Using Molecular Photoswitches to Build Functionality for Microfluidic Systems

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Integration of Optical Control and Photonics with Microfluidics

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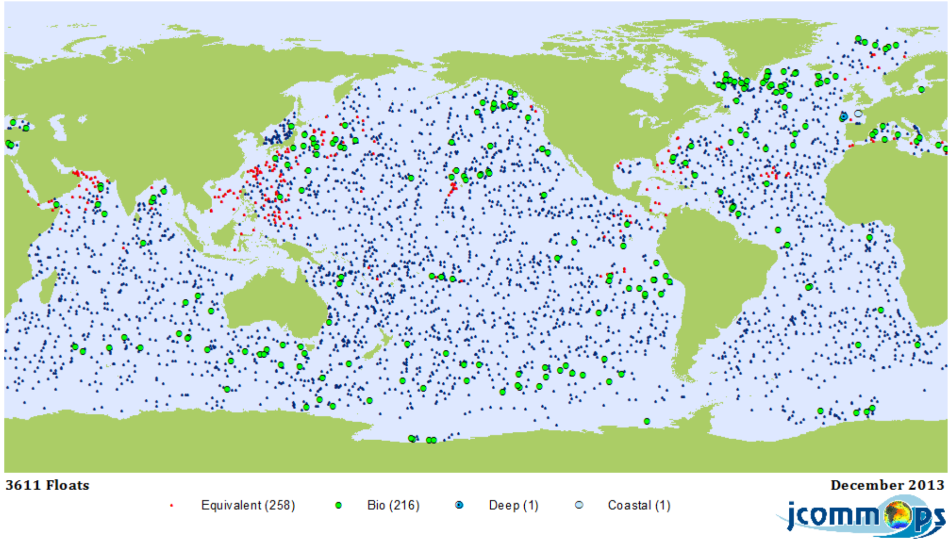
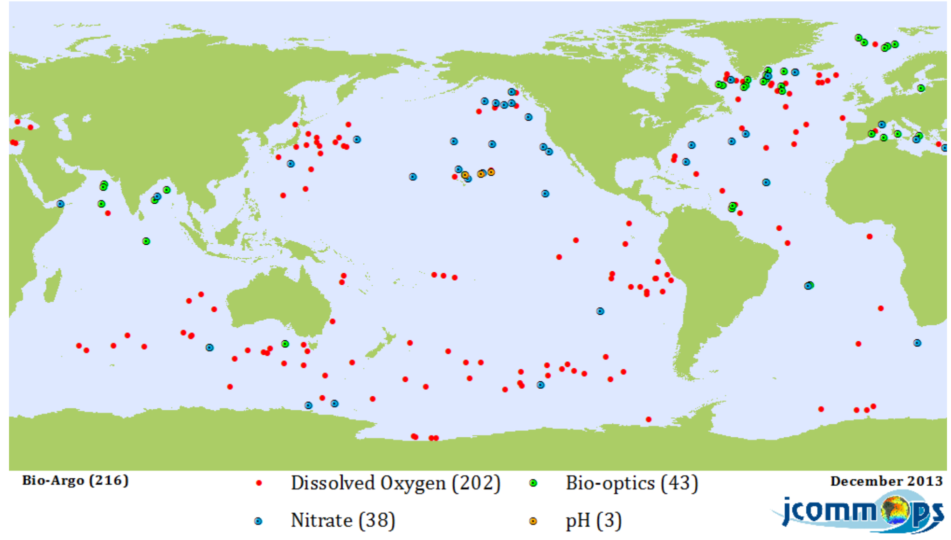
Argo Project (accessed March 9 2014)





- **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)

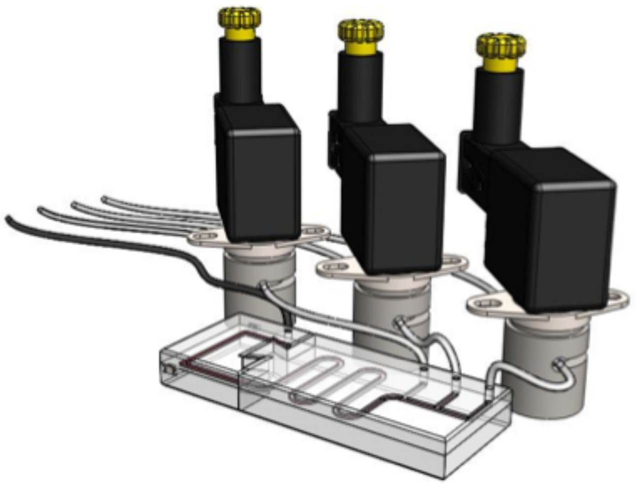
See https://picasaweb.google.com/JCOMMOPS/ArgoMaps?authuser=0&feat=embedwebsite

‘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

After decades of intensive research, our capacity to deliver successful long-term deployments of chemo/bio-sensors in remote locations is still very limited

