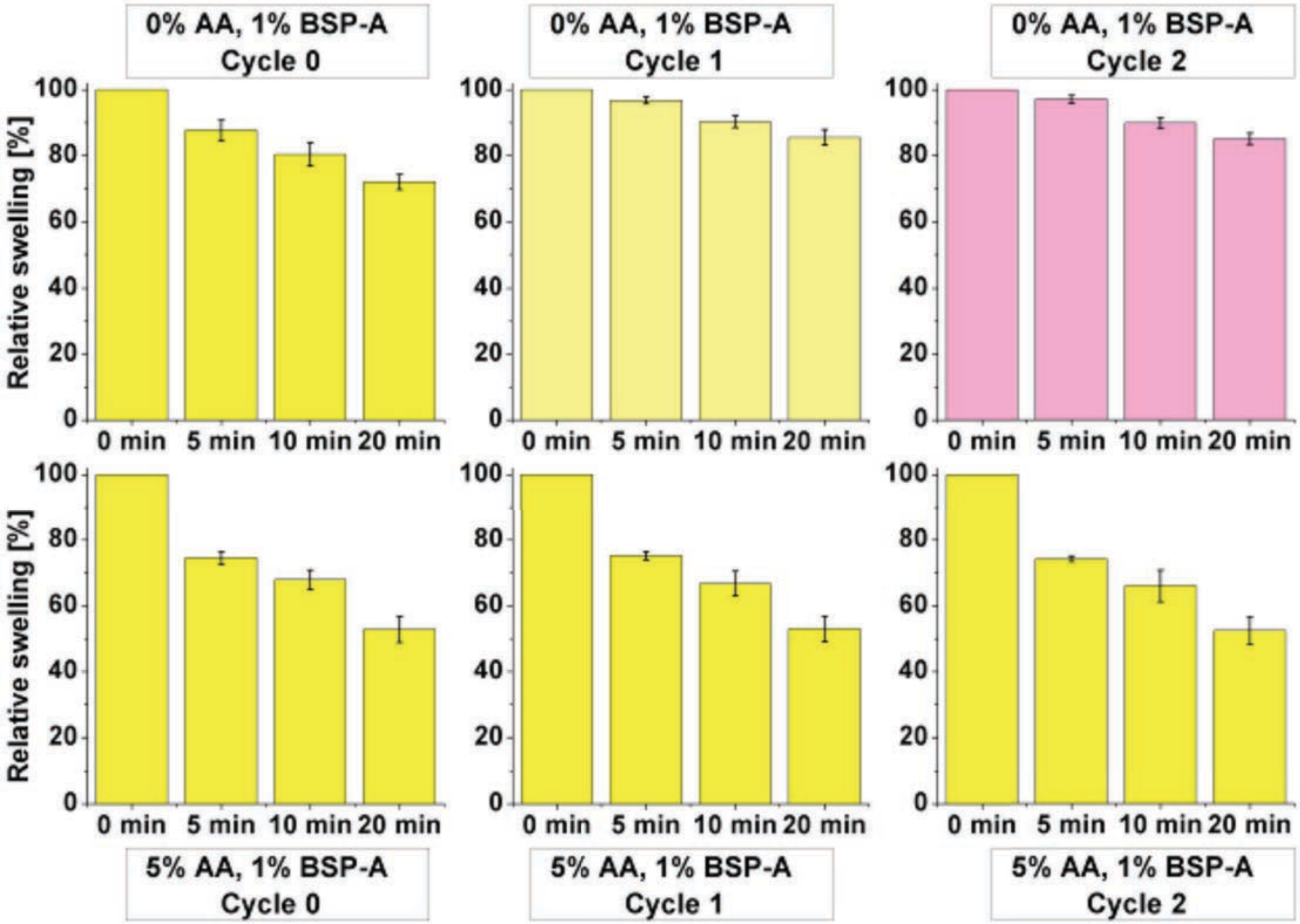
Previously proton source was external (acidic soln. required)
Protons, counter ions & solvent diffuse into/out of the gel

Now the proton exchange is ‘internalised’
The proton population is essentially conserved

