CLARITY
clarity-centre.org

"Stimuli-Responsive Materials: The Fundamental Building Block for New Concepts in Polymer-Based Sensors and Actuators"

Dermot Diamond

National Centre for Sensor Research

Dublin City University

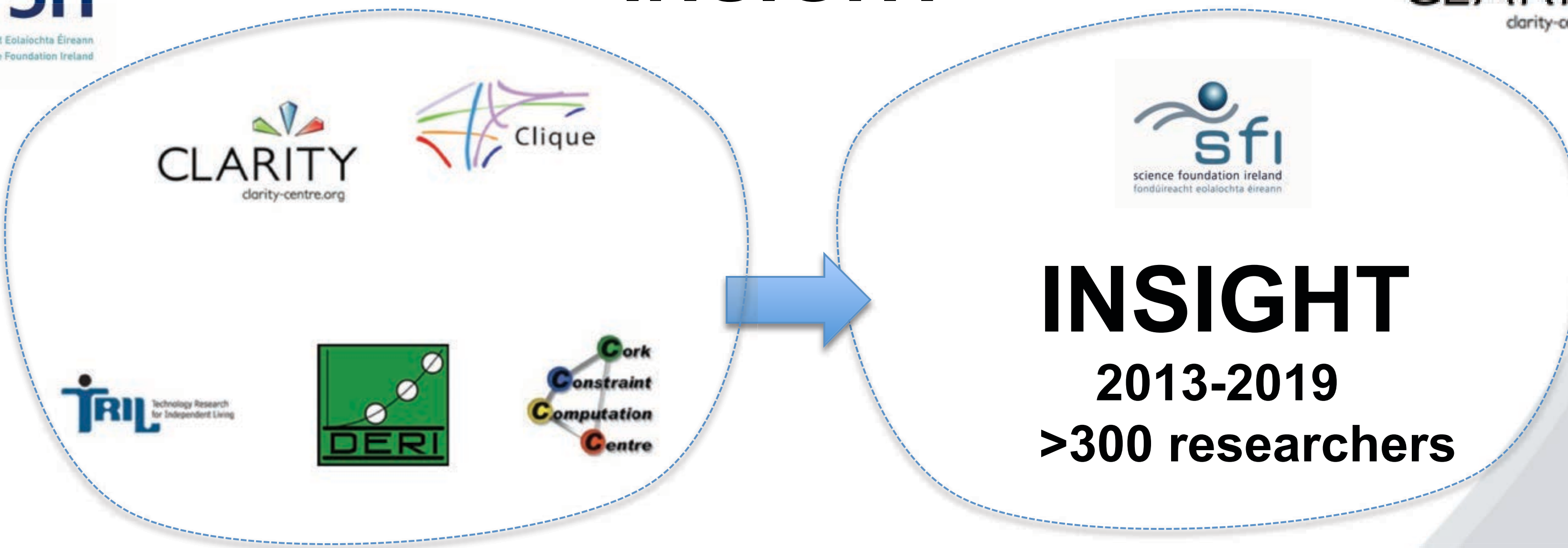
presented at the

RSC Analytical Awards Symposium

Dublin City University

November 27 2013

INSIGHT



- €45 million SFI + ca. €30 million industry
- July 2013-June 2019
- ‘Big Data’; Health focus (inc. exercise, sports, rehabilitation, event detection, clinical applications, cloud database tools)
- Grow dynamically from ‘core’ research through multiple targeted projects and ‘spokes’

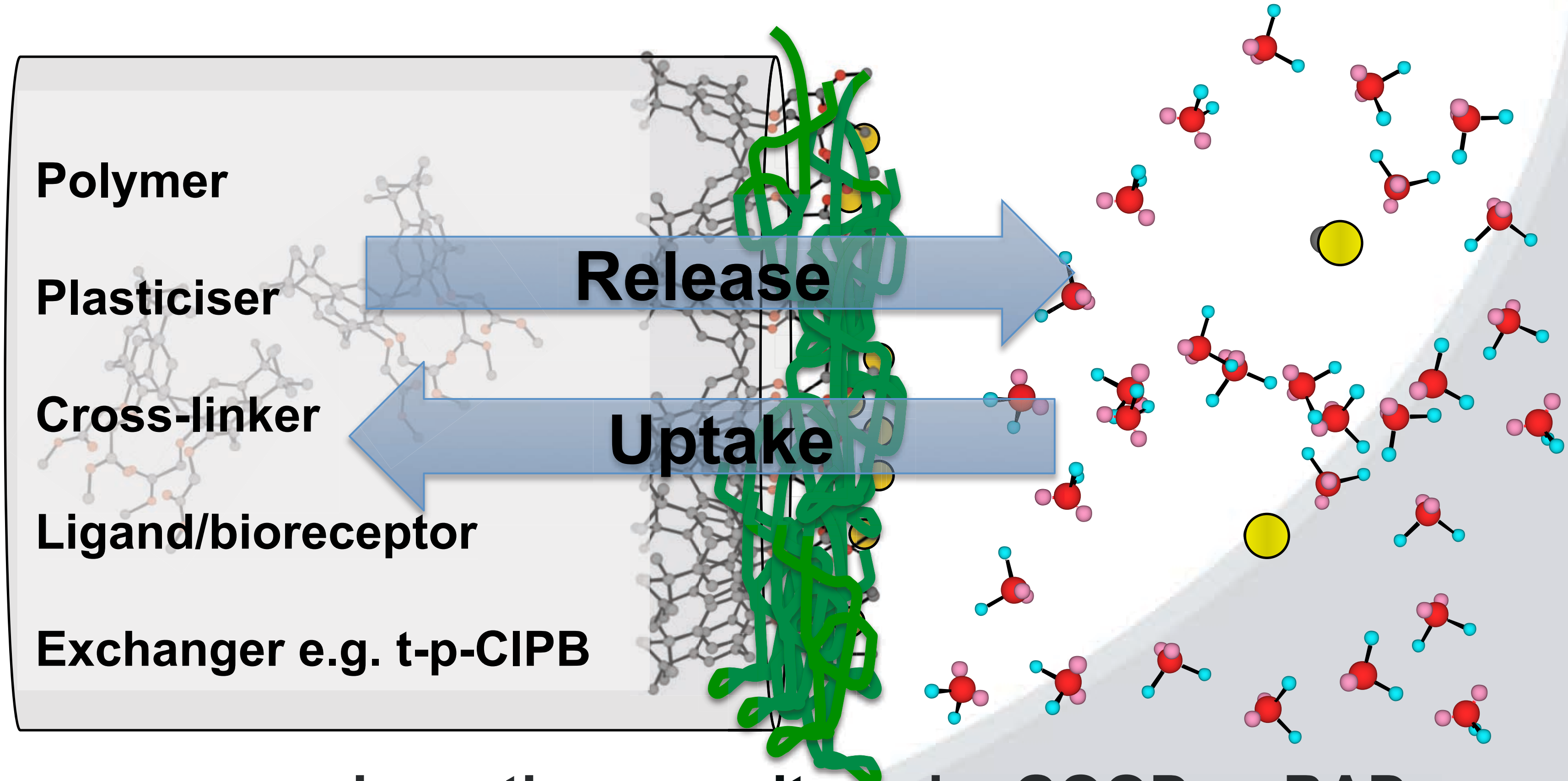
Sensors and Actuators…..

CLARITY
clarity-centre.org

- Polymer (soft membrane based)
- Both require control of interfacial exchanges of charged species and neutral (e.g. solvent) molecules
- For chemo/bio-sensors, a selective exchange or binding process for a particular target species is critical
- For polymer actuators, rapid exchange of solvent is important for fast swelling/ contraction

Control of membrane interfacial exchange & binding processes

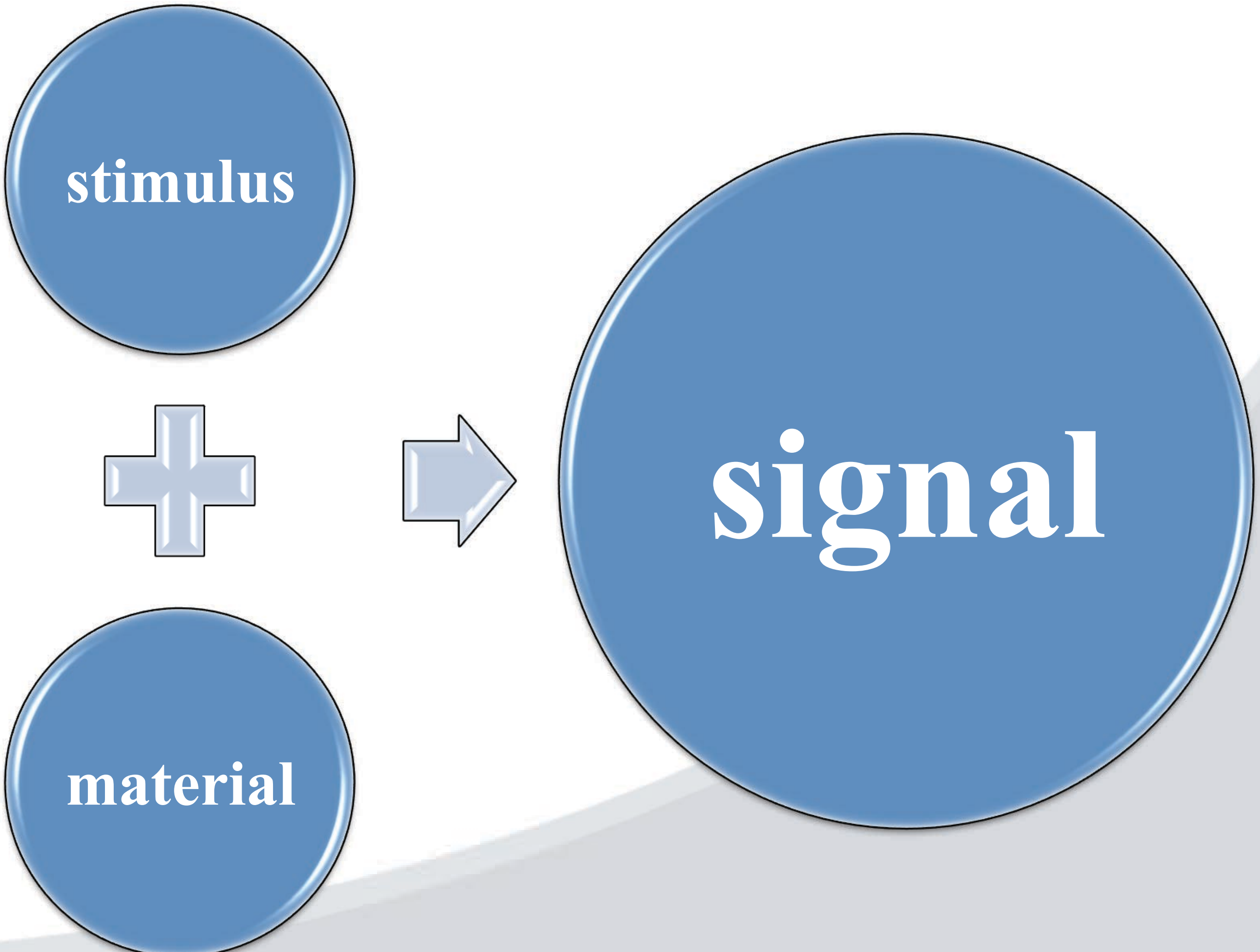
CLARITY
clarity-centre.org



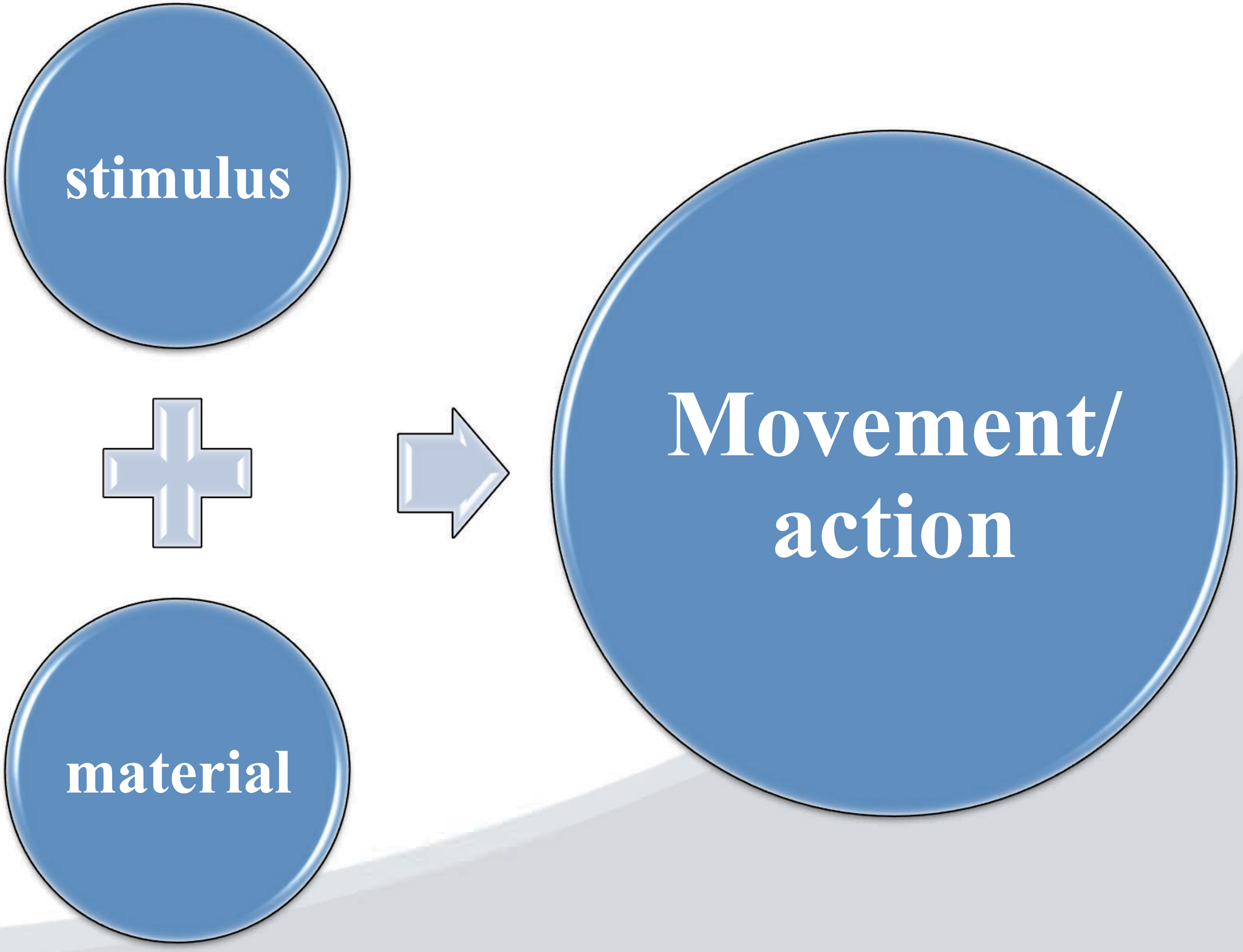
These processes have the capacity to be GOOD or BAD
The key is our ability TO CONTROL them!

- Release is BAD! Changes membrane composition which changes behaviour and can give rise to toxicity issues
- Uptake is GOOD! Facilitates swelling/contraction (actuation), sensing, accumulation of species
- Release is GOOD! Controlled release e.g. drugs, toxins

sensor

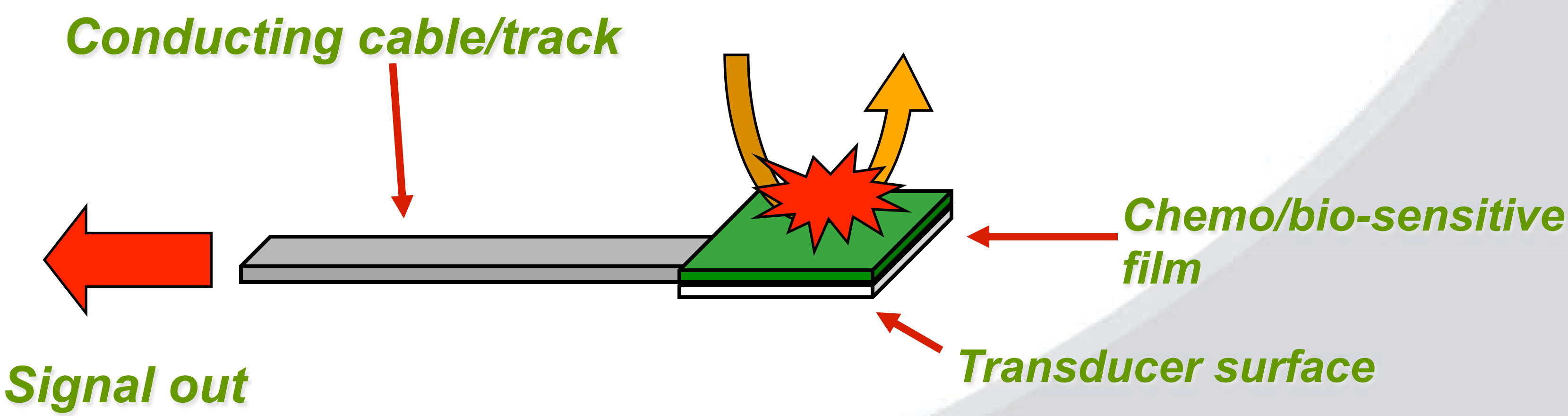


Actuator



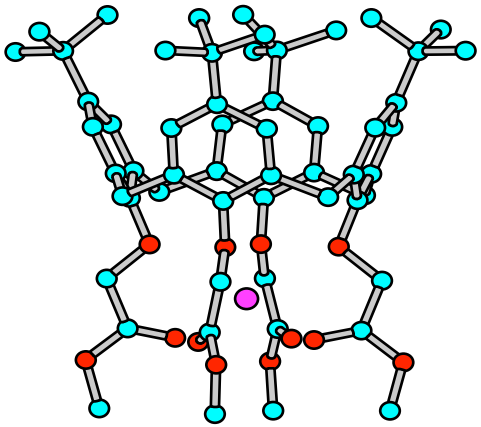
What is a Chemo/Bio-Sensor?

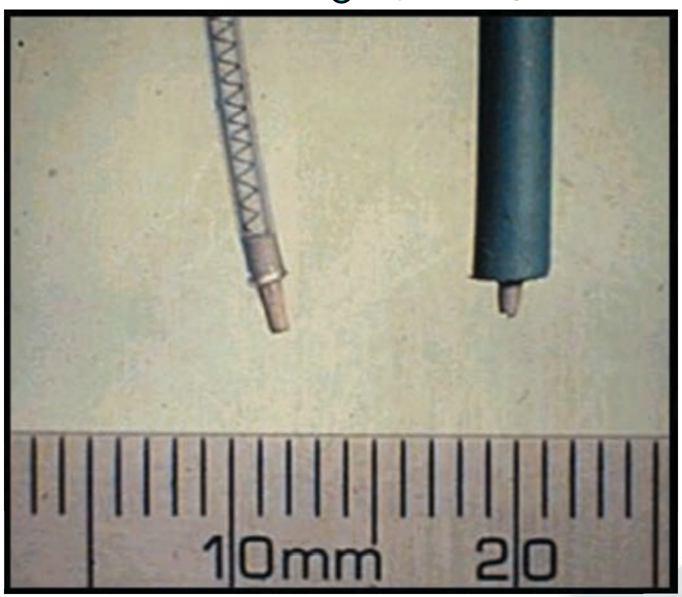
'a device, consisting of a transducer and a chemo/bio-sensitive film/membrane, that generates a signal related to the concentration of particular target analyte in a given sample'



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**)

Blood Analysis; Implantible Sensors





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

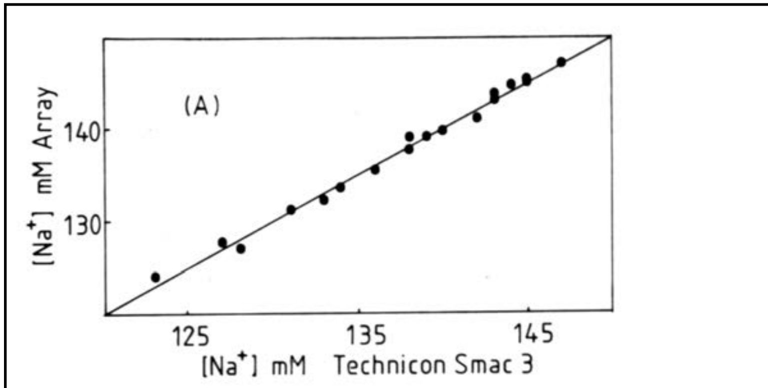
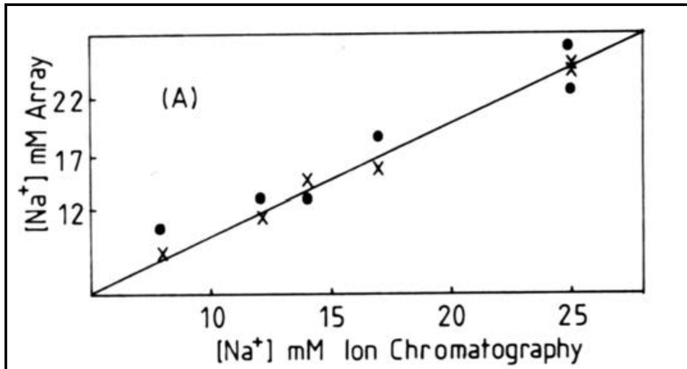


Fig. 3. Comparison of plasma sodium analysis using the array-FIA approach with a SMAC analyser. Good correlation without bias is obtained [5].

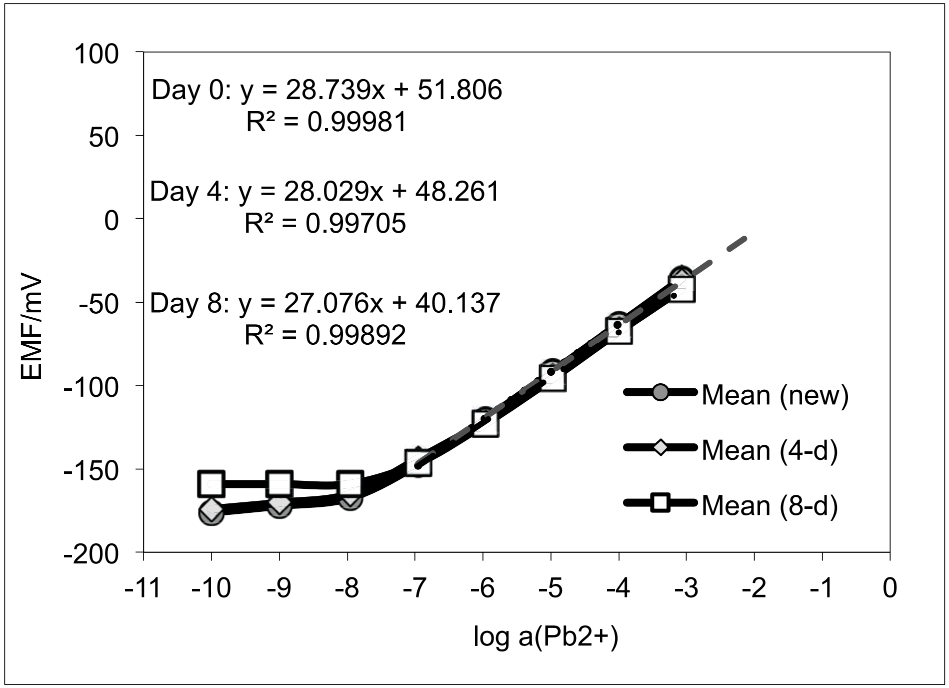


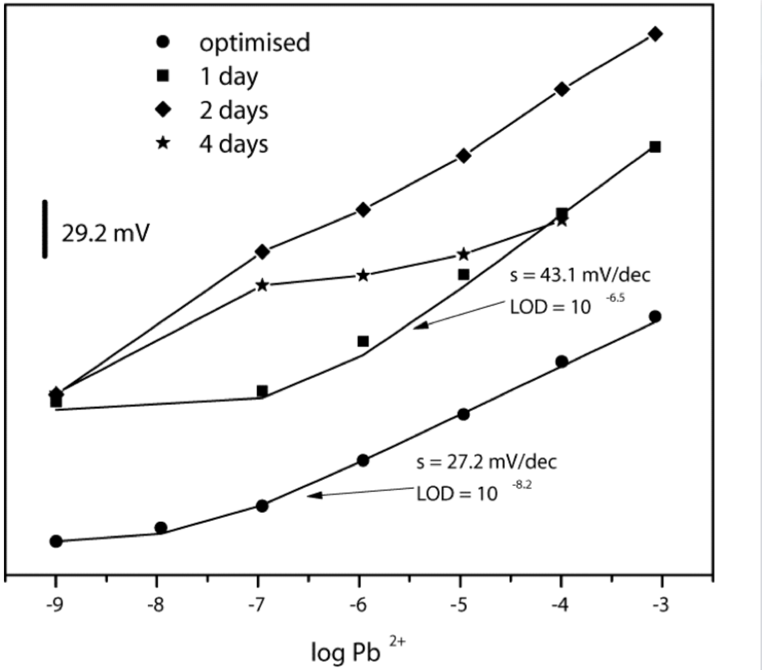
Anal. Chem., ***64*** *(1992) 1721-1728.*