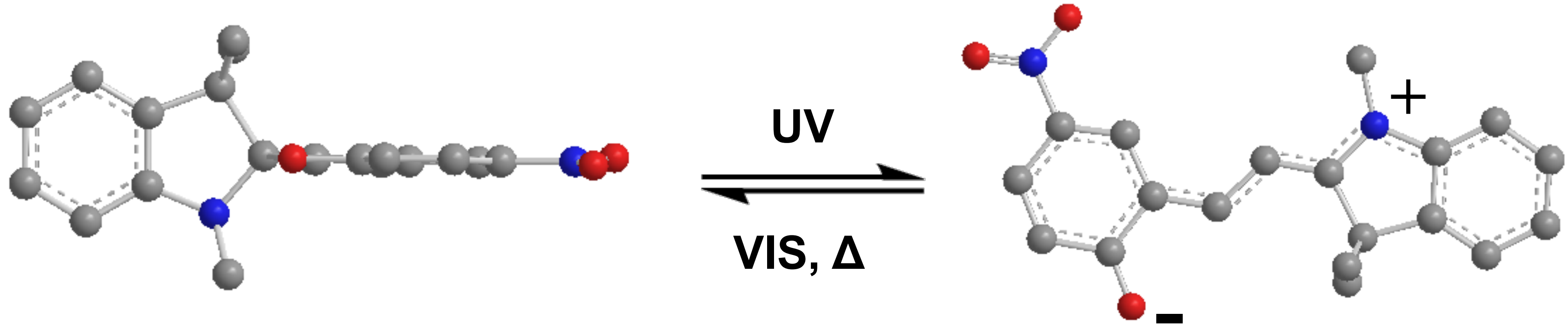
How to advance fluid handling in LOC platforms: re-invent valves (and pumps)!

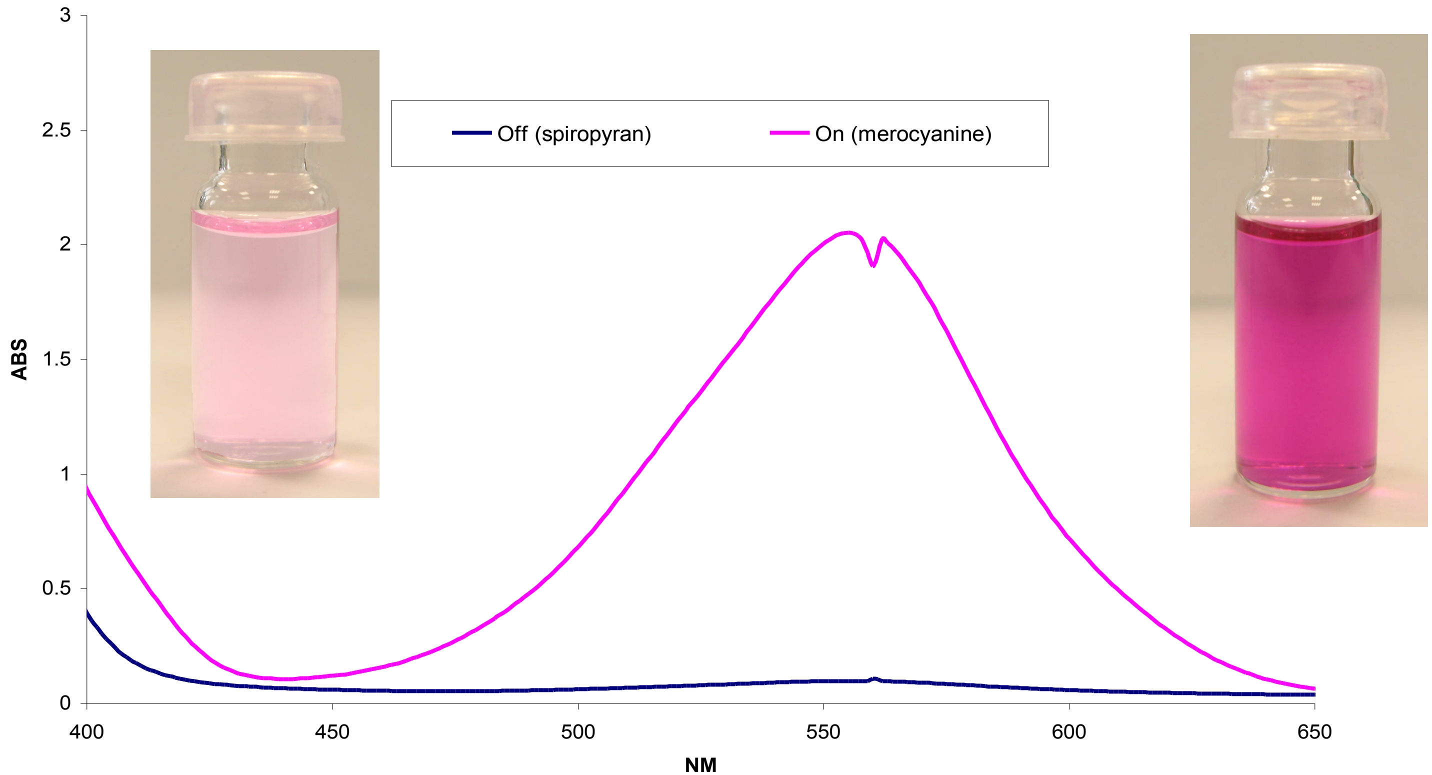
- **Conventional valves cannot be easily scaled down - Located off chip: fluidic interconnects required**
  - Complex fabrication
  - Increased dead volume
  - Mixing effects
- **Based on solenoid action**
  - Large power demand
  - Expensive