Improved Extent and Rate of Contraction

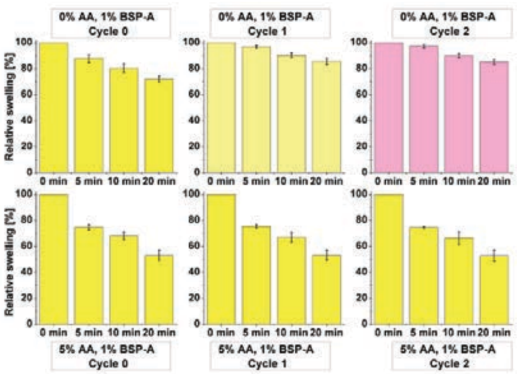


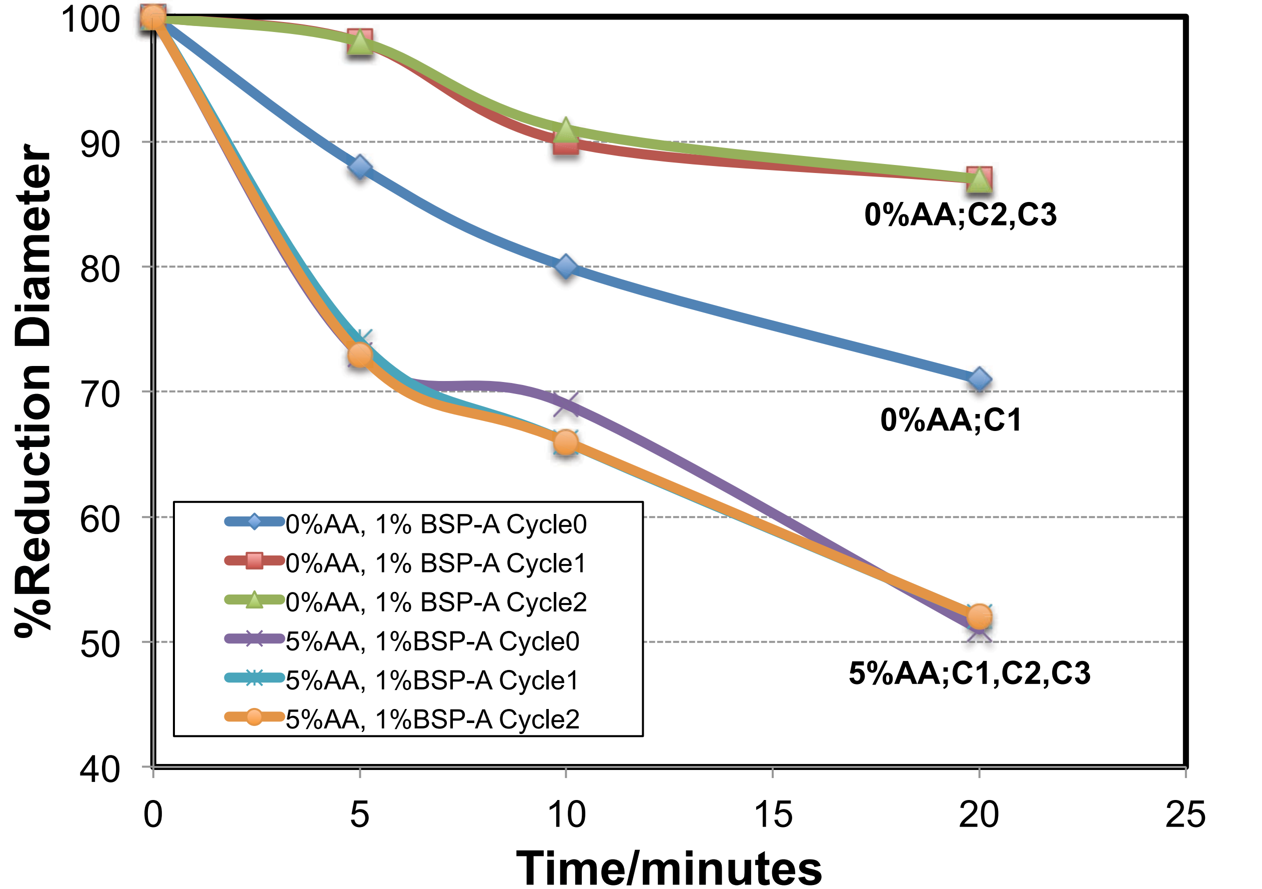
Actuation Cycling without External Acidification



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

Actuation Cycling without External Acidification





Samples have been recycled repeatedly over a period of 2 months

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

Spontaneous Reformation of Acidified Merocyanine during Actuation Cycling in non-acidified water

