

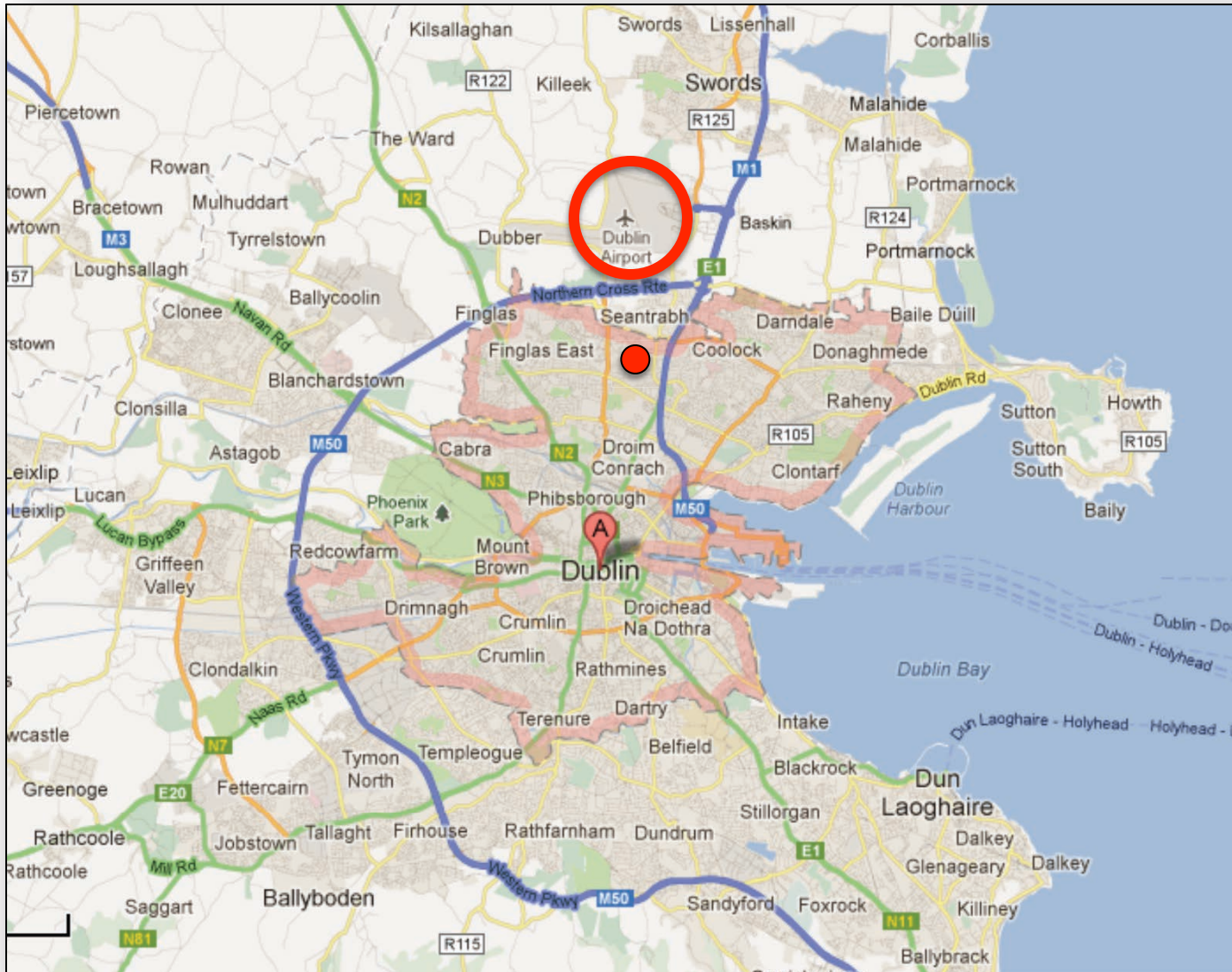
Biomimetic Microfluidics and Stimuli-responsive Materials: The Key to Realising Chemical Sensing Platforms with Revolutionary Capabilities

Prof. Dermot Diamond
Director National Centre for Sensor Research
Funded Investigator, INSIGHT Centre for Data Analytics
Dublin City University

Lecture presented at
1st OrgBio Marie Curie ITN Workshop
Bari, Italy, 30 March – April 1 2015



Dublin & DCU Location





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NEWS AND RESOURCES

MINISTER BRUTON LAUNCHES €88 MILLION SFI RESEARCH CENTRE, BRINGING NEW INSIGHTS TO DATA ANALYTICS

Insight Centre for Data Analytics

- Biggest single research investment ever by Science Foundation
- Biggest coordinated research programme in the history of the state
- Focus is on 'big data' related to health informatics and pHealth

Insight, the Centre for Data Analytics, will position Ireland at the heart of global Data Analytics research

The largest investment in a single research centre in the history of the state

Uniting 4 universities, 30 industry partners, and 200 researchers in one multi-location research centre

Creating 300 direct jobs through 12 funded spin outs, as well as creating indirectly thousands of other job

Research and Innovation, Mr Sean Sherlock T.D. today officially launched Insight, a new Science Foundation Ireland (SFI) Research Centre for Data Analytics. In a joint initiative between DCU, NUI Galway, UCC and UCD, Education institutions, with 30 industry partners, to position Ireland at the heart of global data analytics research.

The Centre will receive funding of €58 million from the Department of Jobs, Enterprise and Innovation through SFI's Research Centres Programme, along with a further contribution of €30 million from 30 industry partners. Insight represents a new approach to research and development in Ireland, by connecting the scientific research of Ireland's leading data analytics researchers with the needs of industry and enterprise.



internet 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.

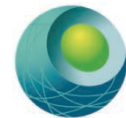
Digital communications networks are at the heart of modern society. The digitalization of communications, the development of the Internet, and the availability of relatively inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions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

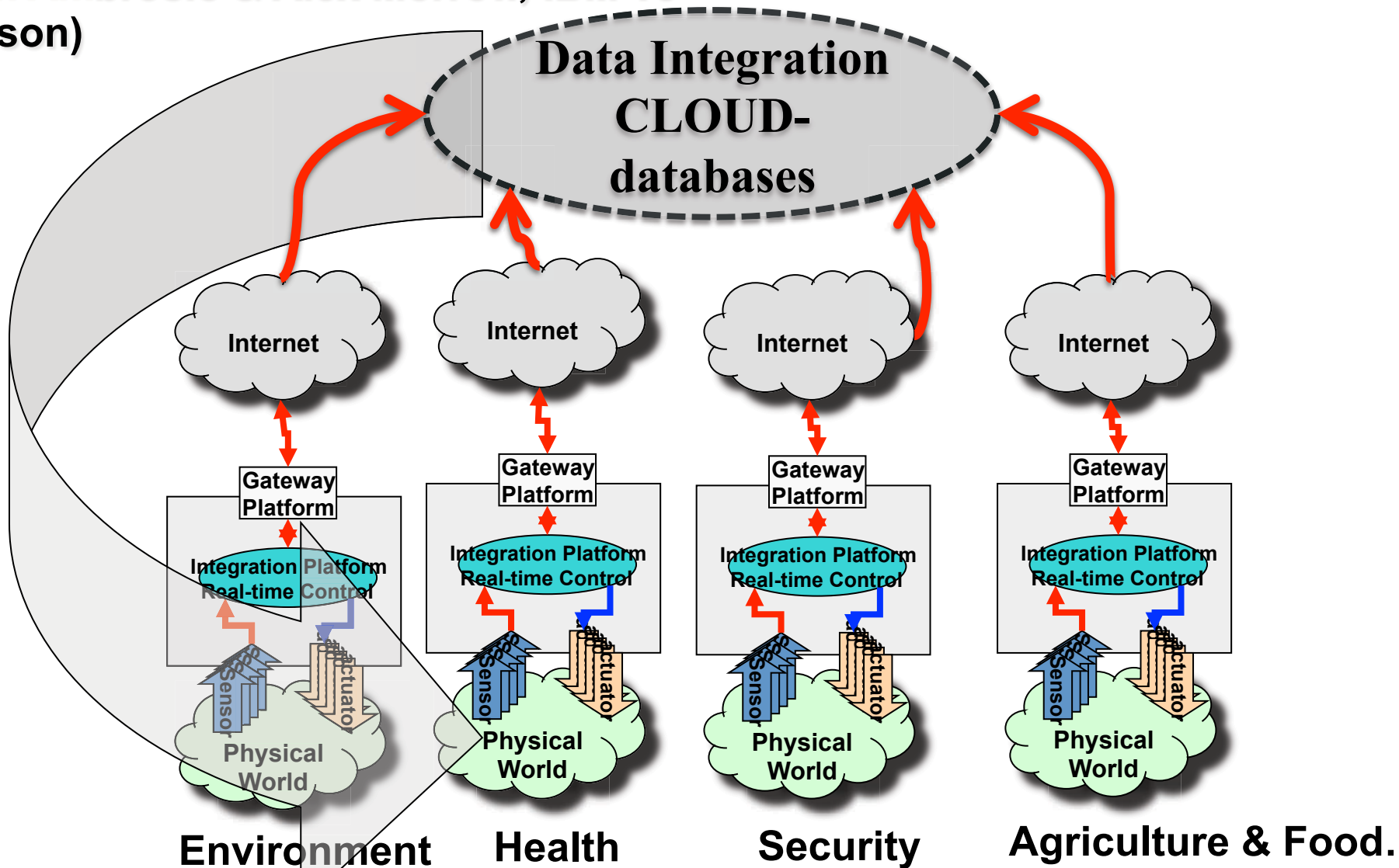
**Dermot Diamond, Anal. Chem., 76 (2004) 278A-286A
(Ron Ambrosio & Alex Morrow, IBM TJ Watson)**

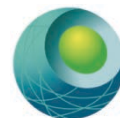


Internet-scale sensing and control



(Ron Ambrosio & Alex Morrow, IBM TJ Watson)



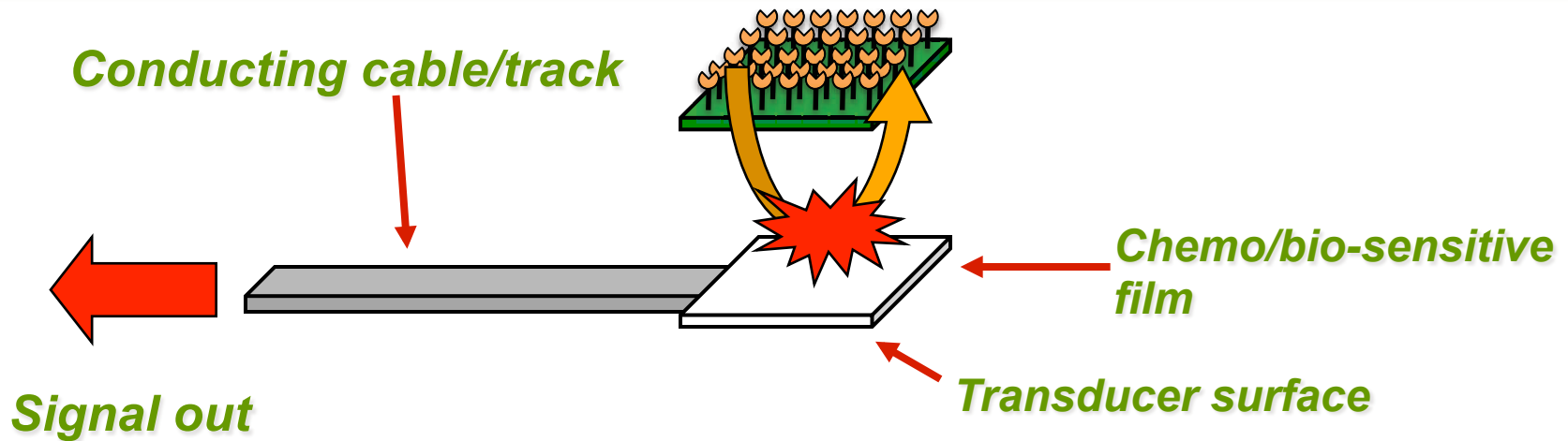


Scalability depends fundamentally of the availability of **affordable** Chem/Bio-sensing devices that can function **autonomously** for **years** in inaccessible/remote locations?



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**)

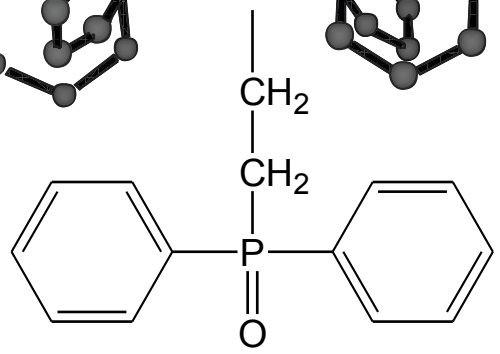
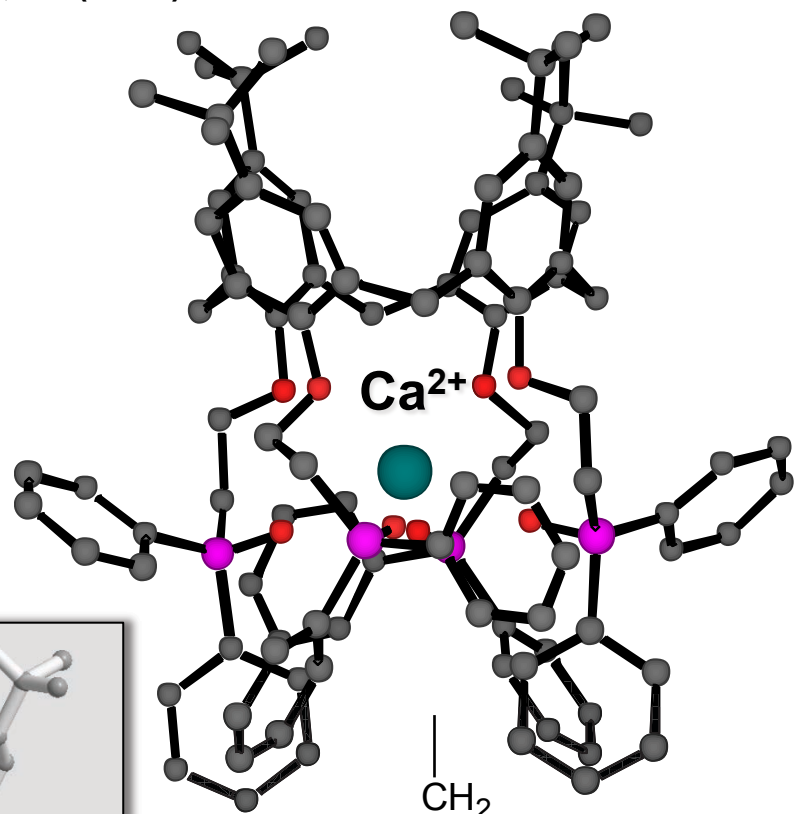
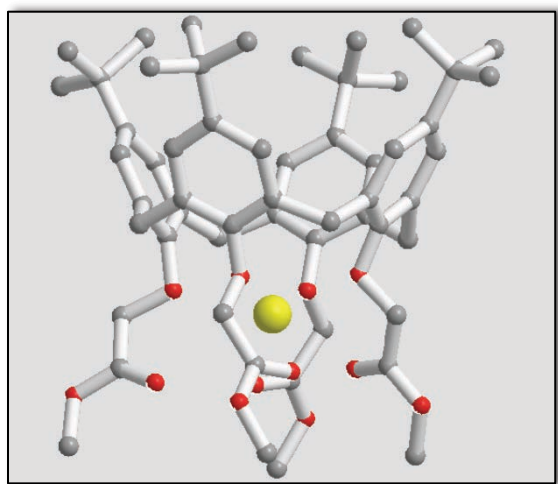
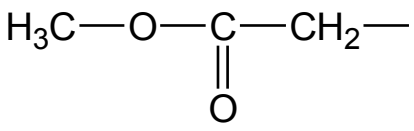
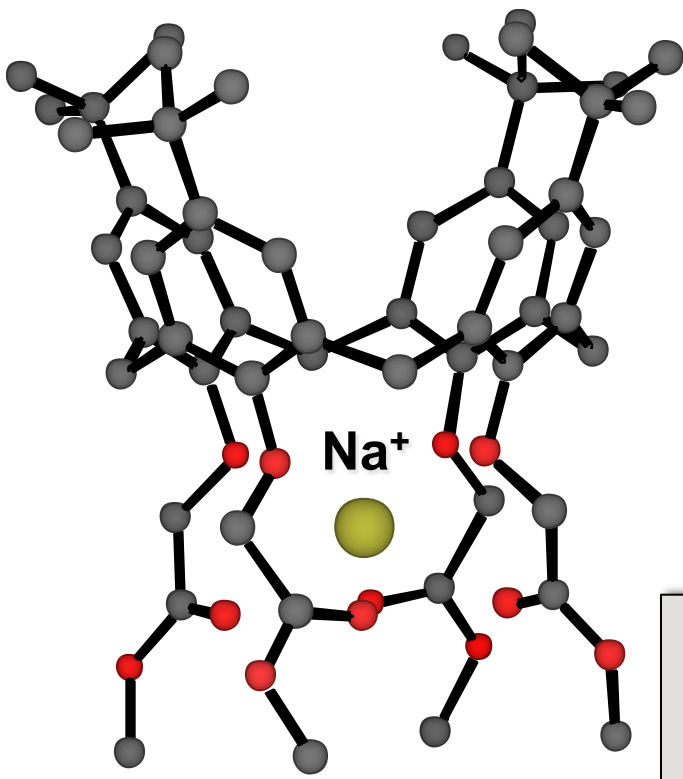


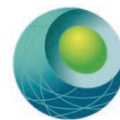


Calixarene Ionophores – controlling the selectivity

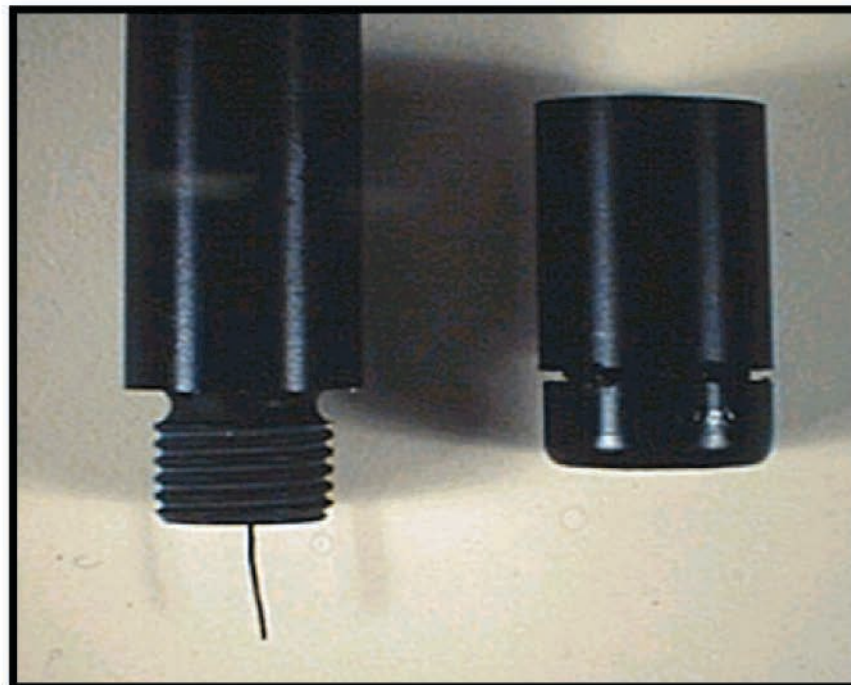
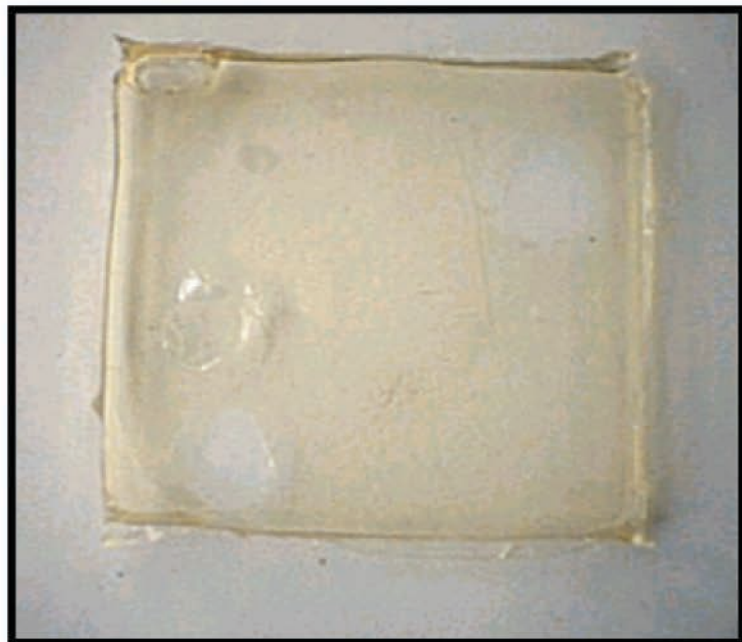


Neutral Carrier Based Ion-Selective Electrodes,
D.Diamond, Anal. Chem. Symp. Ser., 25 (1986) 155.





PVC - Membrane ISEs

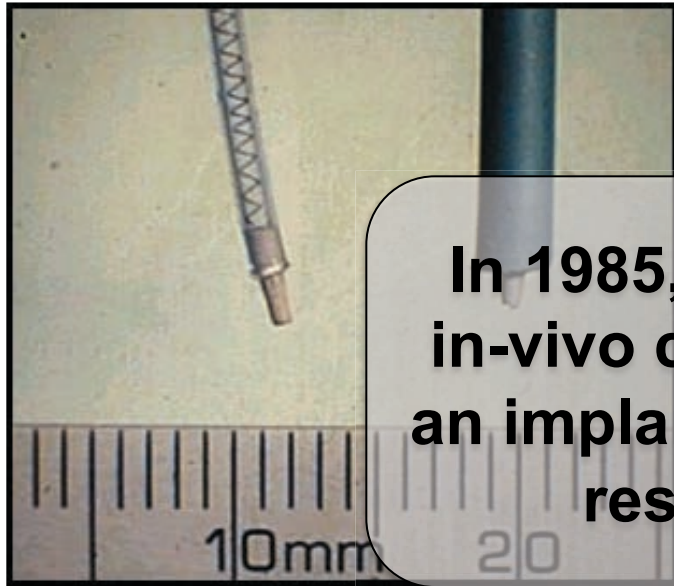


Typical membrane cocktail (%w/w); PVC:33%, NPOE (plasticiser):66%; ionophore/exchanger: 1% (ratio at least 2:1 by mole); dissolve in a volatile solvent e.g. THF and cast membrane from this solution





Blood Analysis; Implantable Sensors



In 1985, the use model for reliable in-vivo continuous monitoring with an implantable chemical sensor was restricted to a day or two

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

Dr. David Band, St Thomas's Hospital London

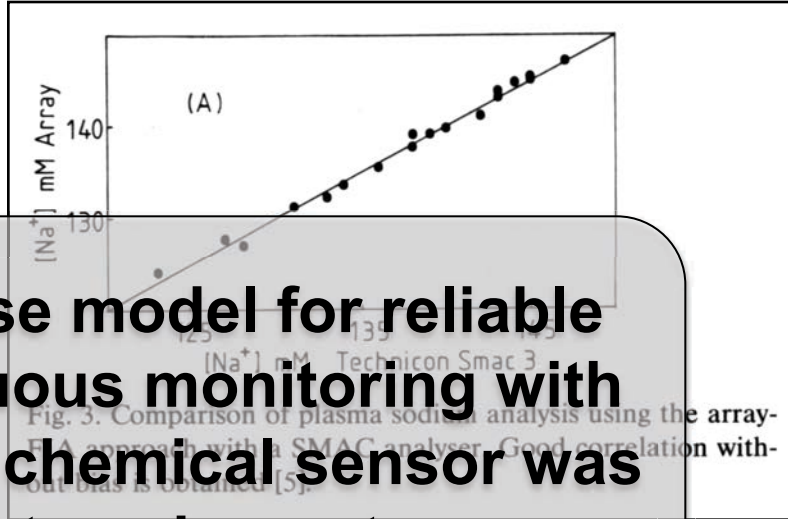
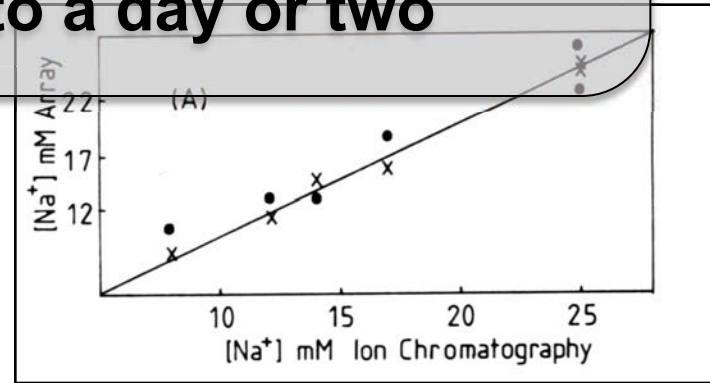


Fig. 3. Comparison of plasma sodium analysis using the array-FIA approach with a SMAC analyser. Good correlation with-out bias is obtained [5].



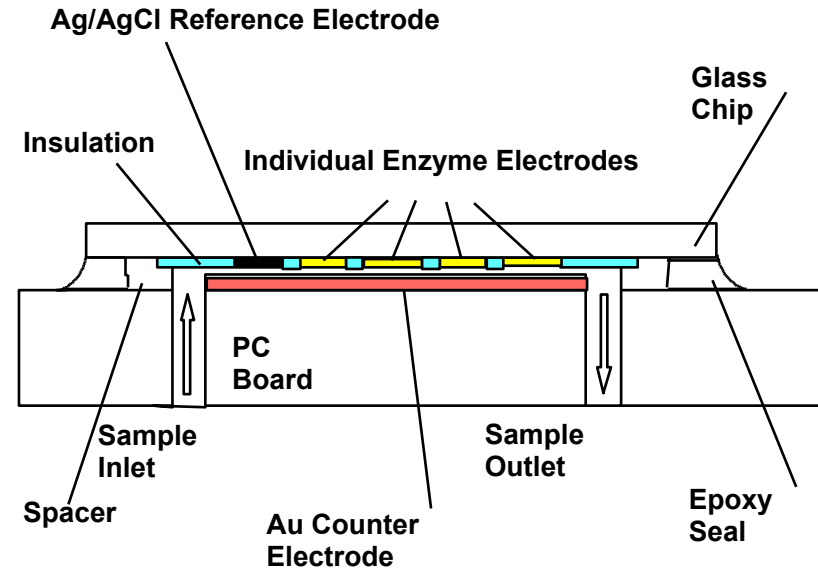
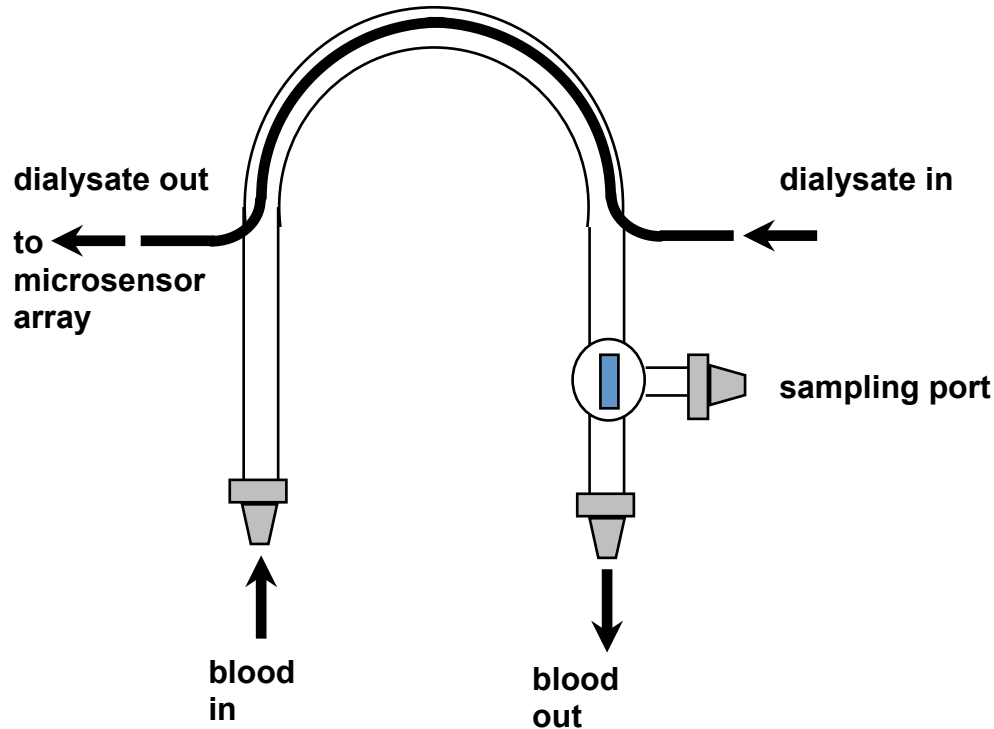
Anal. Chem., **64** (1992) 1721-1728.

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





Microdialysis sampling via arterio-venous shunt



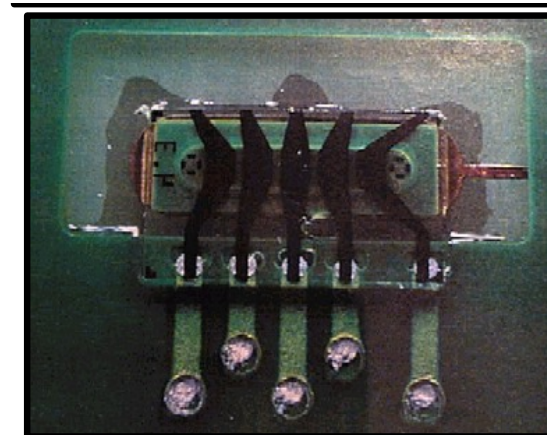
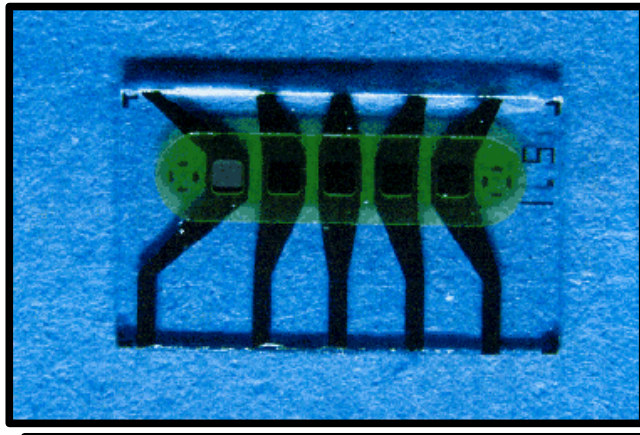
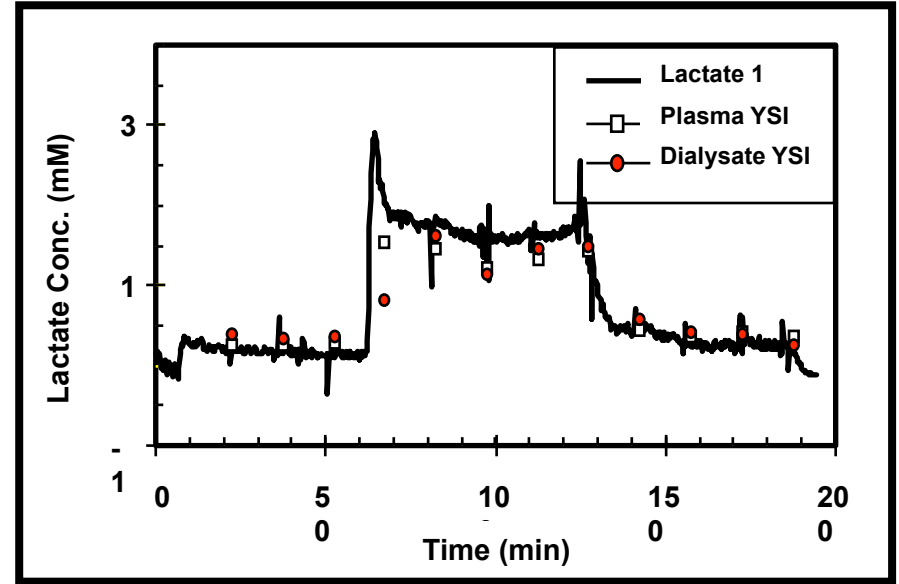
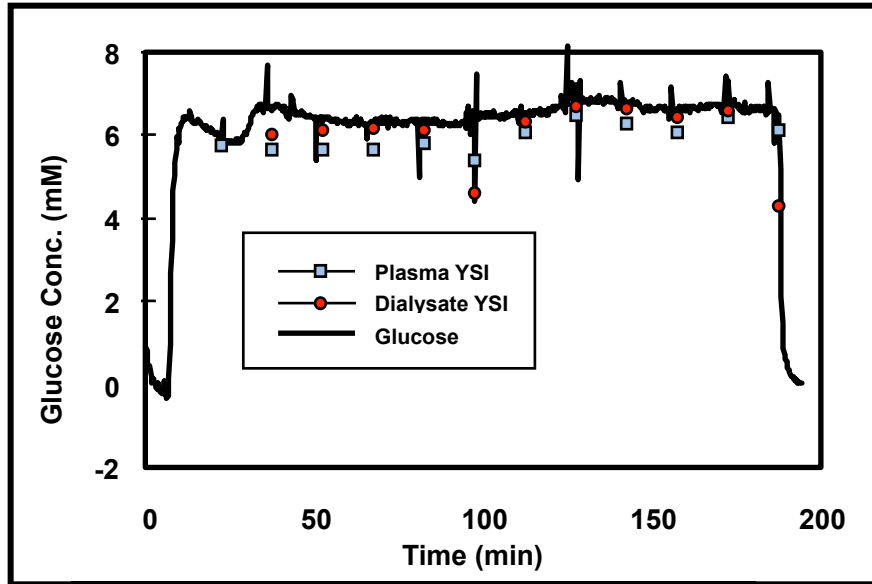
Novel Instrumentation for Real-Time Monitoring Using Miniaturised Flow Cells with Integrated Biosensors, R. Freaney, A. McShane, T.V. Keavney, M. McKenna, K. Rabenstein, F.W. Scheller, D. Pfeiffer, G. Urban, I. Moser, G. Jobst, A. Manz, E. Verpoorte, M.W. Widmer, D. Diamond, E. Dempsey, F.J. Saez de Viteri and M. Smyth, *Annals of Clinical Biochemistry*, 34 (1997) 291-302.

In Vitro Optimisation of a Microdialysis System with Potential for On-Line Monitoring of Lactate and Glucose in Biological Samples, E. Dempsey, D. Diamond, M.R. Smyth, M. Malone, K. Rabenstein, A. McShane, M. McKenna, T.V. Keavney and R. Freaney, *Analyst*, 122 (1997) 185-189.

Design and Development of a Miniaturized Total Chemical-Analysis System for Online Lactate and Glucose Monitoring in Biological Samples, Ethna Dempsey, Dermot Diamond, Malcolm R. Smyth, Gerald Urban, Gerhart Jobst, I. Moser, Elizabeth MJ Verpoorte, Andreas Manz, HM Widmer, Kai Rabenstein and Rosemarie Freaney, *Anal. Chim. Acta*, 346 (1997) 341-349.



Real Time Blood Glucose and Lactate



System functioned continuously for up to three hours!



Artificial Pancreas



A. M. ALBISSER, M.A.SC., PH.D., AND ASSOCIATES

Used a Technicon segmented flow colorimetric glucose analyser

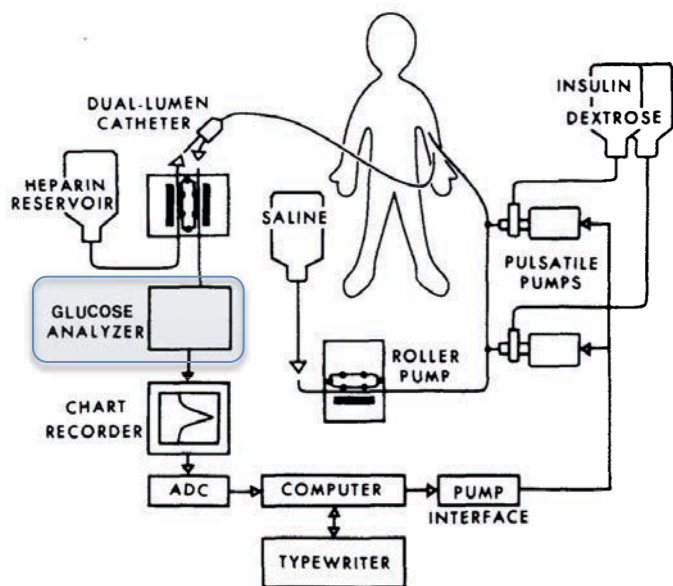
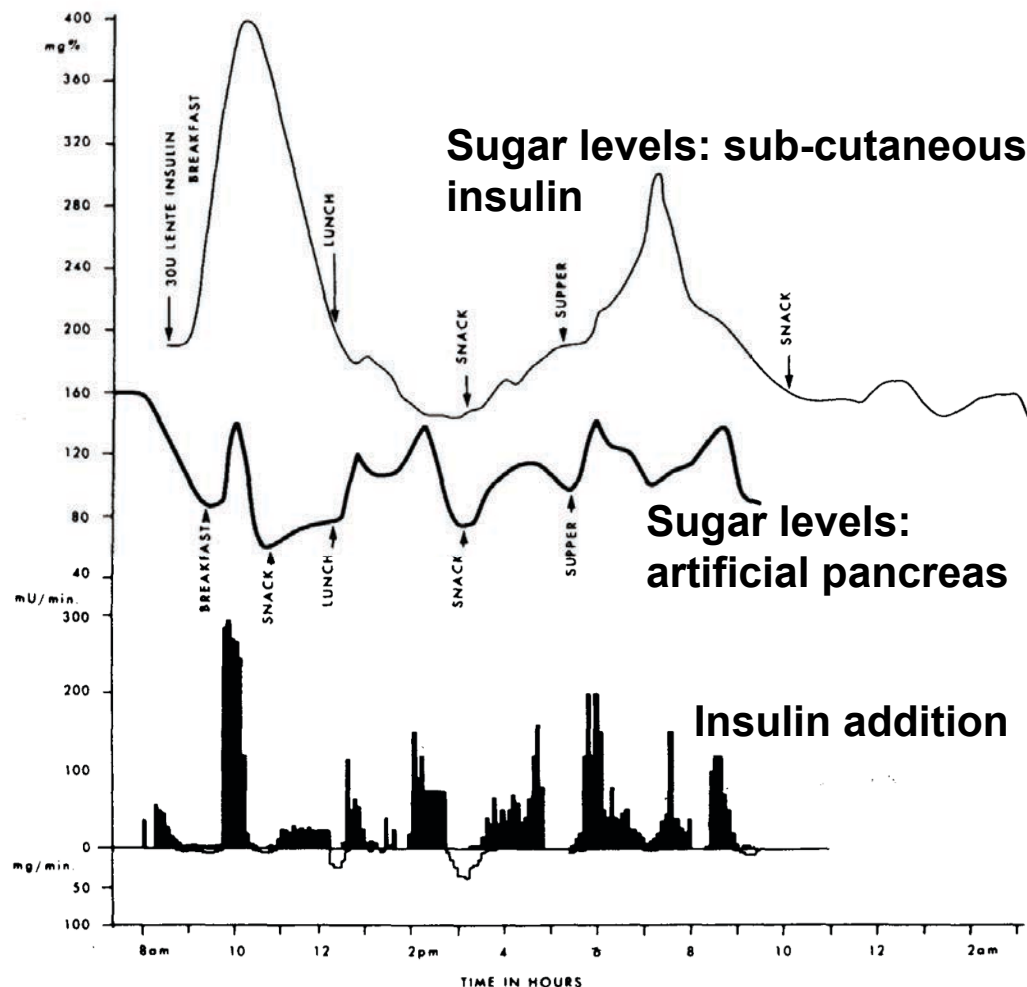


FIG. 1. Schematic diagram of apparatus used for monitoring and automatic regulation of blood sugar.



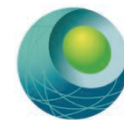
A M Albisser, B S Leibel, T G Ewart, Z Davidovac, C K Botz, W Zingg, H Schipper, and R Gander
Clinical Control of Diabetes by the Artificial Pancreas

Diabetes May 1974 23:5 397-404; doi:10.2337/diab.23.5.397 1939-327X (Toronto)





Implantable Artificial Pancreas



Up to now, implantable pumps for clinical application and suitable for the delivery of insulin have not been developed. However several groups are working on the development of both implantable dosing units and an implantable glucose sensor. Intravascular blood glucose sensing is difficult owing to the complex technology involved, and the foreign-body reaction of blood. The measurement of glucose in tissue would be easier to handle, but it has not been established whether the extravascular tissue concentration of glucose is sufficiently significant to serve as an input signal for a closed-loop system. Only when these questions have been answered and a suitable pumping and dosing unit have been developed, can the closed-loop system for the control of blood glucose be realised and miniaturised for implantation.

An implantable artificial pancreas, W. Schubert, P. Baurischmidt, J. Nagel, R. Thull, M. Schaldach;

Medical and Biological Engineering and Computing, July 1980, Volume 18, Issue 4, pp 527-537

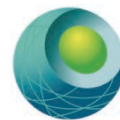
'Intravascular blood glucose sensing is difficult owing to the complex technology involved and the foreign body reaction of blood.'

'The measurement of glucose in tissue would be easier to handle, but it has not been established whether the extravascular tissue concentration of glucose is sufficiently significant to serve as an input signal for a closed-loop system'





Adam Heller



Subcutaneous sampling of interstitial fluid using microneedles to access the fluid through the skin without causing bleeding



San Francisco Business Times; Tuesday, April 6, 2004

'Abbott completes TheraSense acquisition'

Abbott Laboratories said Tuesday it completed its \$1.2 billion acquisition of Alameda-based TheraSense Inc. after a majority of shareholders approved the transaction a day earlier.

- **Abbott Press Release September 29, 2008**
- Abbott Park, Illinois — Adam Heller, Ph.D., a professor at the University of Texas in Austin who created the technology that led to the development of Abbott's FreeStyle Blood Glucose Monitoring Systems® and FreeStyle Navigator® Continuous Glucose Monitoring System, today received the 2007 National Medal of Technology and Innovation from President George W. Bush in an award ceremony at the White House.





Freestyle Navigator



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Indications and Important Safety Information

IFU (Full Version)

FreeStyle Navigator®

Know The FreeStyle Navigator System

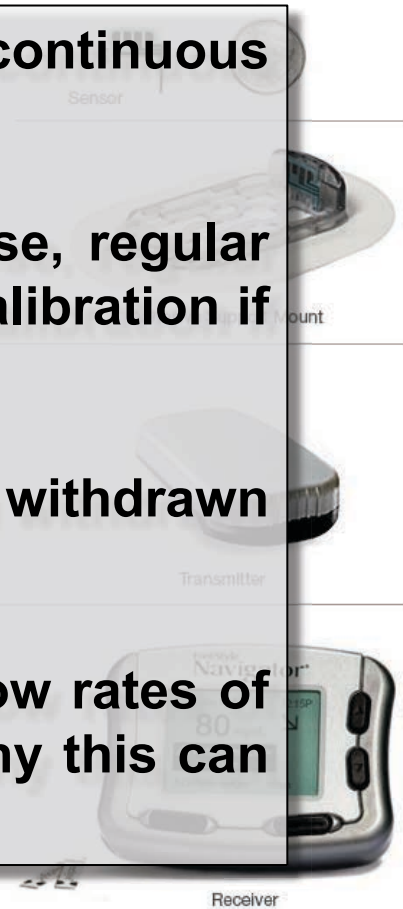
- Combines microfluidics with a micro-dimensioned filament sampling unit which is designed to minimize incidence of infection (therefore for 5 days)
- Measures interstitial fluid (not blood). Diabetics have poor peripheral blood supply, therefore advance.
- Wireless communication used to have continuous data relay to carers and specialists. Enables trending, aggregation, warning....

Target is for several days (up to 7) continuous monitoring; then replace

Use model is good – short periods of use, regular replacement, coulometric detection (no calibration if the enzyme reaction is specific)

Freestyle Navigator appears to have been withdrawn from the US market (2012)

Reasons unclear but may be related to low rates of user uptake – there are many reasons why this can happen





Apple, iWatch & Health Monitoring

Independent.ie 

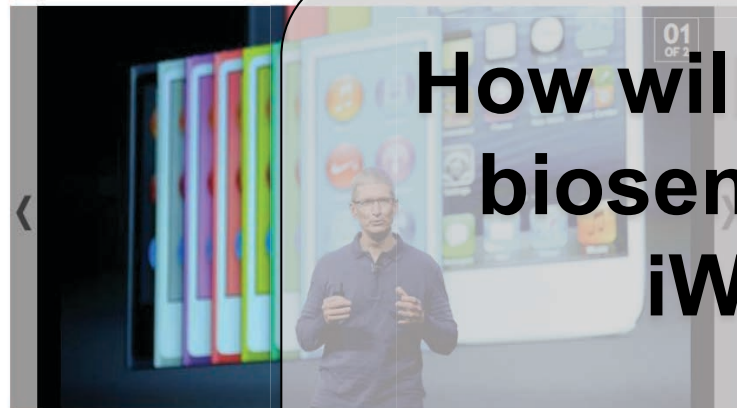
Wednesday 7 May 2014

News Sport Business Woman Entertainment Lifestyle Videos

Independent.ie Business Technology

Apple hiring medical device staff, shares break \$600 mark

0 Comments Recommend 7 Tweet 89 +1 Share



Apple Inc CEO Tim Cook

How will they integrate biosensing with the iWatch....?

'Over the past year, Apple has snapped up at least half a dozen prominent experts in biomedicine, according to LinkedIn profile changes.

May 7th 2014

Much of the hiring is in sensor technology, an area Chief Executive Tim Cook singled out last year as primed to explode."

Industry insiders say the moves telegraph a vision of monitoring everything from blood-sugar levels to nutrition, beyond the fitness-oriented devices now on the market.'

"This is a very specific play in the bio-sensing space," said Malay Gandhi, chief strategy officer at Rock Health, a San Francisco venture capital firm that has backed prominent wearable-tech startups, such as Augmedix and Spire.





Google Contact Lens

United States Patent Application 20140107445

Google Smart Contact Lenses Move

Kind Code A1 Liu; Zenghe April 17, 2014

Closer to Reality

Microelectrodes
Sensor
Abstract

Use model is 24 hours max, then replace;
likely to leverage Google Glass* infrastructure;
Novartis now working with Google.

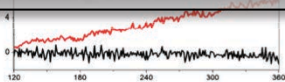
An eye-mountable device includes an electrochemical sensor embedded in a polymeric material configured for mounting to a substrate. The electrochemical sensor includes a working electrode, a reference electrode, and a reagent that selectively reacts with an analyte to generate a sensor measurement of a concentration of the analyte in a fluid to which the eye-mountable device is exposed.

Google's Smart Contact Lens is like your contact lens, except it's a whole lot smarter.



*Google Glass project has been abandoned! (Jan 15 2015) see

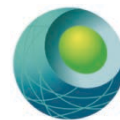
<https://plus.google.com/+GoogleGlass/posts/9uiwXY42tvc>



Biosensors & Bioelectronics, 2011, 26, 3290-3296.

<http://www.gmanetwork.com/news/story/360331/scitech/technology/google-s-smart-contact-lenses-may-arrive-sooner-than-you-think>

Fig. 2. Images of the sensor as it goes through surface functionalization and the related measured responses: (a) sequential images of sensor pre-treatment with GOD/titania/Nafion®; (b) measured amperometric response for the sensor just incubated with GOD; (c) measured amperometric response for the sensor prepared with GOD/titania sol-gel film; (d) measured amperometric response for the sensor prepared with GOD/titania/Nafion®; (e) three controls (signals for buffer) for the same pre-treatment of (b), (c), and (d); (f) the enlarged view of curve (b) and control of (b) for 120–300s.



After decades of intensive research, our capacity to deliver chemo/bio-sensors capable of long-term autonomous use for in-vivo monitoring is still very limited.

Blood is by far the best diagnostic medium, but no sensor will function acceptably for more than a few days continuous exposure to blood





What about the environment?





Remote (Continuous) Sensing Challenges: Platform and Deployment Hierarchies



Physical Transducers –low cost, reliable, low power demand, long life-time

Thermistors (temperature), movement, location, power,, light level, conductivity, flow, sound/audio,

Chemical Sensors – more complicated, need regular calibration, more costly to implement

Electrochemical, Optical, .. For metal ions, pH, organics...

Biosensors – the most challenging, very difficult to work with, die quickly, single shot (disposable) mode dominant use model

Due to the delicate nature of biomaterials enzymes, antibodies....

Increasing difficulty & cost

Increasing scalability

Gas/Air Sensing – easiest to realise

Reliable sensors available, relatively low cost

Integrate into platforms, develop IT infrastructure, GIS tools, Cloud Computing

On-land Water/ Monitoring

More accessible locations

Target concentrations tend to be higher

Infrastructure available

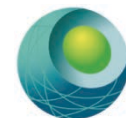
Marine Water

Challenging conditions

Remote locations & Limited infrastructure

Concentrations tend to be lower and tighter in range





pH sensing – wasn't that solved by Nikolskii in the 1930's?

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

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



OVERVIEW

Overview

The Challenge: Improve Our Understanding of Ocean Acidification

Competition Guidelines

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.

Competition Schedule

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

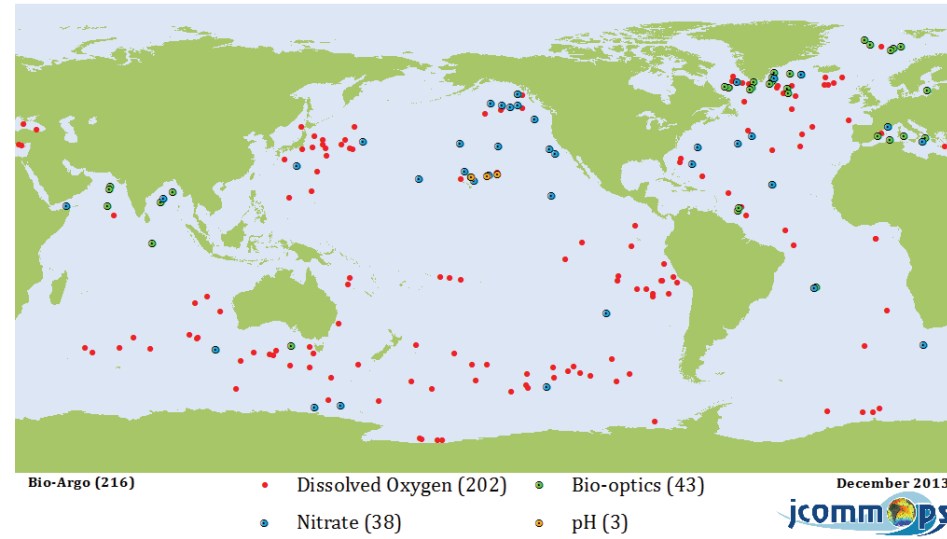
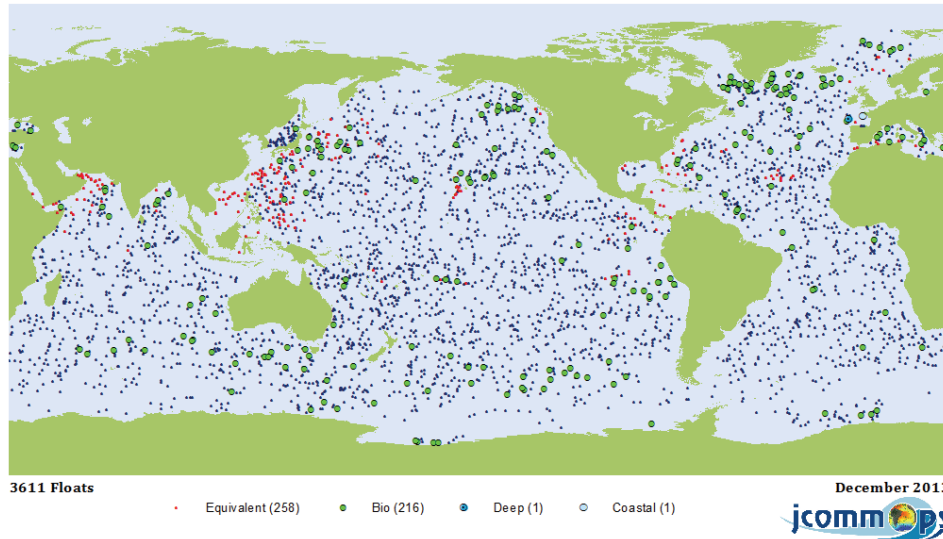
Registration Process

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.





Argo Project (accessed March 9 2014)



- Ca. 3,600 floats: temperature and salinity
 - Only 216 reporting chem/bio parameters (ca. 6%)
 - Of these nitrate (38), DO (202), Bio-optics (43), pH (3) @€60K ea!
- DO is by Clark Cell (Sea Bird Electronics) or Dynamic fluorescence quenching (Aanderaa)
- See <https://picasaweb.google.com/JCOMMOPS/ArgoMaps?authuser=0&feat=embedwebsite>

‘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





And for nutrients....



ALLIANCE FOR COASTAL TECHNOLOGIES

SUPPORTING INNOVATION TO BETTER UNDERSTAND, PREDICT AND MANAGE COASTAL, OCEAN AND GREAT LAKES ENVIRONMENTS.

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The Challenge

- Register Now
- The Problem
- Timeline
- Awards
- Market Information
- Reports
- Provide Your Input
- Registered Participants - Spring 2015
- Frequent Questions

Thinking about registering for the Challenge?

Info and Q&A webinar
12 Feb 2015



Nutrient Sensor Challenge

A Water Sensor Market Stimulation Challenge

Federal agencies, the Alliance for Coastal Technologies, and other partners **CHALLENGE YOU** to join the effort to develop affordable, accurate, and reliable nutrient sensors!

Registration closes March 16, 2015



Nutrient Sensor Features

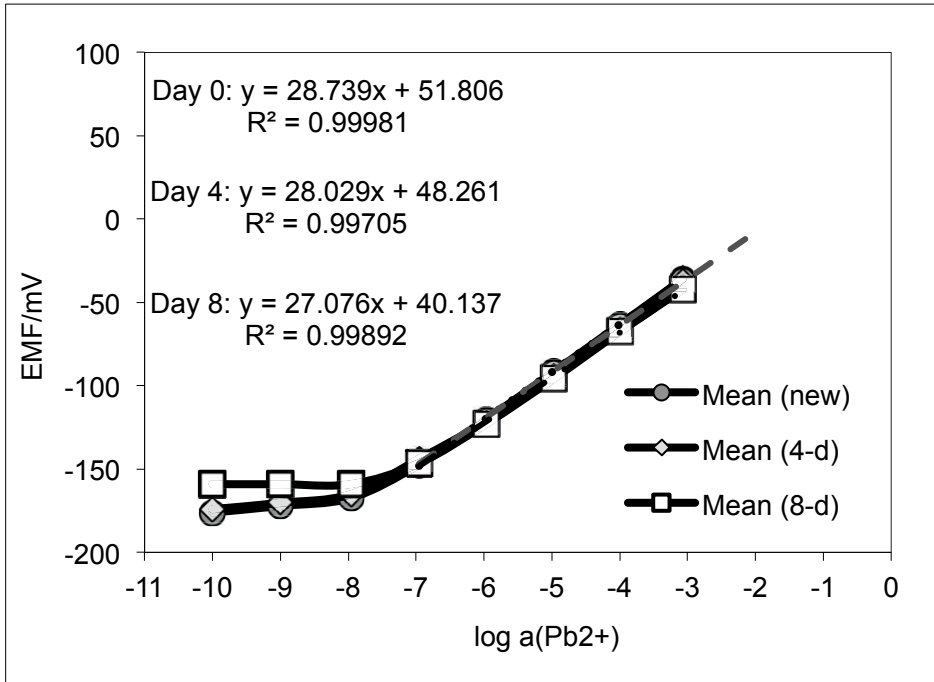
- Measures dissolved nitrate and/or phosphate
- Provides real-time data
- Easy to use
- Less than \$5,000 purchase price
- Unattended deployments for 3 months
- Highly accurate and precise



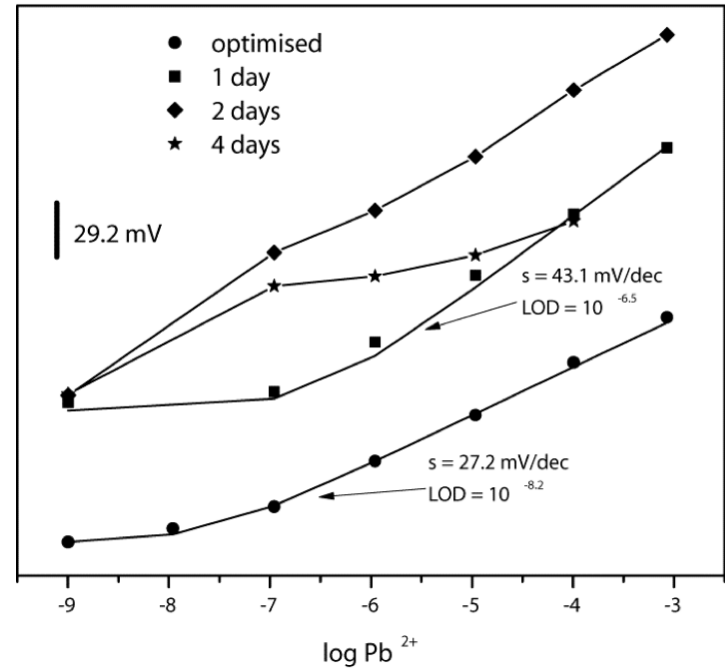


Change in Electrode Function over Time

See *Electrochimica Acta* 73 (2012) 93–97



stored in 10^{-9}M Pb^{2+} , pH=4

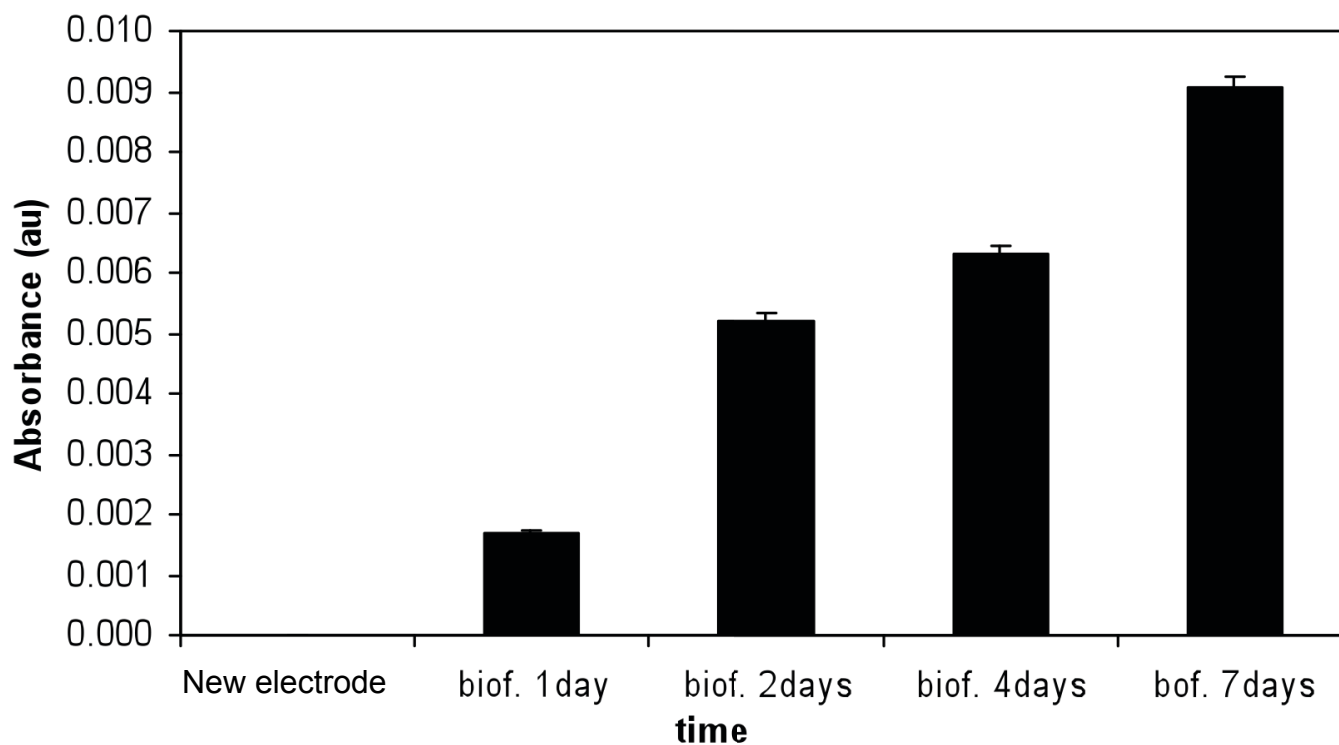


Continuous contact with river water

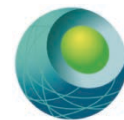
PVC-membrane based ISEs



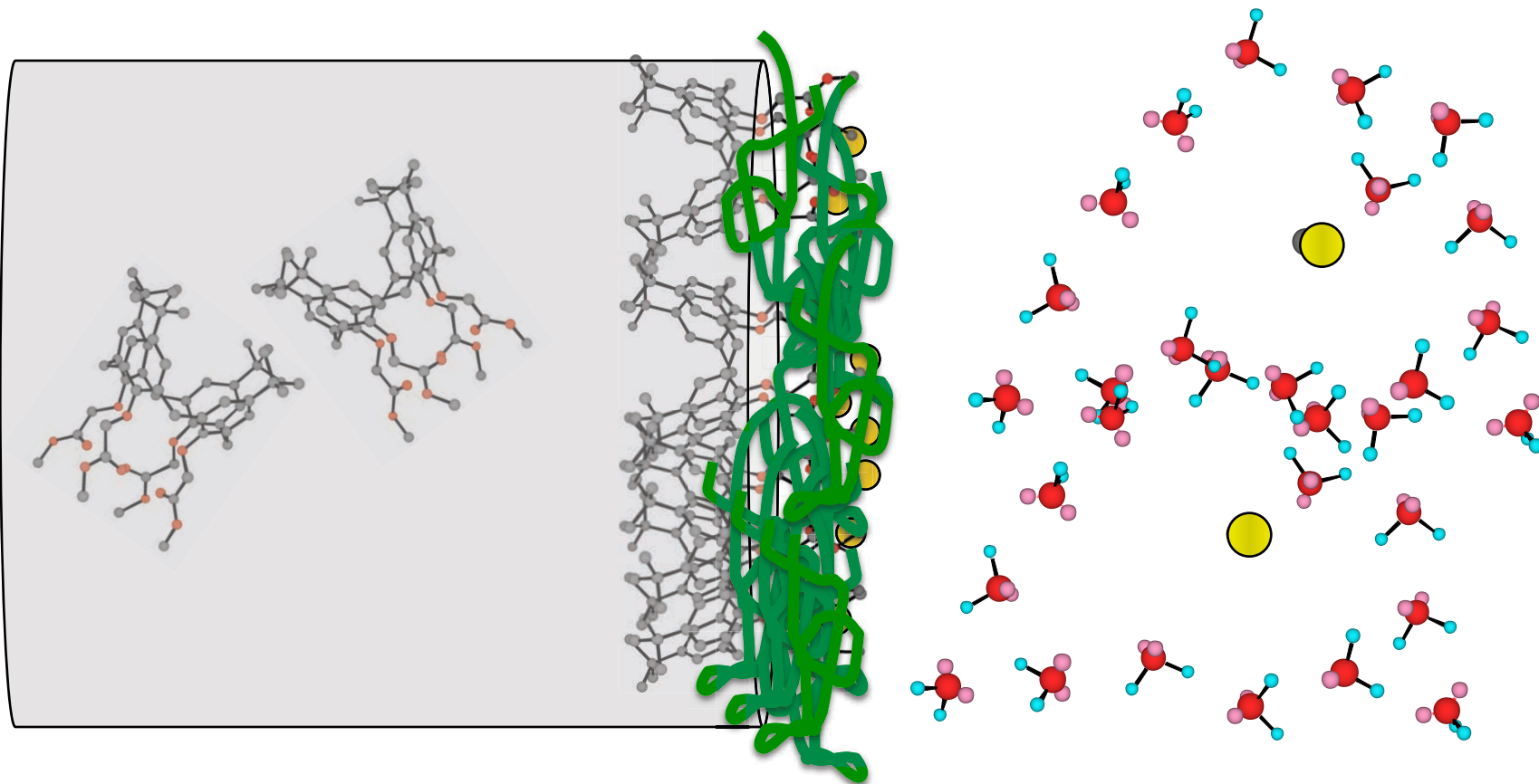
Biofilm Formation on Sensors



- **Electrodes exposed to local river water (Tolka)**
- **‘Slime test’ shows biofilm formation happens almost immediately and grows rapidly**



Control of membrane interfacial exchange & binding processes



Remote, autonomous chemical sensing is a tricky business!



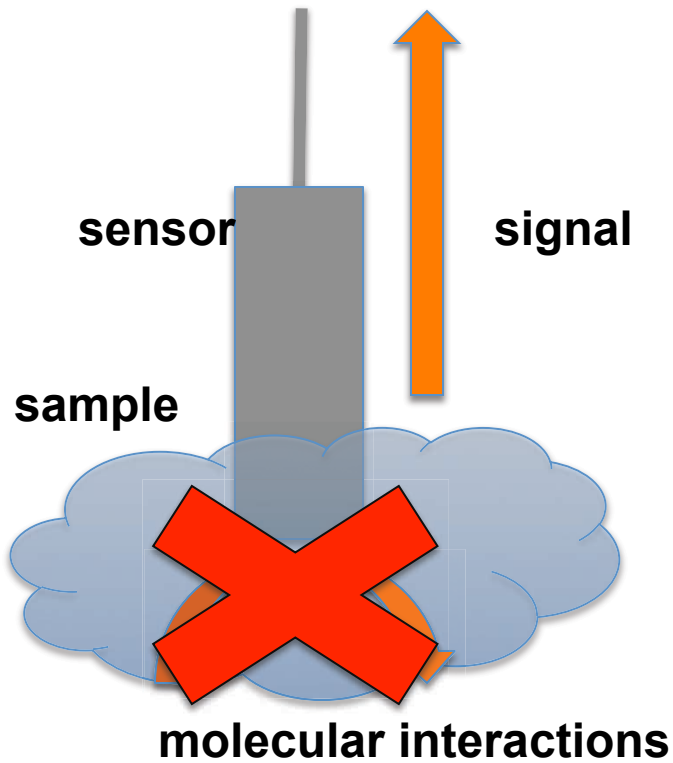


Direct Sensing vs. Reagent Based LOAC/ufluidics

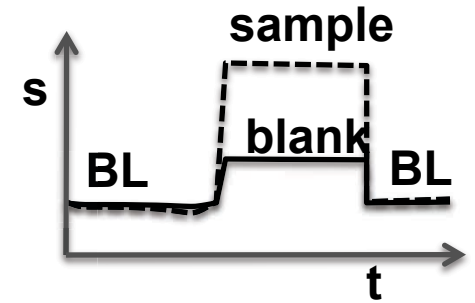
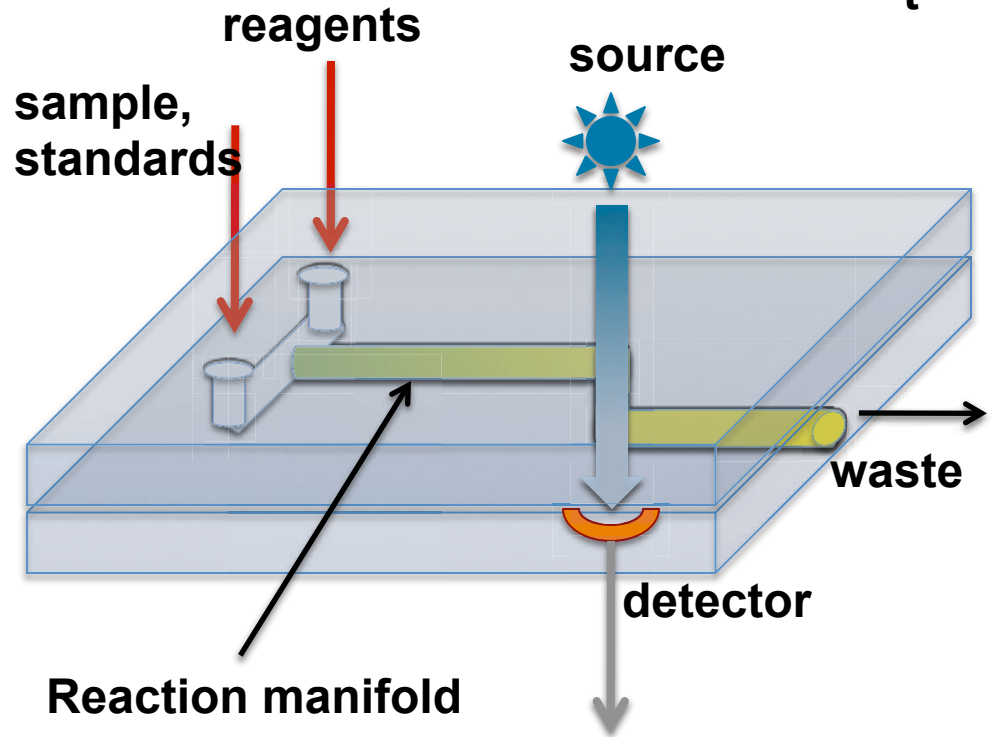


Direct Sensing

outside world

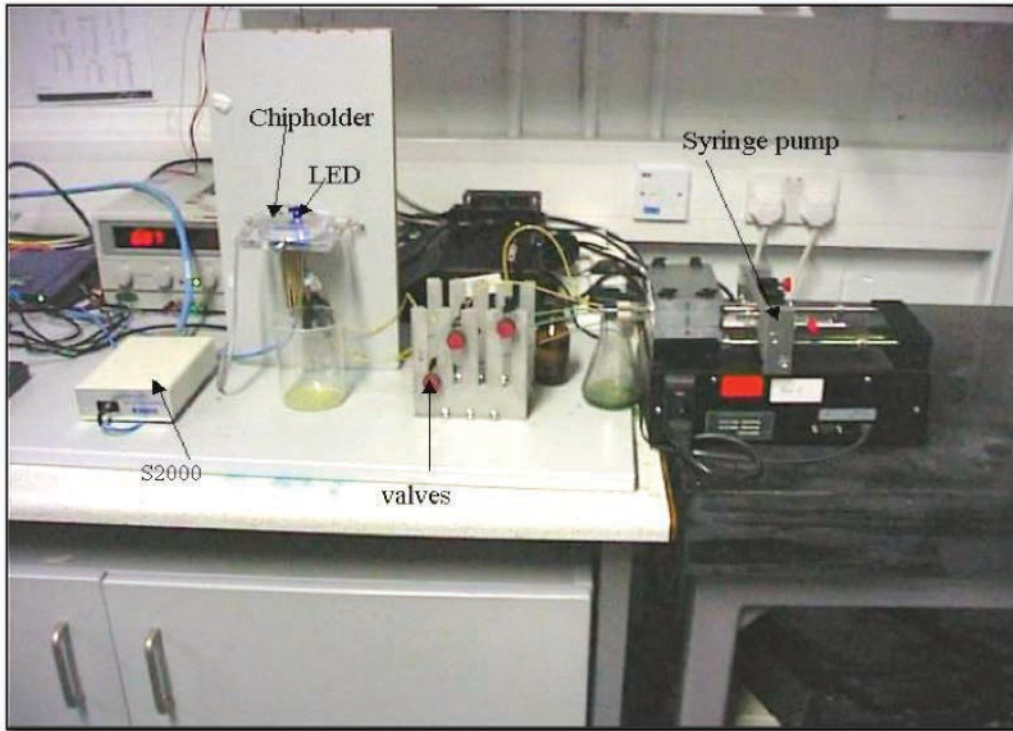


LOAC Analyser



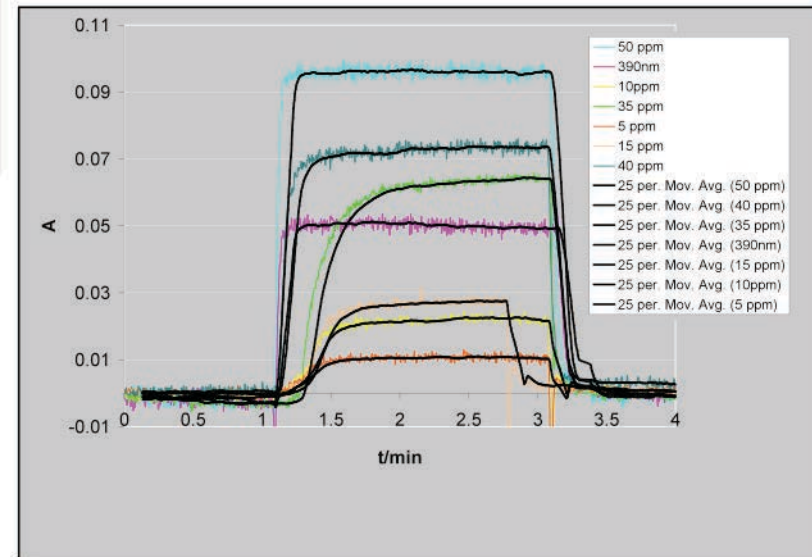


Reagent based Nutrient Analyser



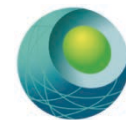
- Setup ca. 1999
- Worked well but not an integrated system

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, M Sequiera, G. Pennarun-Thomas, J Lichtenberg, E Verpoorte, D Diamond and NF de Rooij, Sensors and Actuators B, 76/1-3, (2001) 235-243.

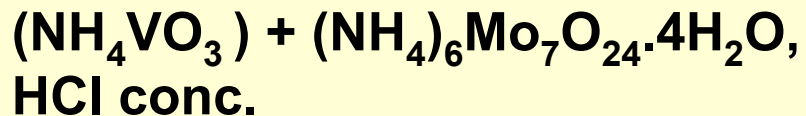




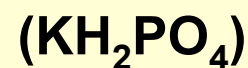
Phosphate: The Yellow Method



Mixture (Reagent)



Sample



+

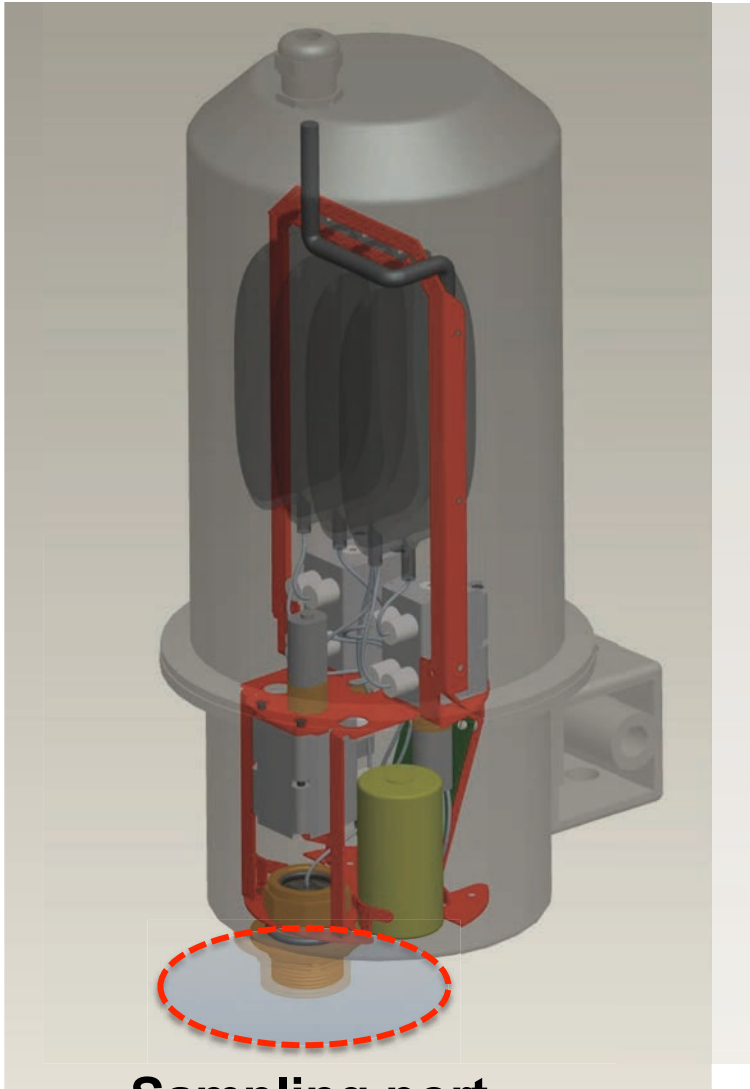


- yellow vanaomolybdophosphoric acid is formed when ammonium metavanadate and ammonium molybdate (mixture) reacts with phosphate (acidic conditions)
- In conventional (molybdate) method, **ascorbic acid** is used to generate the well-known deep blue complex (**v. fine precipitate**)
- Could not be exploited in LOAC devices until UV-LEDs became available!!!!

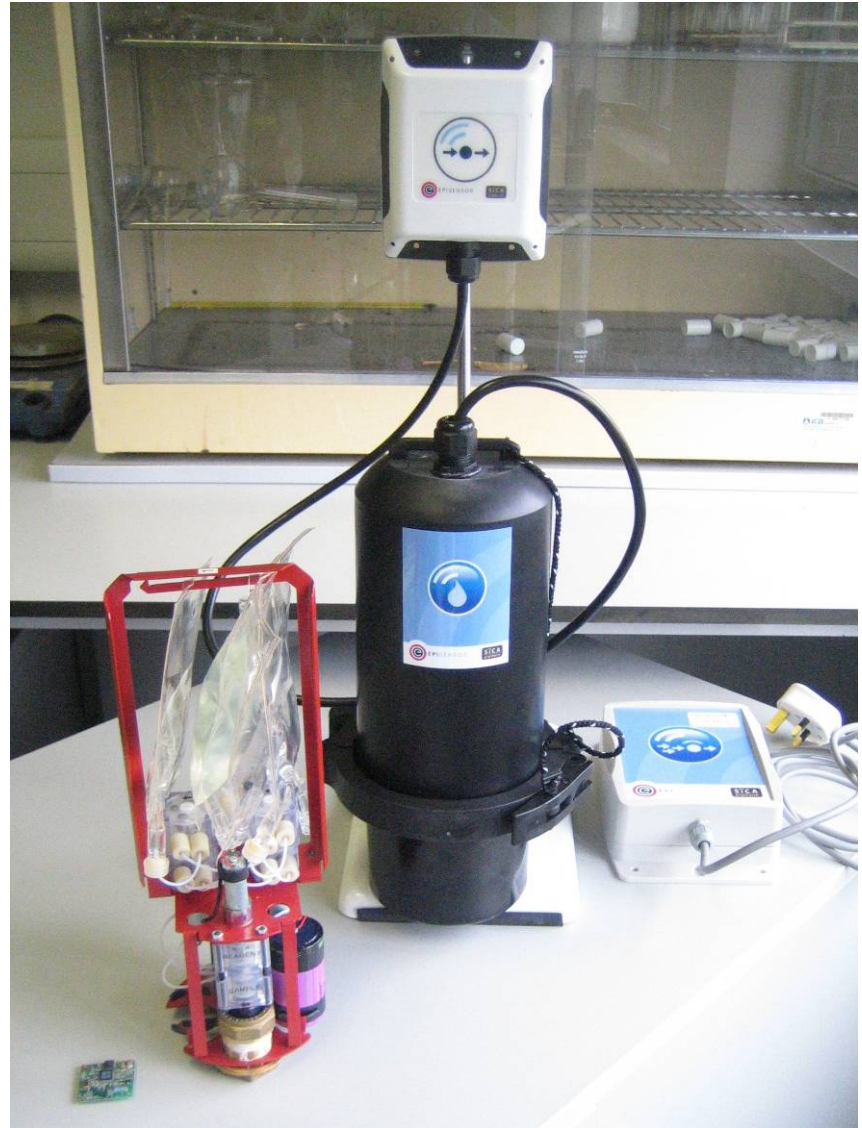




2nd Generation Analyser: Design



Sampling port





Deployment at Osberstown WWTP

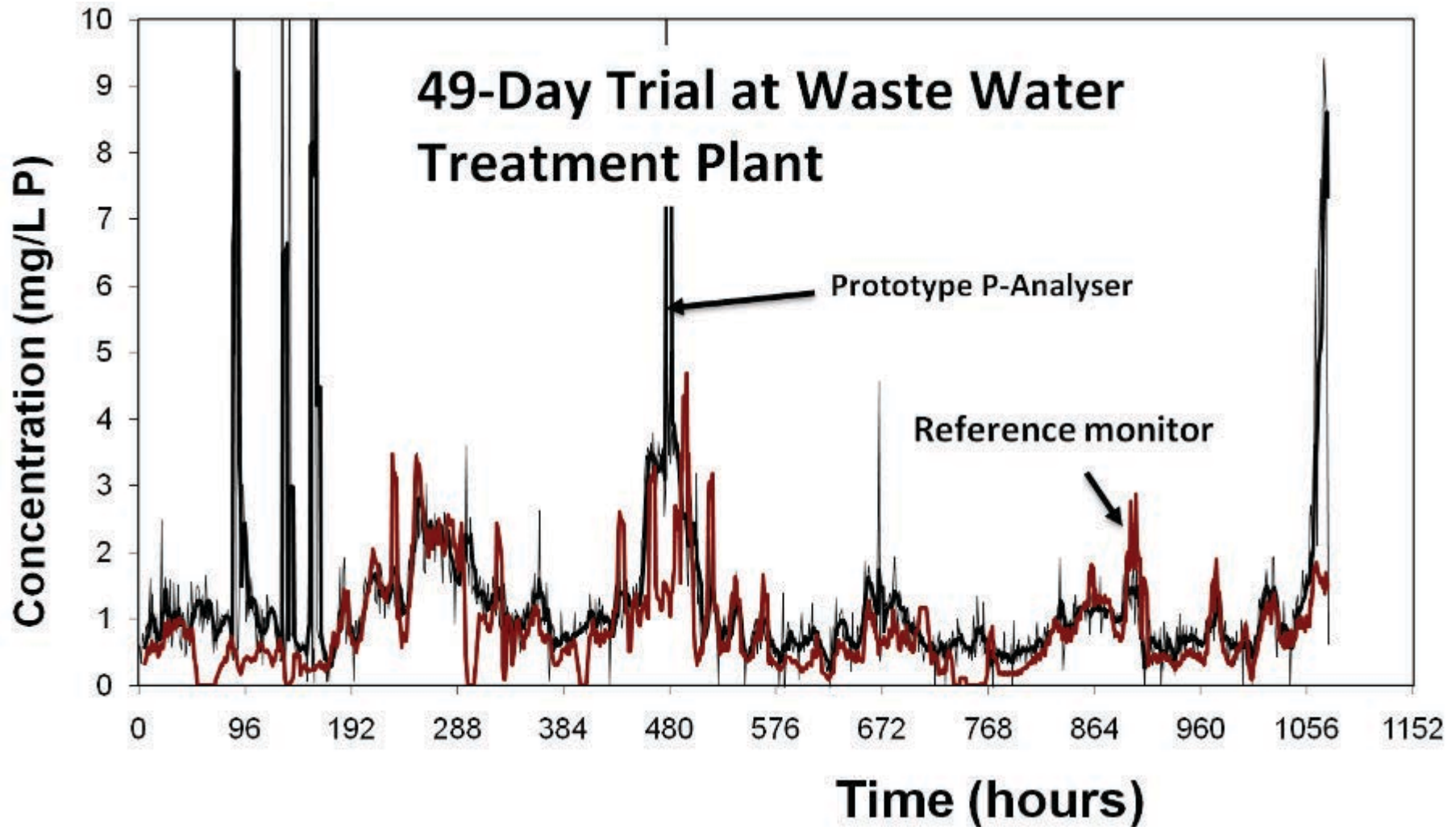


- Phosphate monitoring unit deployed
- System is fully immersed in the treatment tank
- Wireless communications unit linked by cable
- Data transmitted to web





Autonomous Chemical Analyser



Phosphate monitoring using the Yellow Method





Osberstown – 3 week deployment

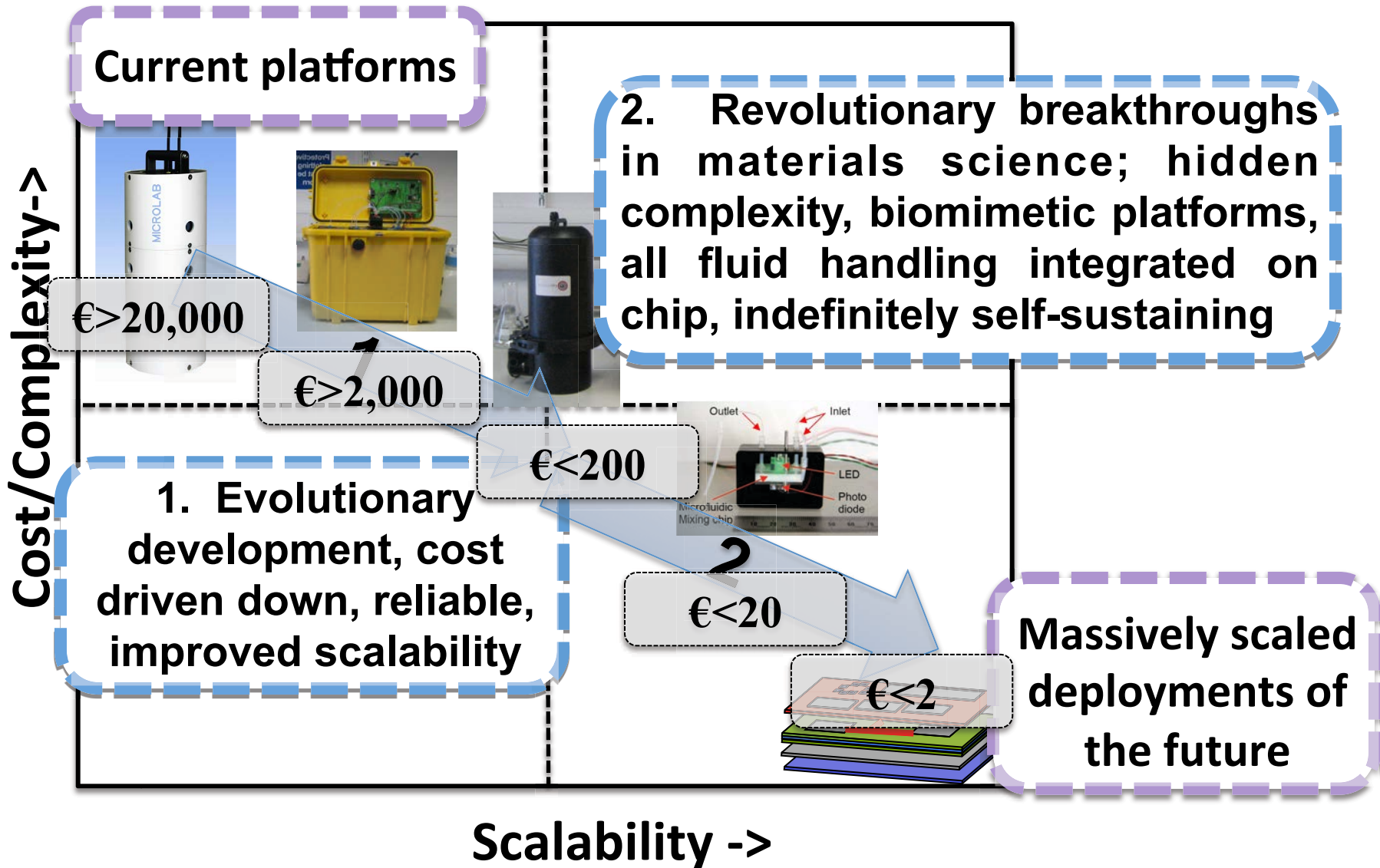


Biofouling of sensor surfaces is a major challenge for remote chemical sensing – both for the environment and for implantable sensors



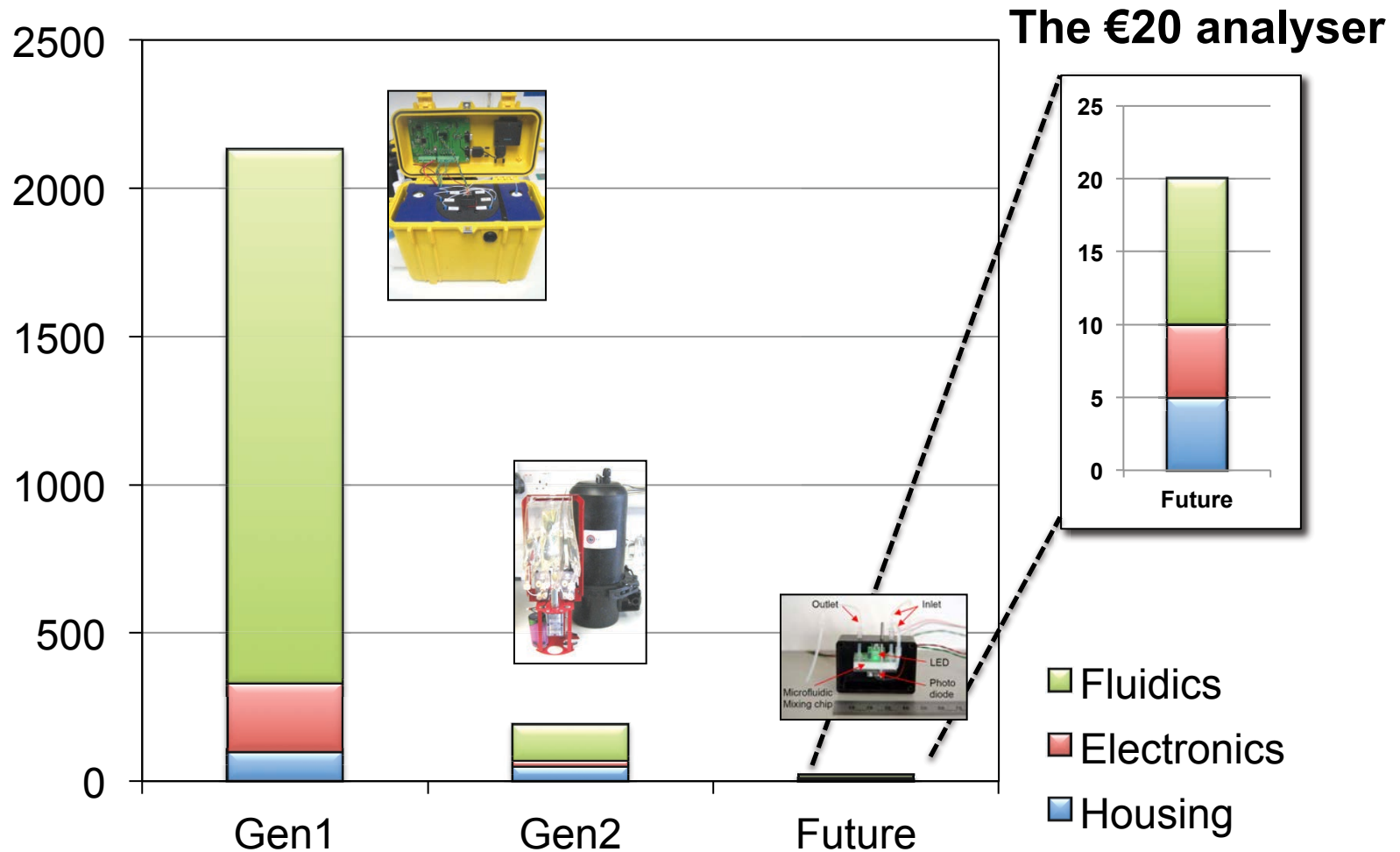


Achieving Scale-up





Cost Comparison Analyser (€)

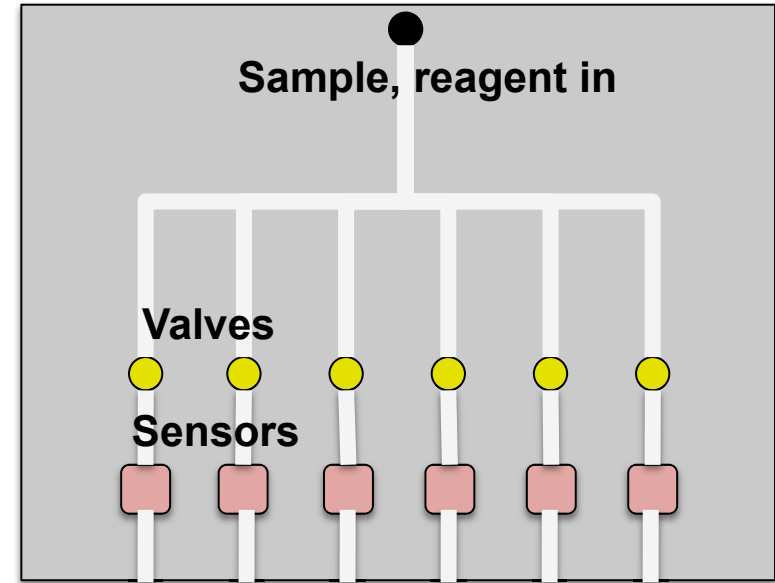




Extend Period of Use via Arrays of Sensors....?

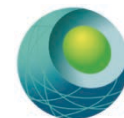


- If each sensor has an in-use lifetime of 1 week....
- And these sensors are very reproducible....
- And they are very stable in storage (up to several years)....



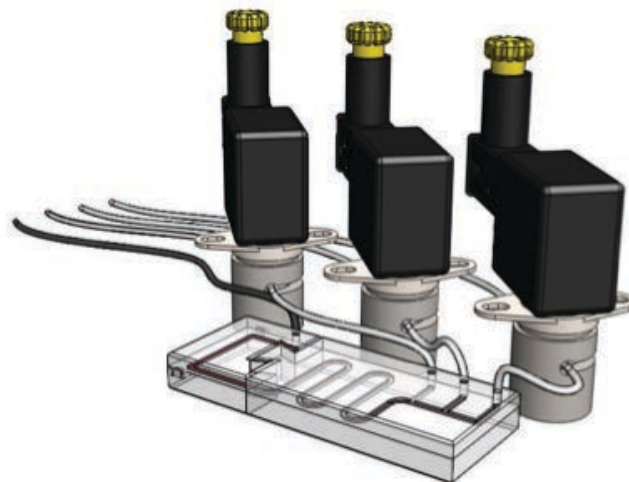
Then 50 sensors when used sequentially could provide an aggregated in-use lifetime of around 1 year

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

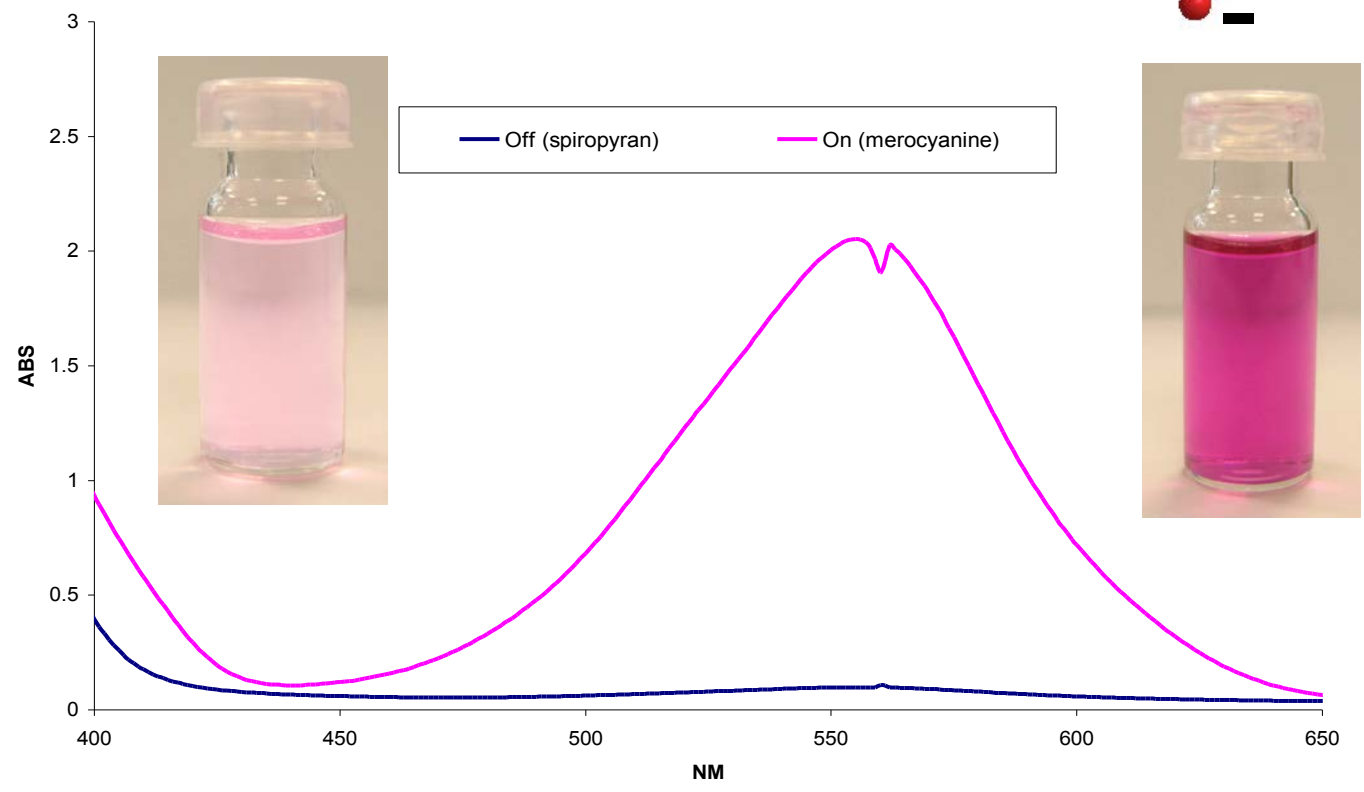
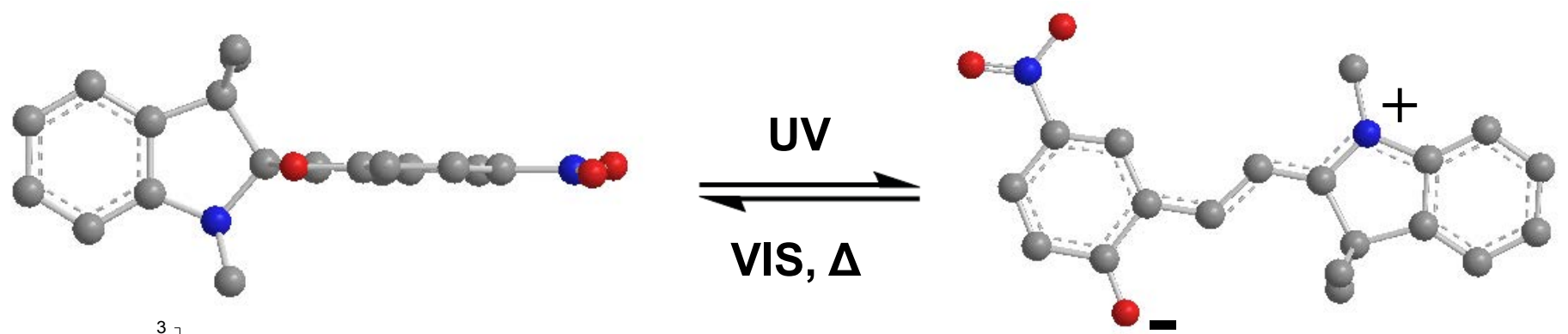
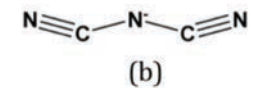
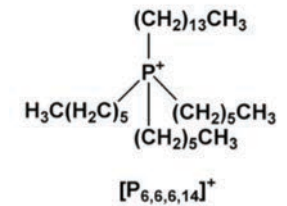
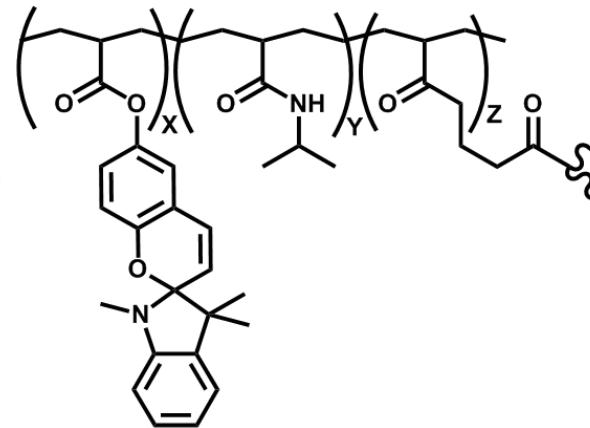
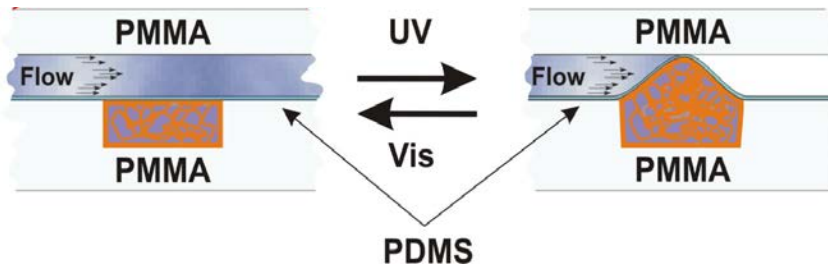
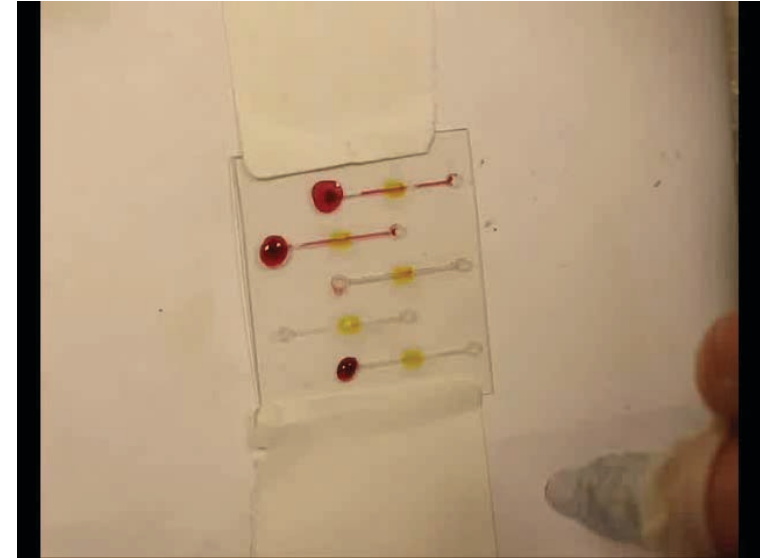
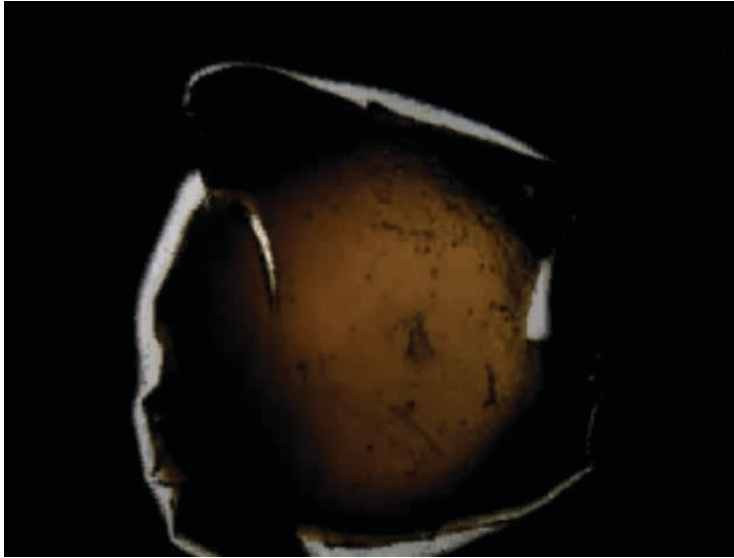




Photo-actuator polymers as microvalves in microfluidic systems



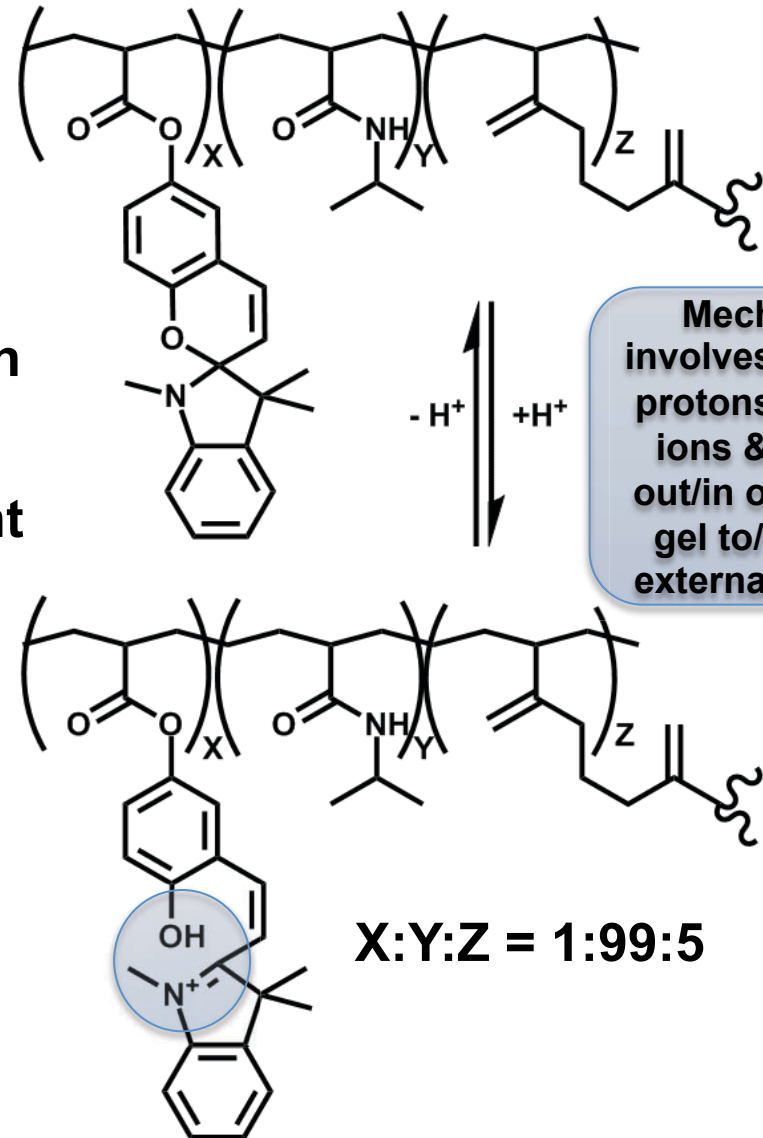
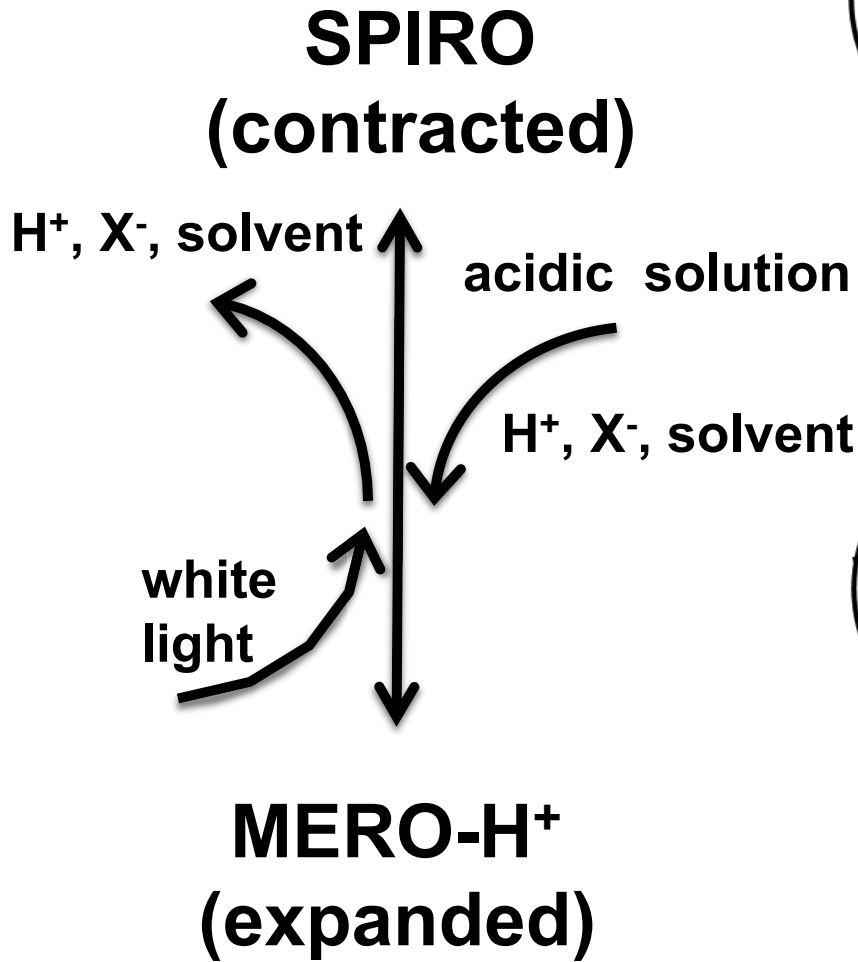
trihexyltetradecylphosphonium dicyanoamide $[\text{P}_{6,6,6,14}]^+[\text{dca}]^-$

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



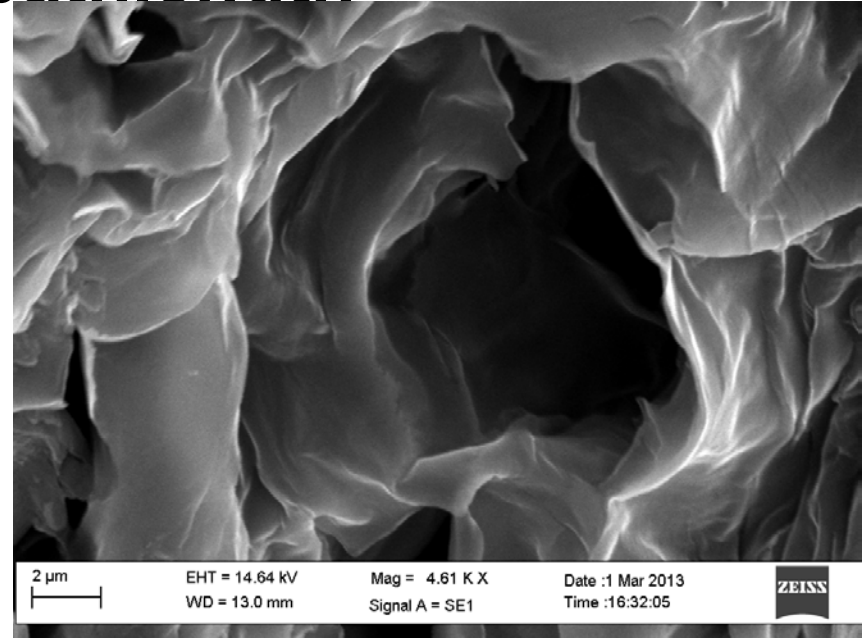
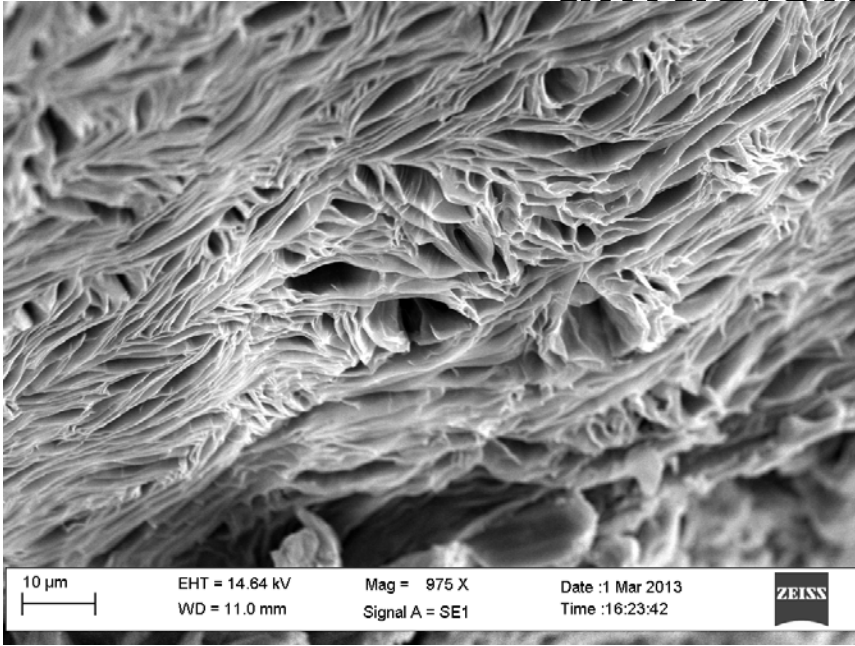


So far, so good: but what are the limitations?

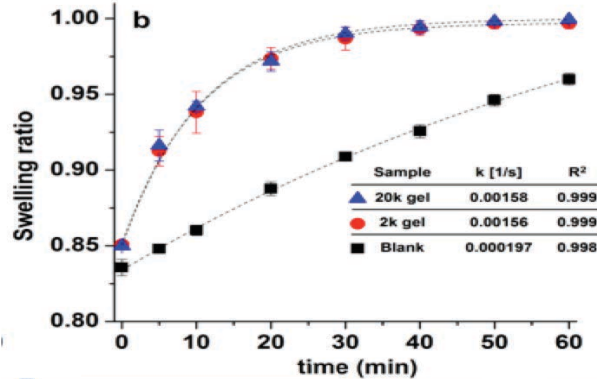
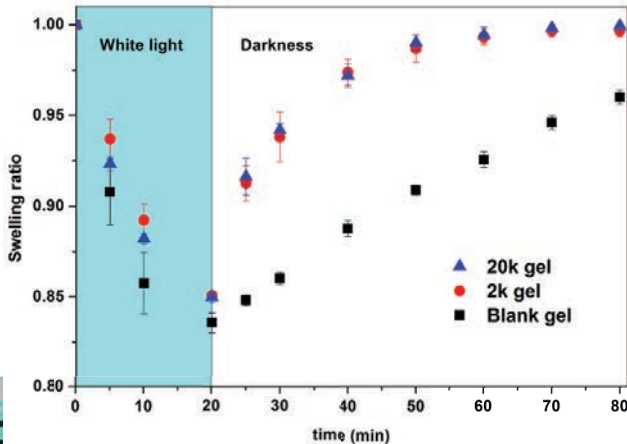
- Response time for re-swelling is slow - 10's of minutes due to diffusion mechanism
- Swelling requires protonation of the MC to MC-H⁺ within the ionogel by the external bathing solution – which must be acidic, typically pH 3
- These issues more or less limit the applicability of the valves to single use



Improve response time: Porous Gels → reduce diffusion pathlength



Highly porous pNIPAAm gel structures generated using PEG as the porogen. This dramatically increases the surface area to bulk ratio, reducing the diffusion pathlength for water to penetrate to the gel interior, which in turns results in faster swelling/contraction rates



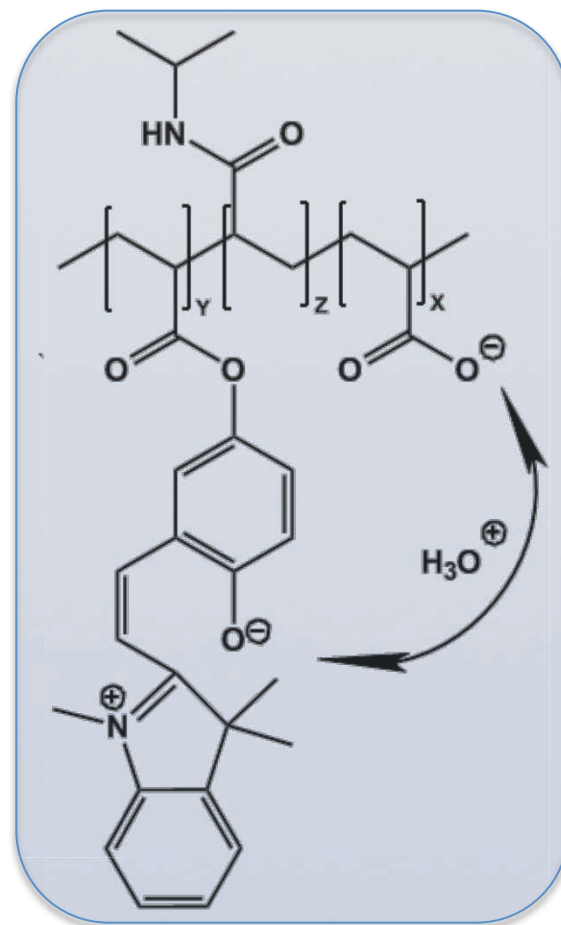
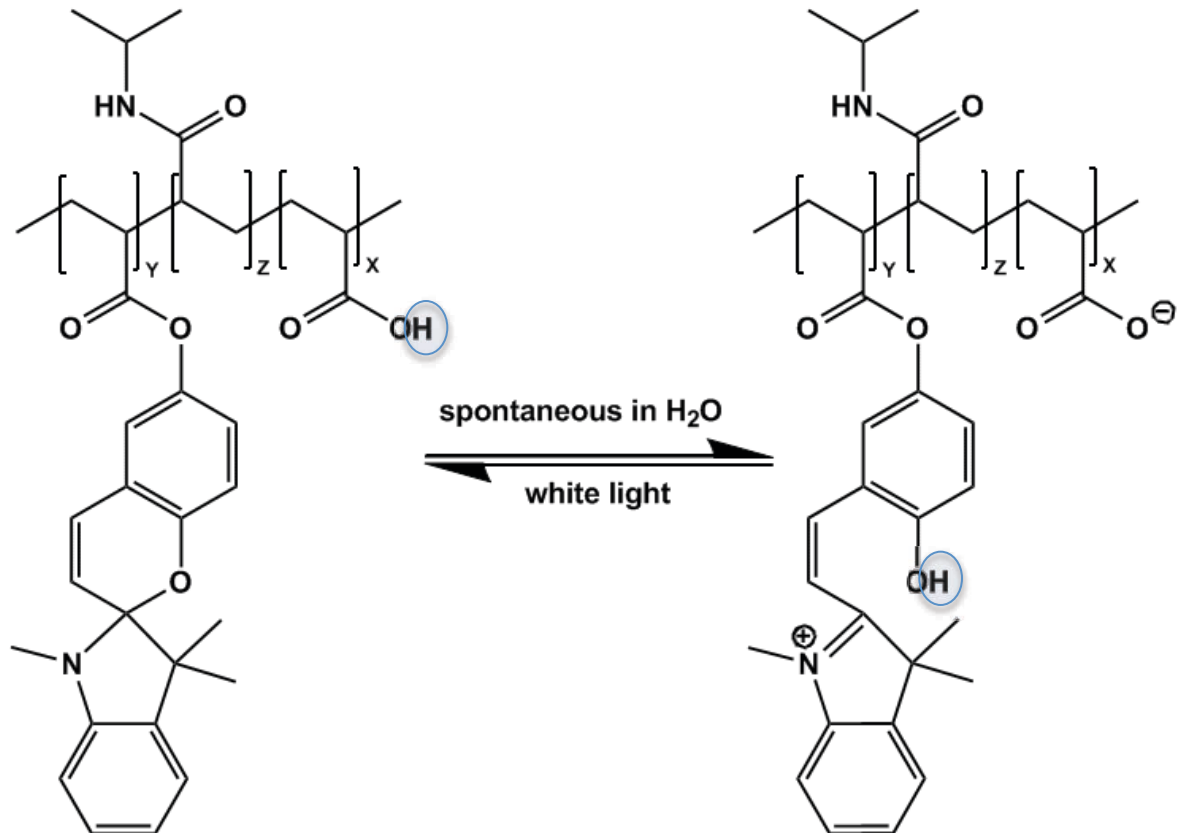
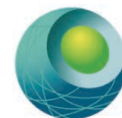
On the re-swelling side; highly porous gels now recover ca. an order of magnitude faster;