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

Change in Electrode Function over Time

See Electrochimica Acta 73 (2012) 93–97



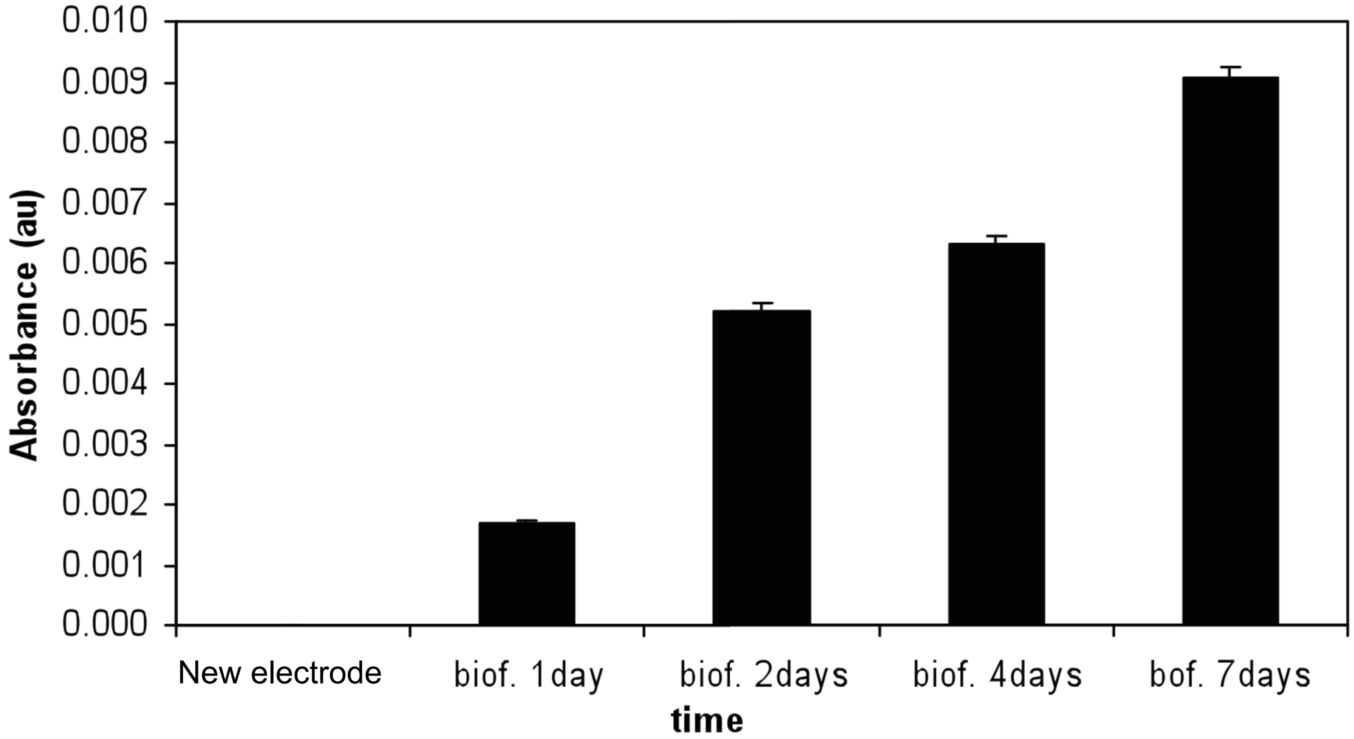


stored in 10^{-9}M Pb^{2+}, pH=4

Continuous contact with river water

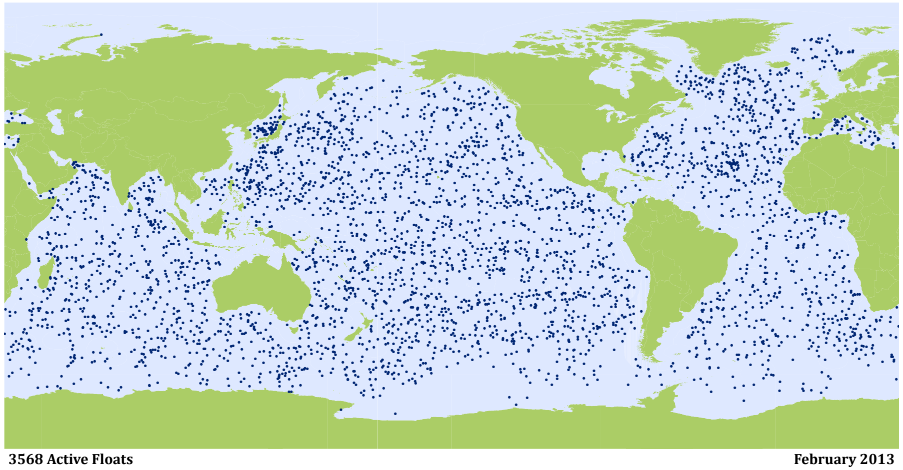
Conventional PVC-membrane based ISEs

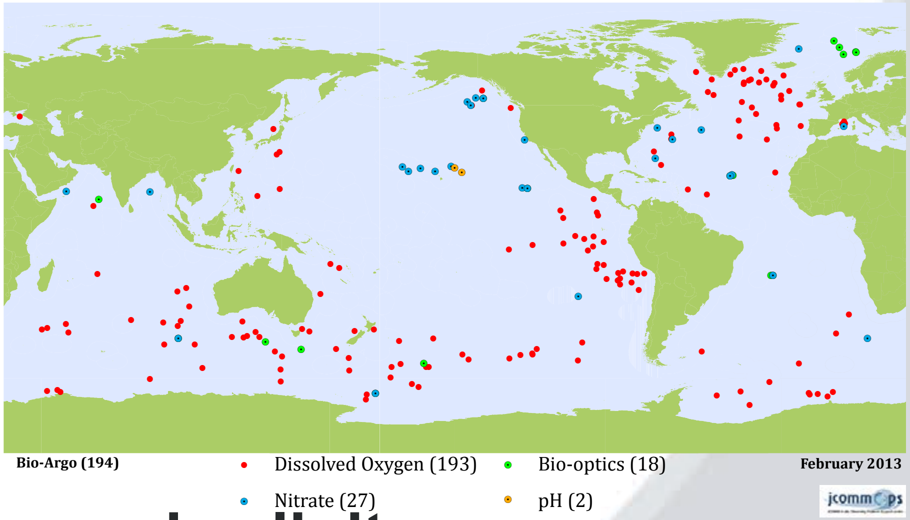
Biofilm Formation on Sensors



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

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

CLARITY
clarity-centre.org

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 still very limited

Keynote Article: August 2004, Analytical Chemistry (A

internet scale sensing

Dermot Diamond
Dublin City University
(Ireland)

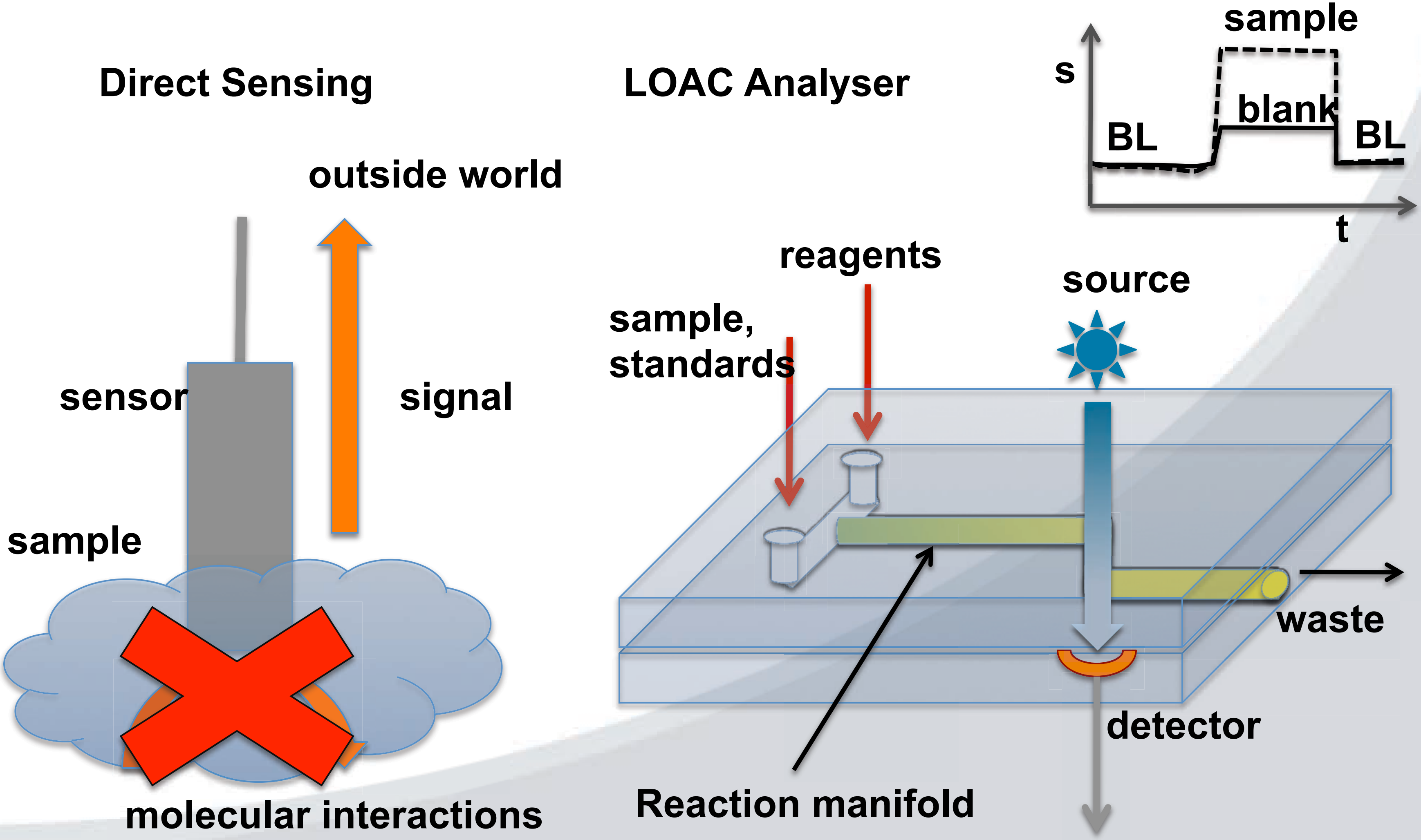
Incredible advances in digital communications and computer power have profoundly changed our lives. One chemist shares his vision of the role of analytical science in the next communications revolution.

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

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

Direct Sensing vs. Reagent Based LOAC/ufluidics



MicroTAS/Lab on a Chip/Microfluidics

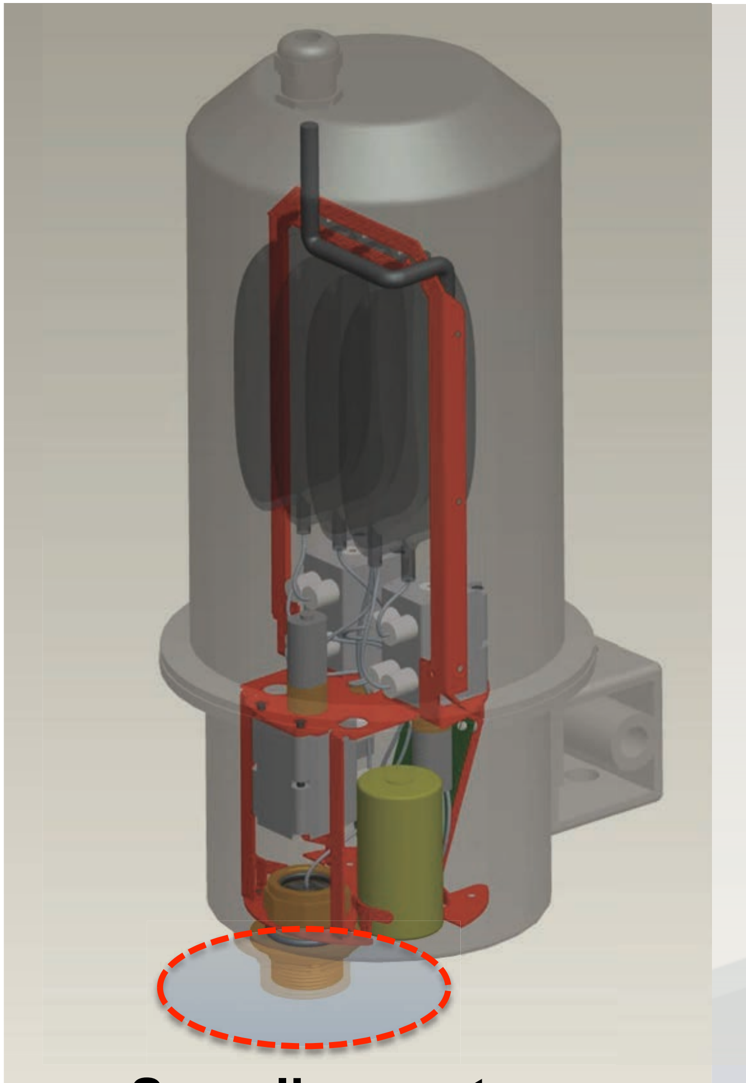
CLARITY
clarity-centre.org

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

2nd Generation Analyser: Design

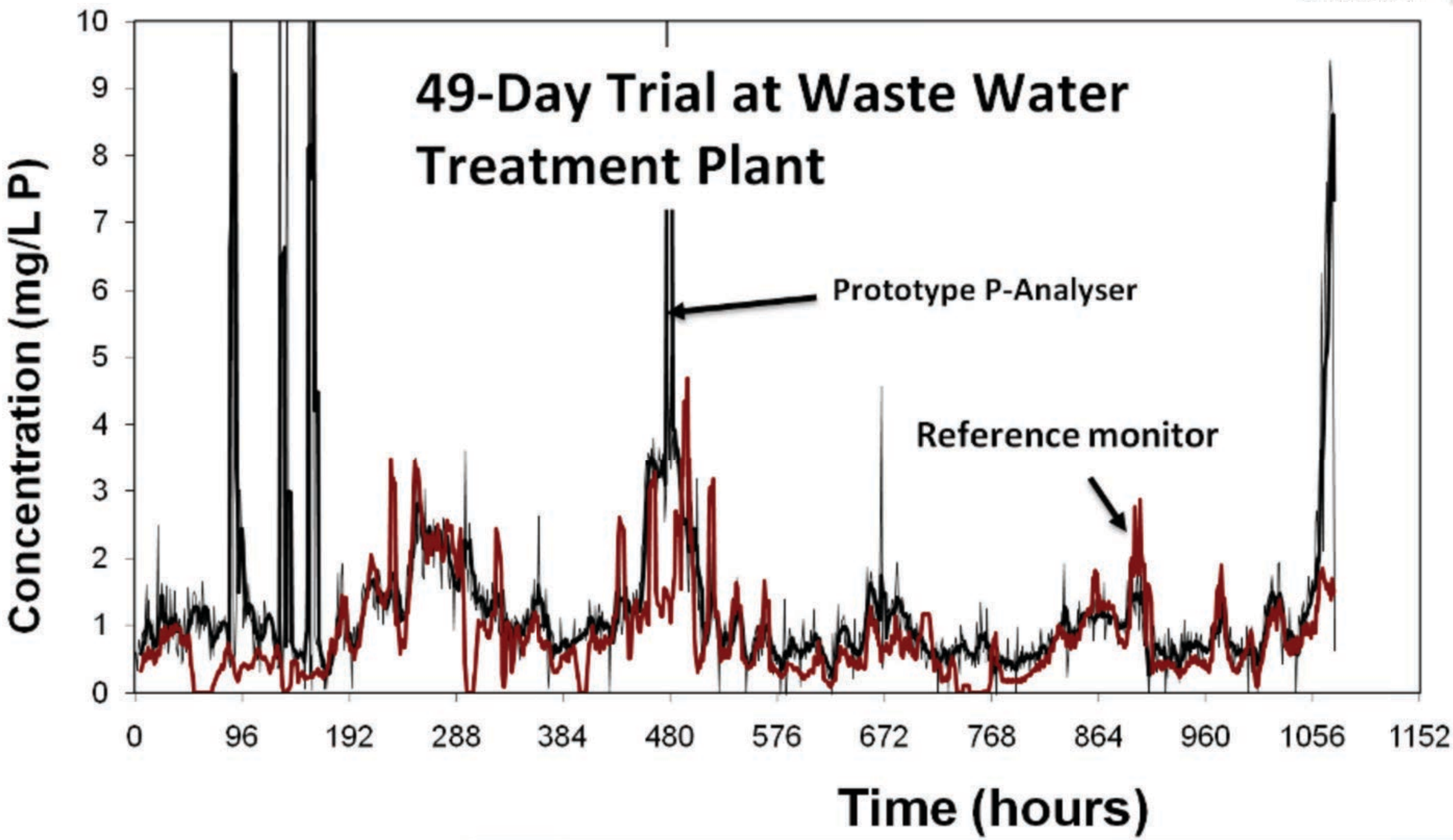


Sampling port

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

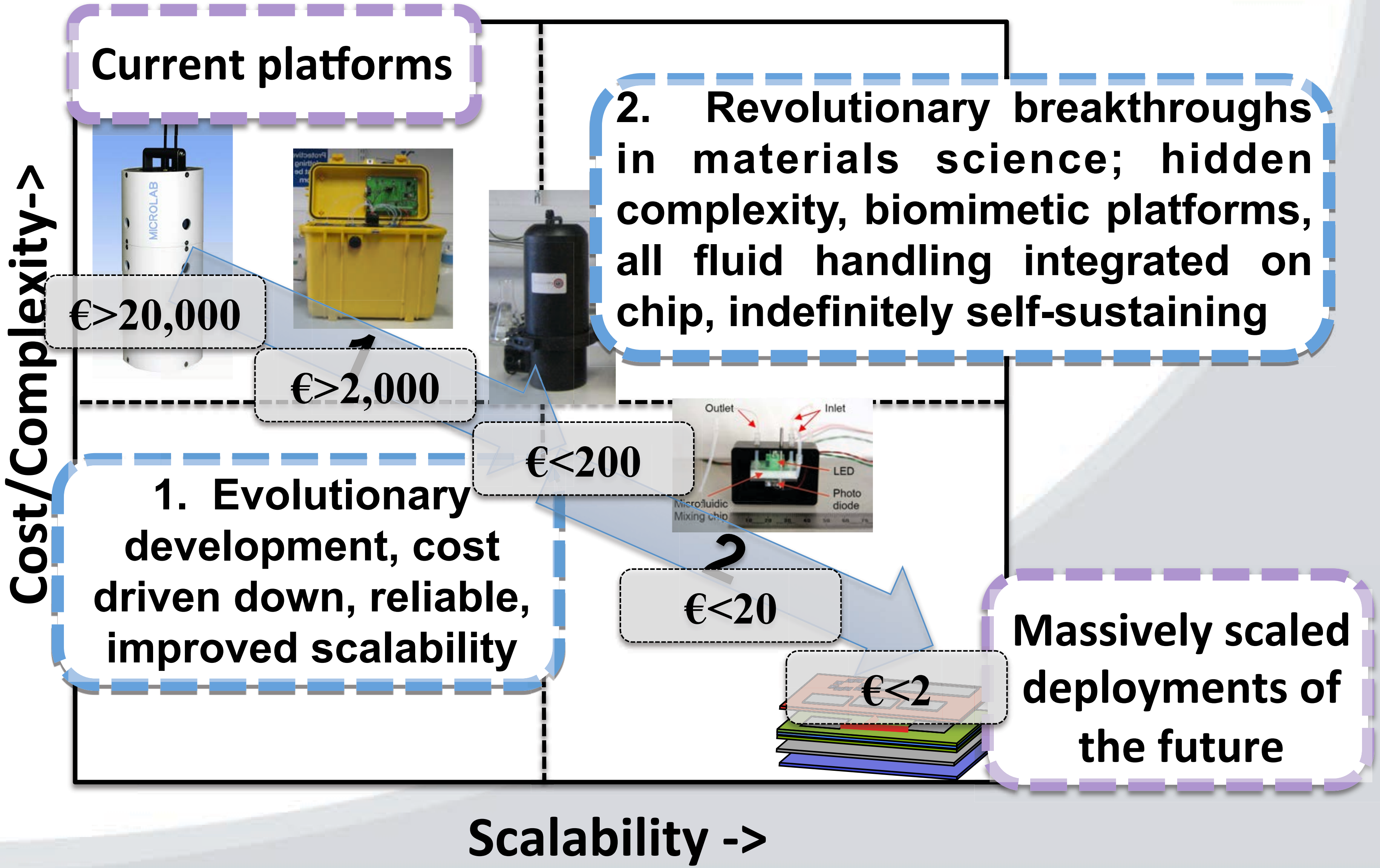
Autonomous Chemical Analyser



Osberstown – 3 week deployment

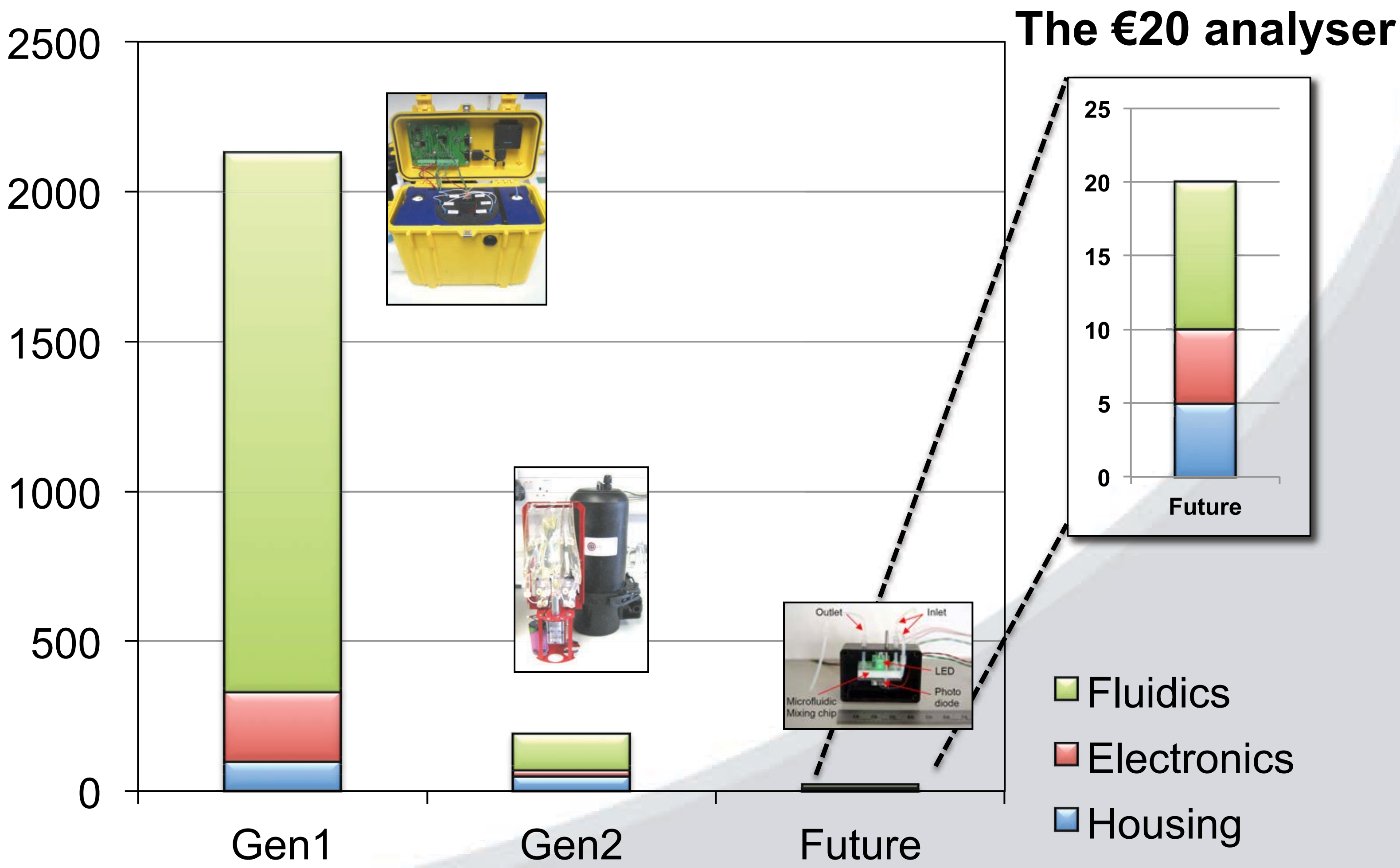
Biofouling of sensor surfaces is a major challenge for remote chemical sensing – both for the environment and for implantable sensors

Achieving Scale-up



Cost Comparison Analyser (€)

CLARITY
clarity-centre.org



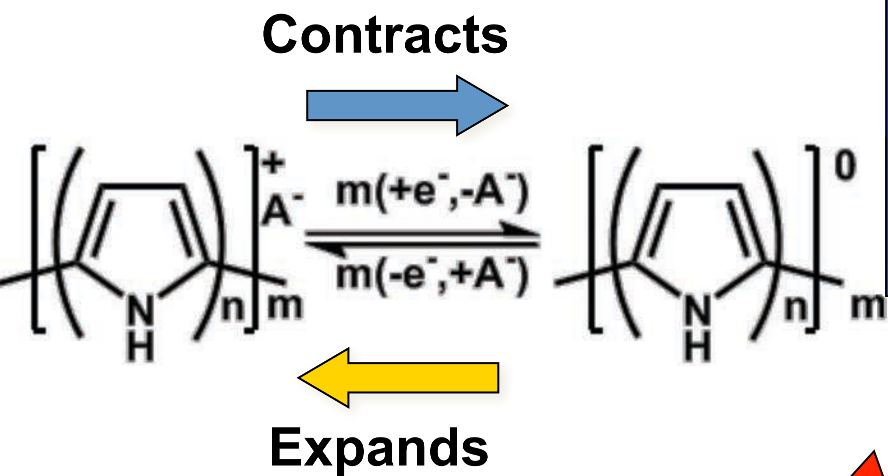
How to advance fluid handling in LOC platforms: re-invent valves (and pumps)!

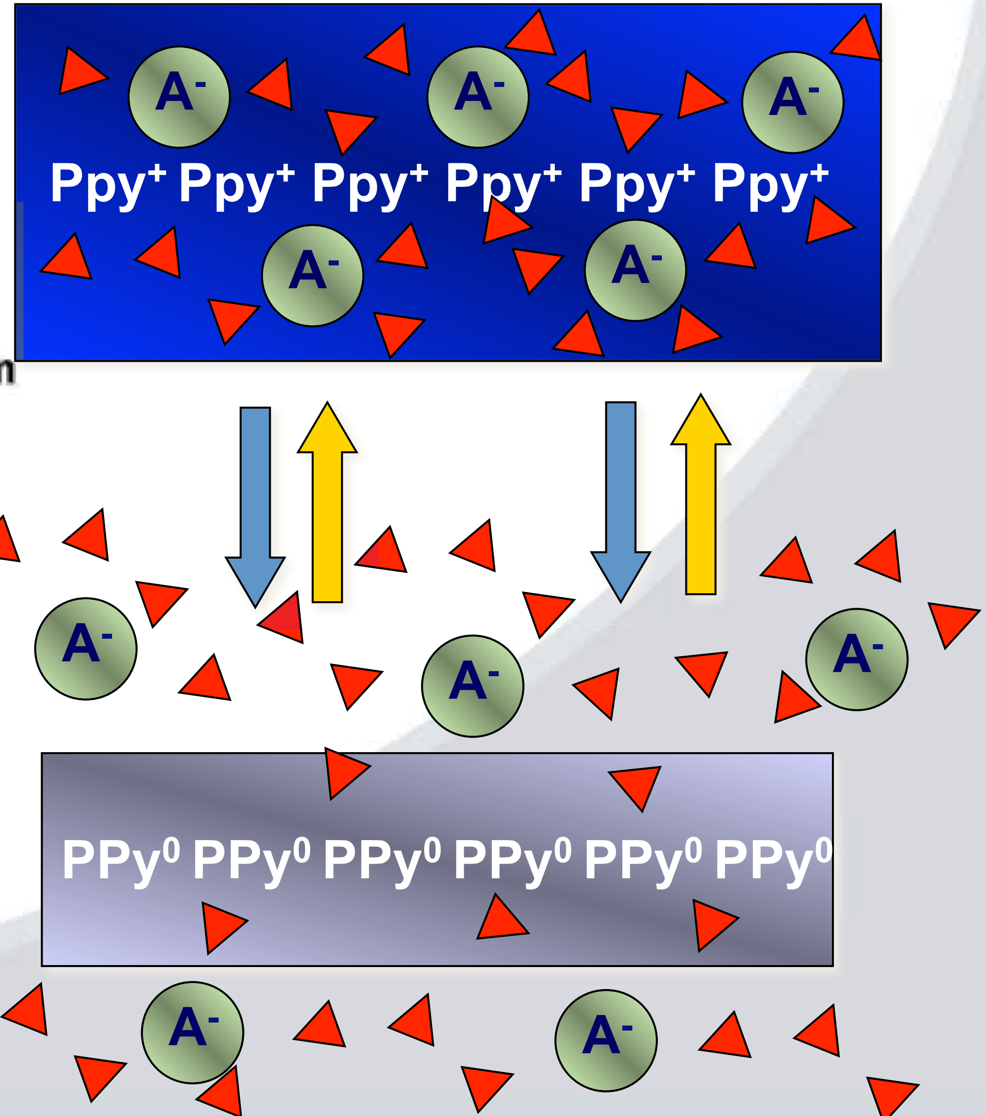
- **Conventional valves cannot be easily scaled down - Located off chip: fluidic interconnects required**
  - Complex fabrication
  - Increased dead volume
  - Mixing effects
- **Based on solenoid action**
  - Large power demand
  - Expensive

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

Switchable Materials: Soft Polymer Actuators

CLARITY
clarity-centre.org

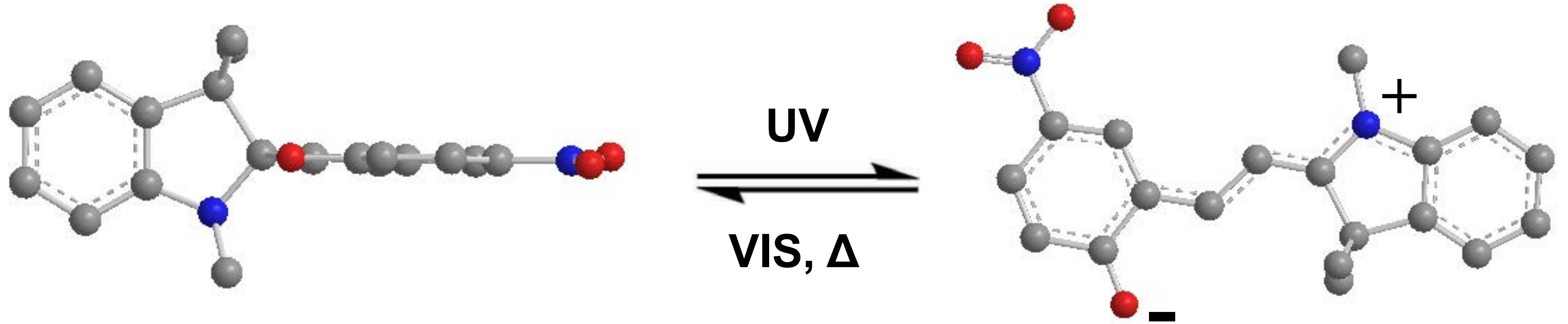


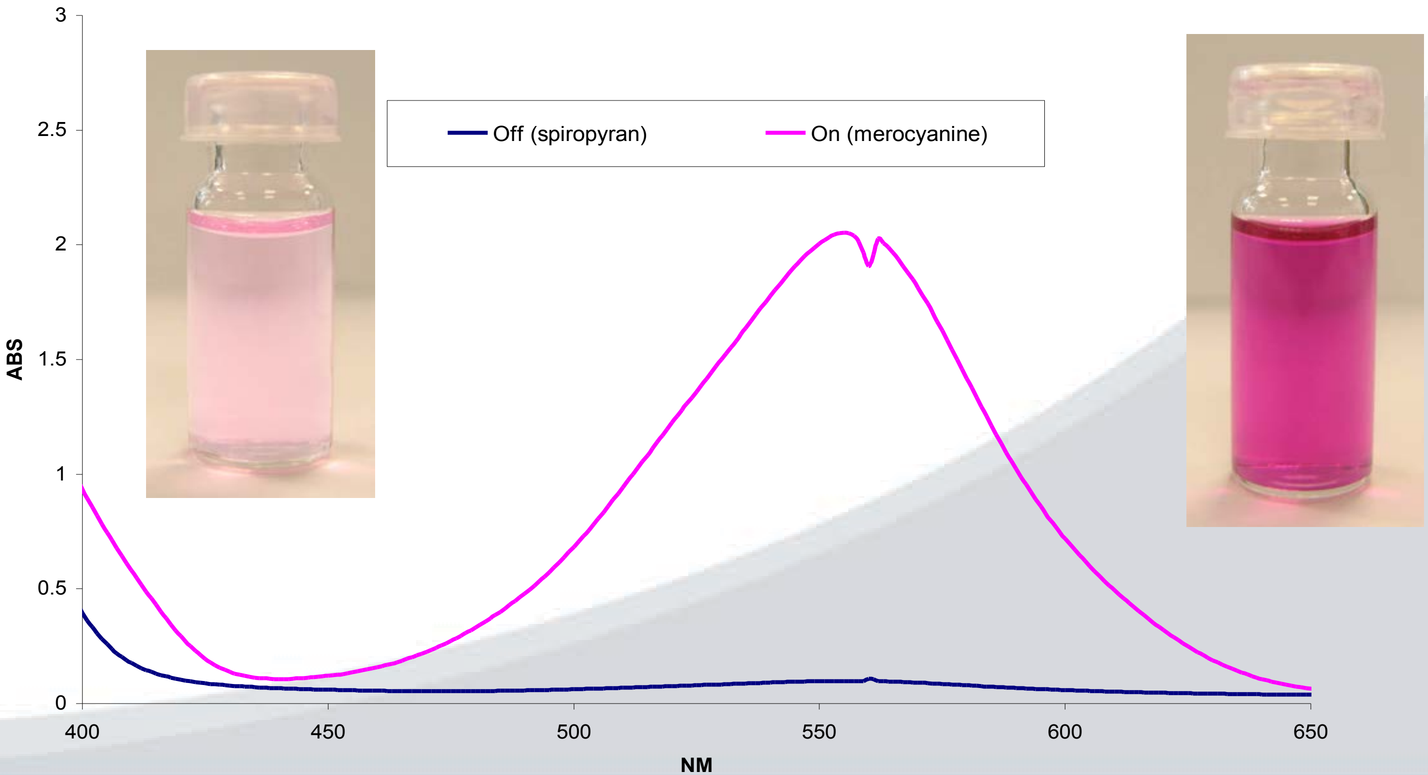


Principle can be used to make soft polymer (biomimetic, artificial muscle) actuators

Photoswitchable Materials

CLARITY
clarity-centre.org

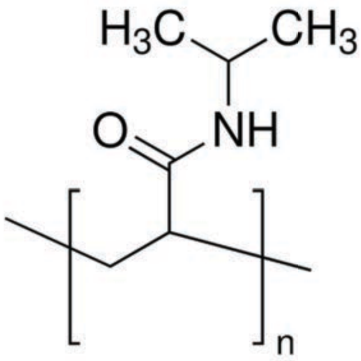


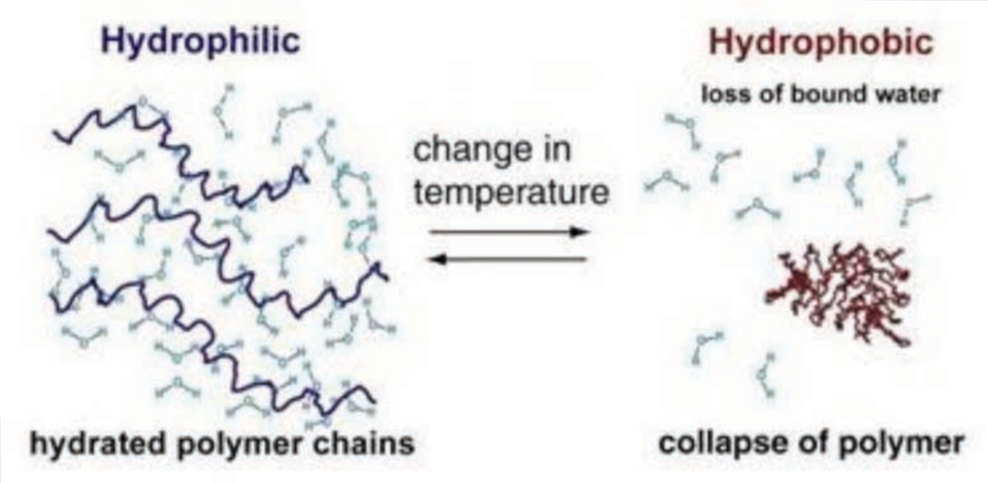


Poly(*N*-isopropylacrylamide)

- PNIPAM posses 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 isa 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

PNIPAM





Polymer based photoactuators based on pNIPAAm

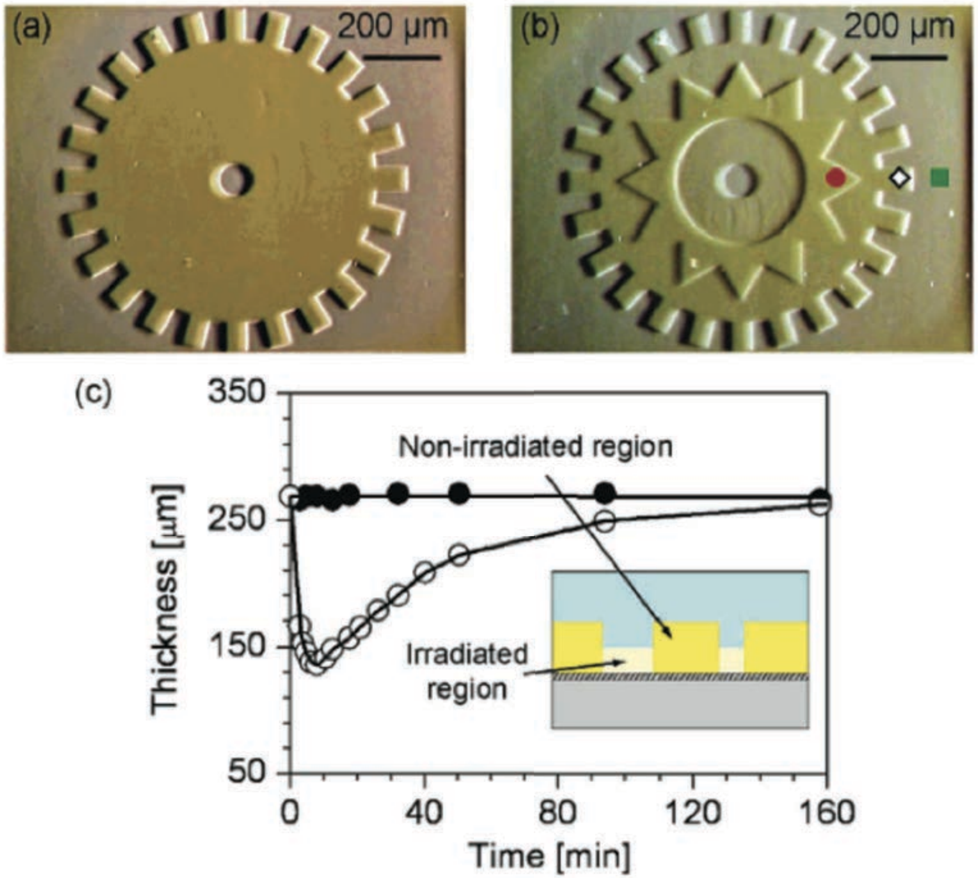
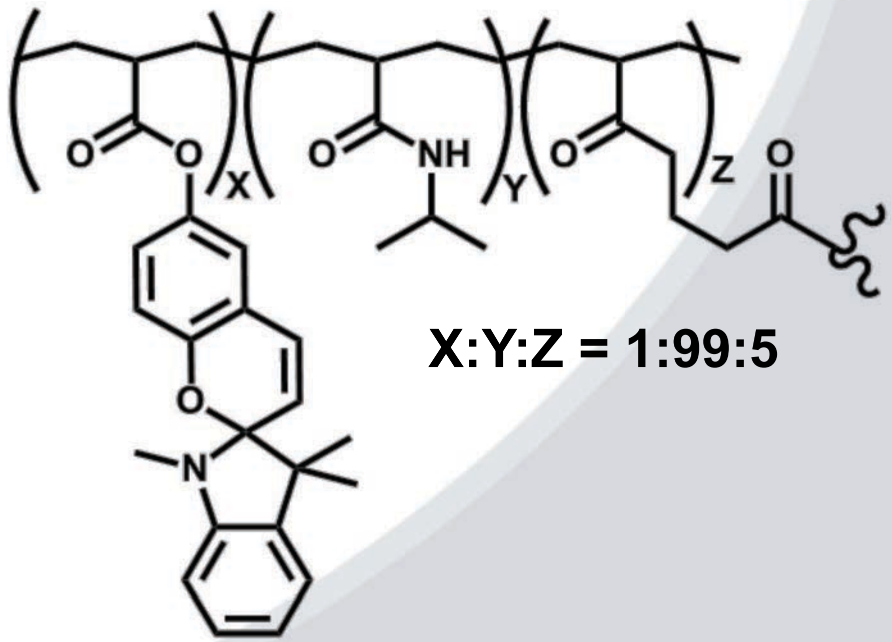


Figure 3. (a, b) Images of the pSPNIPAAm hydrogel layer just after the micropatterned light irradiation. Duration of irradiation was (●, red) 0, (◇) 1, and (■, green) 3 s. (c) Height change of the hydrogel layer in (●) non-irradiated and (○) irradiated region as a function of time after 3 s blue light irradiation.



X:Y:Z = 1:99:5

poly(N-isopropylacrylamide) (PNIPAAm)
Formulation as by Sumaru et al[1]
1) Chem. Mater., **19 (11), 2730 -2732, 2007.**

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

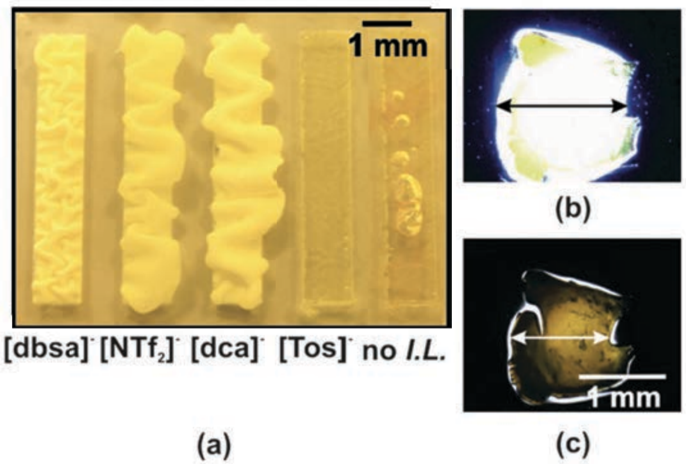


Fig. 3 (a) Photo-responsive polymer gels after immersion of the mould in a 1 mM HCl solution for 2 h. Right: $[dca]^-$ ionogel shrinking process; (b) ionogel before illumination and (c) the same sample after 2 s illumination with a white light LED, size decrease is *ca.* 30% by volume.

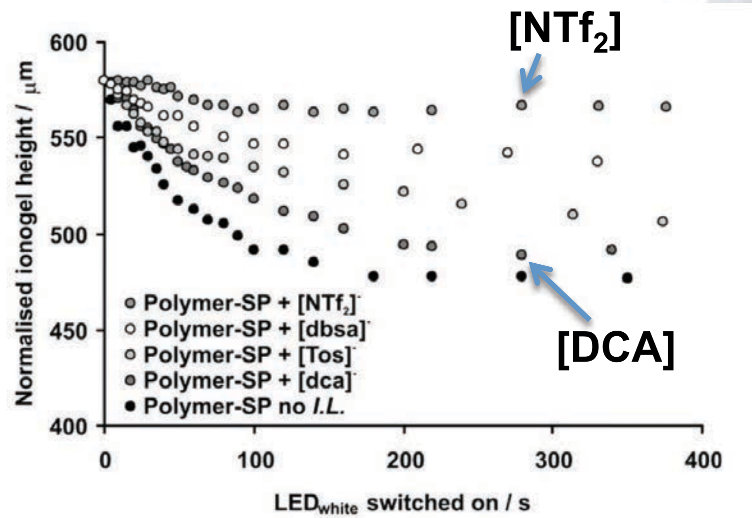
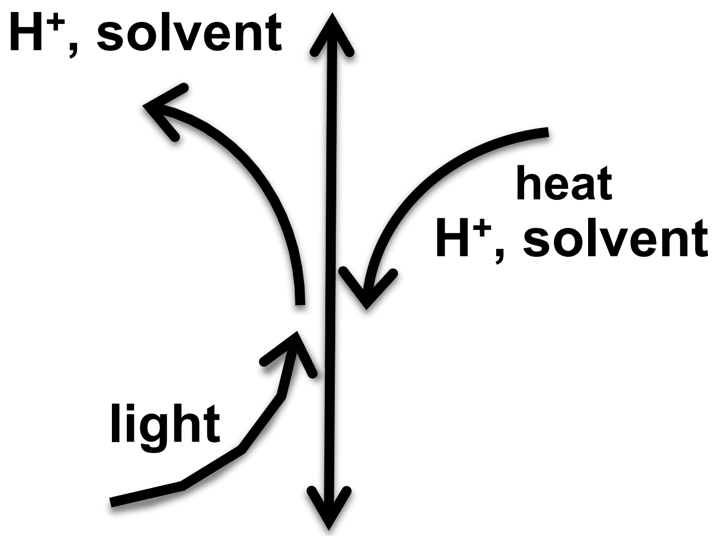


Fig. 6 Response kinetics of ionogels upon irradiation with white light (ionogel height error: ±5 µm).

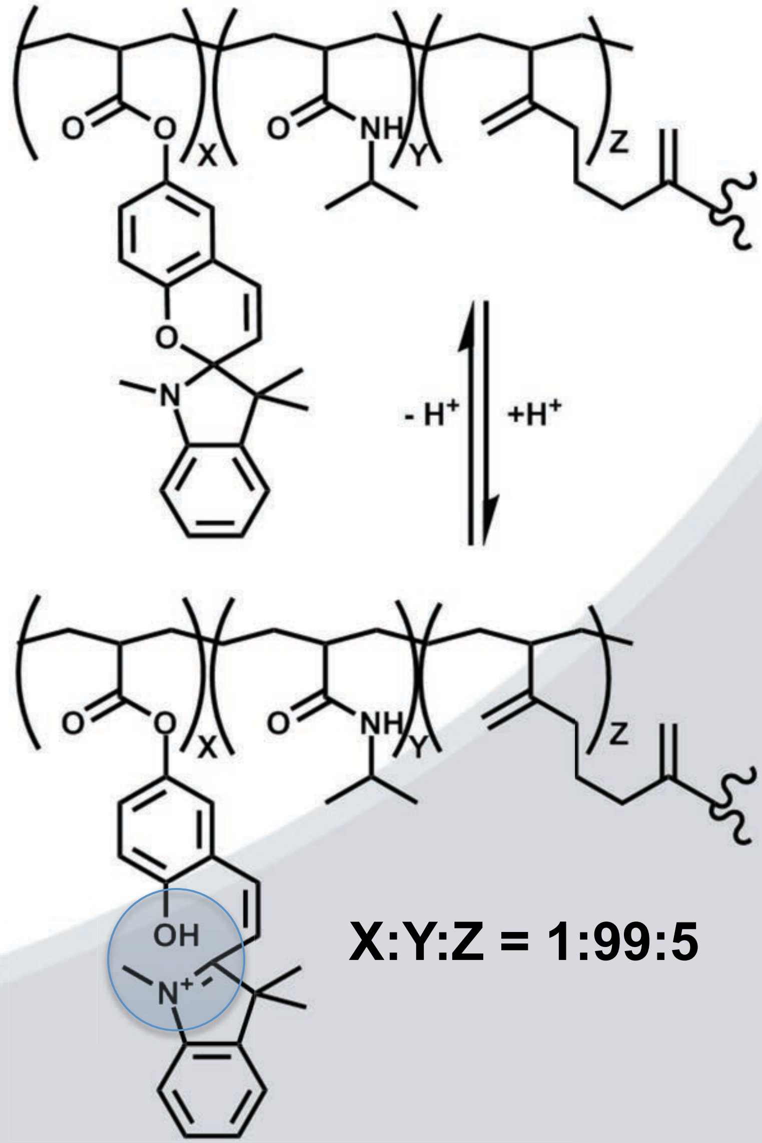
Actuation Mechanism

CLARITY
clarity-centre.org

SPIRO
(contracted)



MERO-H^+
(expanded)

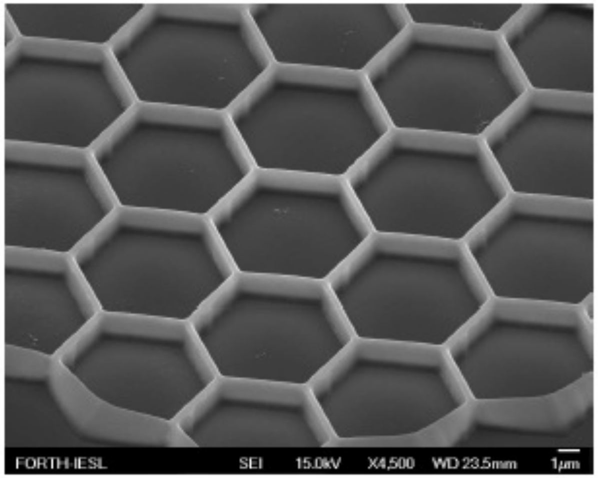


X:Y:Z = 1:99:5

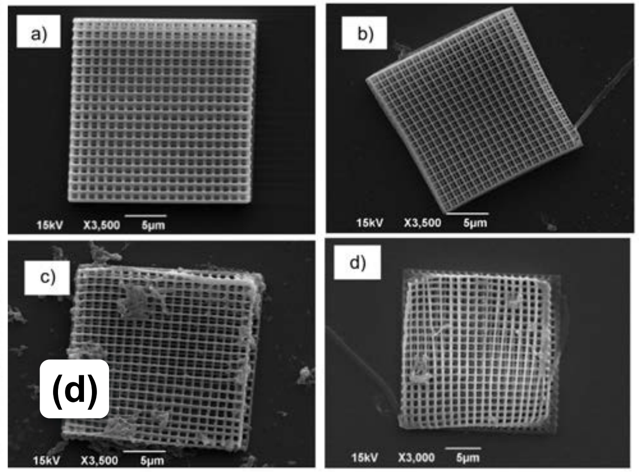
So far, so good: but what are the limitations?

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

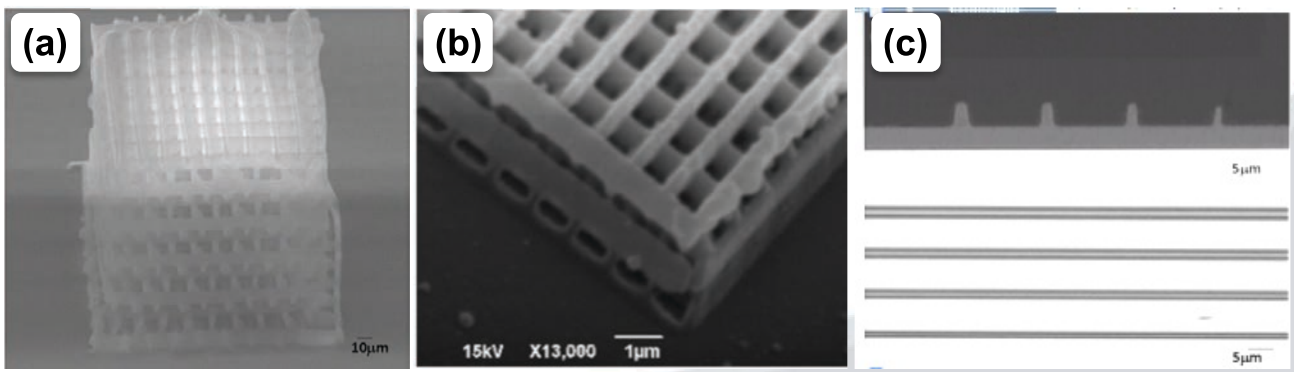
Reduce scale – increase response time
3-d Spiro-doped sol-ionogels



SEM of surface pattering produced by multi-photon polymerisation of hybrid graphene-doped ionogels



SEM images of woodpiles fabricated from material D containing a) 0%, b) 20%, c) 40% and d) 50% IL



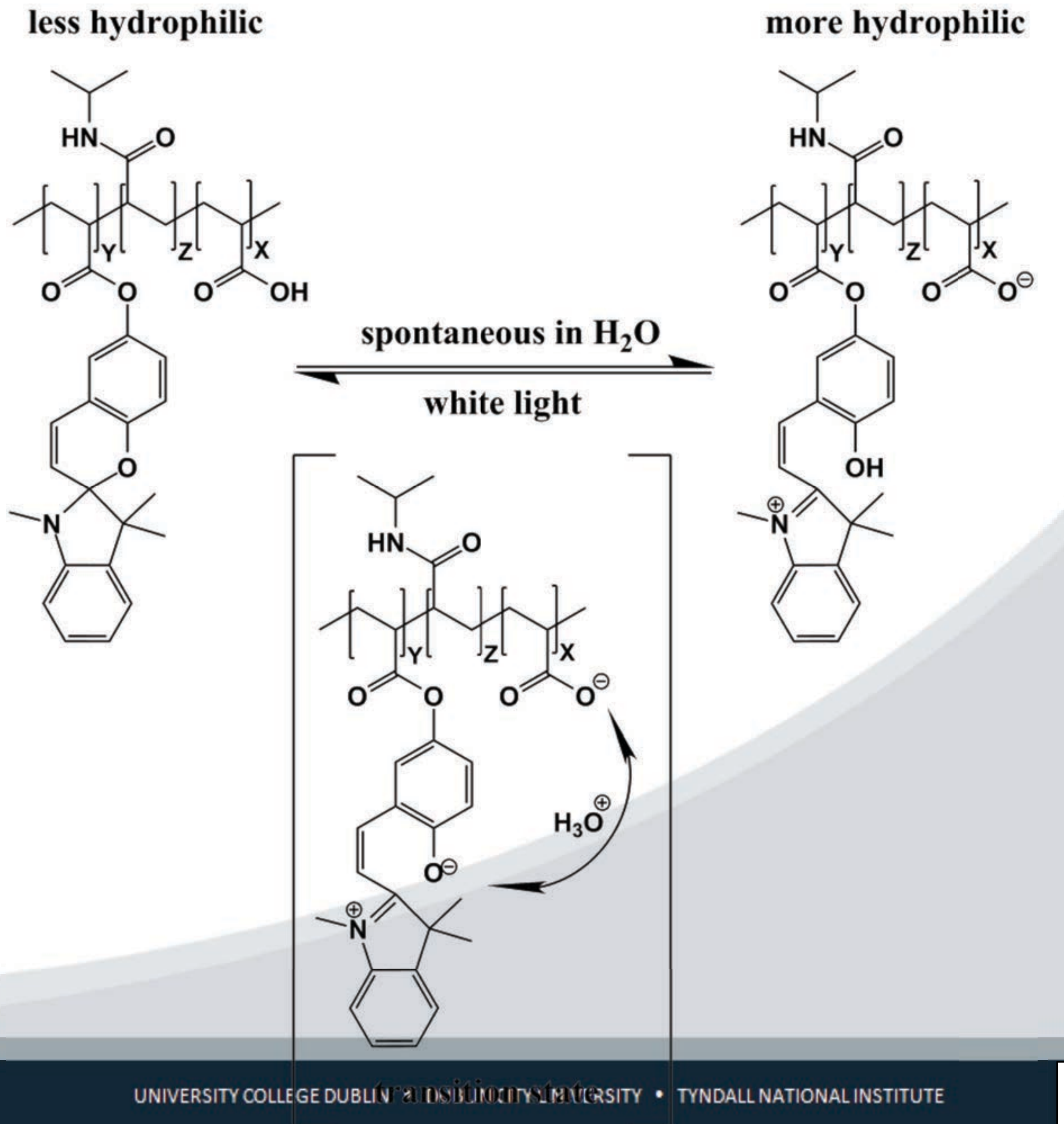
Two photon polymerised (2PP), patterned ionogels (a) and (b), and (c) feature resolution down to 150 nm or less; (d) spiropyran co-polymerised in a gel 'woodpile' structure.

The ionogels were based on photo-curable silicato-zirconate hybrid sol-gel materials and phosphonium (trihexyltetradecylphosphonium dicyanamide [$P_{6,6,6,14}$][DCA] ionic liquid (IL). To optimise the dispersion of graphene within the ionogel matrices, aqueous solutions of graphene were prepared, as opposed to the conventional graphene powder approach, and employed as catalysts for the hydrolysis and condensation reactions occurring in the sol-gel process.

With Gabija Bickauskait *and* Maria Farsari, Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, N. Plastira 100, GR-70013 Heraklion, Crete, Greece

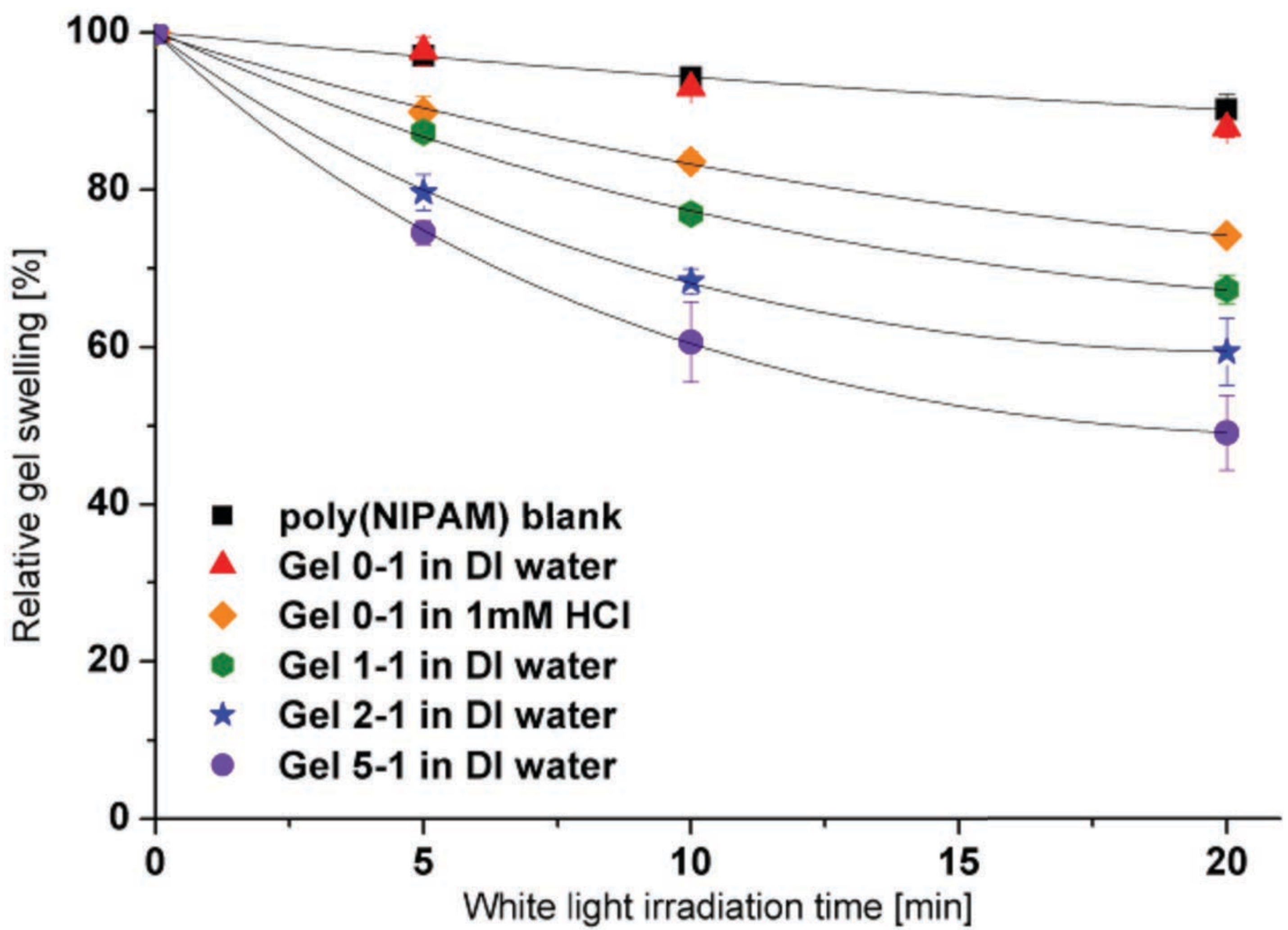
Self protonating photoresponsive gel

CLARITY
clarity-centre.org

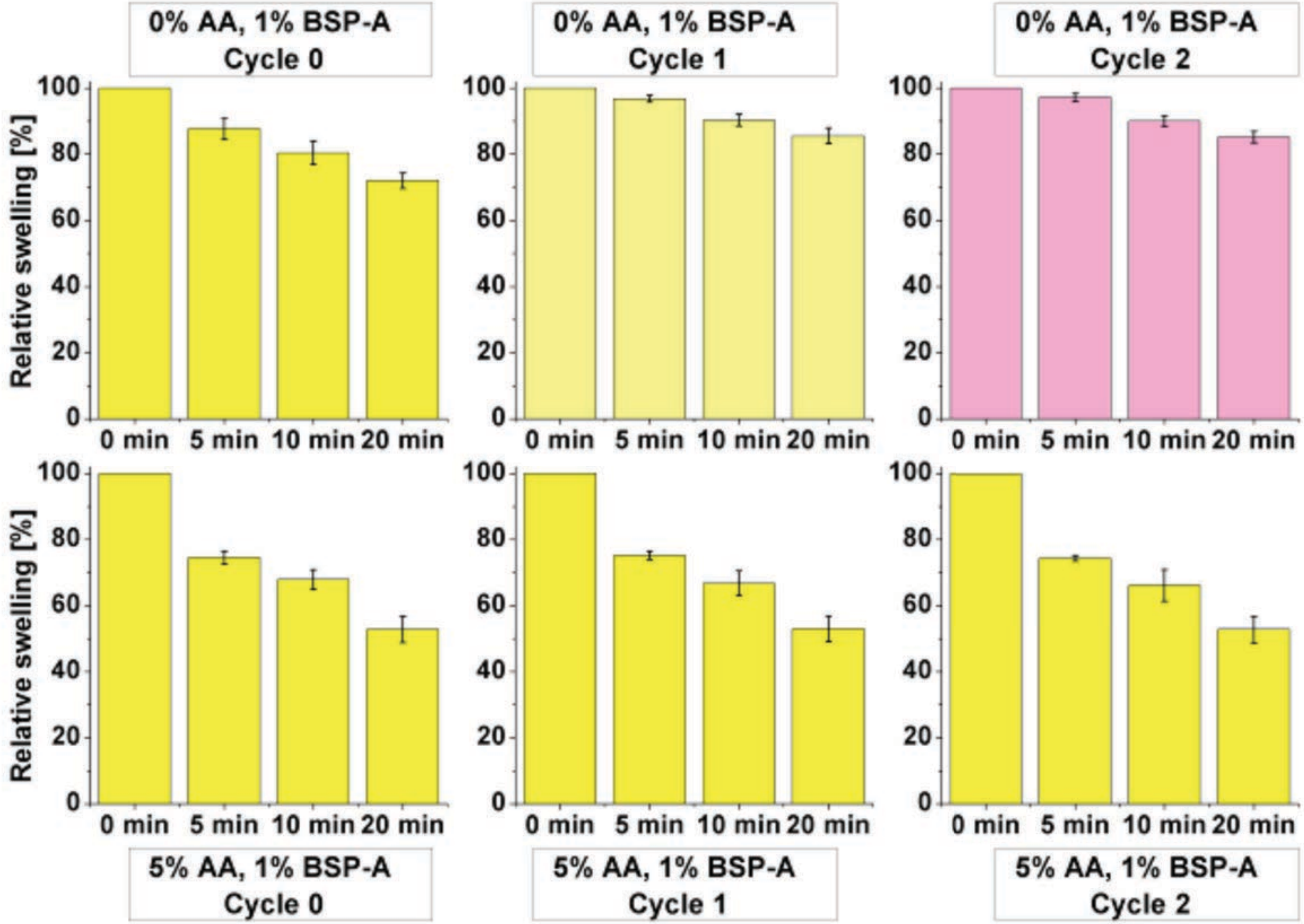


Improved Extent and Rate of Contraction

CLARITY
clarity-centre.org



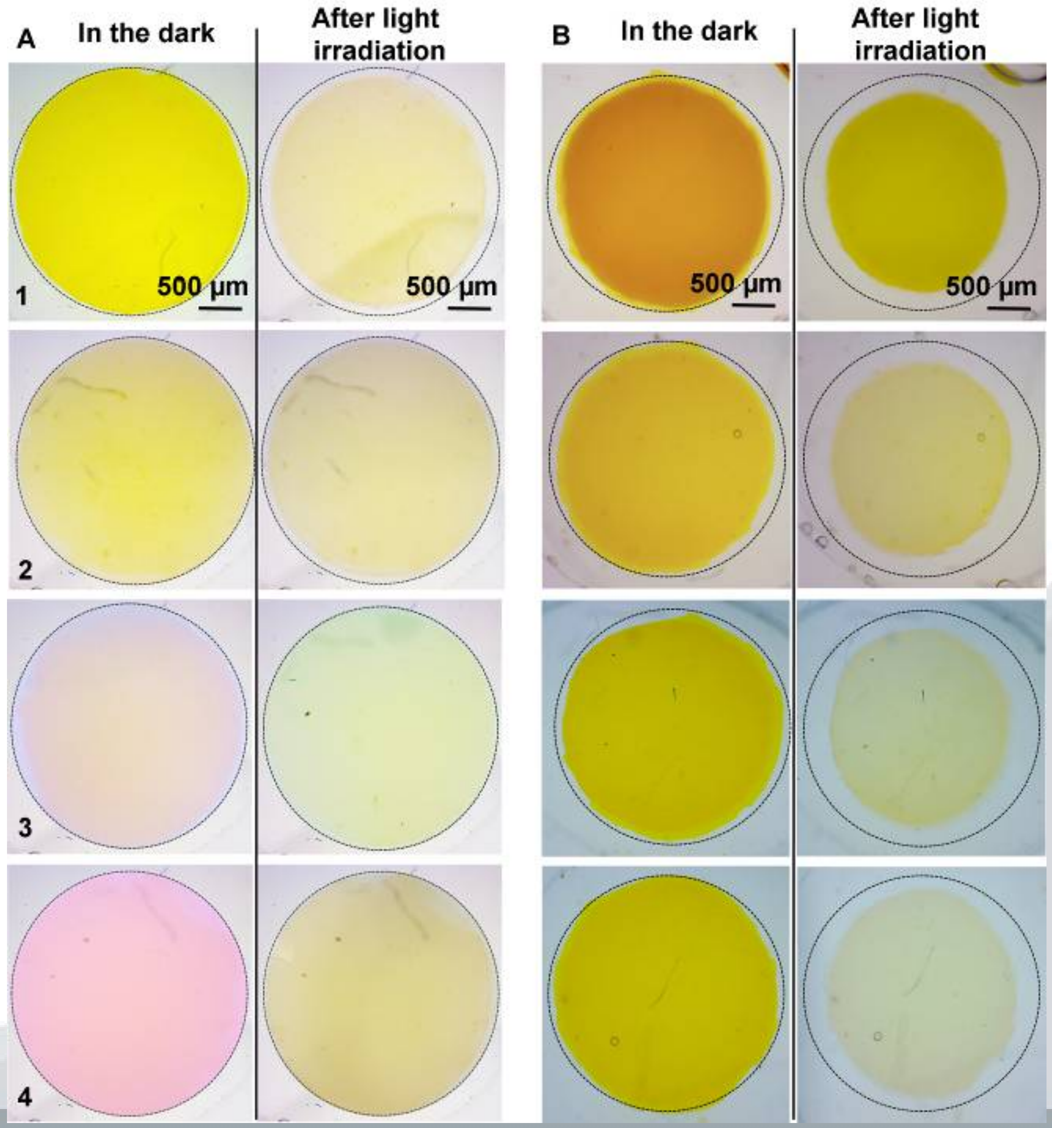
Actuation Cycling without External Acidification



Spontaneous Reformation of Acidified Merocyanine during Actuation Cycling

CLARITY
clarity-centre.org

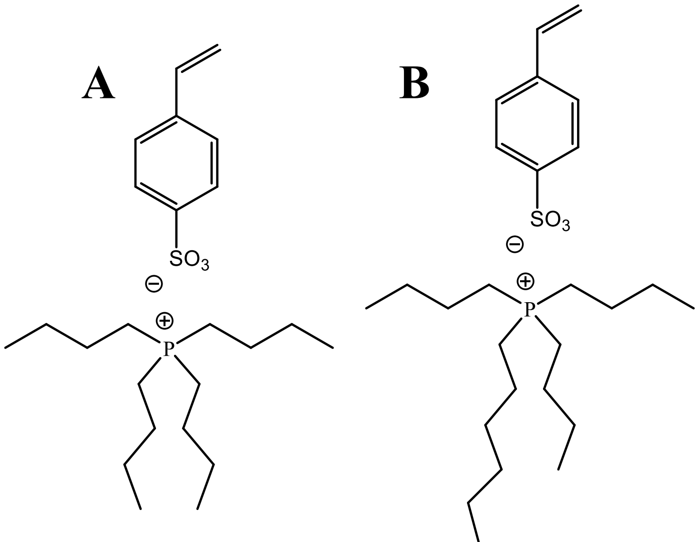
Gel with 0 % AA

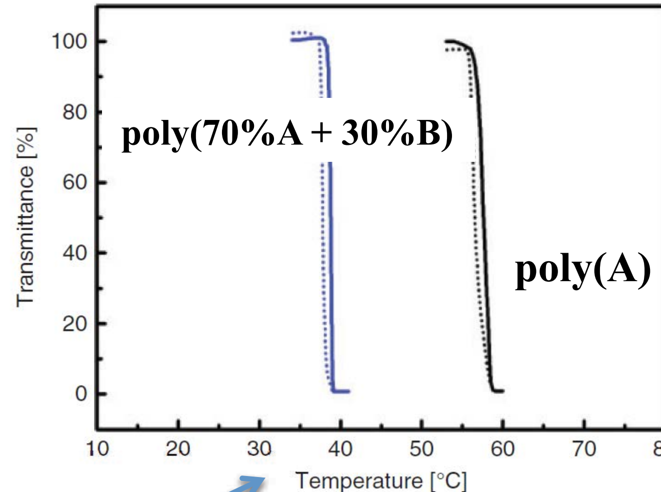


Gel with 5 % AA

Stimuli-Thermo-responsive poly(ILs)

New polymeric ionic liquids that are thermoresponsive have been recently reported



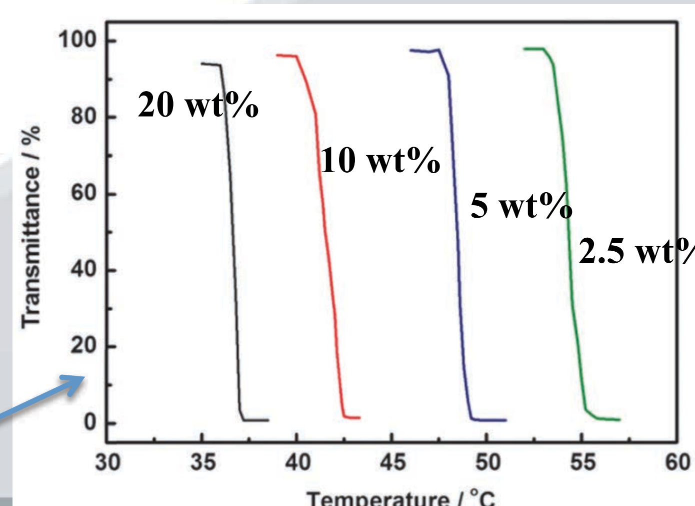


Y. Kohno and H. Ohno, *Aust. J. Chem.*, 2011, 65, 91-94

LCST depends on the proportion of each IL used

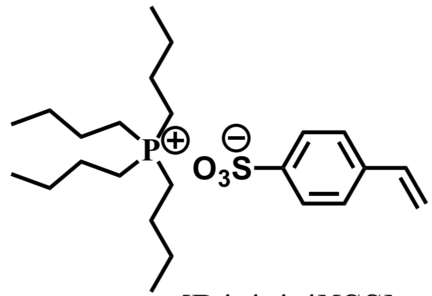
Y. Kohno, Y. Deguchi and H. Ohno, *Chem. Commun.*, 2012, 48, 11883-11885.

LCST depends on the concentration of the IL in water

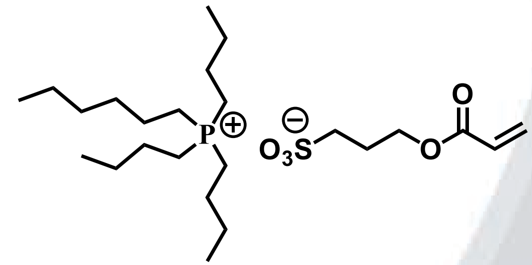


Preparation of thermo-responsive poly(IL) gels

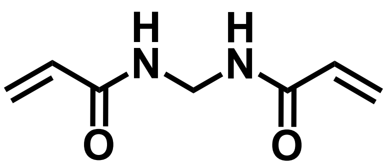
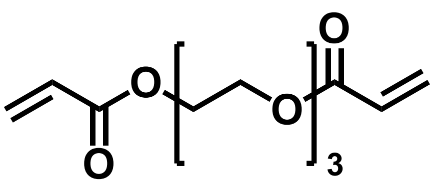
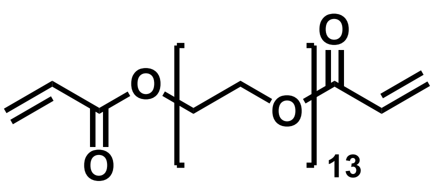
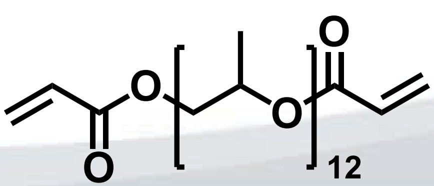
1. **Longer cross-linkers produce stable poly(IL) gels**
2. **Amount of cross-linker enables LCST effect to be tuned**
3. **Cross-linking broadens the LCST peak**



[P4,4,4,4][SS]



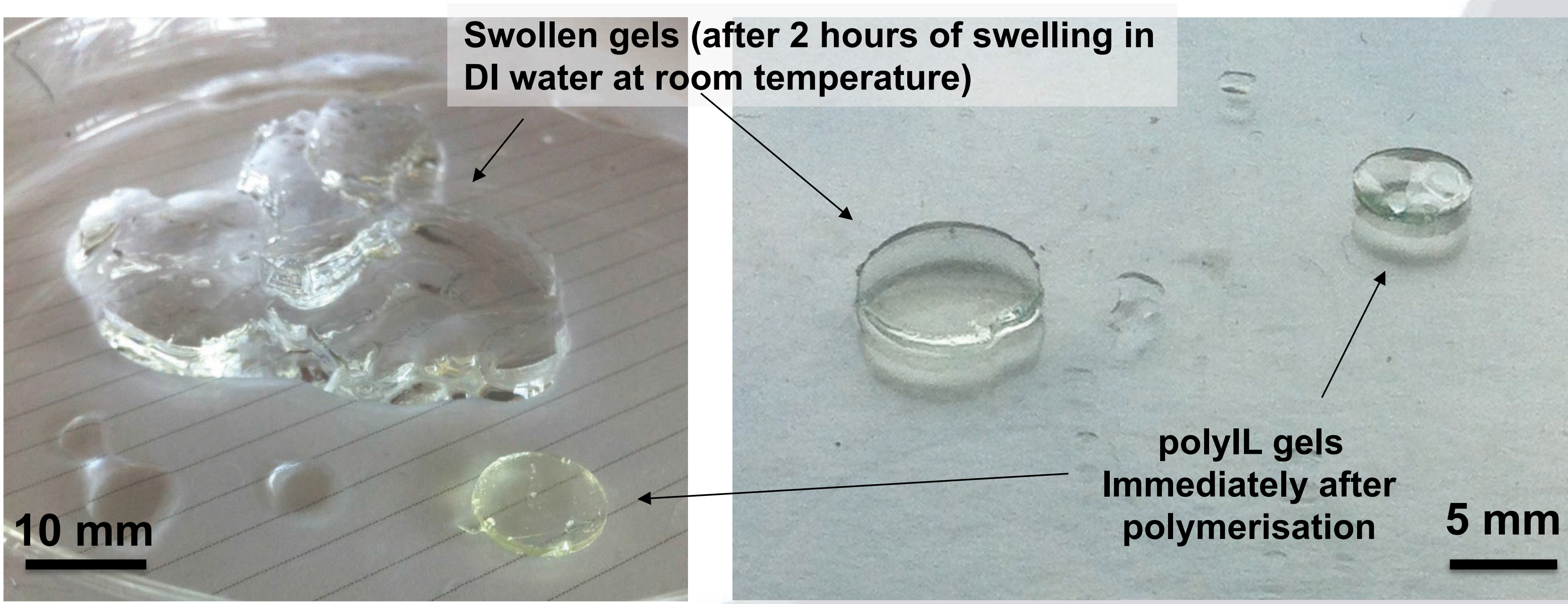
[P4,4,4,6][SPA]

		[P4,4,4,4][SS]	[P4,4,4,6][SPA]
	MBIS	Cracks, no stable shape, excessive swelling	Cracks, no stable shape, excessive swelling
	PEG 256 diacrylate	Cracks, no stable shape	Cracks, no stable shape
	PEG 700 diacrylate	Stable, transparent gel	Stable, transparent gel
	PPO 800 diacrylate	Stable, transparent gel (up to 9 %mol)	Stable, transparent gel (up to 9 %mol)

Preparation of thermo-responsive poly(IL) gels

$[P_{4,4,4,4}][SS]$ + 10 % MBIS

$[P_{4,4,4,6}][SPA]$ + 5 % PPO800 diacrylate



Only longer chain crosslinkers seem to allow mechanically stable hydrogels

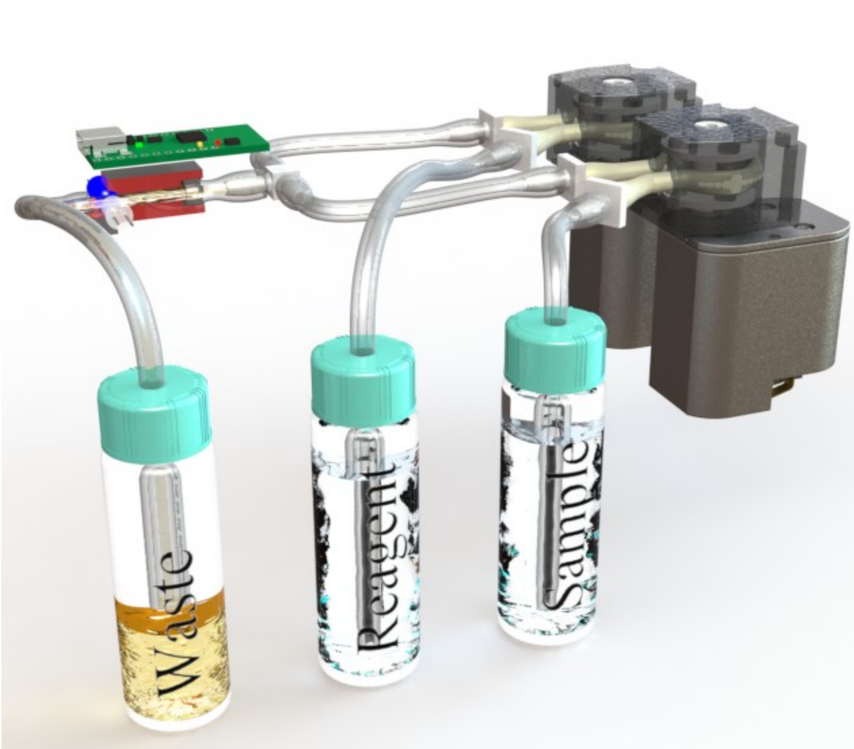
Why move the solvent at all?

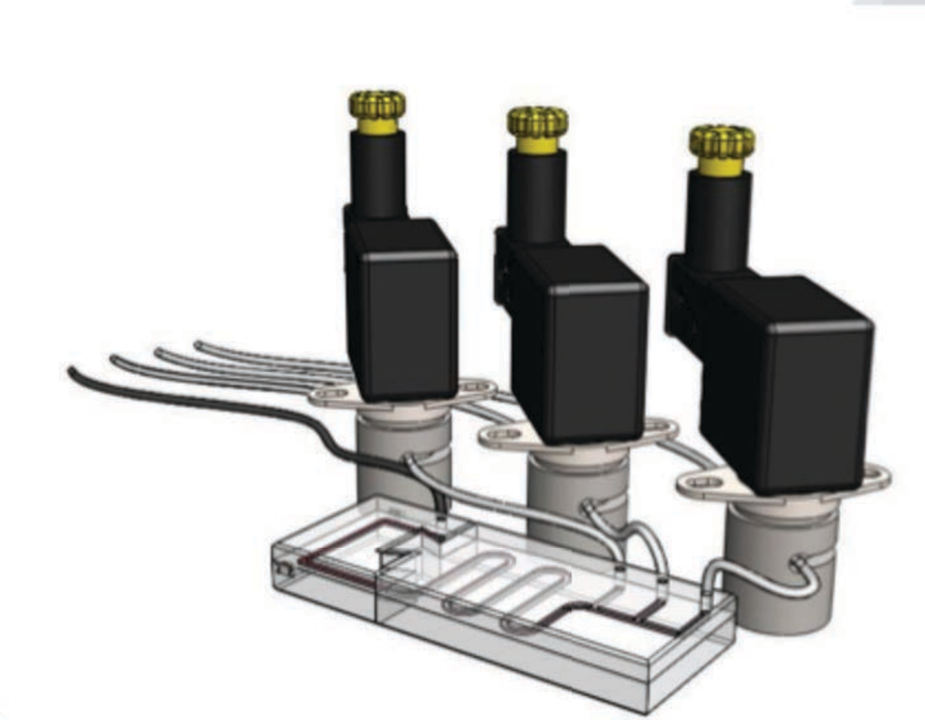
[sample]/mol l^{-1}	Ratio H_2O/Sample
1.0×10^{-6}	5.56×10^{7}
1.0×10^{-9}	5.56×10^{10}
1.0×10^{-12}	5.56×10^{13}

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

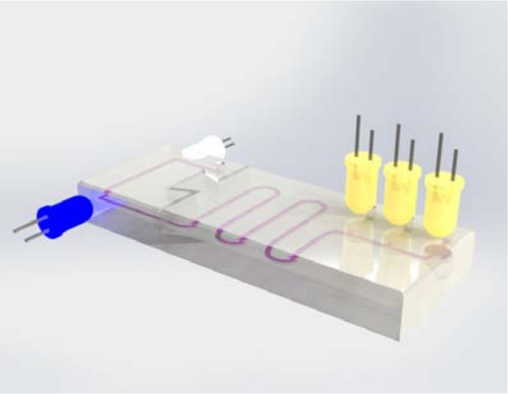
Can we go from this:

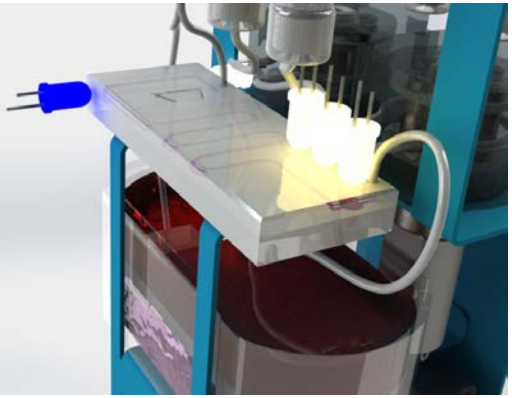


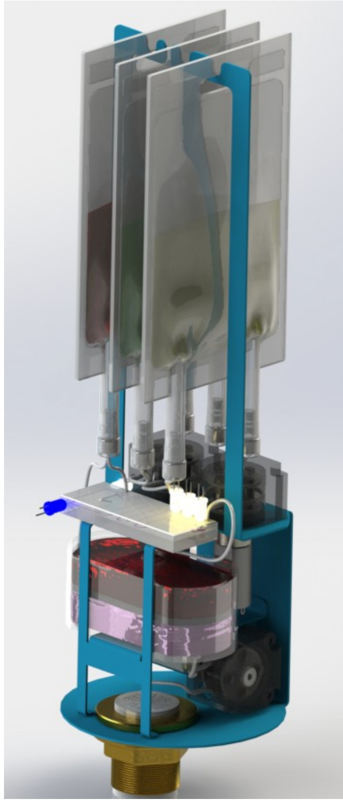


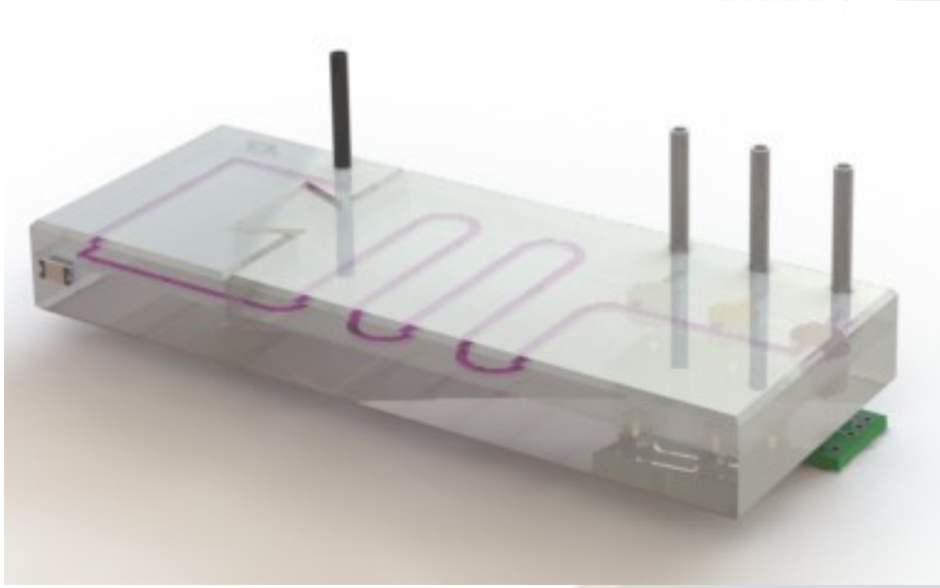
To Photo-Fluidics & Detection

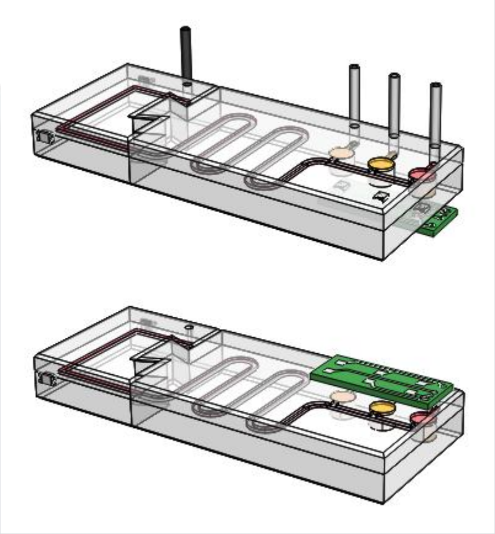
CLARITY
clarity-centre.org











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

Conclusions

CLARITY
clarity-centre.org

- **Linking 'Applied' and 'Fundamental' Research is important**
- **There is great value in building teams/networks with true multidisciplinary capabilities**
  - Merge engineering and materials science capabilities
  - Talk to people who have real applications needs: sports science, exercise, personal health, environment, food, agriculture, marine….
  - Fundamental research can be 'informed' by potential impacts and applications
- **A multitude of disruptive technologies will emerge from fundamental research in Materials Science!**