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

Gel with 0 % AA

Colour gradually changing from yellow to purple as H^+ leaves the gel on each cycle

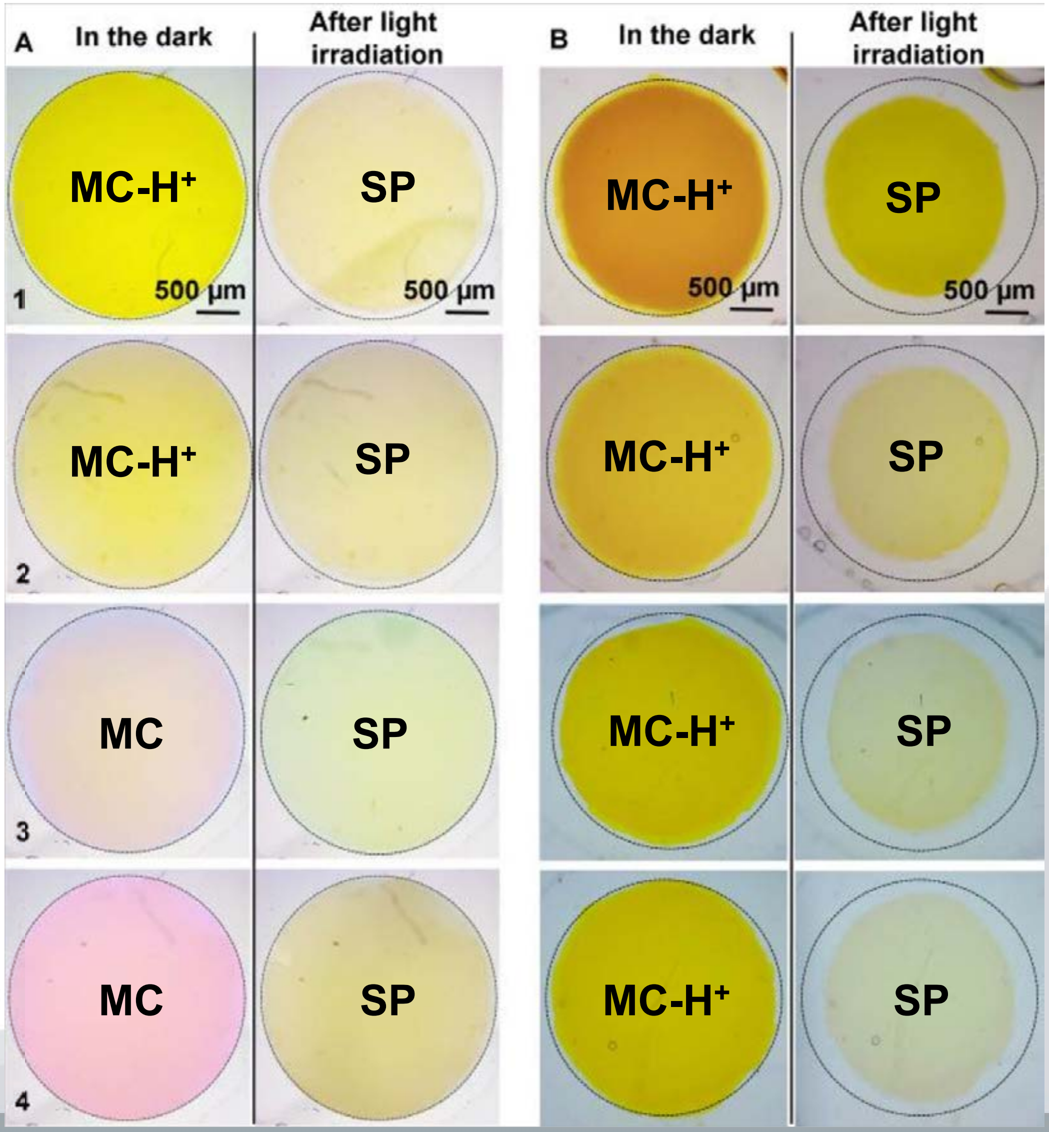
Switching changes from primarily

$MC\text{-}H^+ \rightarrow SP + H^+$

to

$MC \rightarrow SP$

Gel actuation stops



Gel with 5 % AA

Colour remains essentially the same, as H^+ stays in the gel during cycling

Switching stays primarily as

$MC\text{-}H^+ \rightarrow SP + H^+$