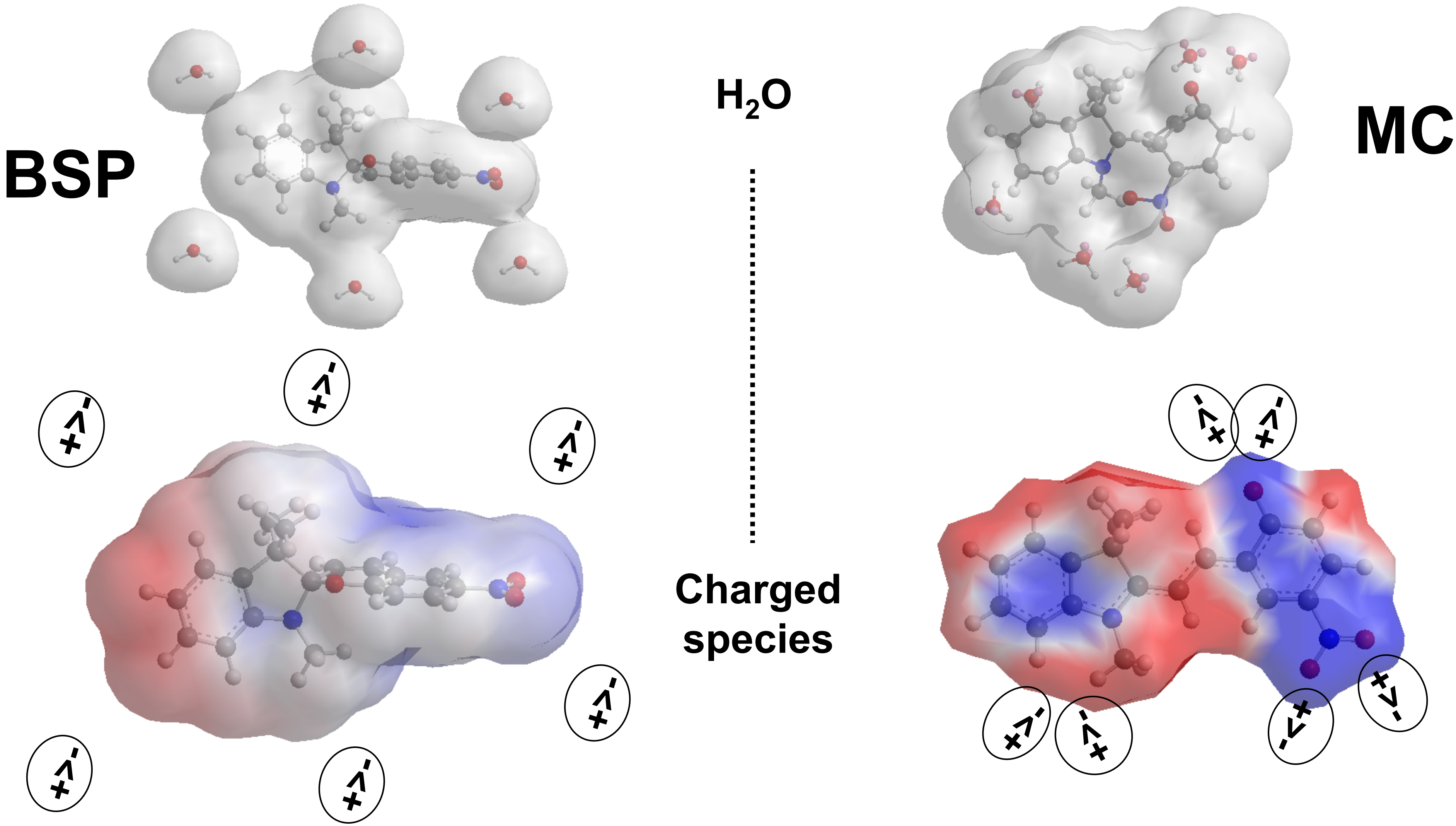
Solution: soft-polymer (biomimetic) valves fully integrated into the fluidic system

Photoswitchable Materials





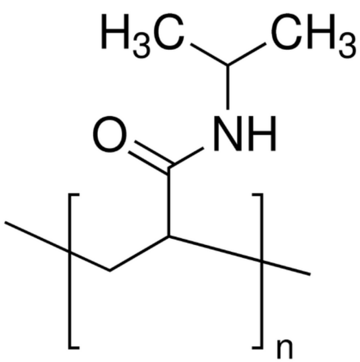
Non-specific (BSP) and specific (MC) