“Tuning the Behaviour of Sensors and Actuators using Ionic Liquids”

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presented at

ILMAT 2013
Espace Jacques 1er d’Aragon
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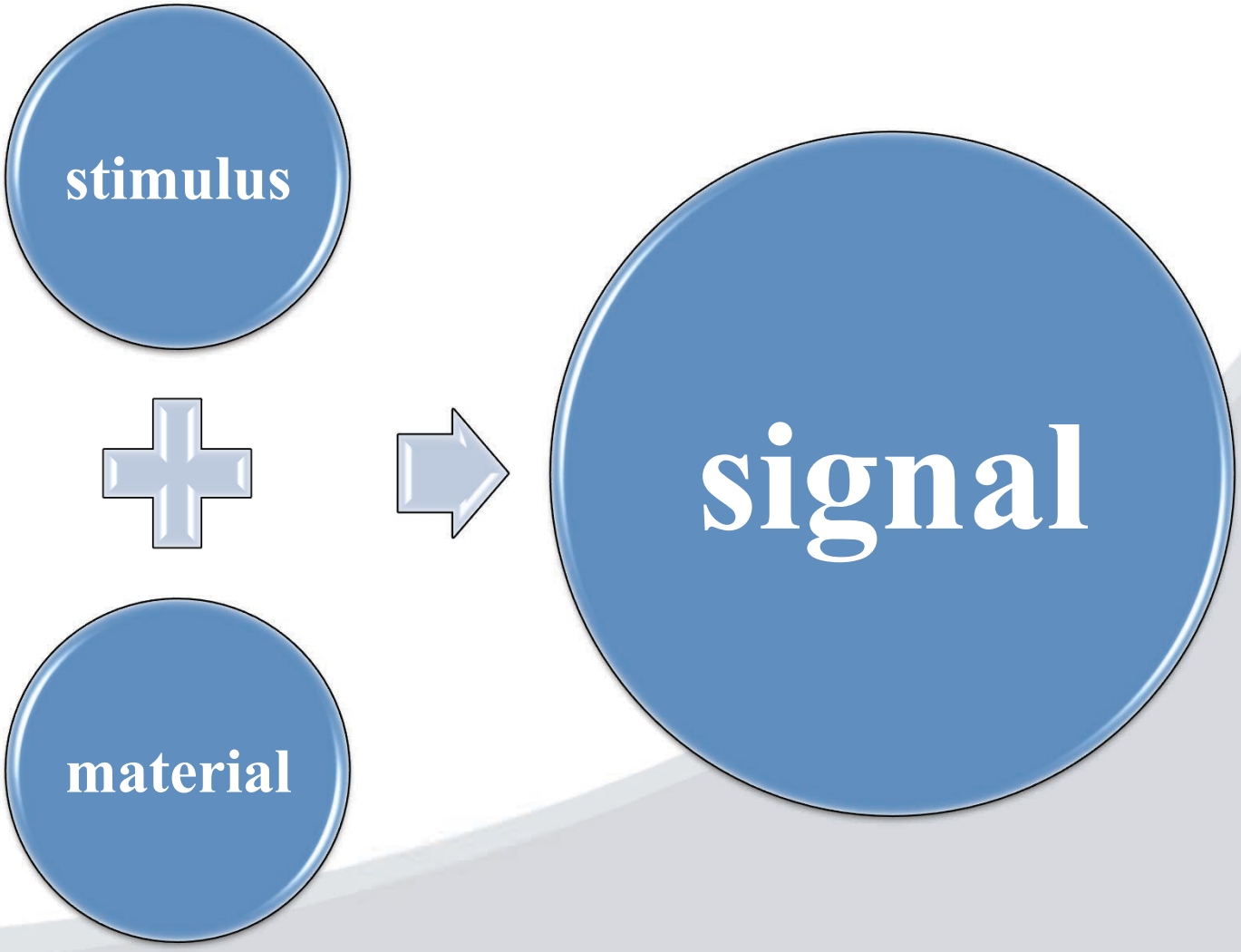
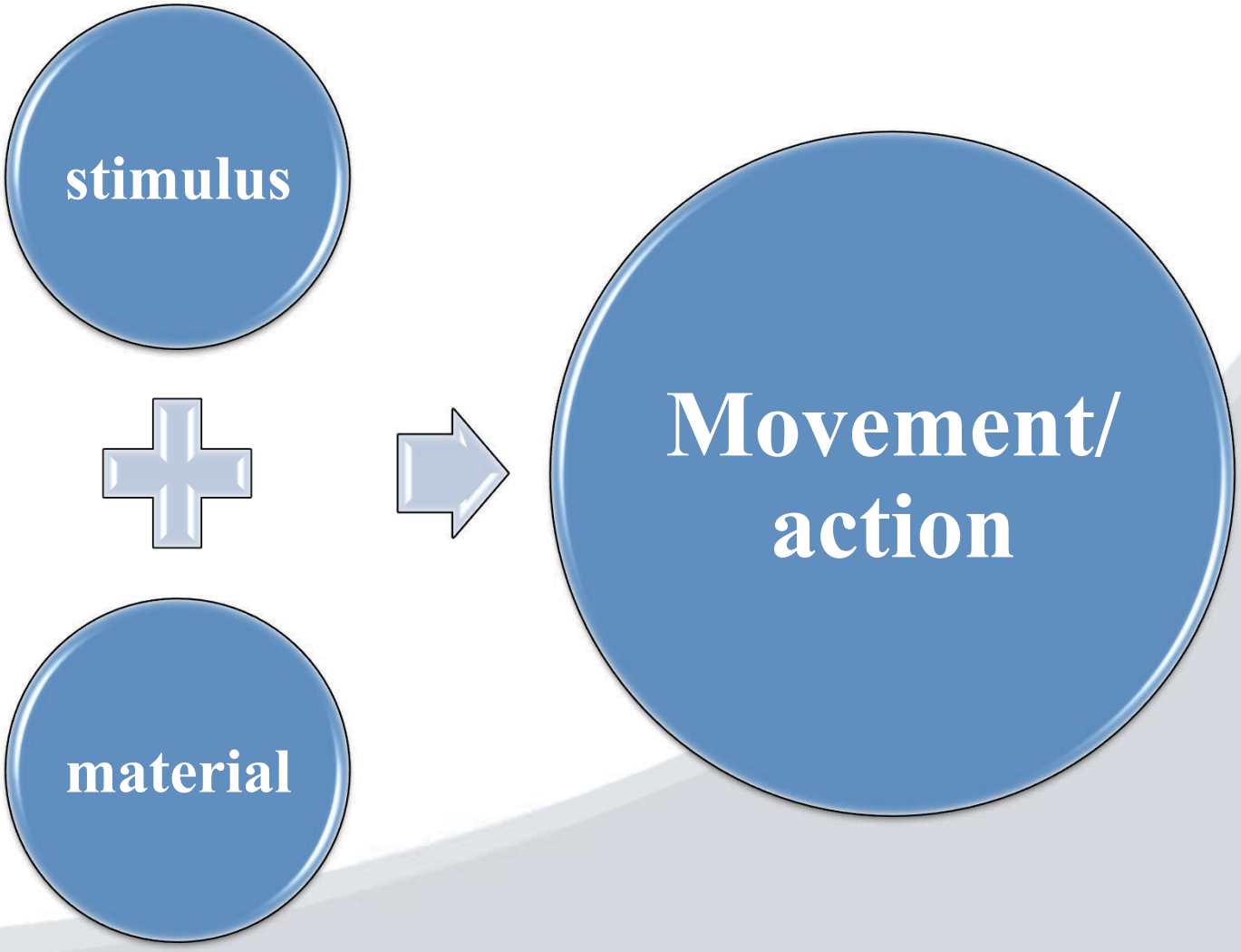
Sensors and Actuators…..

- 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

sensor



Actuator



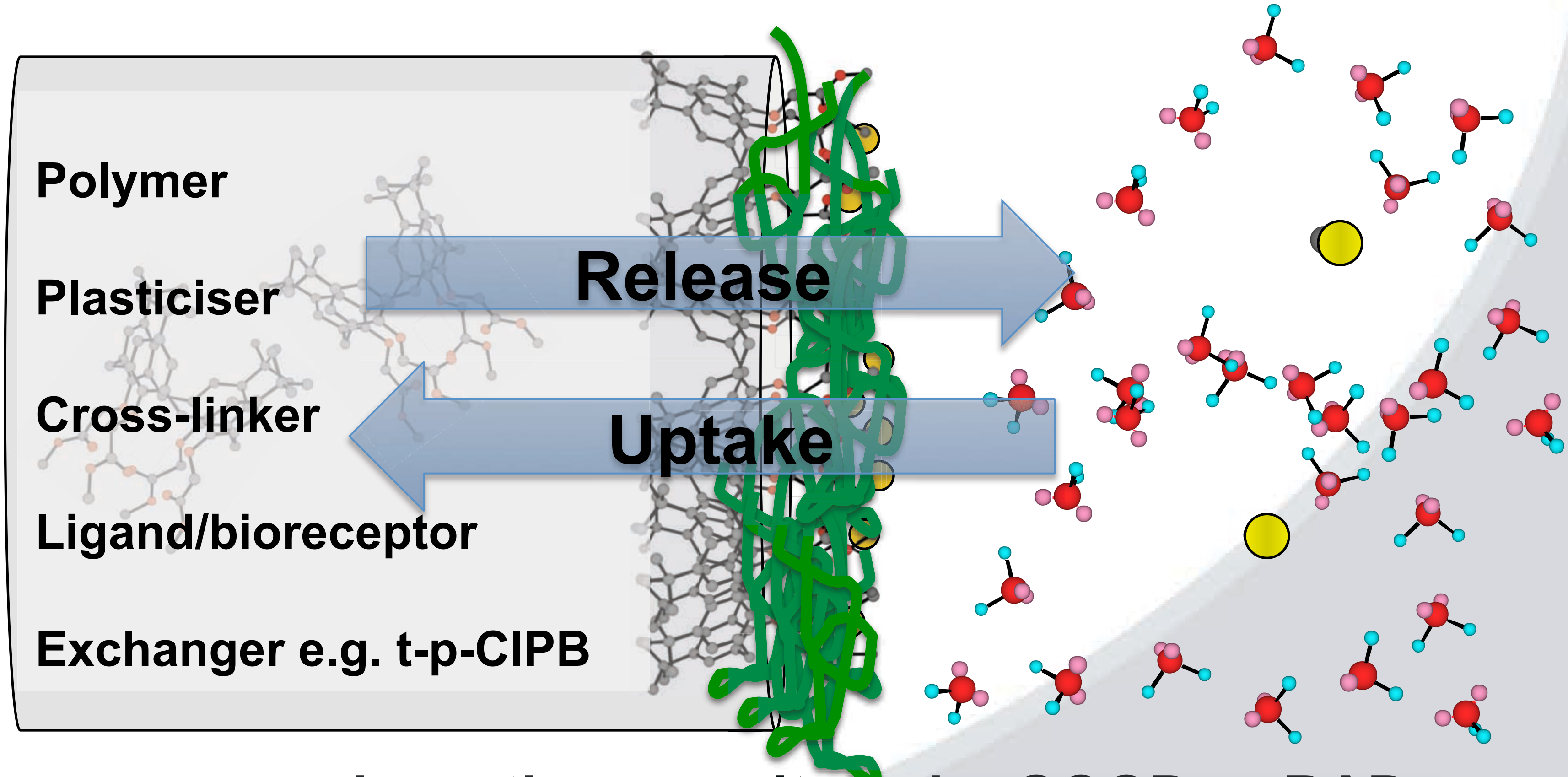
Why Ionic Liquids?

- Long-term stability of overall system
- Zero vapour pressure – do not evaporate over time
- Control of membrane bulk/surface charge and polarity
- Control of relative transfer characteristics of membrane and sample components across the sample/membrane interface

The ideal SENSOR and ACTUATOR is both Reactive AND Passive

Introducing switchable functionality is particularly interesting; i.e. capacity to switch between ACTIVE and PASSIVE states

Control of membrane interfacial exchange & binding processes



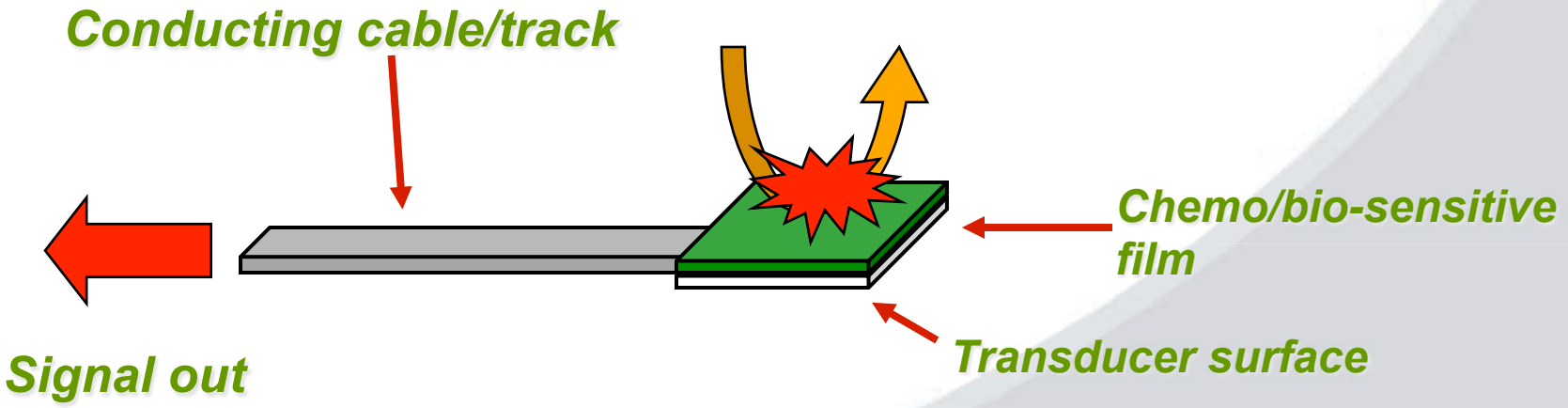
The processes have the capacity to be GOOD or BAD

The key is our ability TO CONTROL them!

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

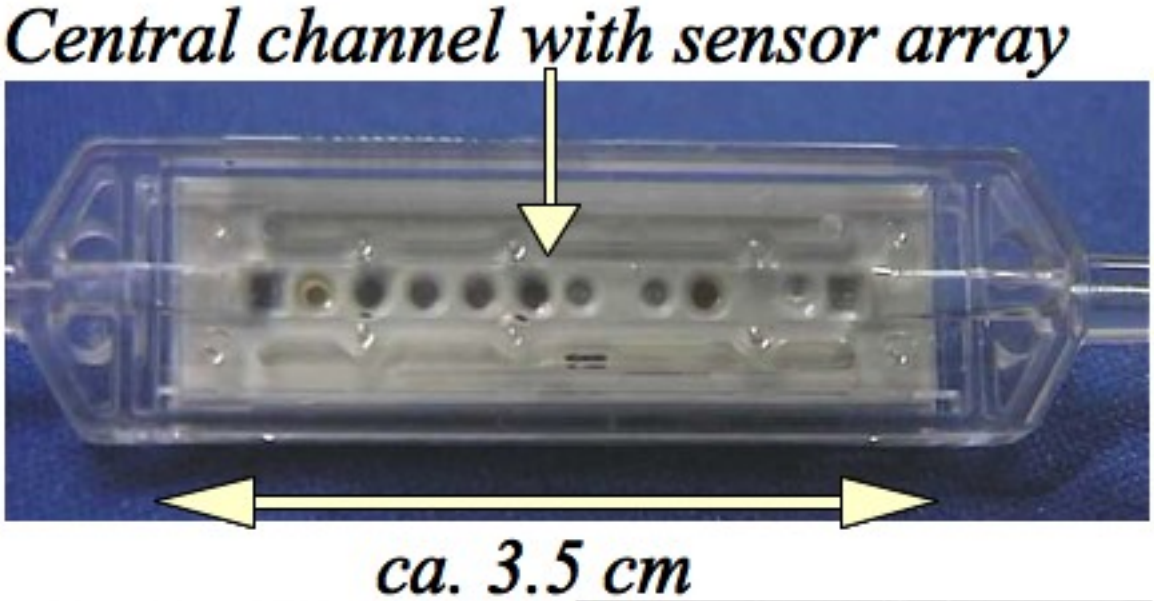
What is a Chemo/Bio-Sensor?