Gel actuation continues

Photoactuator Summary

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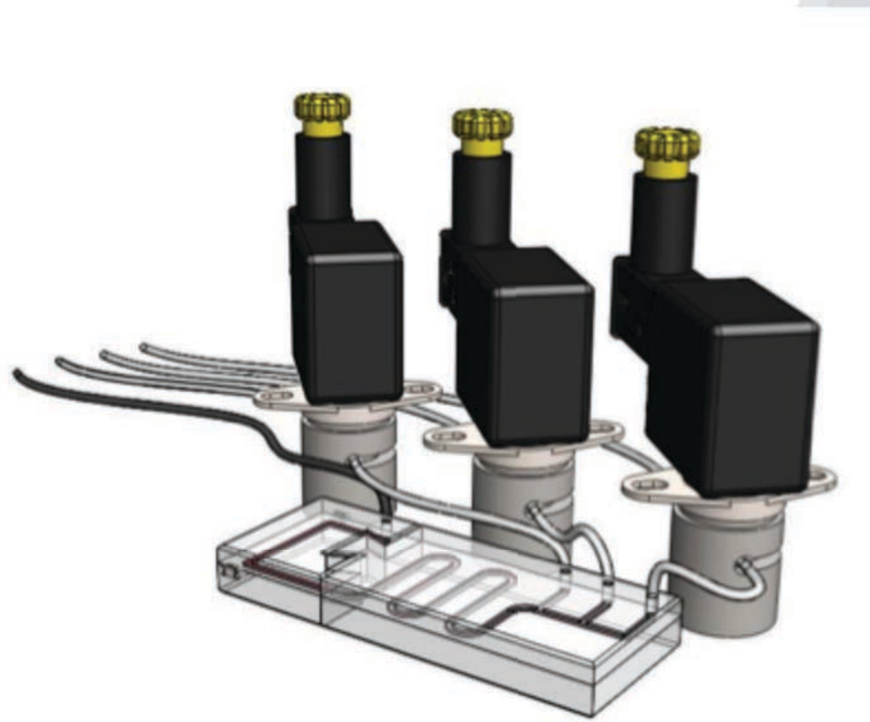
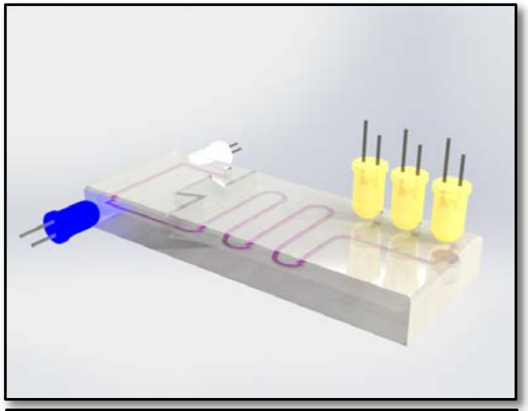
- **Need to optimise**
  - Response kinetics
  - Extent of effect
  - Repeatability over time
  - Physical Ruggedness
  - Effective lifetime
  - Ease of fabrication; in-situ, spatial control/resolution
  - Cost per unit
  - …………

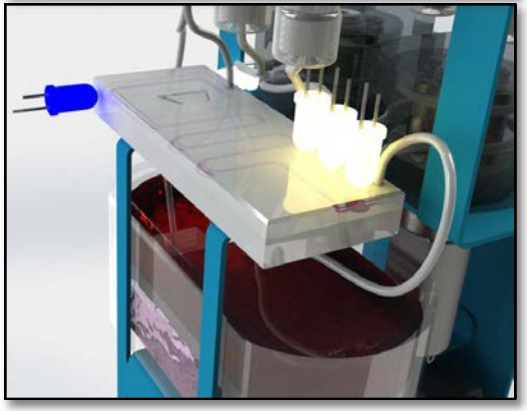
Lots of opportunity for materials science!

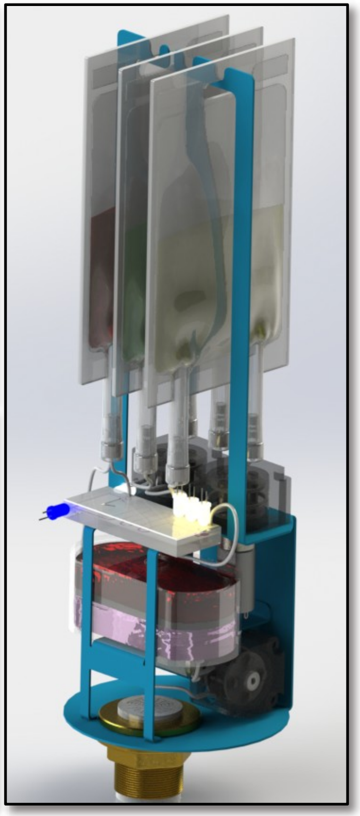
Can we go from this:

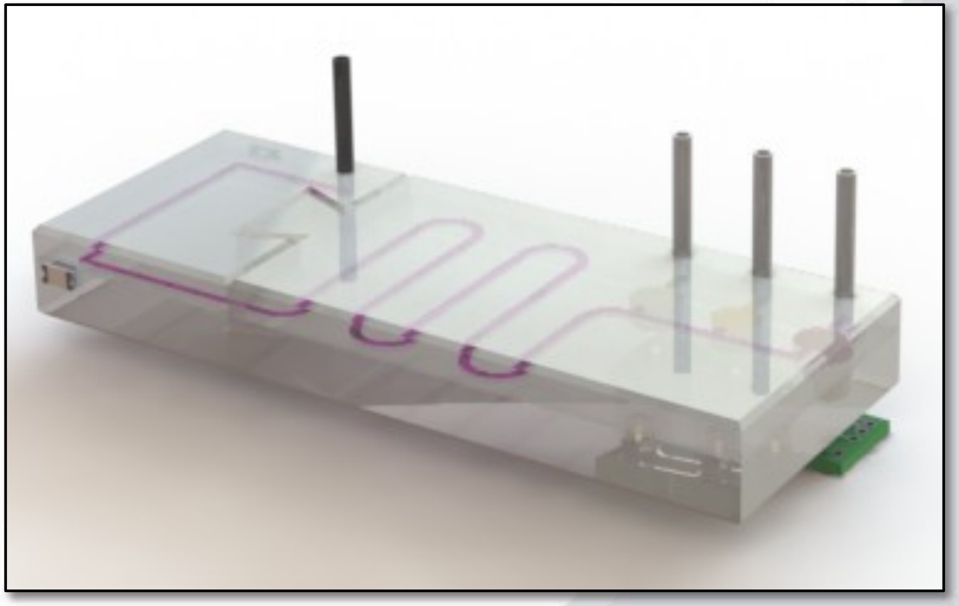


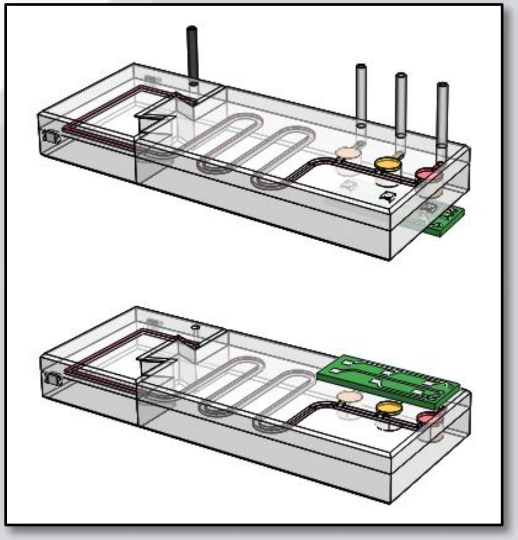
To Photo-Fluidics & Detection











- Fluidic handling completely integrated into the microfluidic chip
- Valves actuated remotely using light (LEDs)
- Detection is via LED colorimetric measurements

Conclusions

- **Linking 'Applied' and 'Fundamental' Research is critical**
- **Build micro/nano-scaled platforms capable of**
  - Movement/intelligent location
  - Controlled binding and release of molecular pay-loads
  - Integrated communications capability

Disruptive approaches to remote chemo/bio-sensing will emerge from fundamental research in Materials Science!

- NCSR, DCU
- CLARITY/INSIGHT
- Research Partners – academic and industry
- Funding sources – SFI, HEA, EI, MI, EPA, ARC, EU-FP7, IRCSET…

Thanks for the invitation