$k = 1.6 \times 10^{-3} \text{ S}^{-1}$
vs. $2.0 \times 10^{-4} \text{ S}^{-1}$



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





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

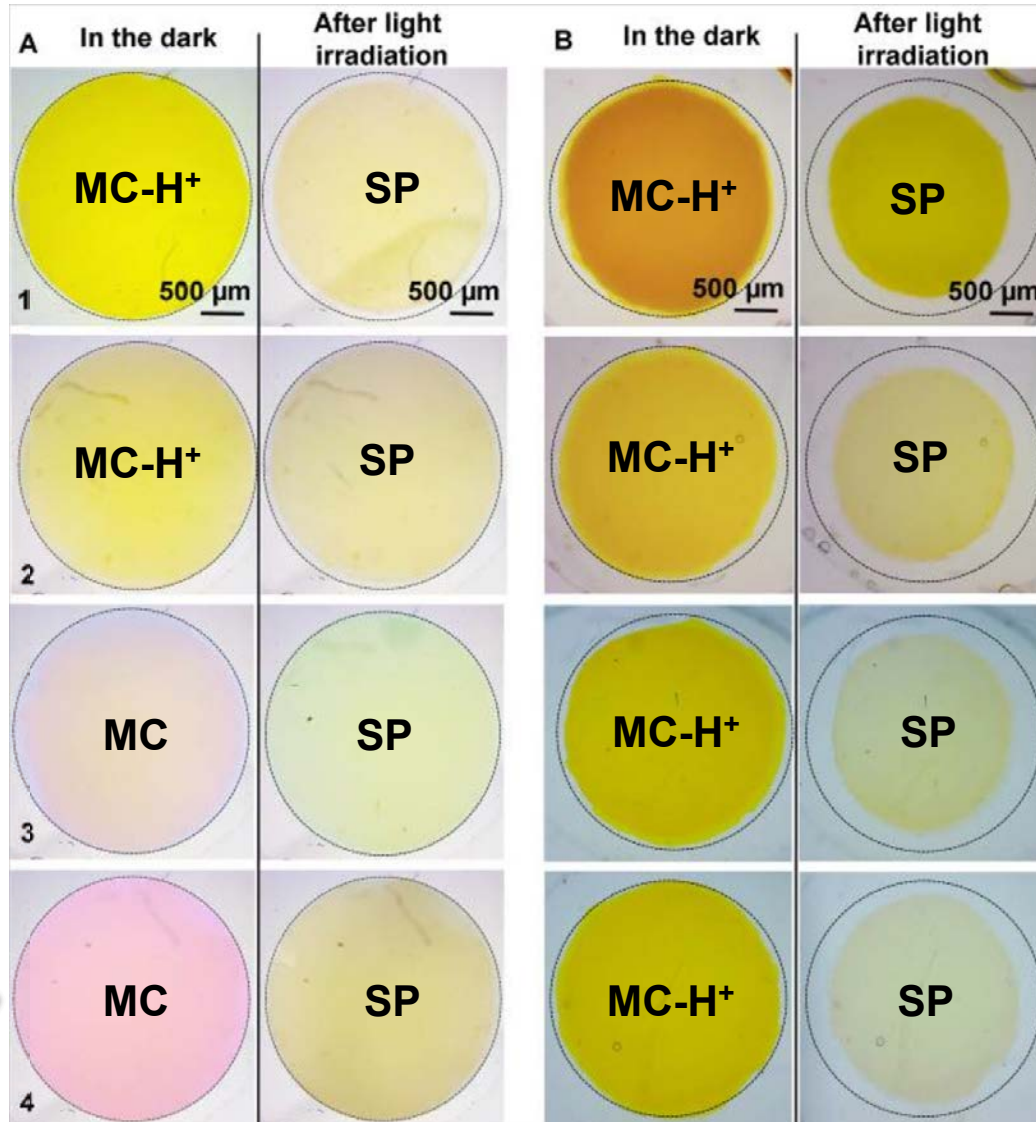
Switching changes from primarily

$MC-H^+ \rightarrow SP+H^+$

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

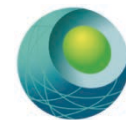
$MC-H^+ \rightarrow SP+H^+$

Gel actuation continues





Why move the solvent at all?

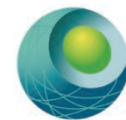


[sample]/mol l ⁻¹	Ratio H ₂ O/Sample
1.0x10 ⁻⁶	5.56x10 ⁷
1.0x10 ⁻⁹	5.56x10 ¹⁰
1.0x10 ⁻¹²	5.56x10 ¹³

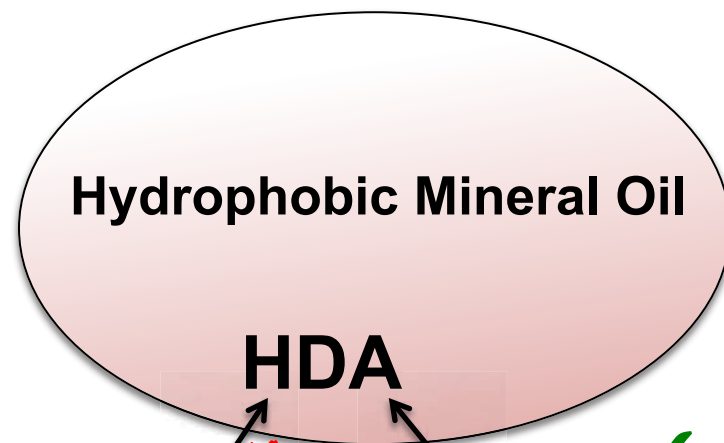
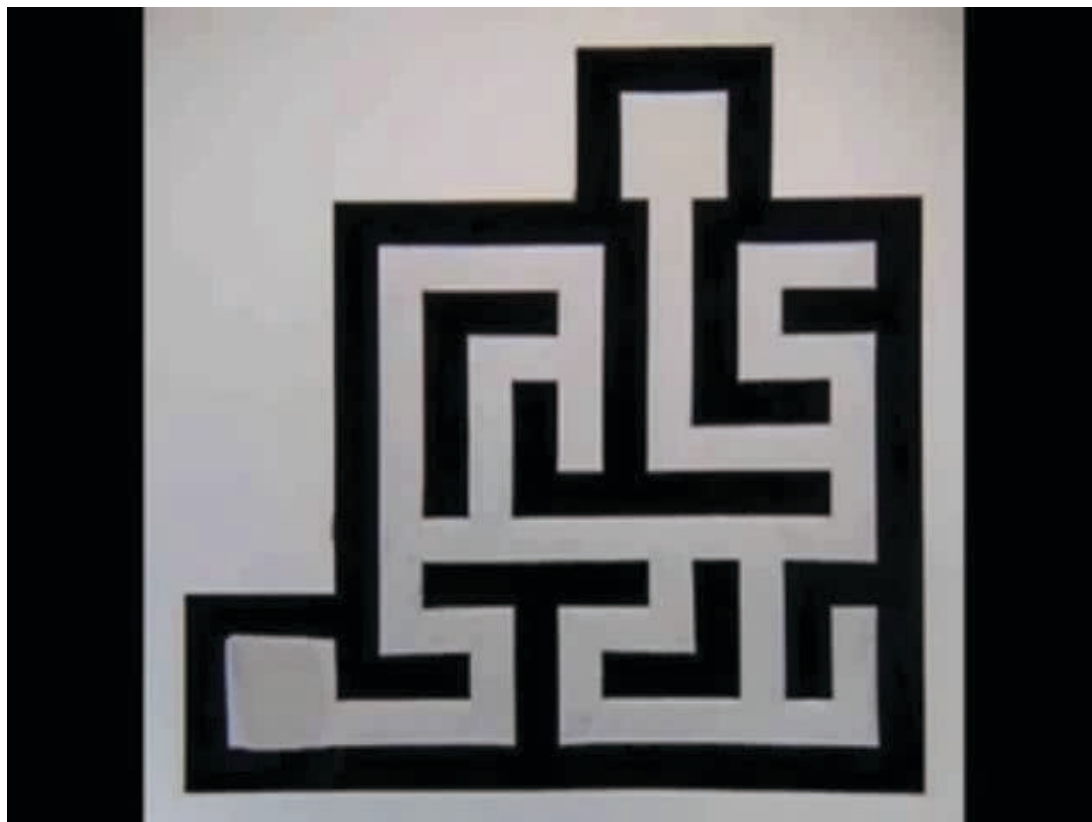
Strategy:

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



Chemotactic Systems



In a pH gradient, DA^- is preferentially transferred to the aqueous phase at the more basic side of the drop.

Published on Web 11/01/2010 (speed $\sim x4$): channels filled with KOH (pH 12.0-12.3 + surfactant; agarose gel soaked in HCl (pH 1.2) sets up the pH gradient; droplets of mineral oil or DCM containing 20-60% 2-hexyldecanoic acid + dye. Droplet speed ca. 1-10 mm/s; movement caused by convective flows arising from concentration gradient of HDA at droplet-air interface (greater concentration of DA^- towards higher pH side); $\text{HDA} \leftrightarrow \text{H}^+ + \text{DA}^-$

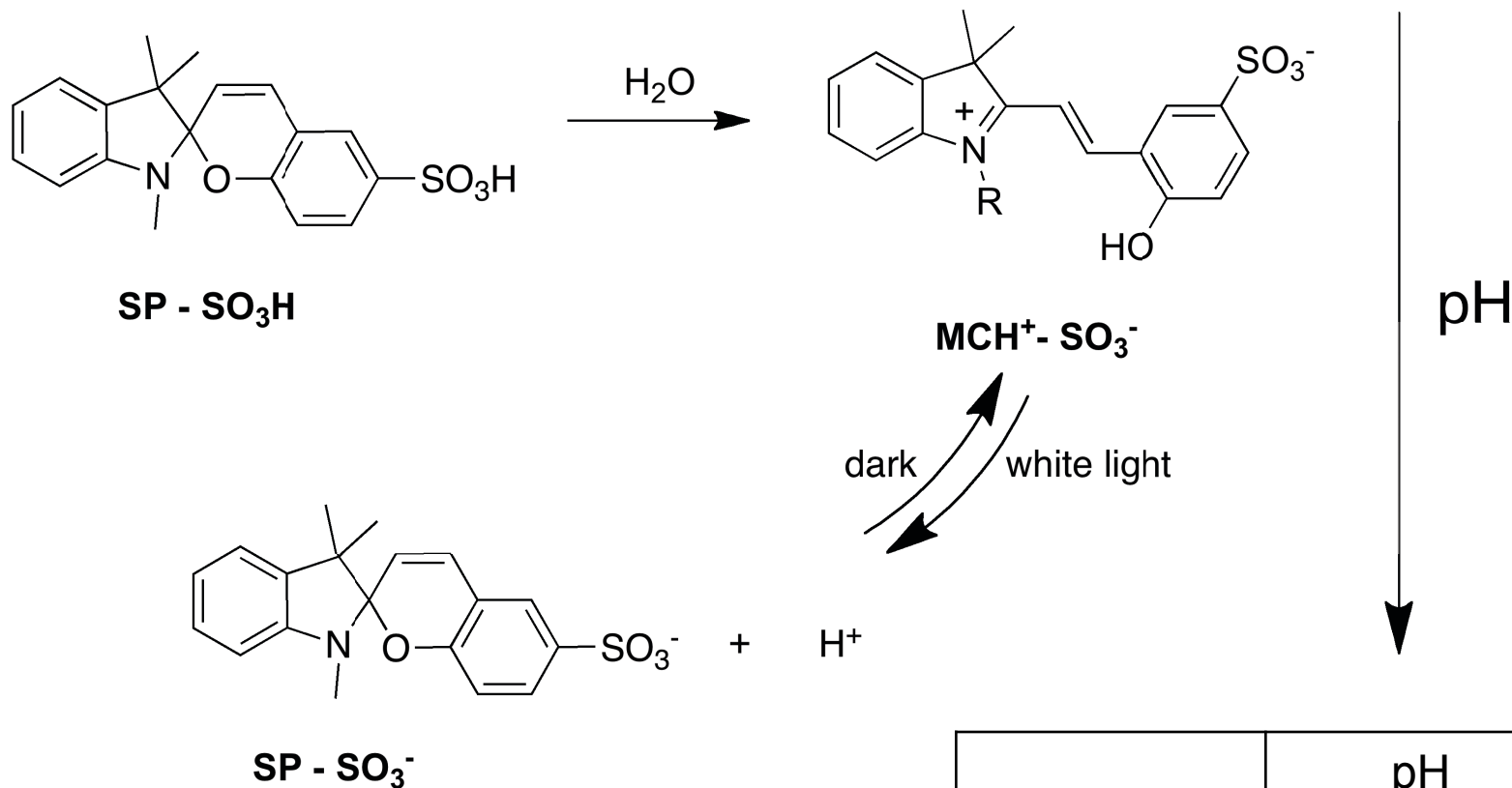
Maze Solving by Chemotactic Droplets; Istvan Lagzi, Siowling Soh, Paul J. Wesson, Kevin P. Browne, and Bartosz A. Grzybowski; *J. AM. CHEM. SOC.* 2010, 132, 1198–1199

Fuerstman, M. J.; Deschatelets, P.; Kane, R.; Schwartz, A.; Kenis, P. J. A.; Deutch, J. M.; Whitesides, G. M. *Langmuir* 2003, 19, 4714.





Photo-modulation of pH



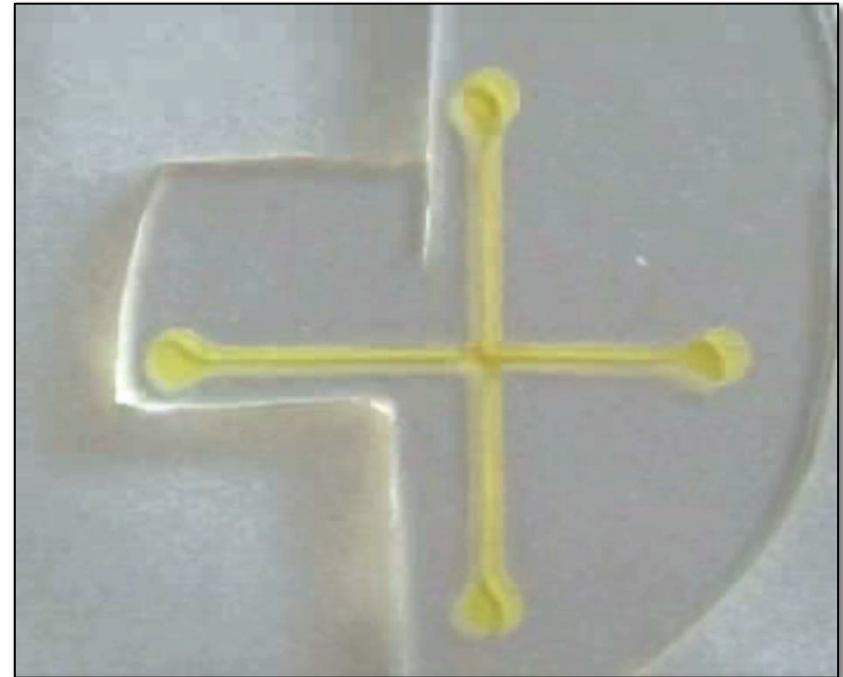
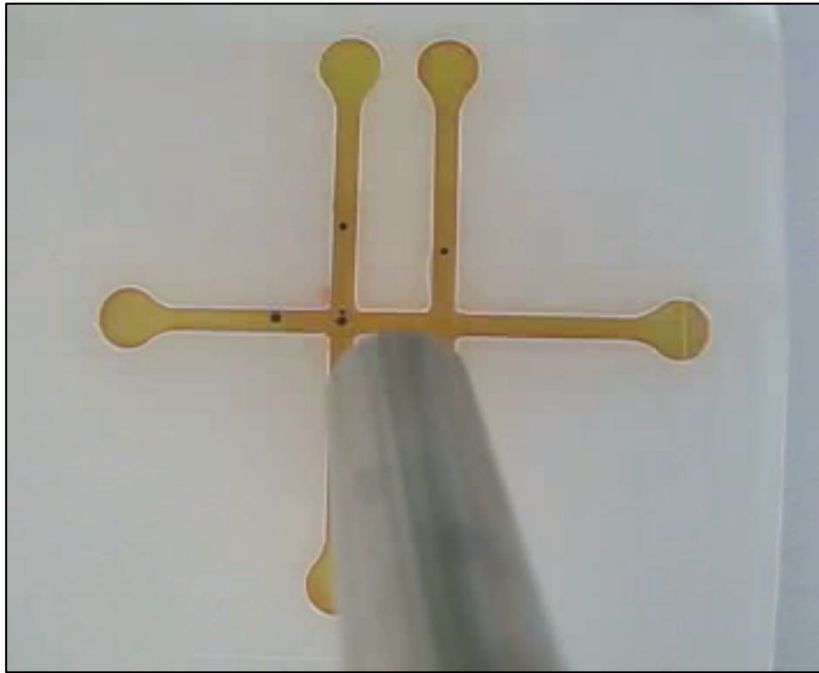
Channel Solution: Spiropyran Sulfonic Acid 10^{-3}M (H_2O)

	pH
H_2O	6.5
$\text{MCH}^+\text{-SO}_3^-$	4.8
SP-SO_3^-	3.4



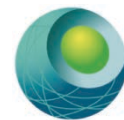


Movement of Droplets in Channels using Light



- 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





Mechanism of Photo-Stimulated Droplet Movement

(with David Officer, UOW)

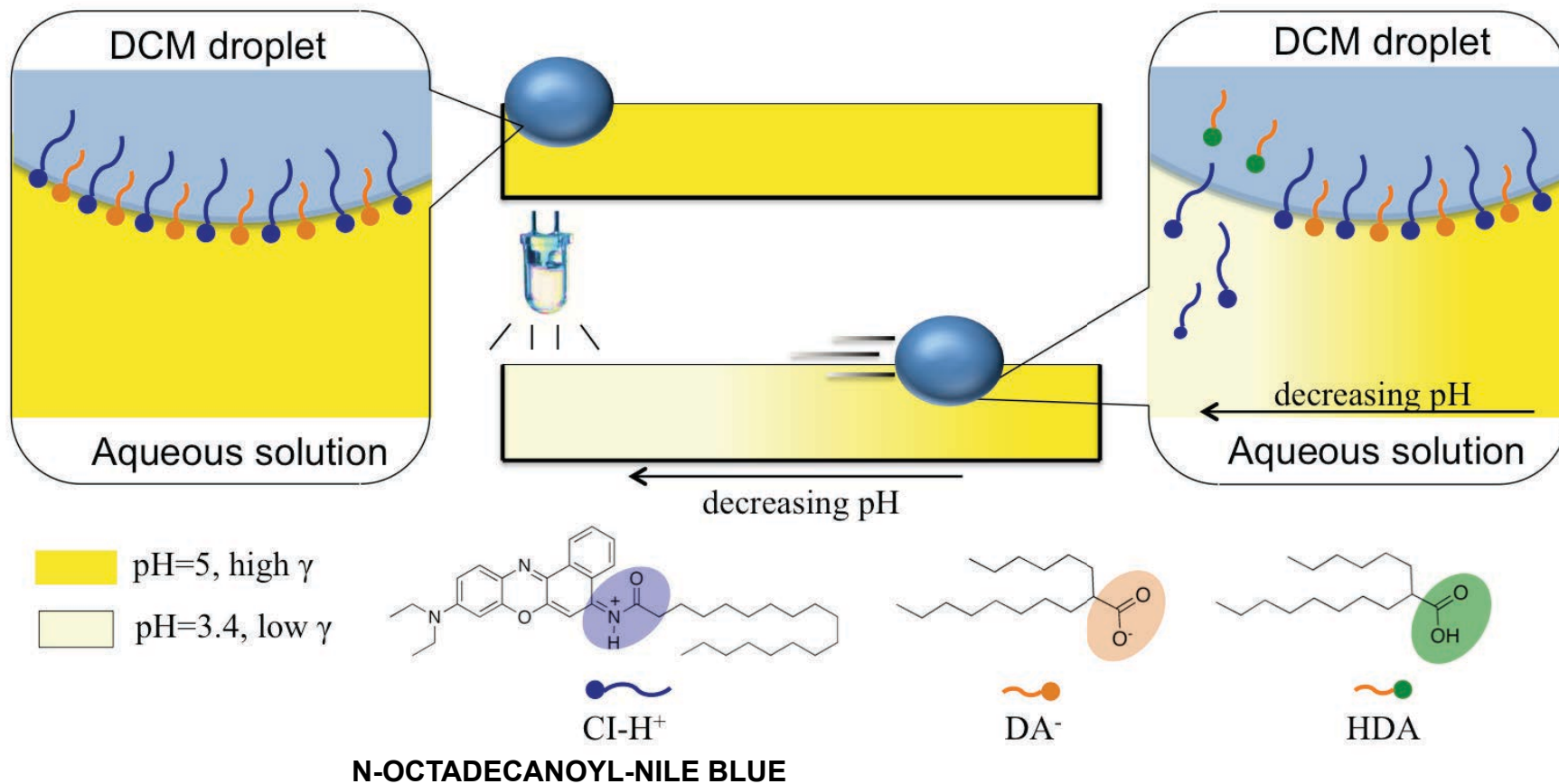
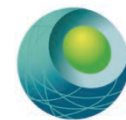


Photo-Chemopropulsion – Light-Stimulated Movement of Microdroplets, Larisa Florea, Klaudia Wagner, Pawel Wagner, Gordon G. Wallace, Fernando Benito-Lopez, David L. Officer, and Dermot Diamond, *Adv. Mater.* 2014, DOI: 10.1002/adma.201403007





Photocontrol of Assembly and Subsequent Switching of Surface Features



ACS APPLIED MATERIALS & INTERFACES

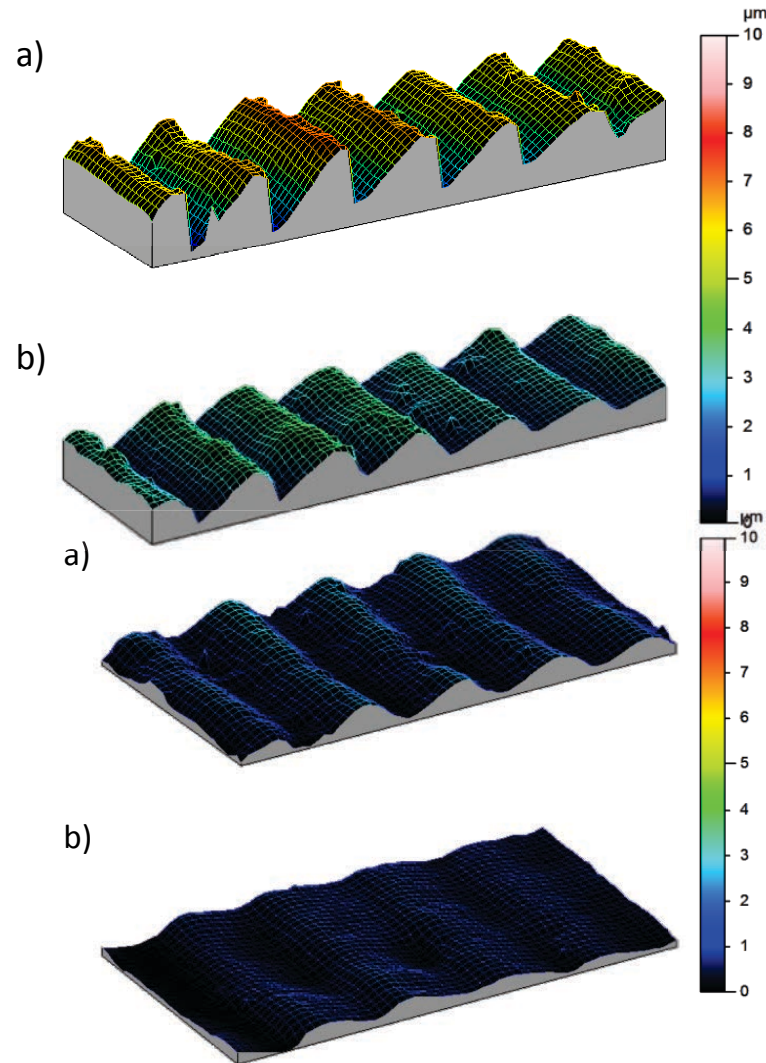
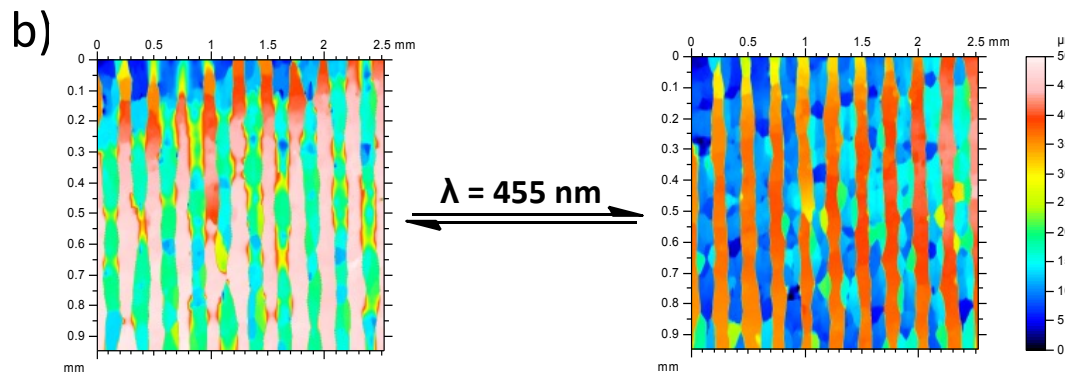
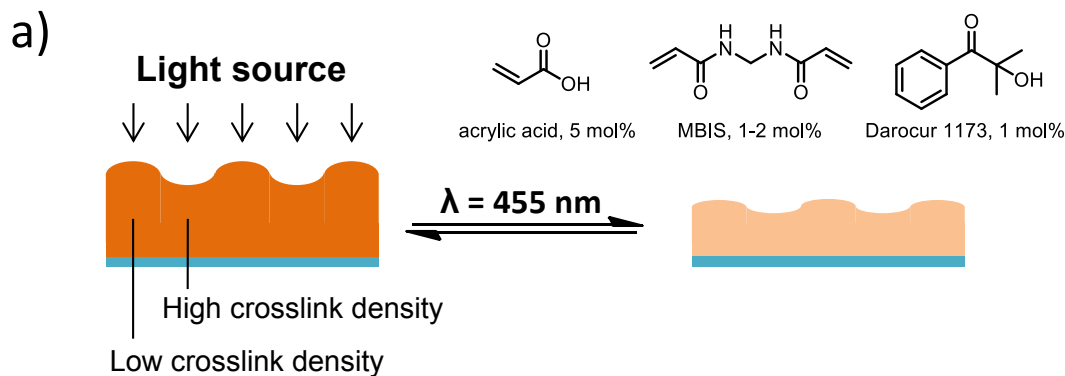
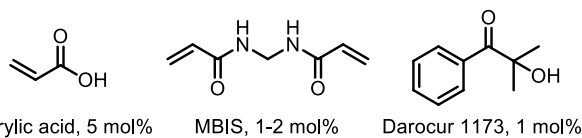
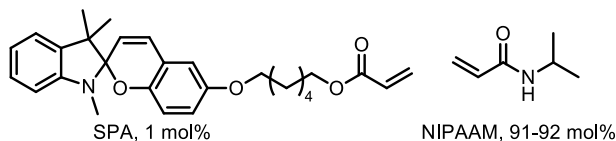
Research Article

www.acsami.org

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

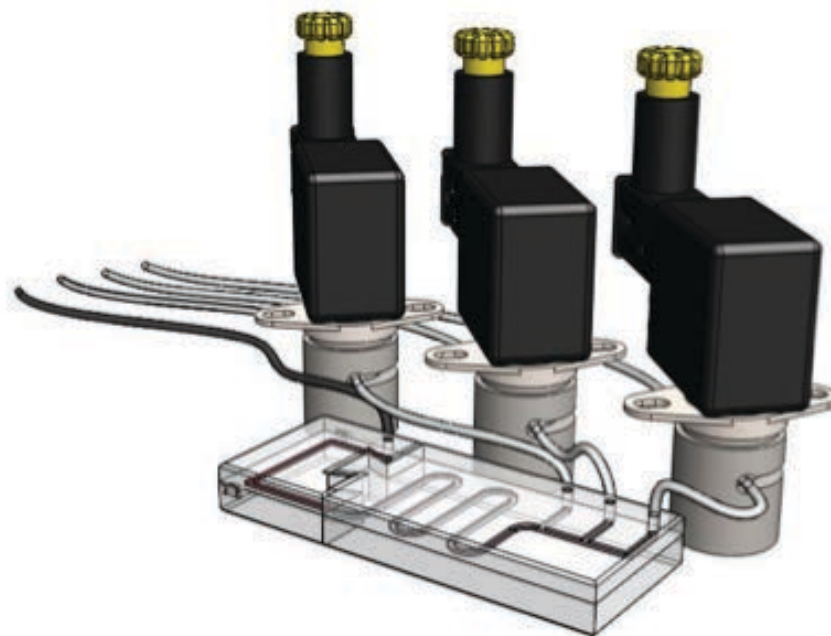
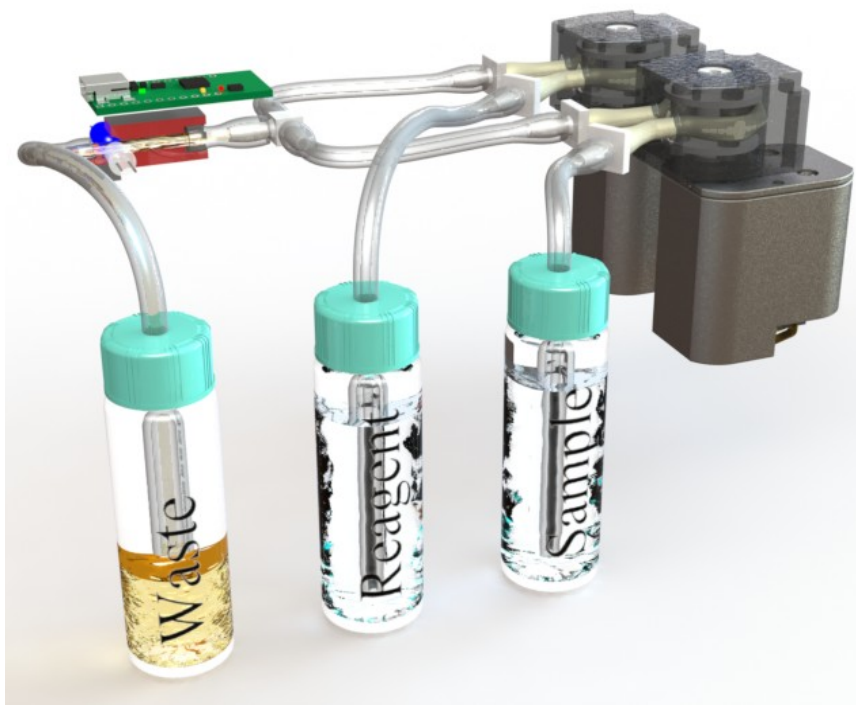
Photoswitchable Ratchet Surface Topographies Based on Self-Protonating Spiropyran–NIPAAm Hydrogels

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



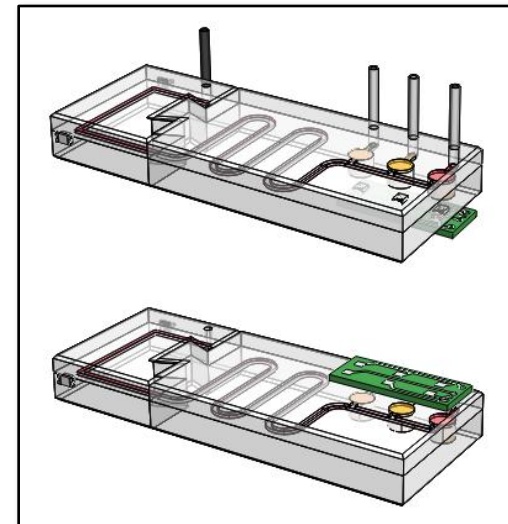
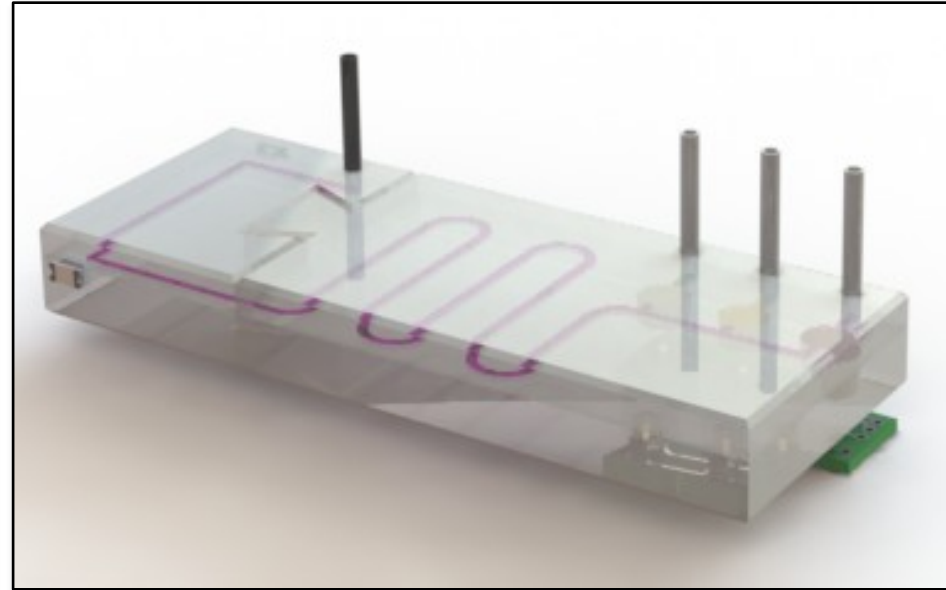
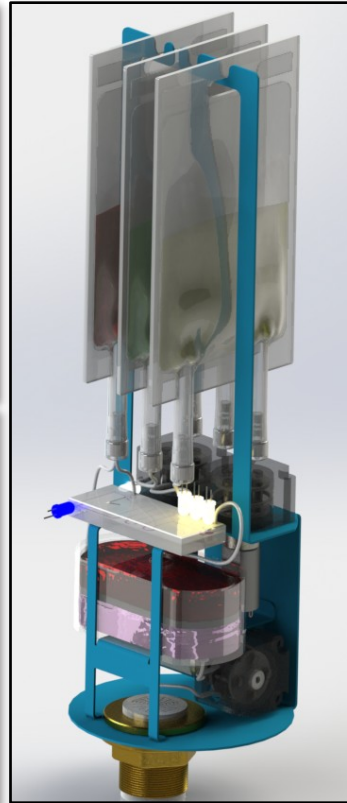
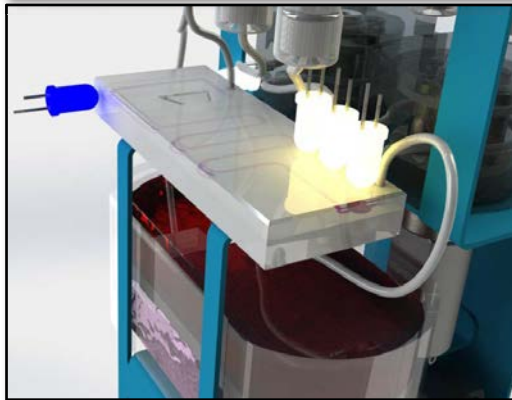
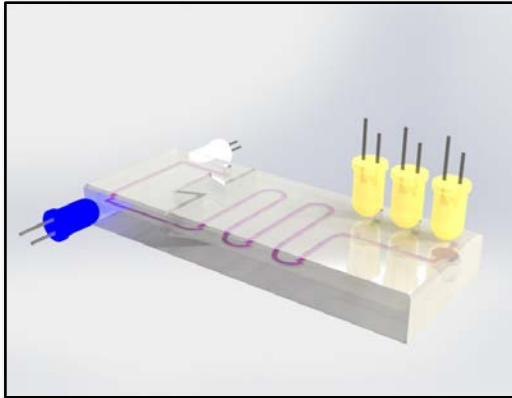


Can we go from this:





To Photo-Fluidics & Detection



- **Fluidic handling completely integrated into the microfluidic chip**
 - Valves actuated remotely using light (LEDs)
 - Detection is via LED colorimetric measurements
 - Photo-controlled uptake and release





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

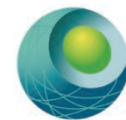
Integration and commercialization

• O. Martimort

Dissemination and Outreach

• T. Simmons (Eurice)

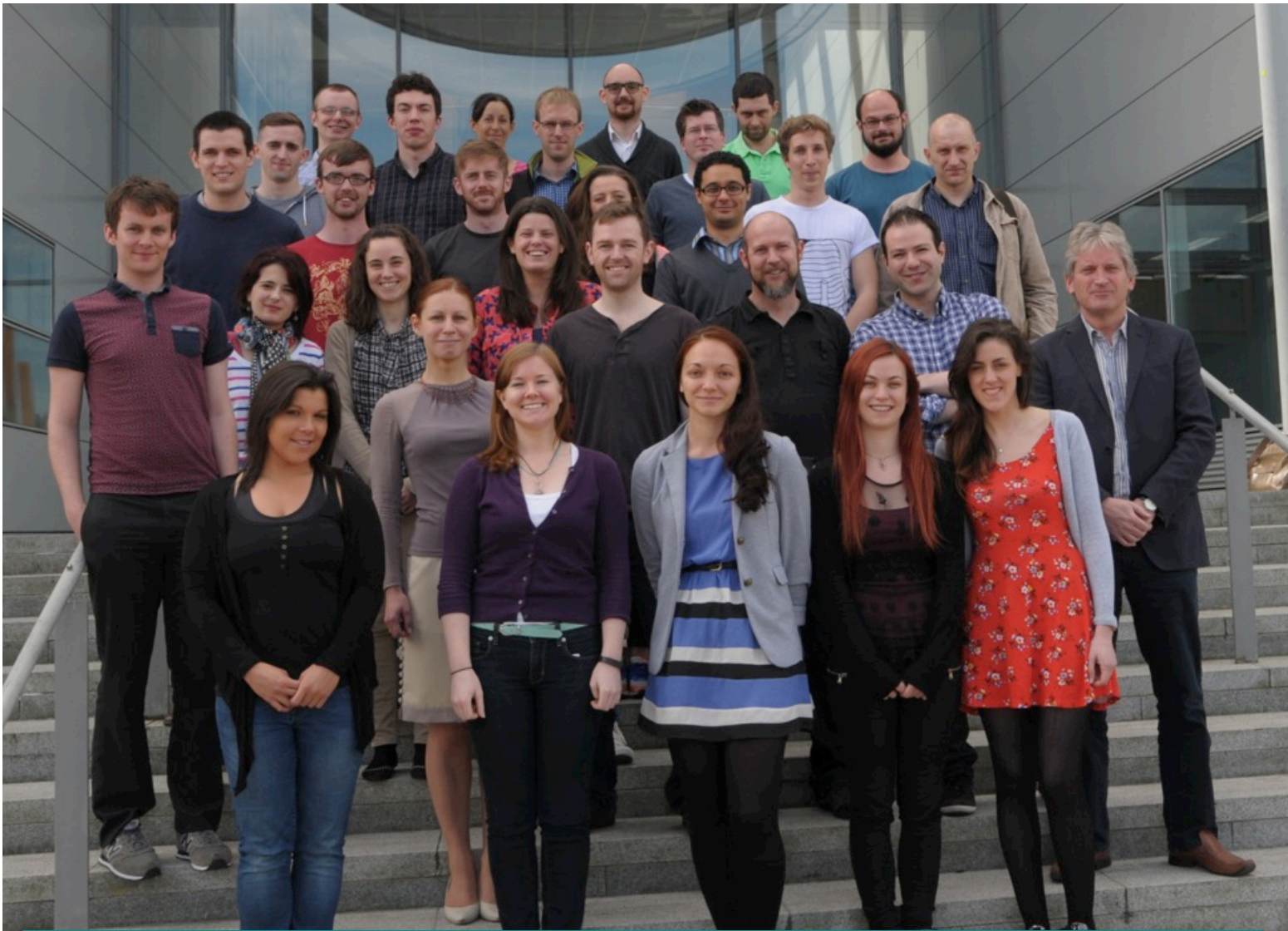




Time to re-think the game!!!

- **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!



Thanks for listening



OÉ Gaillimh
NUI Galway