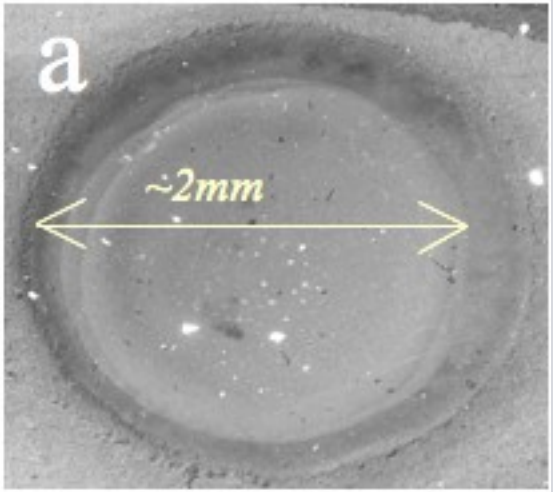
'a device, consisting of a transducer and a chemo/bio-sensitive film/membrane, that generates a signal related to the concentration of particular target analyte in a given sample'

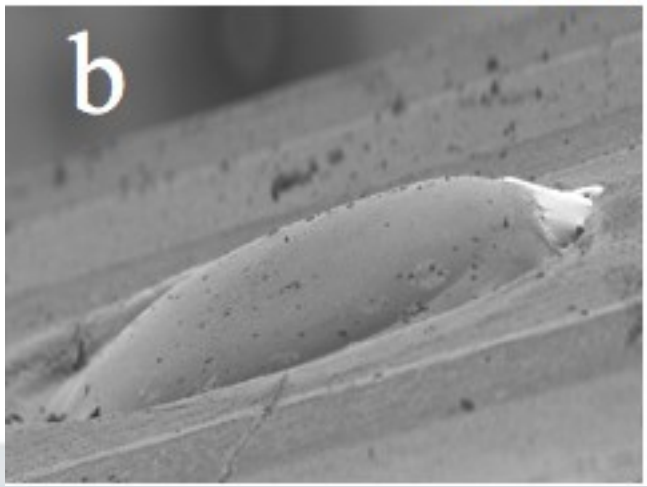


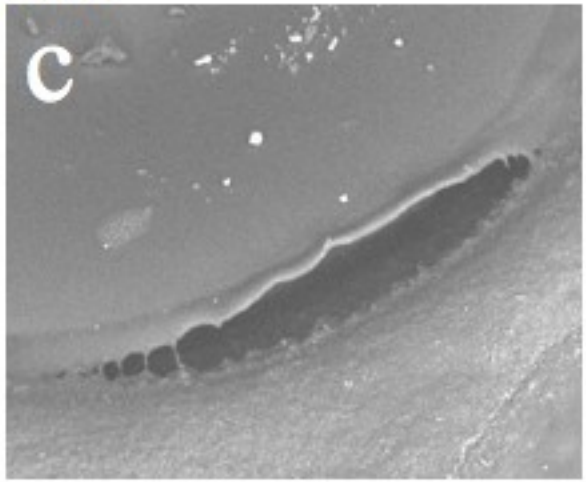
Chemo/Bio-sensing involves selective **BINDING** & **TRANSDUCTION** on the device surface; this also implies the target analyte MUST meet the device surface (**LOCATION** & **MOVEMENT**). It provides a signal observable in the macroscopic world (**COMMUNICATION**)

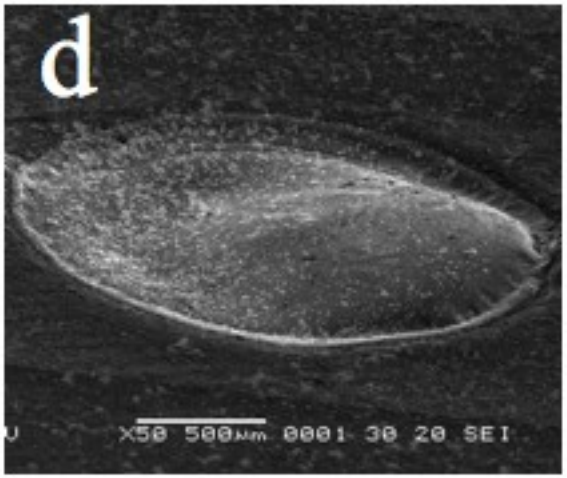
Planar ISE arrays for blood profiling: VP-SEM *(SenDx Corporation)*





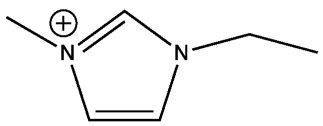




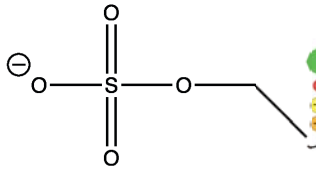


OCET Biosensing Platform: Lactate and Glucose

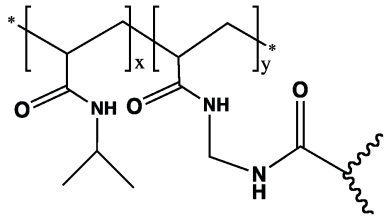
(A)



1-Ethyl-3methylimidazolium $[C_2mIm]^+$

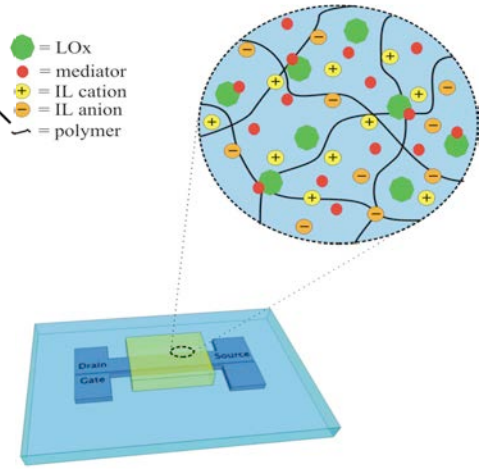


ethyl sulfate $[EtSO_4]^-$

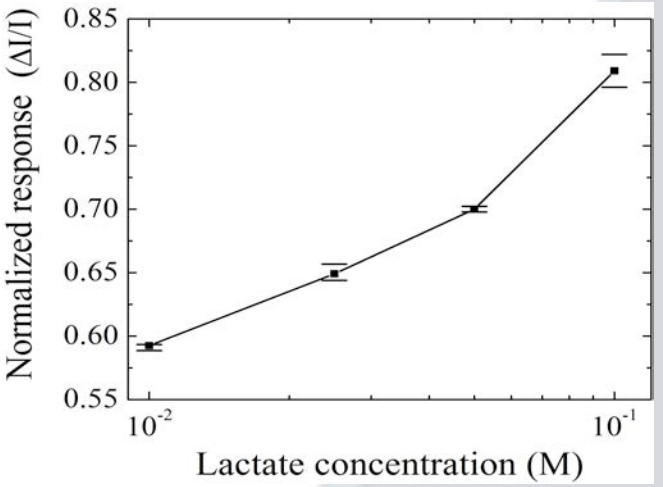


poly(*N*-isopropylacrylamide-co-*N*,*N*'-methylenebisacrylamide)

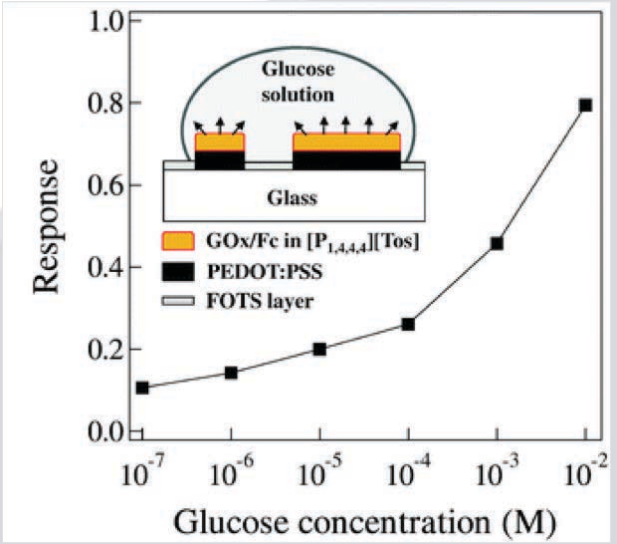
(B)



(c)



(d)



With George Malliaris and Roisin Owens, Centre Microélectronique de Provence, Ecole Nationale Supérieure des Mines de Saint Etienne

IL based Solid-State reference electrode

See Electroanalysis 2011, 23, No. 8, 1881–1890

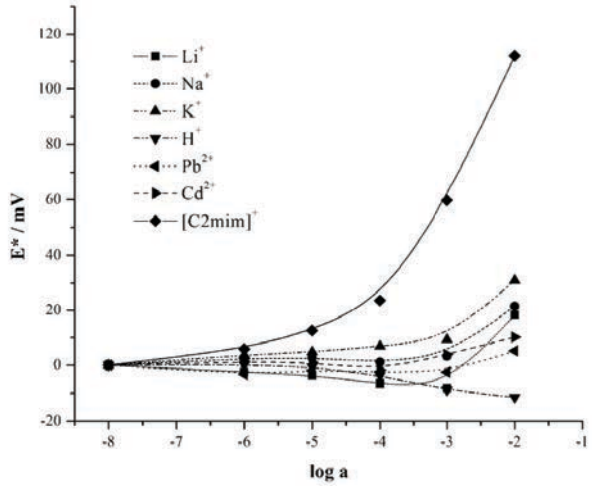


Fig. 3. Potentiometric responses of solid-contact electrodes prepared using PVC and [C_2mim][NTf2] to a range of ions.

Based on PVC:[C_2mim][NTf_2] membrane 1:2 m/m

IL acts as plasticiser for PVC and source of sparingly soluble ions that form a stable interfacial potential with the sample solution
(Left) titrations of SSRE vs. Ag/AgCl ref electrode for a range of ions; only significant response is to [C2mim]$^+$, confirming that this ion defines the potential

Electrodes are produced by

1. screen printing Ag/AgCl contact track
2. Screen printing carbon sub-electrode layer
3. Screen printing insulating regions
4. Drop casting or electrochemically growing PEDOT layer
5. Drop-casting IL:PVC capping layer

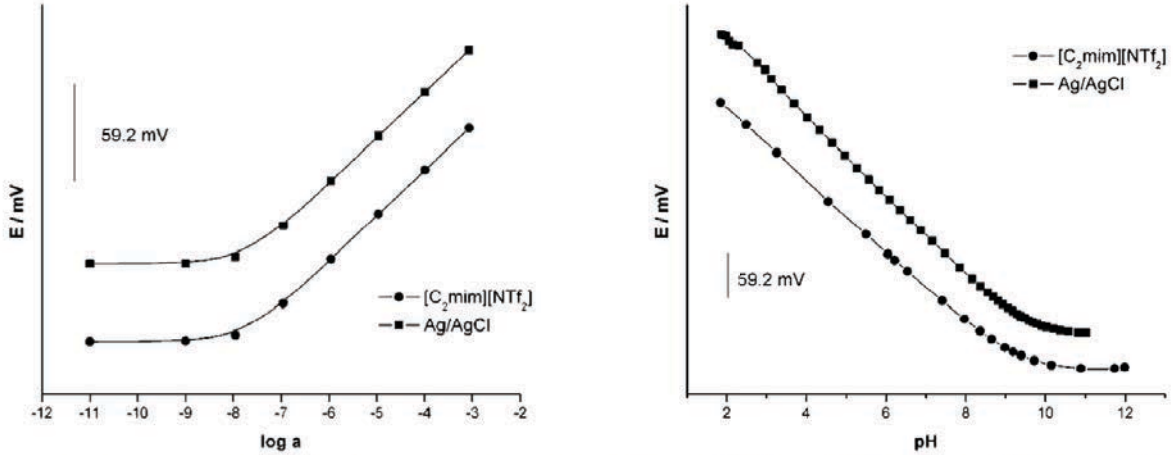
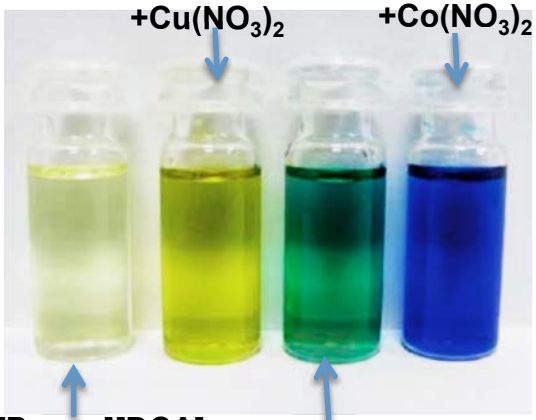


Fig. 6. Left) Response of the SC Pb-selective electrode coupled with [C_2mim][NTf2]-based SCRE (circles) and Methrom Ag/AgCl RE (squares). The slopes are 28.1 mV/decade and 26.5 mV/decade, respectively. The detection limit of 2×10^{-8} M is identical for both electrodes. Right) Response of the SC pH-selective electrode coupled with [C_2mim][NTf2]-based SCRE (circles) and Methrom Ag/AgCl RE (squares). The slopes are 55.4 mV/decade and 51.2 mV/decade, respectively.

Colour Sensitive [P6,6,6,14][DCA] membranes

See Analyst, 2011, 136, 348–353



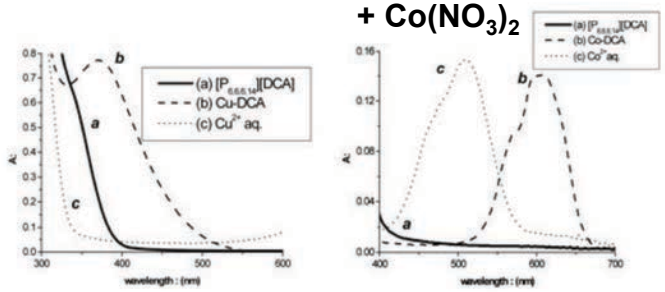


Fig. 2 Absorption spectra of IL (a), upon complexation with metal ion (b), and the original metal ion solution (c).

DCA acts as a pseudo halide and binds certain metal ions; with Cu^{2+} and Co^{2+}, striking colours are obtained; can be used to form the basis of optical sensors.

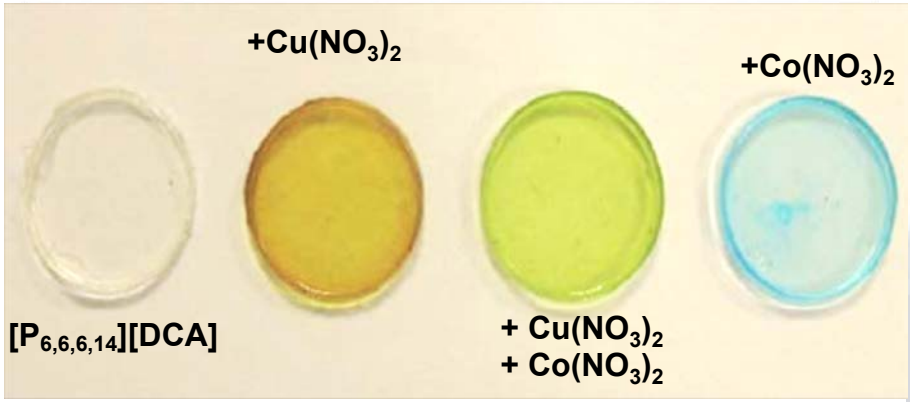


Fig. 4 Two-component IL–PVC polymeric optode membranes capable of generating 3 distinct optical responses.

Membranes prepared 1:2 m/m PVC:$P_{6,6,6,14}$][DCA] using THF

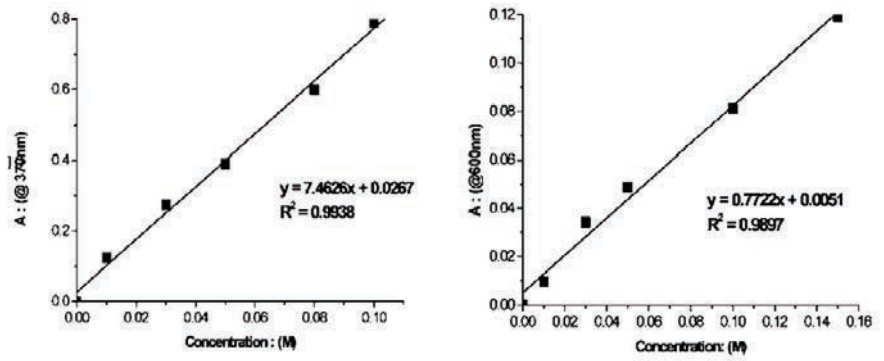
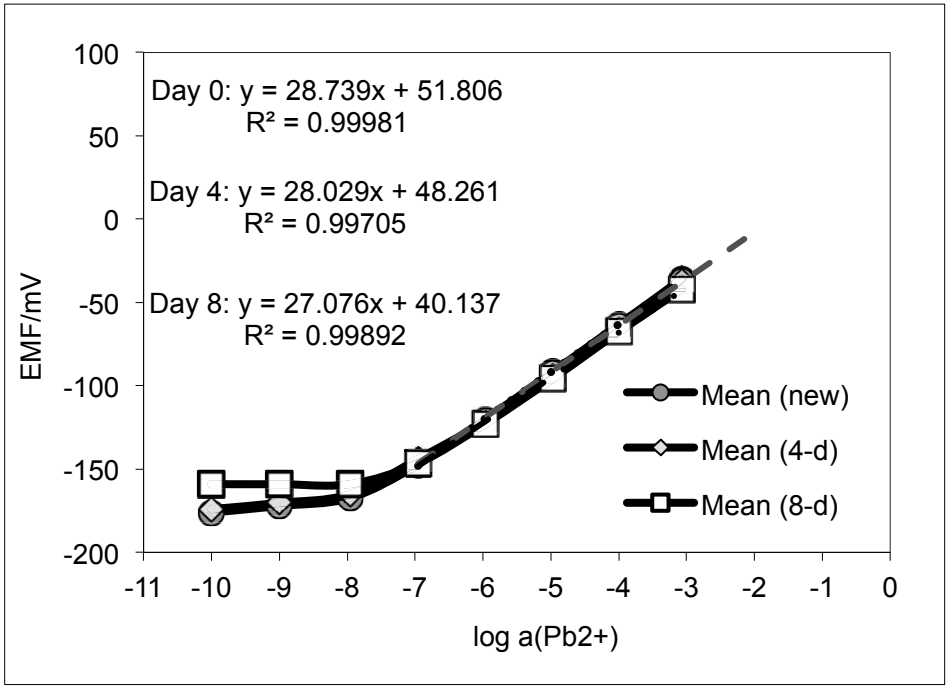
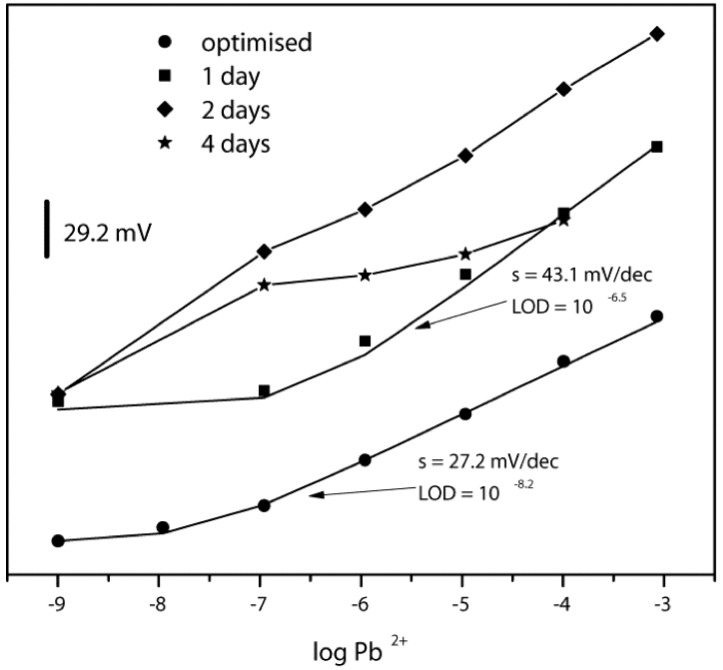


Fig. 6 Calibration curves obtained for copper (left) and cobalt (right) complexation.

Change in Electrode Function over Time

See Electrochimica Acta 73 (2012) 93–97



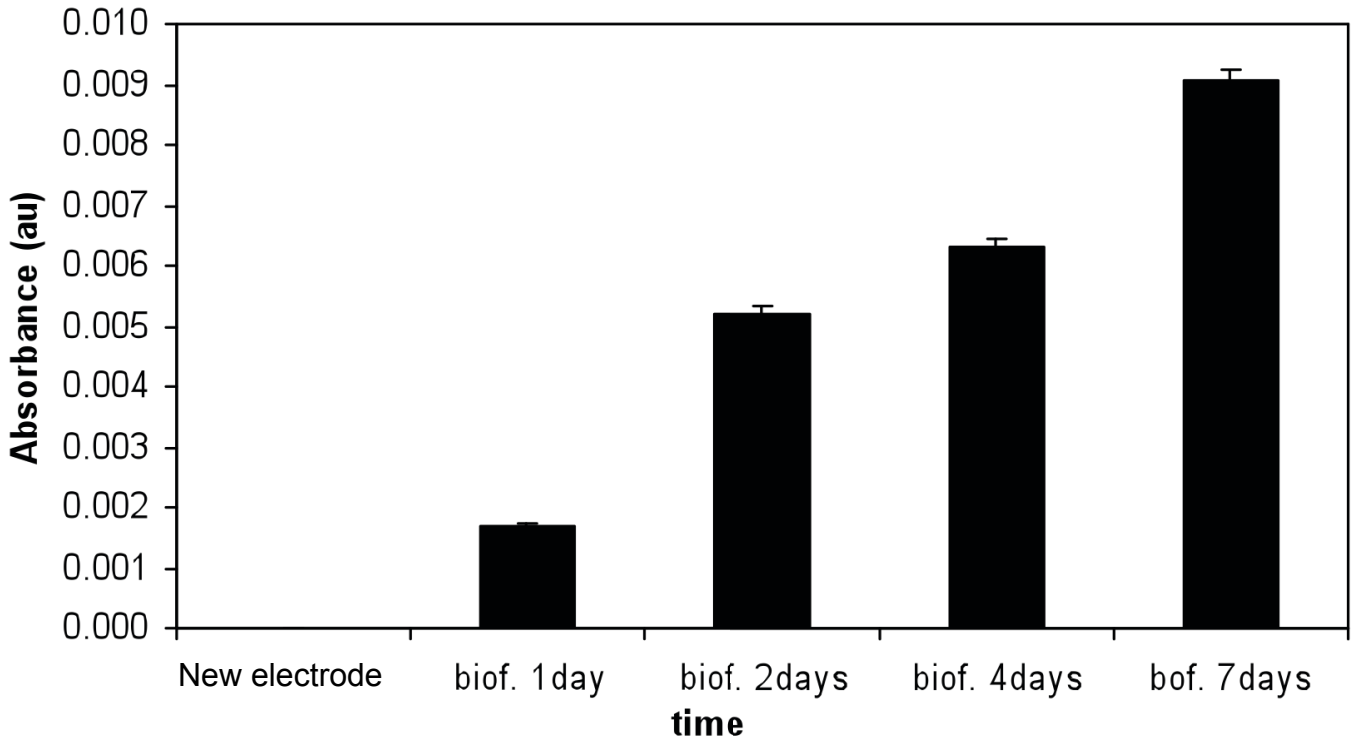


stored in 10^{-9}M Pb^{2+}, pH=4

Continuous contact with river water

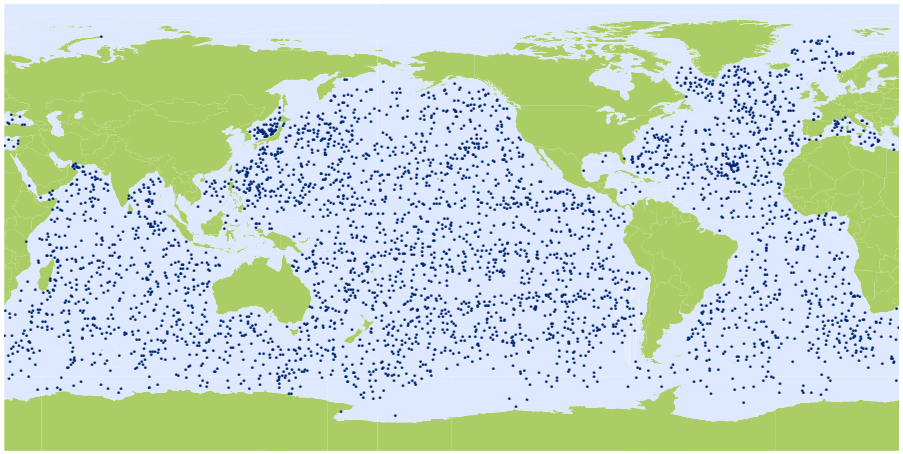
Conventional PVC-membrane based ISEs

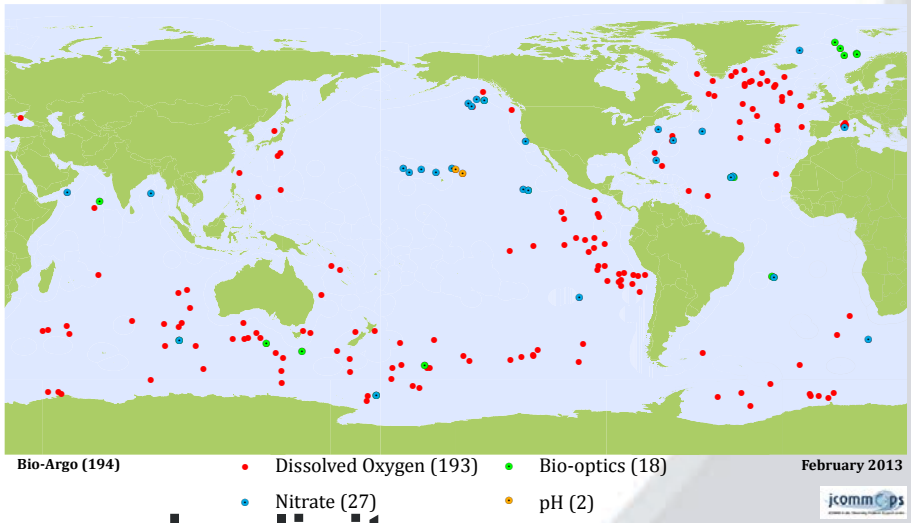
Biofilm Formation on Sensors



- 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

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

Progress will require advances emerging from fundamental research in materials chemistry

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

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

CLARITY
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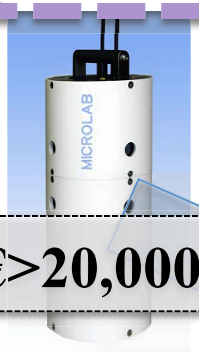
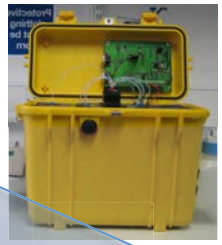
Current platforms





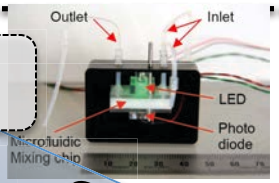
€>20,000

1

€>2,000

2. Revolutionary breakthroughs in materials science; hidden complexity, biomimetic platforms, all fluid handling integrated on chip, indefinitely self-sustaining

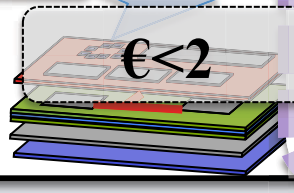
€<200



2

€<20

1. Evolutionary development, cost driven down, reliable, improved scalability



€<2

Massively scaled deployments of the future

Cost/Complexity->

Scalability ->

Cost Comparison Analyser (€)

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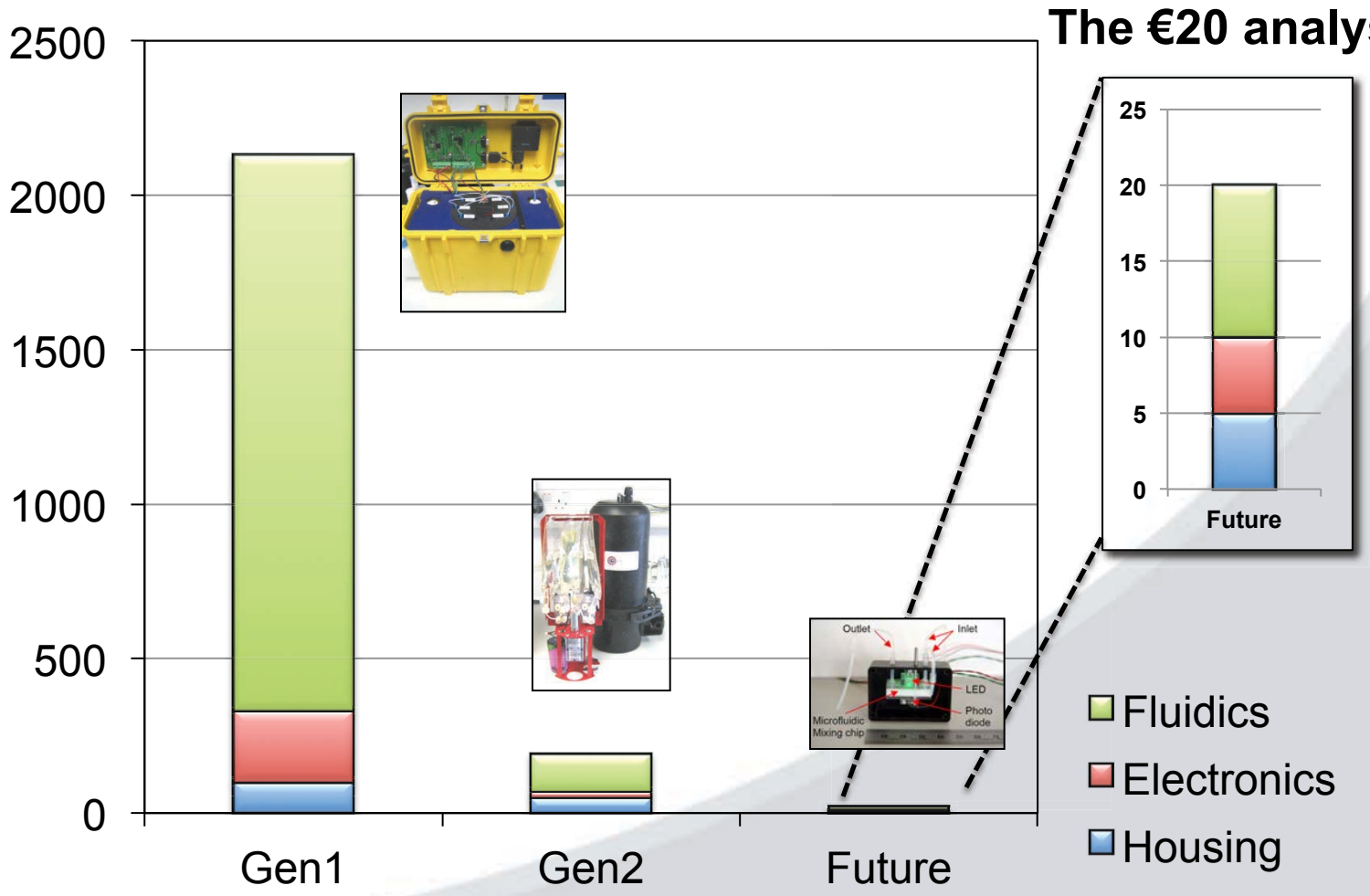
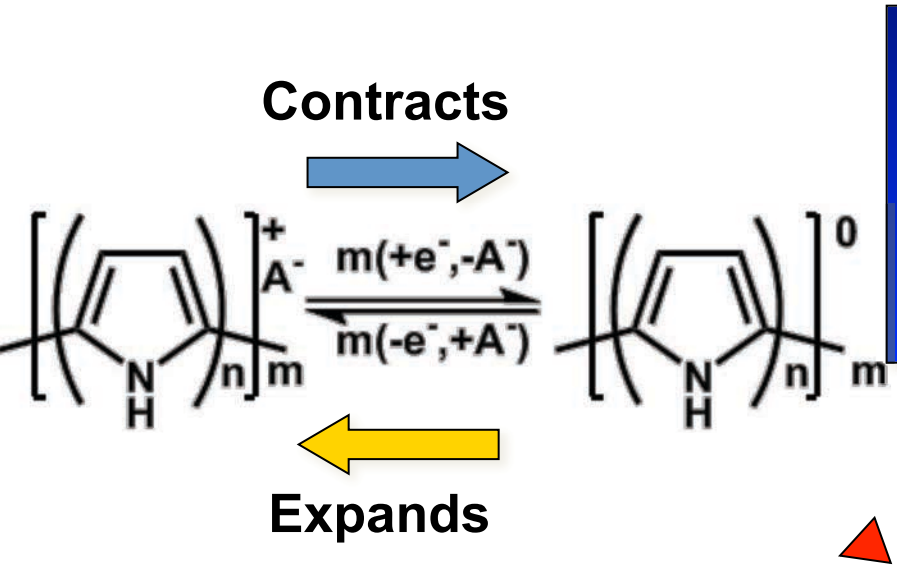


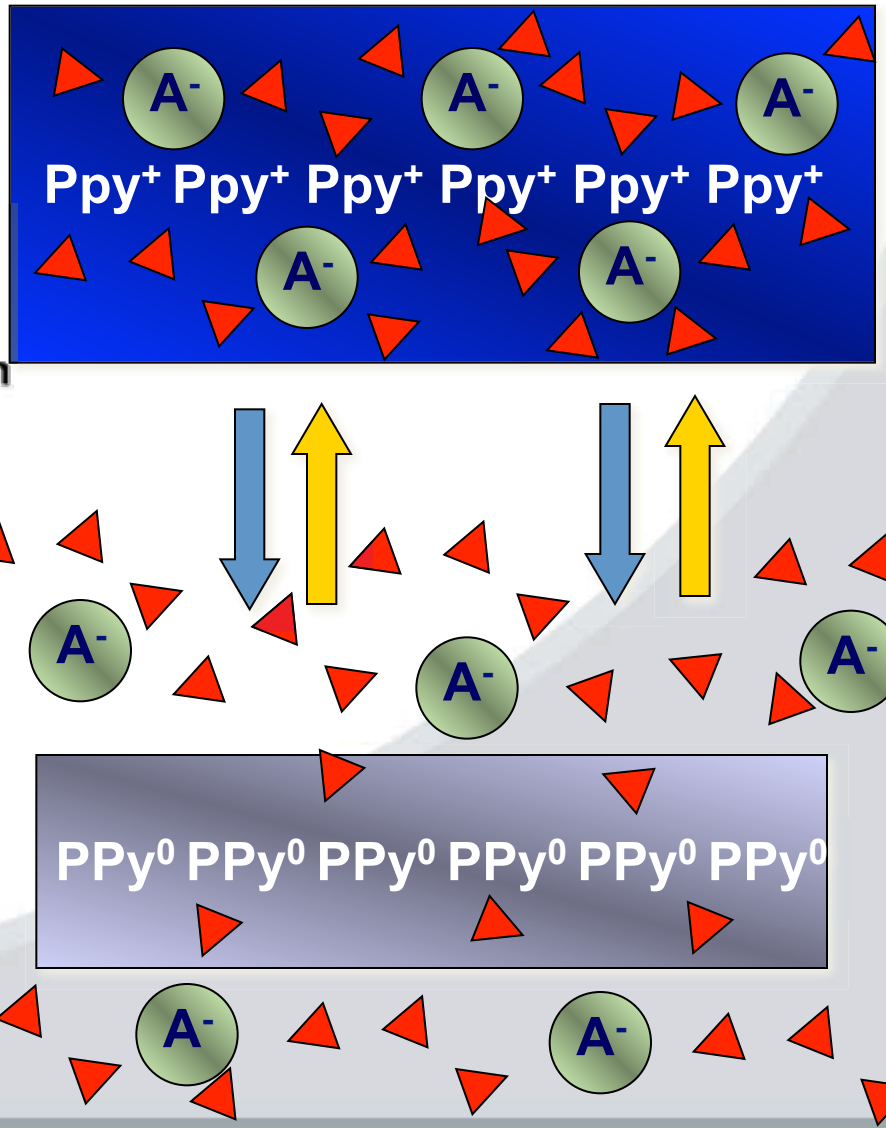
How to advance fluid handling in LOC platforms: re-invent valves (and pumps)!

- **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

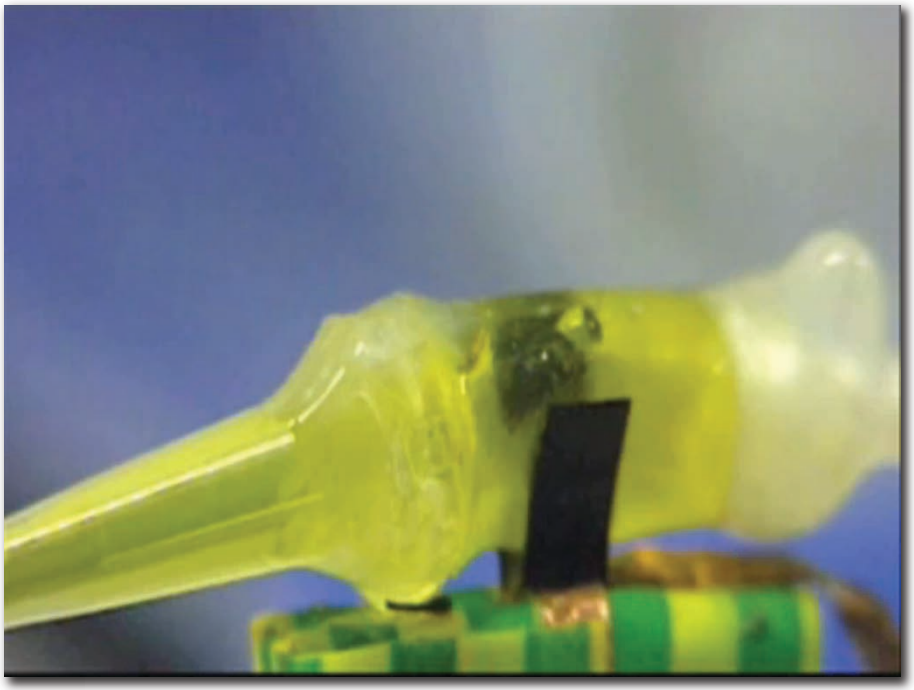
Switchable Materials: Soft Polymer Actuators

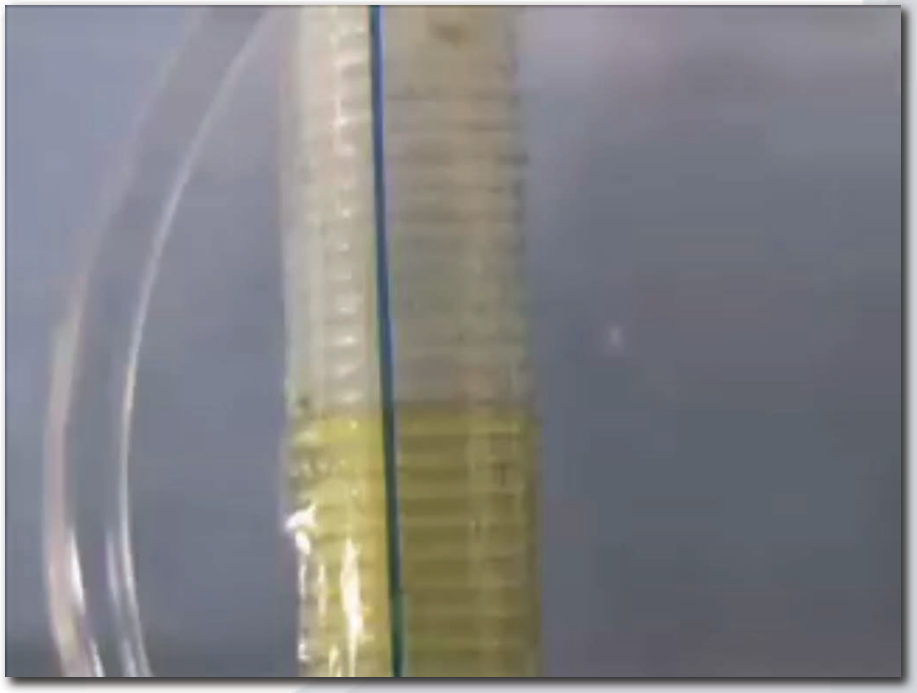




Principle can be used to make soft polymer (biomimetic, artificial muscle) actuators

Towards the €20 Analyser: Biomimetic low-power soft pump



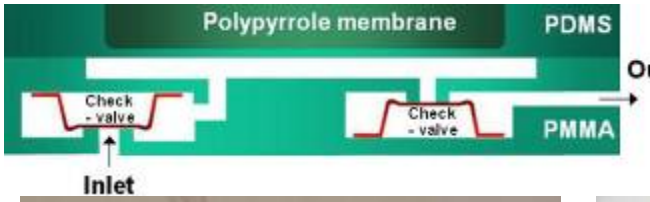


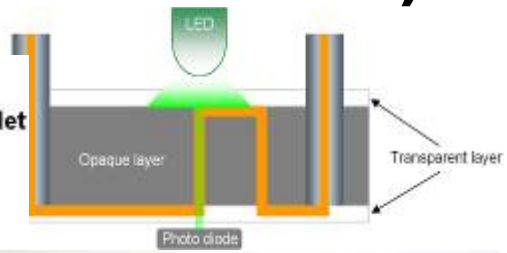
Low Power control of fluid movement in channels and on surfaces is possible using electrochemically switched actuators!

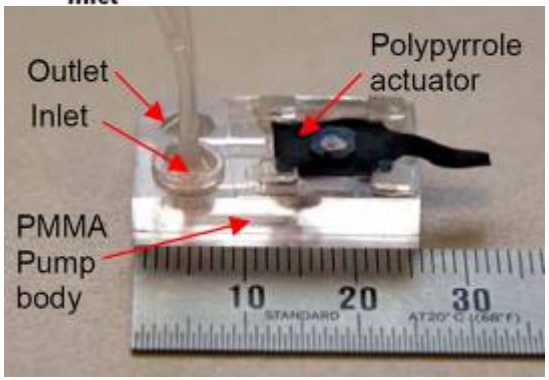
Internet-scale Sensing: Are Biomimetic Approaches the Answer?, Sonia Ramirez-Garcia and Dermot Diamond, Journal of Intelligent Material Systems and Structures, 18 (2) (2007) 159-164.

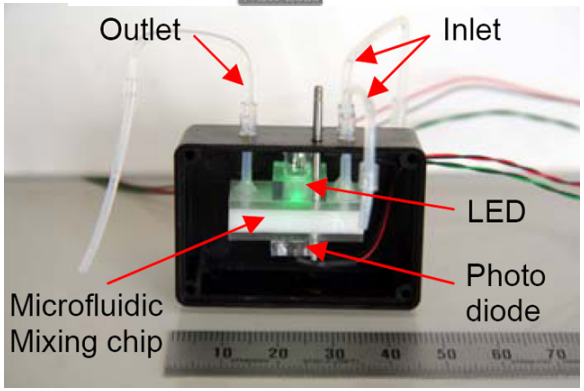
Biomimetic, low power pumps based on soft actuators, Sonia Ramirez-Garcıa and Dermot Diamond, Sensors and Actuators A 135 (2007) 229–235.

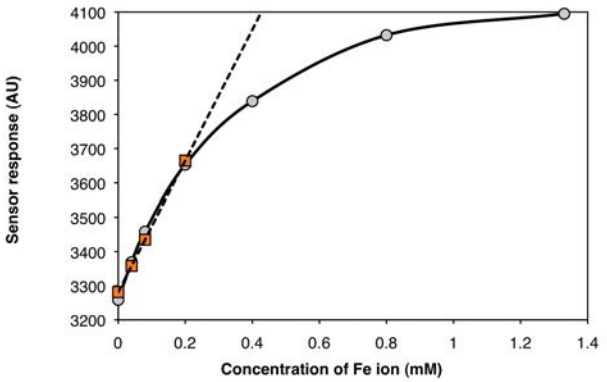
Prototype Gen3 (Matchbox) System

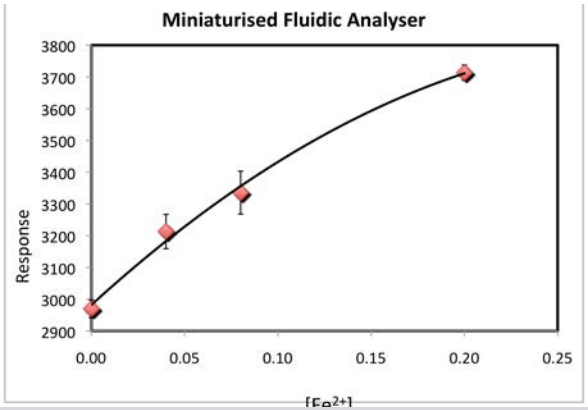


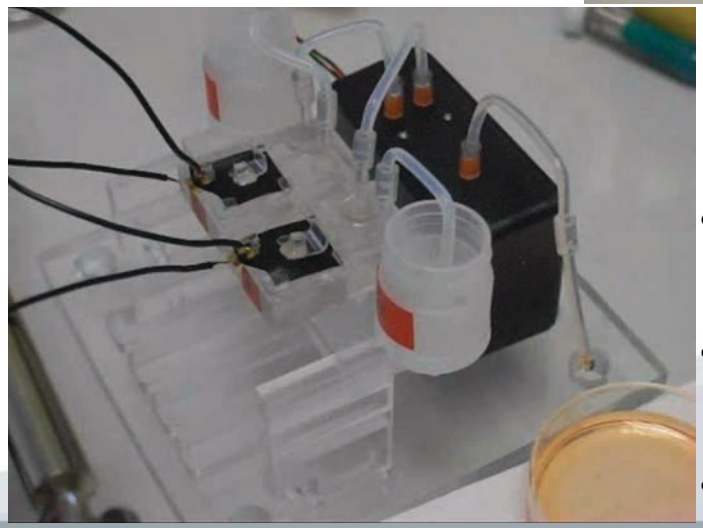






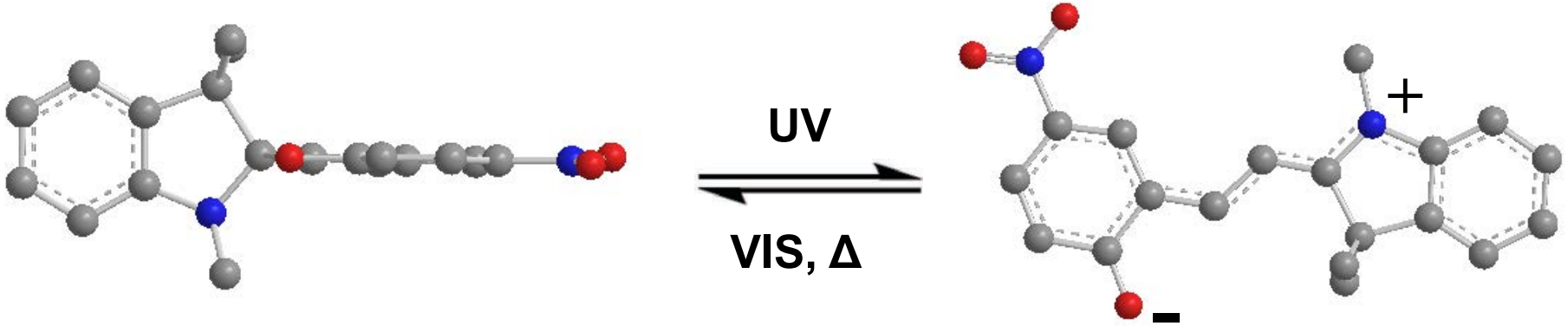


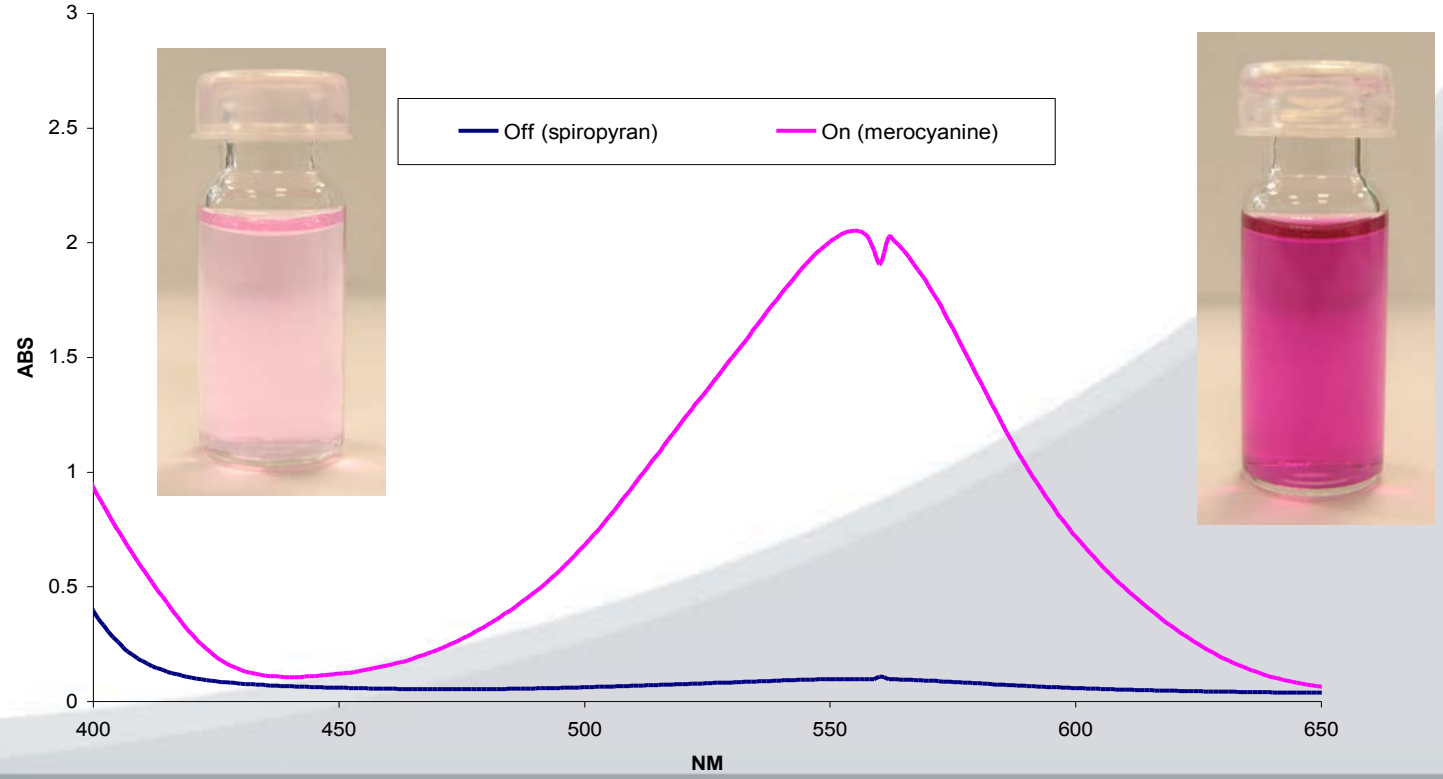




- Linear range of detection: 0.04~0.20mM of Fe^{2+} ions (n=3)
- Upper limit (saturation) of detection occurs over 1.33mM
- Can be applied to other colorimetric methods

Photoswitchable Materials

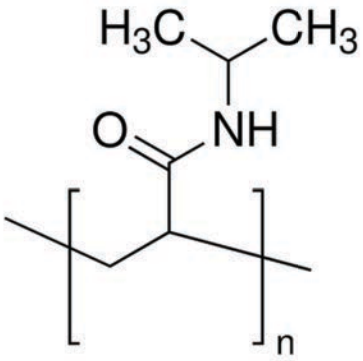


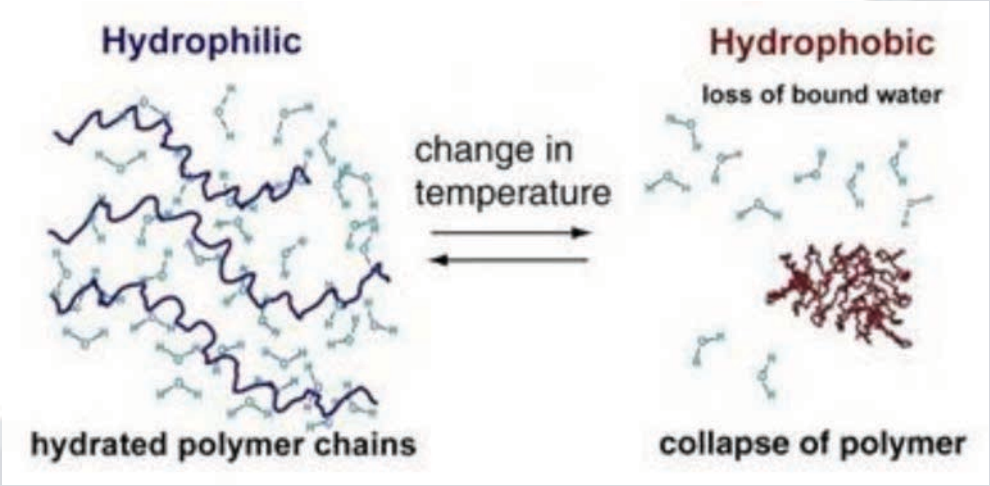


Poly(*N*-isopropylacrylamide)

- 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

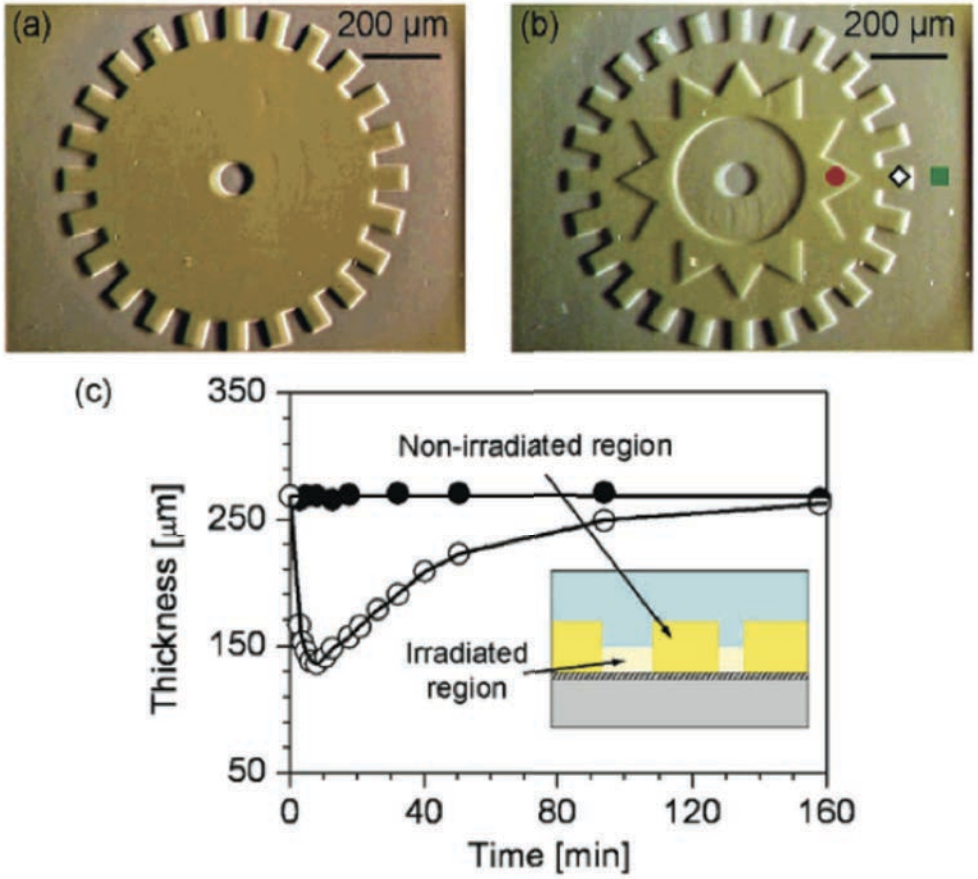
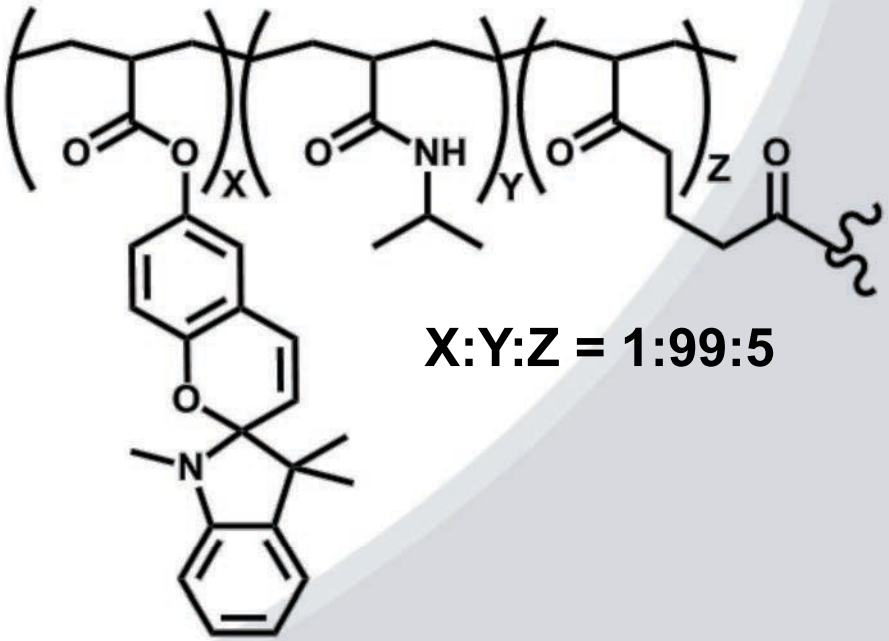


Figure 3. (a, b) Images of the pSPNIPAAm hydrogel layer just after the micropatterned light irradiation. Duration of irradiation was (●, red) 0, (◇) 1, and (■, green) 3 s. (c) Height change of the hydrogel layer in (●) non-irradiated and (○) irradiated region as a function of time after 3 s blue light 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 ([P6,6,6,14] 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

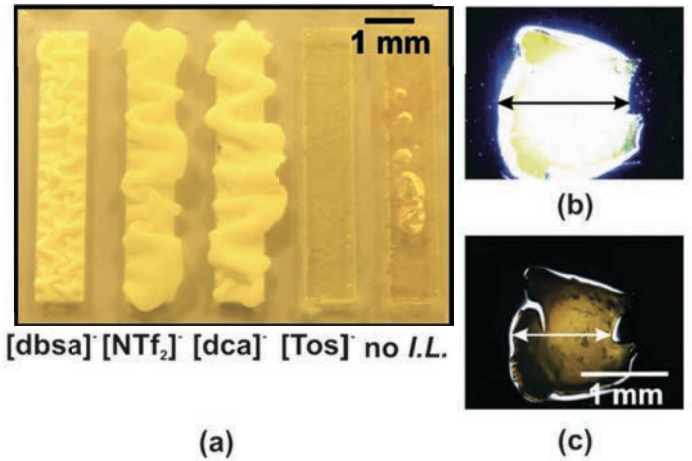


Fig. 3 (a) Photo-responsive polymer gels after immersion of the mould in a 1 mM HCl solution for 2 h. Right: $[dca]^-$ ionogel shrinking process; (b) ionogel before illumination and (c) the same sample after 2 s illumination with a white light LED, size decrease is *ca.* 30% by volume.

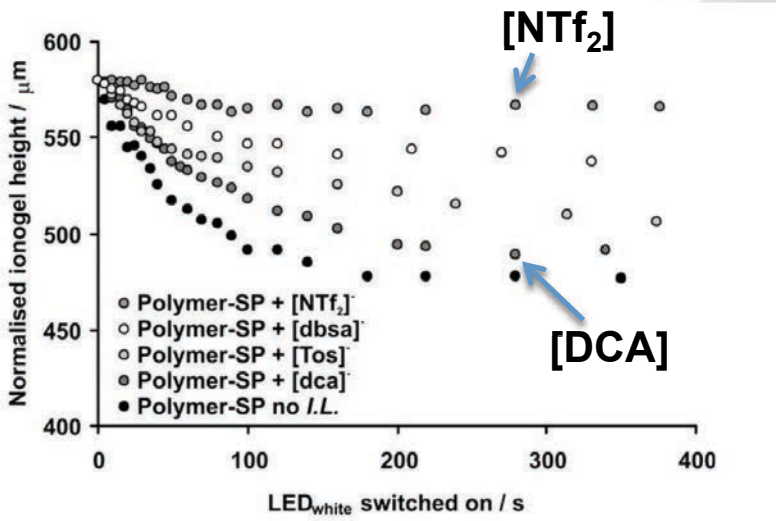
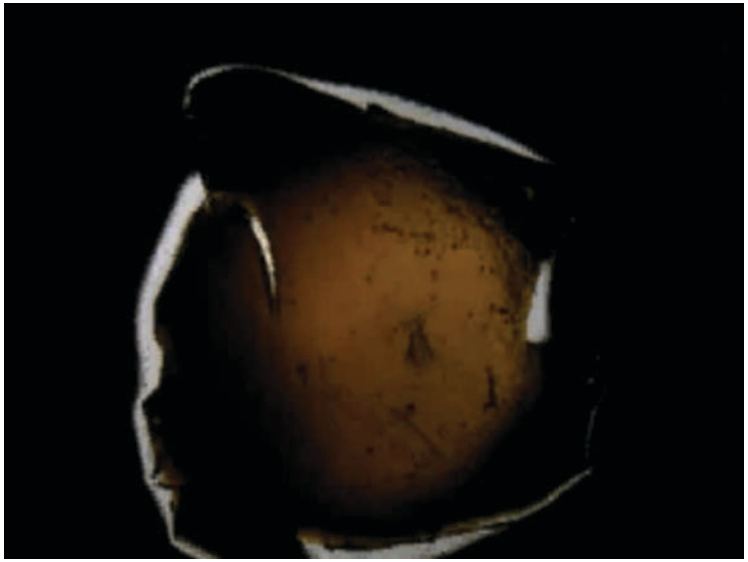
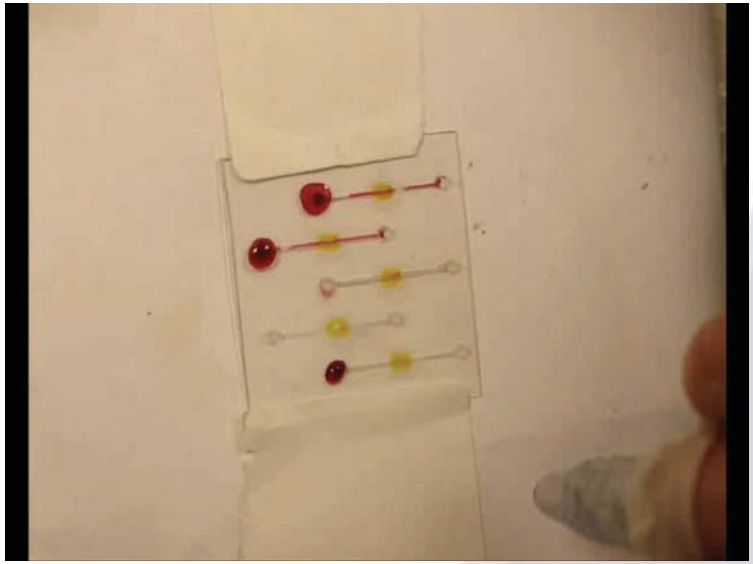
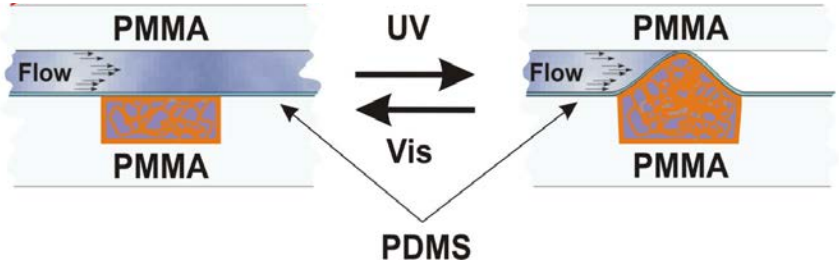


Fig. 6 Response kinetics of ionogels upon irradiation with white light (ionogel height error: ±5 µm).

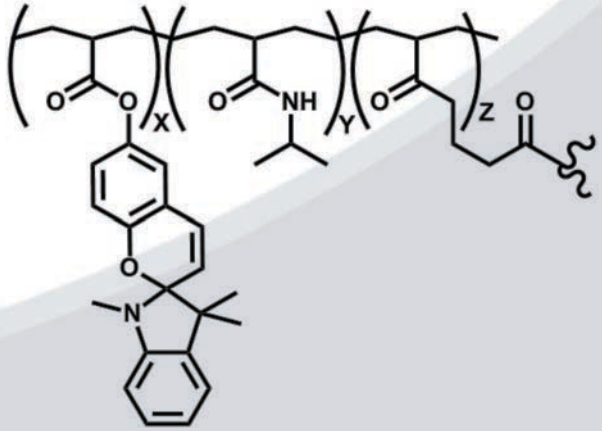
Photo-actuator polymers as microvalves in microfluidic systems

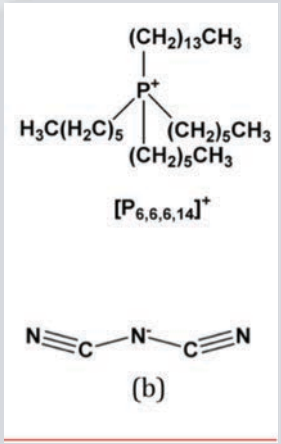






trihexyltetradecylphosphonium dicyanoamide $[P_{6,6,6,14}]^+[dca]^-$

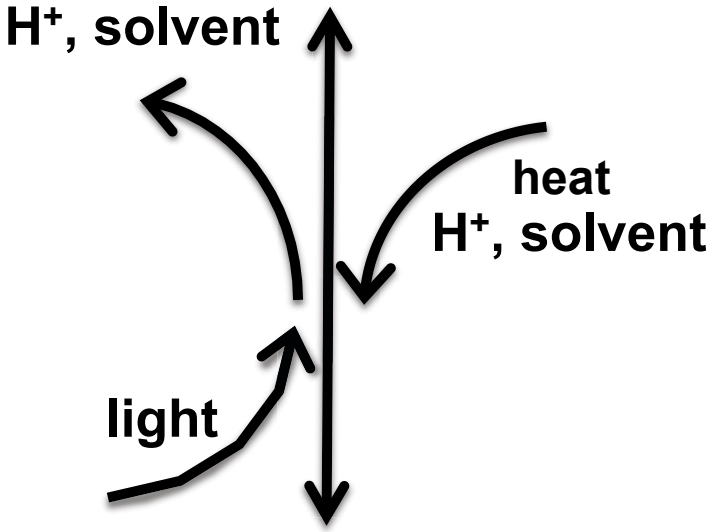




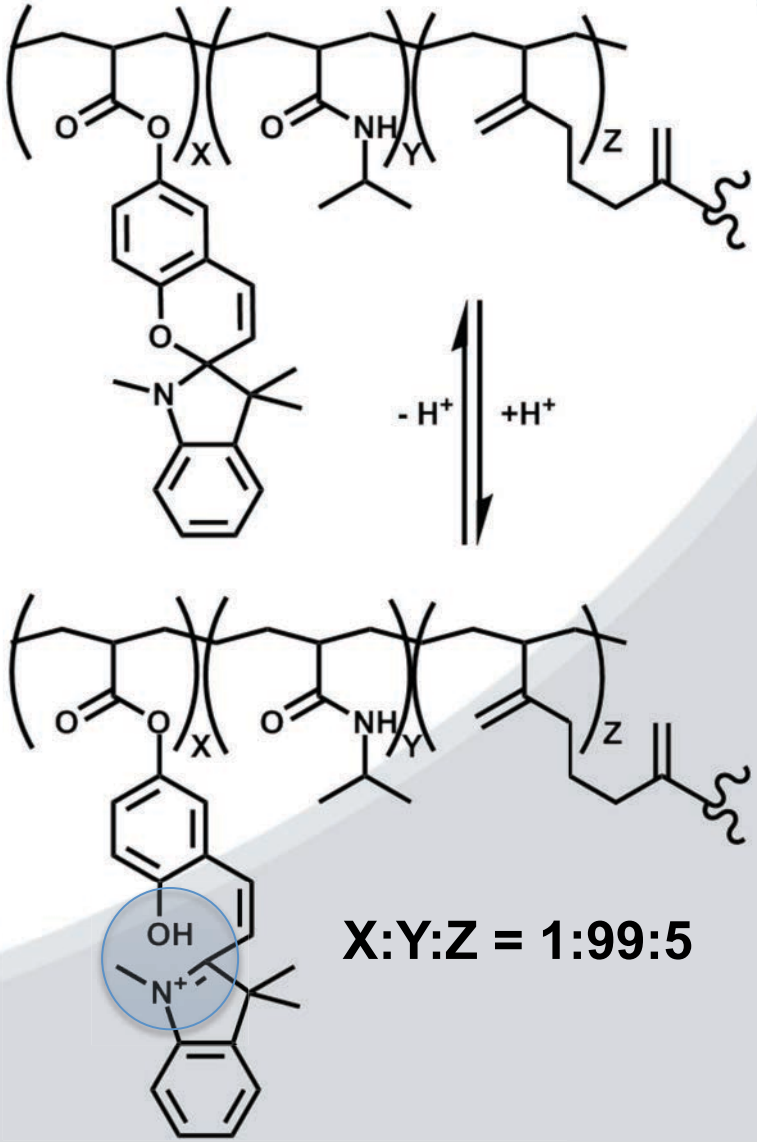
Ionogel-based light-actuated valves for controlling liquid flow in micro-fluidic manifolds, Fernando Benito-Lopez, Robert Byrne, Ana Maria Raduta, Nihal Engin Vrana, Garrett McGuinness, Dermot Diamond, Lab Chip, 10 (2010) 195-201.

Actuation Mechanism

SPIRO
(contracted)



MERO-H+
(expanded)

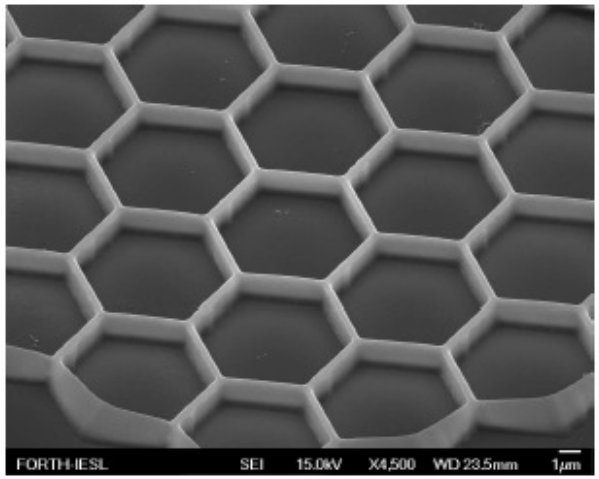


X:Y:Z = 1:99:5

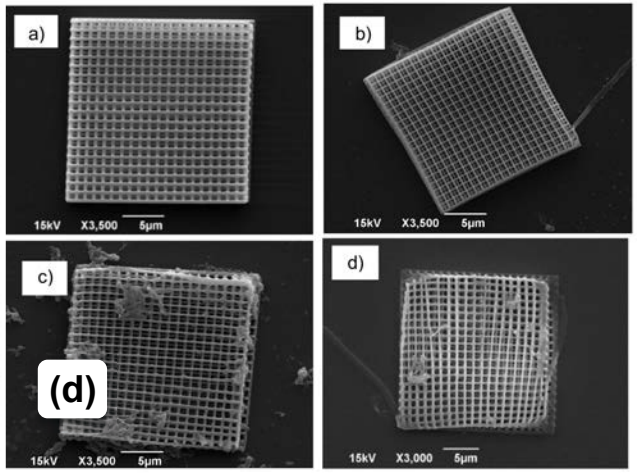
So far, so good: but what are the limitations?

- 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

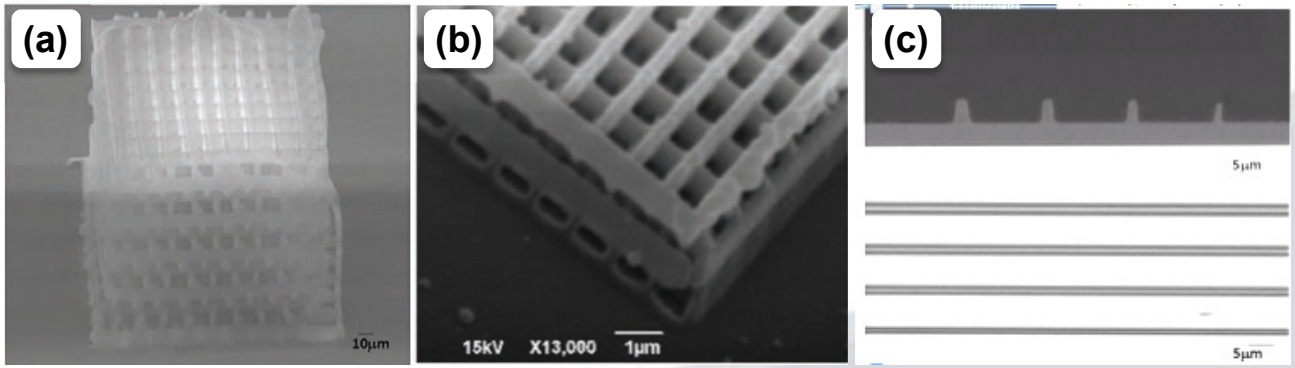
Reduce scale – increase response time
3-d Spiro-doped sol-ionogels



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

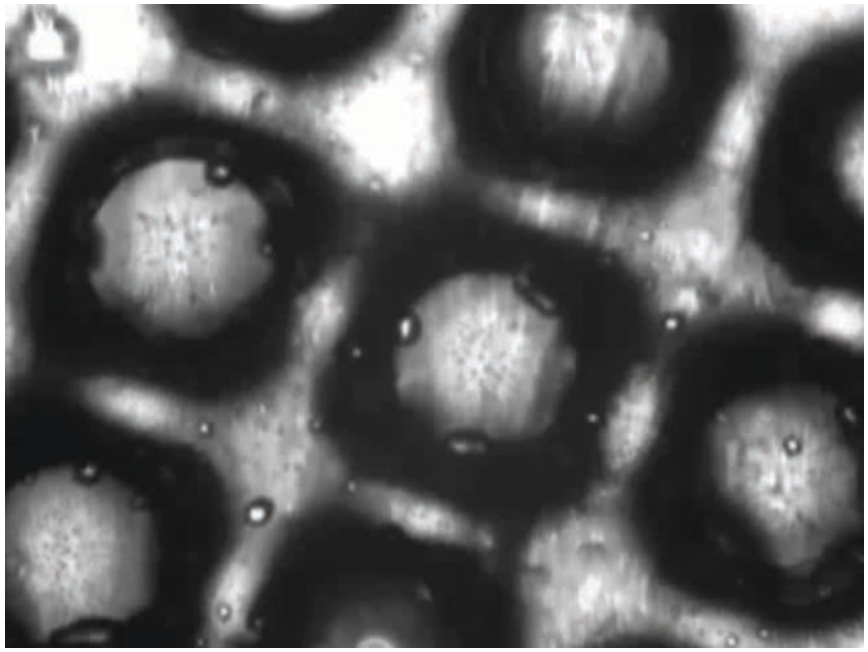


Two photon polymerised (2PP), patterned ionogels (a) and (b), and (c) feature resolution down to 150 nm or less; (d) spiropyran co-polymerised in a gel 'woodpile' structure.

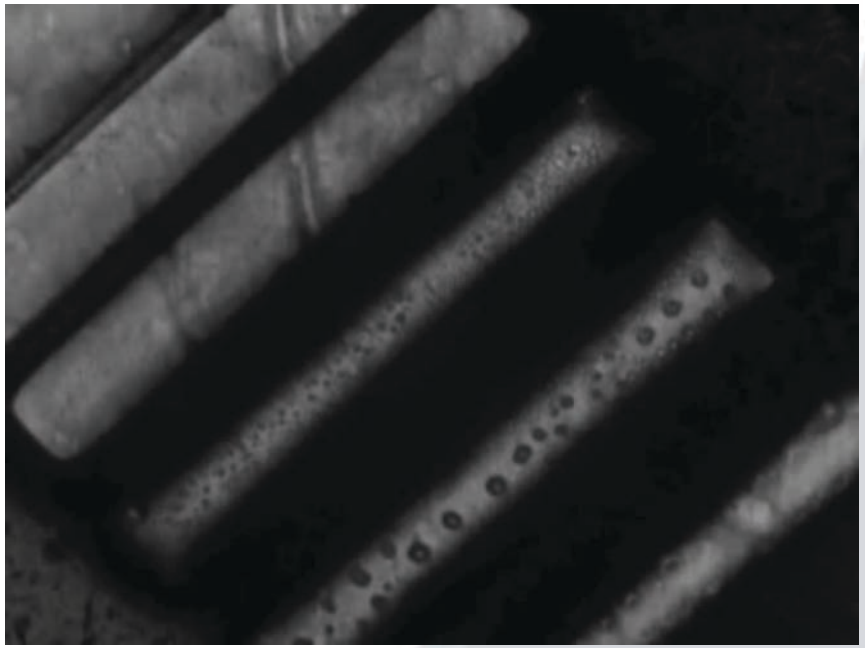
The ionogels were based on photo-curable silicato-zirconate hybrid sol-gel materials and phosphonium (trihexyltetradecylphosphonium dicyanamide [$P_{6,6,6,14}$][DCA] ionic liquid (IL). To optimise the dispersion of graphene within the ionogel matrices, aqueous solutions of graphene were prepared, as 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

Build Dynamic pNIPAAm Structures within Microchannels



Ntf2 pillars speed x3

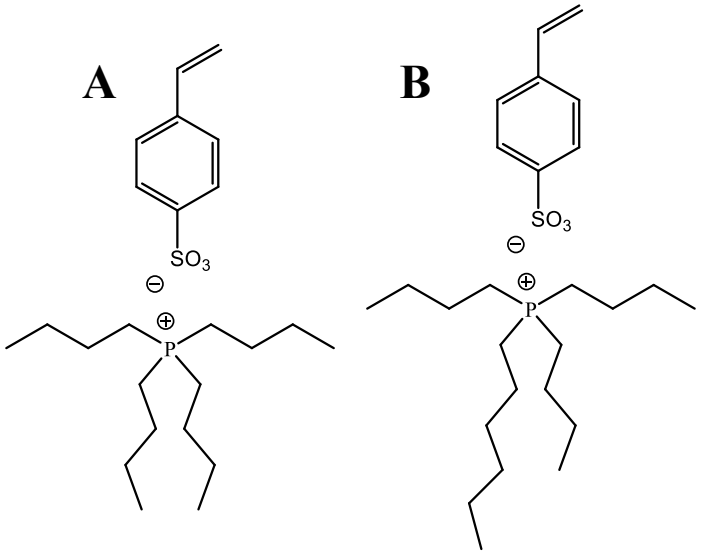


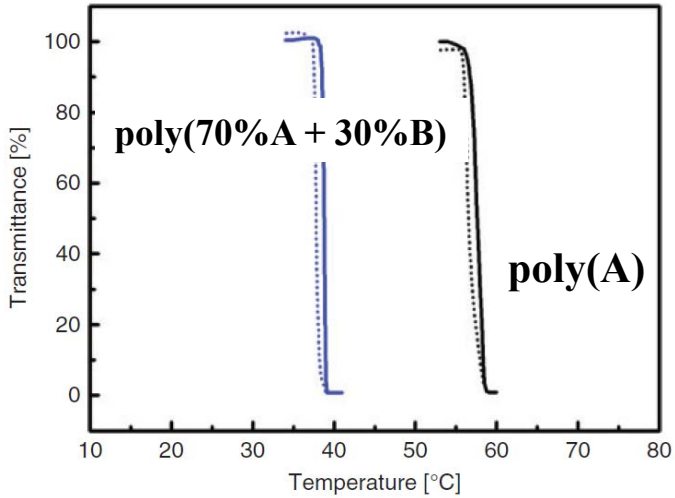
DCA lines speed x4

With Dr Peer Fischer, Fraunhofer-Institut für Physikalische Messtechnik (IPM), Freiburg

Other stimuli- Thermo-responsive poly(ILs)

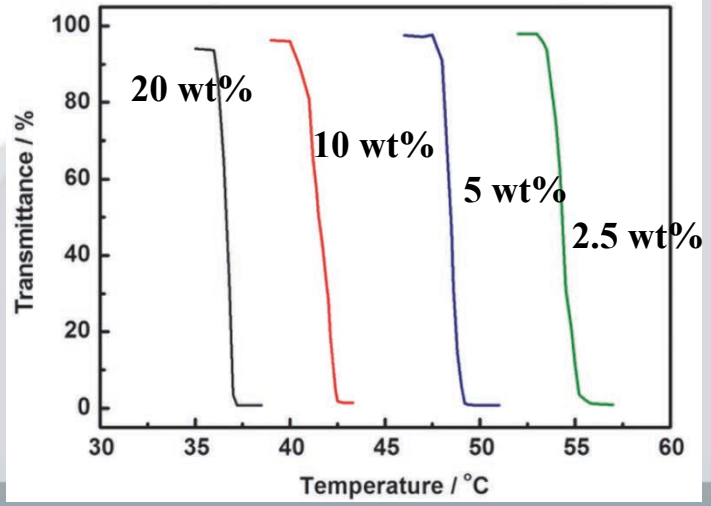
New polymeric ionic liquids that are thermoresponsive have been recently reported





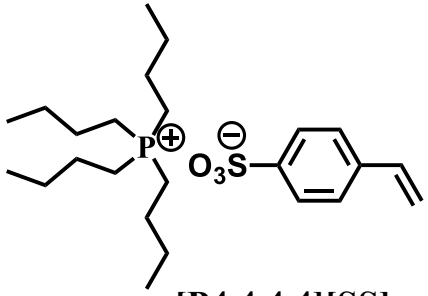
Y. Kohno and H. Ohno, *Aust. J. Chem.*, 2011, 65, 91-94

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

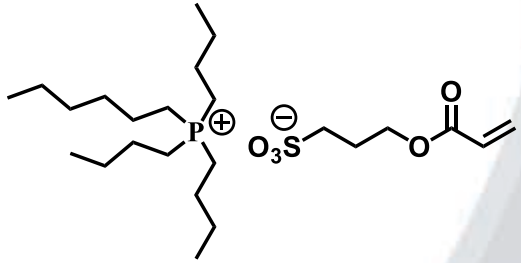


Preparation of thermo-responsive poly(IL) gels

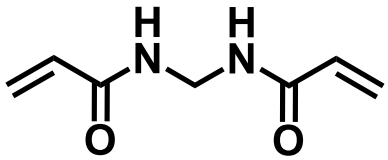
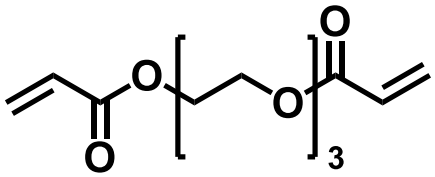
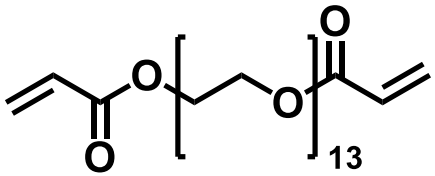
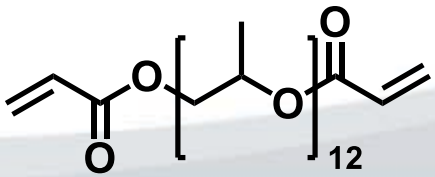
1. Longer cross-linkers produce stable poly(IL) gels
2. Amount of cross-linker enables LCST effect to be tuned
3. Cross-linking broadens the LCST peak



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



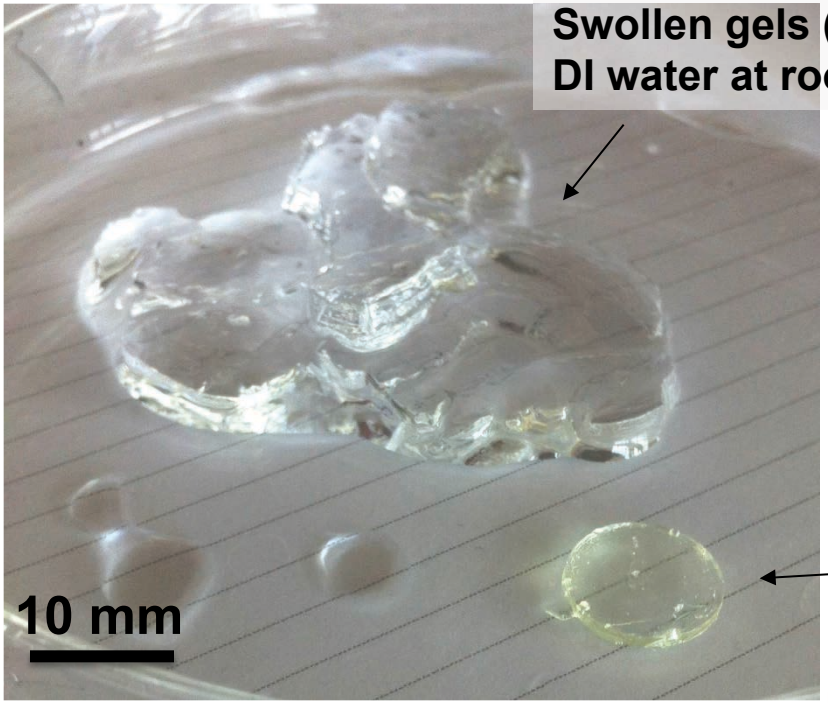
[P4,4,4,6][SPA]

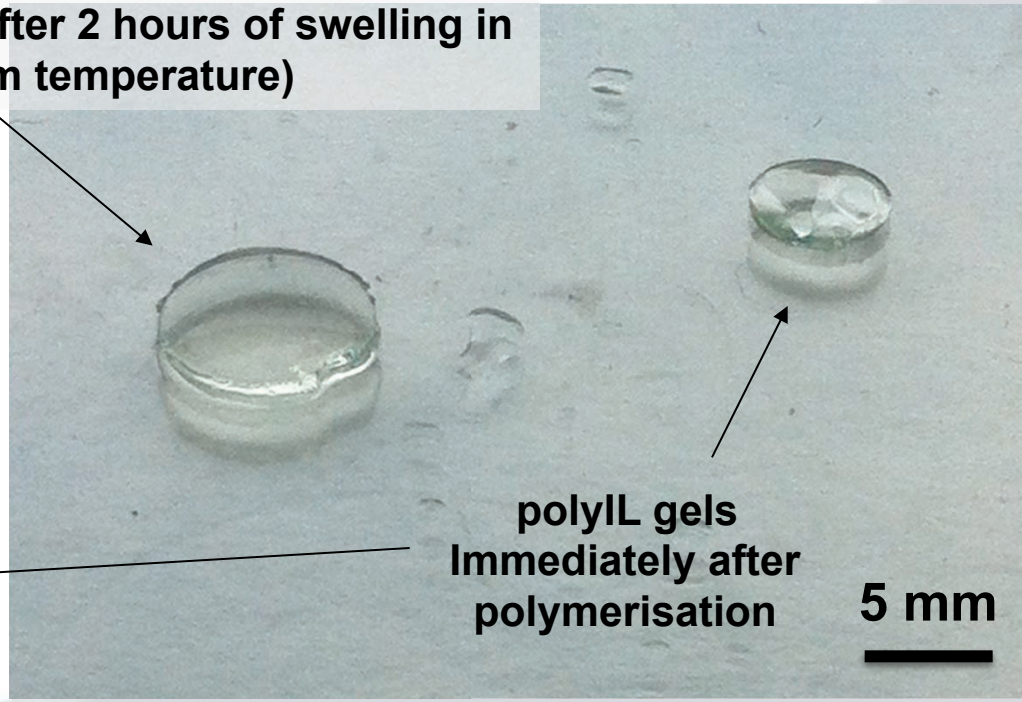
 MBIS	Cracks, no stable shape, excessive swelling	Cracks, no stable shape, excessive swelling
 PEG 256 diacrylate	Cracks, no stable shape	Cracks, no stable shape
 PEG 700 diacrylate	Stable, transparent gel	Stable, transparent gel
 PPO 800 diacrylate	Stable, transparent gel (up to 9 %mol)	Stable, transparent 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

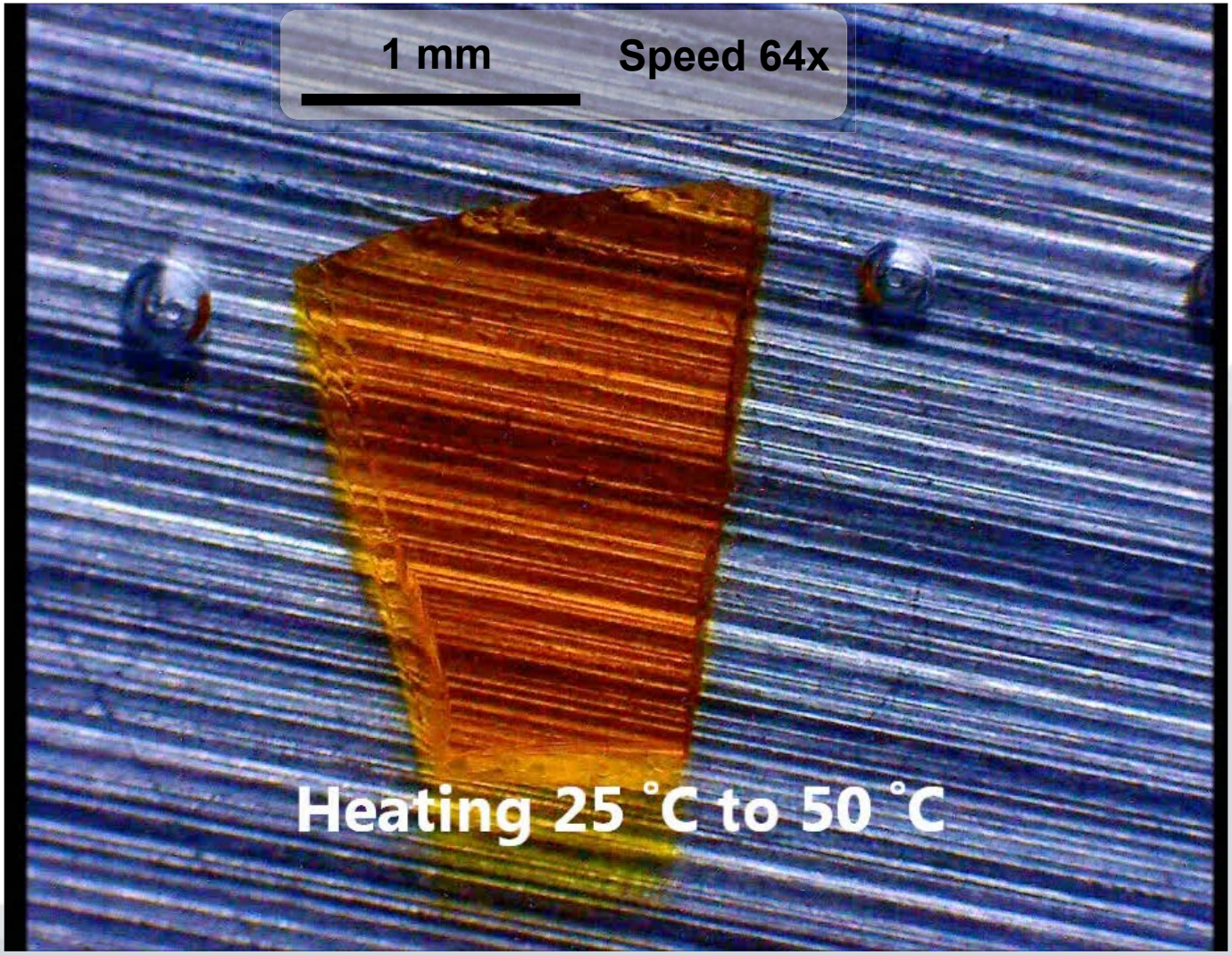




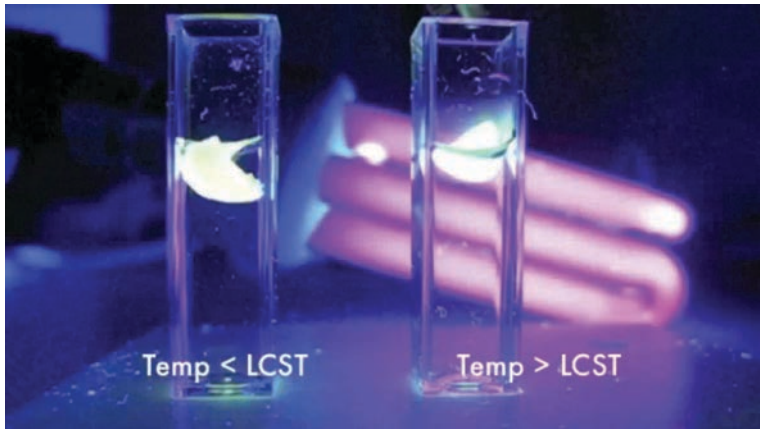
Only longer chain crosslinkers seem to allow mechanically stable hydrogels

Thermal behaviour of poly(IL) gel

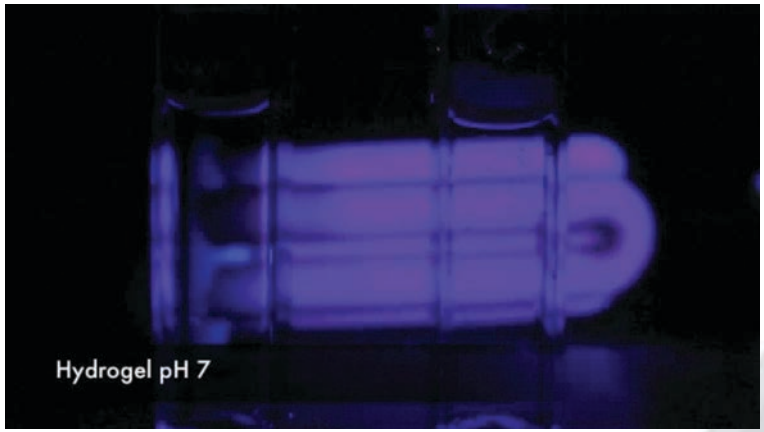
Poly(tetrabutyl phosphonium styrenesulphonate) hydrogel crosslinked with 8mol% polypropylene glycol diacrylate (Mn=800) and 2% spiropyran acrylate bound to the backbone as well. All measurements were performed in water.



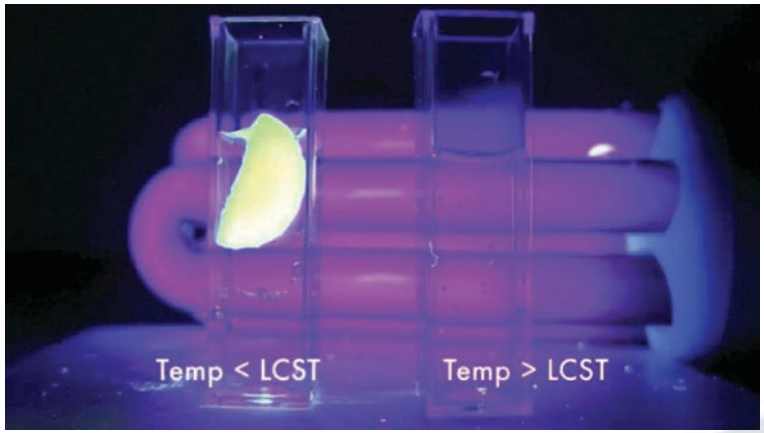
Controlled Release – depends on pH AND temperature



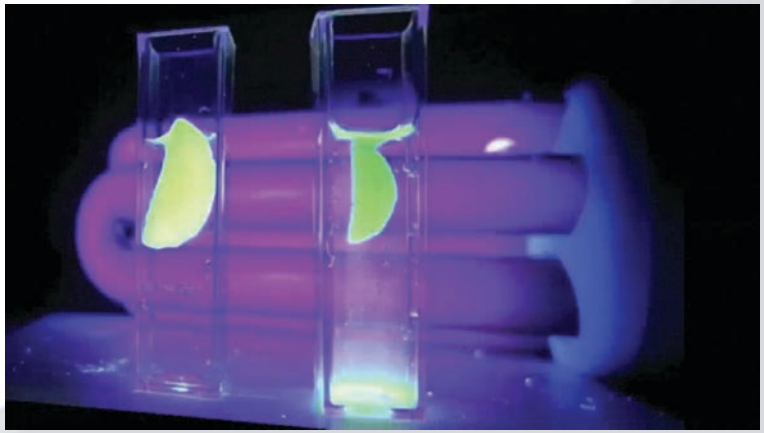
Hydrogel pH 4



Hydrogel pH 7

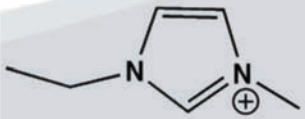


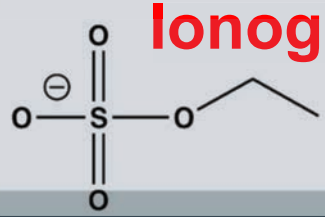
Ionogel pH 4



Ionogel pH 7

$[C_2mIm][EtSO_4]$

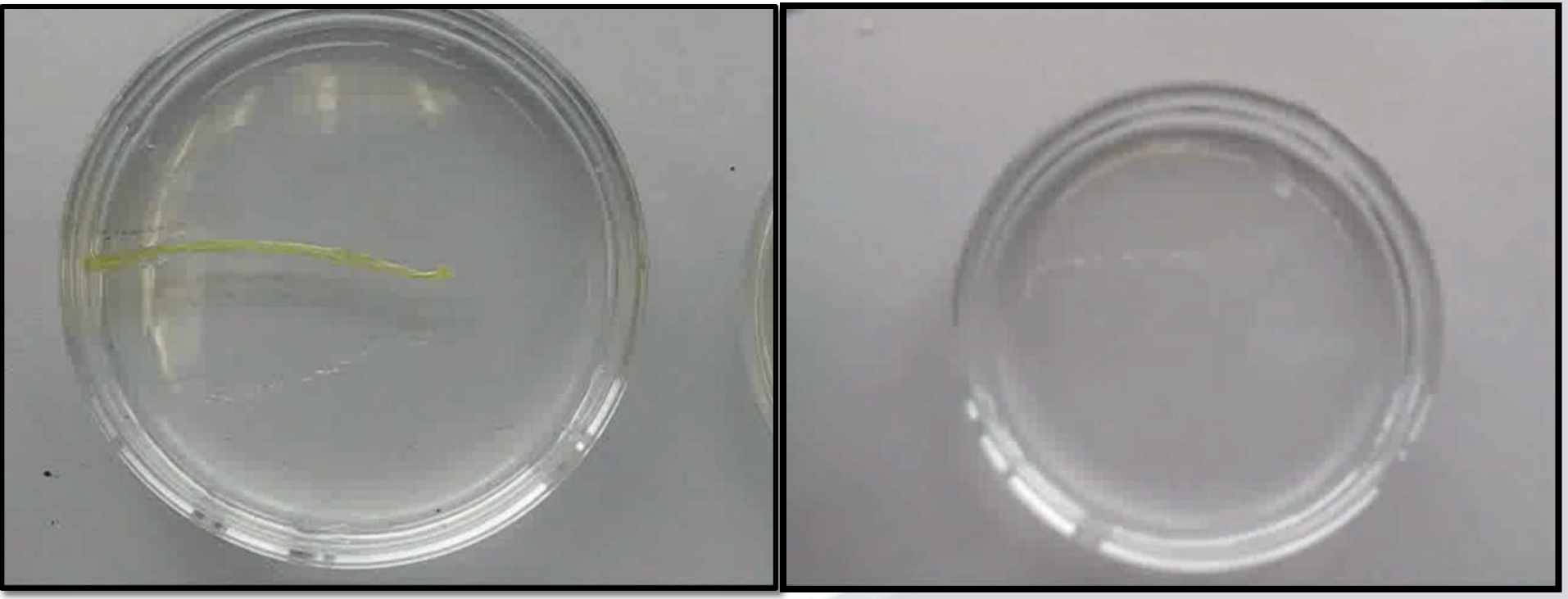




Mobile platforms with chemical actuation: No external power required

DBSA ionogel

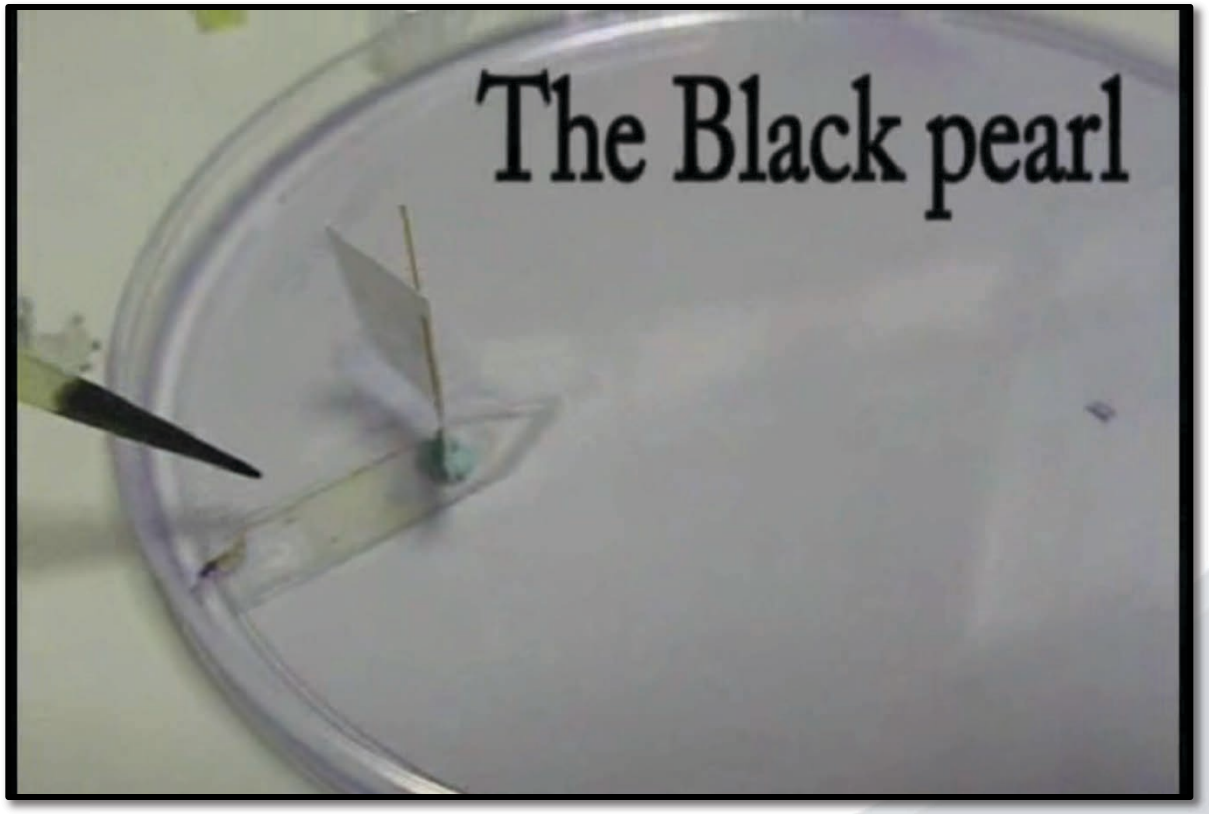
TOS ionogel



Based on solvent exchange within ionogel (water/ethanol)

Robert Byrne and Fernando Lopez

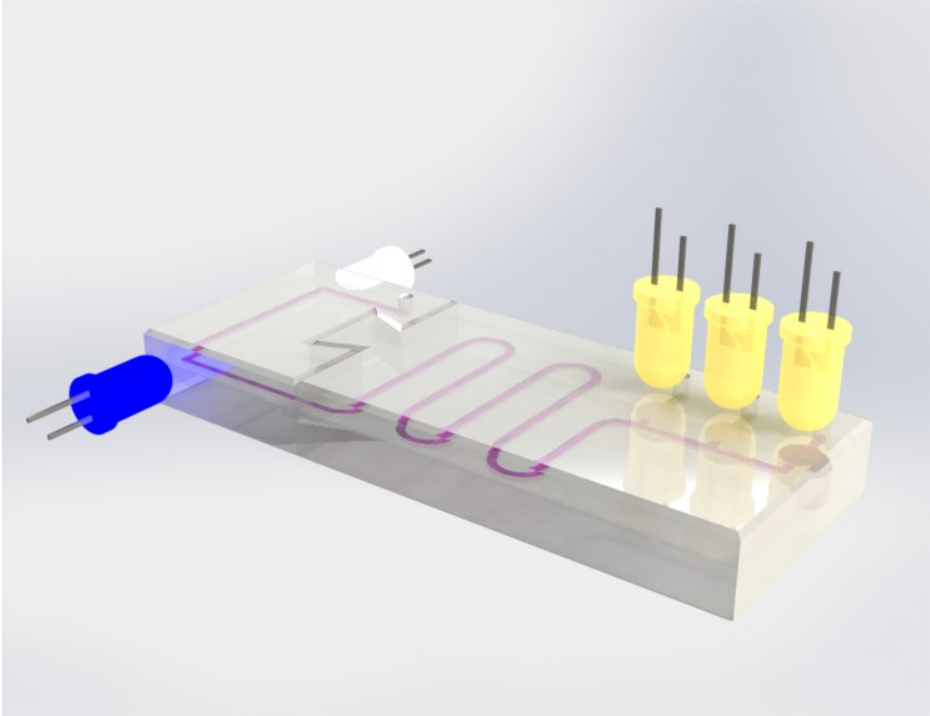
A mobile platform for incorporating sensors….

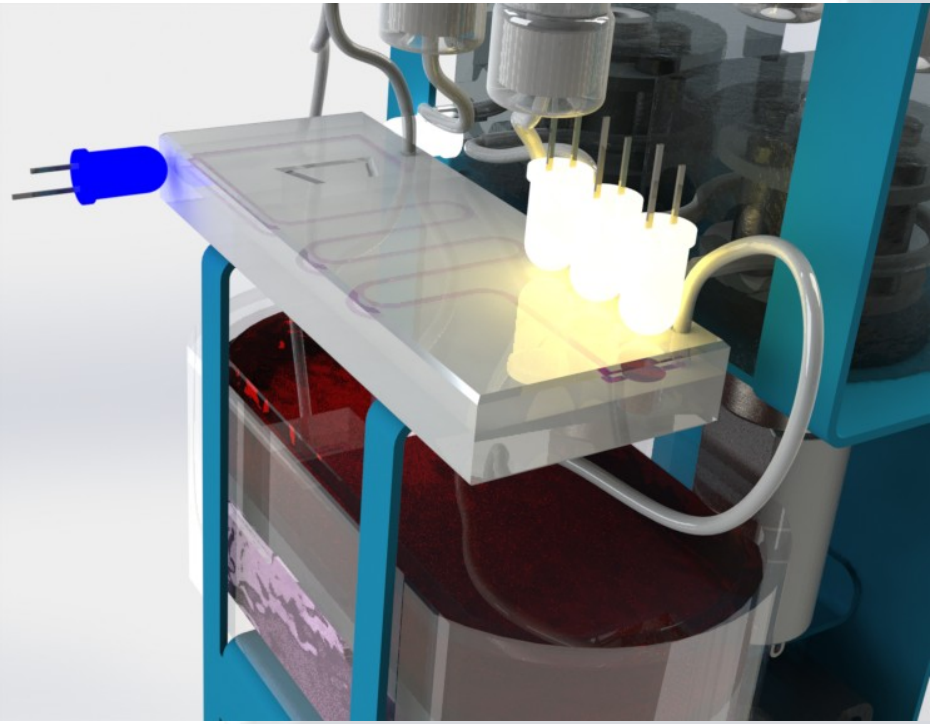


Ionogel rapidly propels ethanol out of the reservoir generating driving force
Combines polymer reorganisation combined with solvent expulsion;
'Solvent Driven Motion of Lithographically Fabricated Gels', Noy Bassik, Beza T. Abebe, and David H. Gracias, *Langmuir 2008, 24, 12158-12163.*
Velocity of alcohol spreading on water is ca. 53 cm/s
Structures exhibited remarkably high linear and rotational velocities of up to 31 cm/s and 3529 rpm over time spans of seconds to minutes'

Can we go from this:

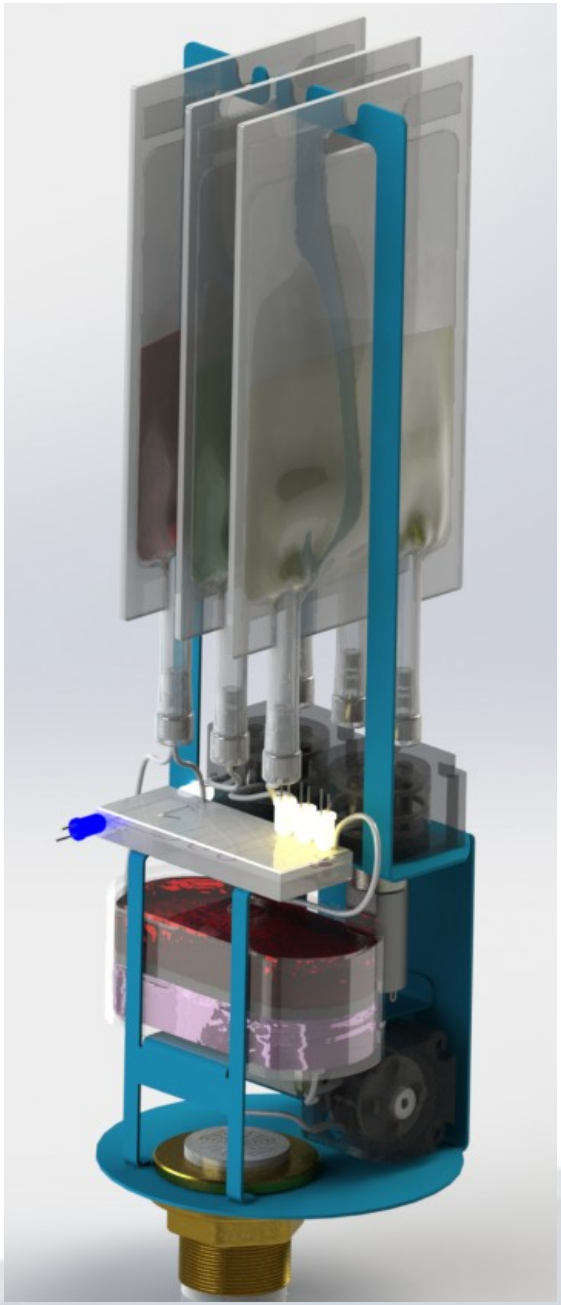
To Photo-Fluidics & Detection

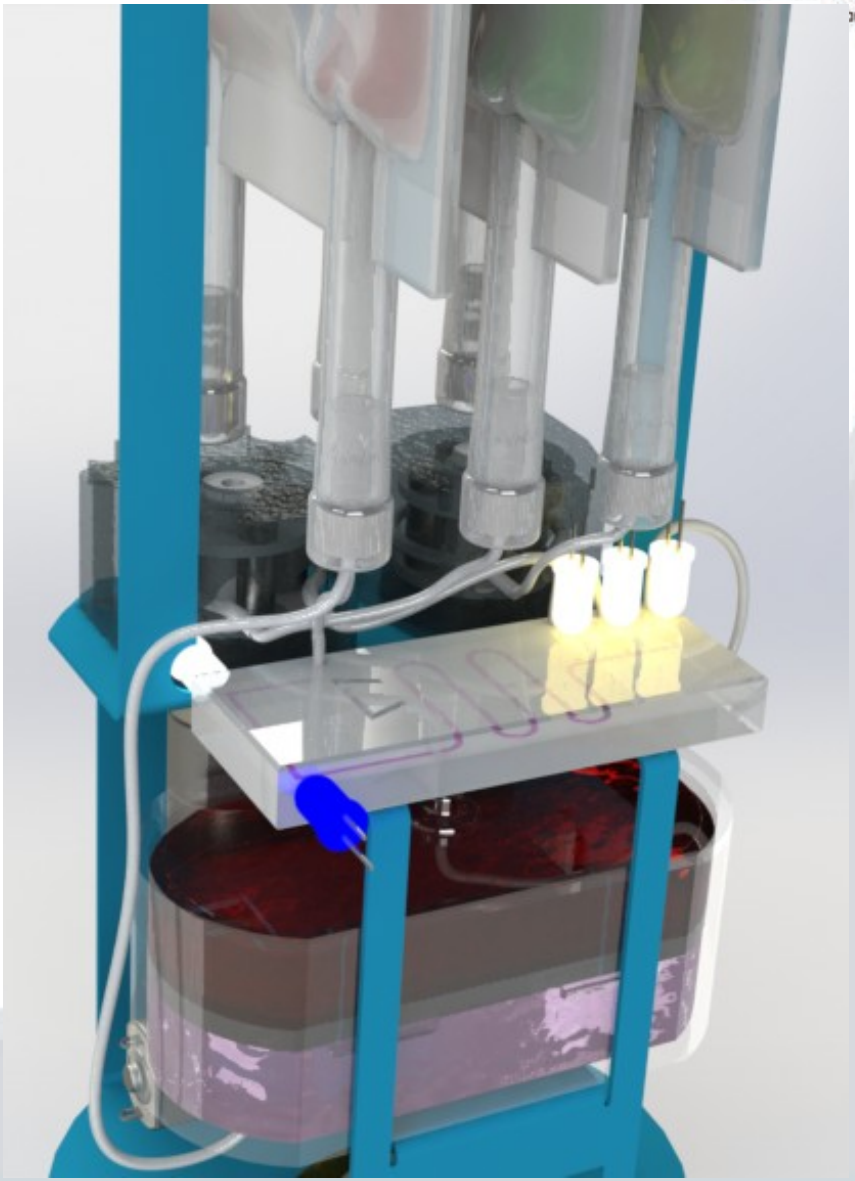




- Fluidic handling completely integrated into the microfluidic chip
- Valves actuated remotely using light (LEDs)
- Detection is via LED colorimetric measurements

Vision





Conclusions

- **Linking ‘Applied’ and ‘Fundamental’ Research is important**
- **Create teams/networks with true multidisciplinary capabilities**
  - Merge engineering and materials science
  - Talk to people who have real applications needs: sports science, exercise, personal health, environment, food, agriculture, marine….
  - Point to potential impacts of your research
- **A multitude of disruptive technologies will emerge from fundamental research in Materials Science – Ionic Liquids can play a leading role in this process!**

Thanks to…..

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

Thanks for the invitation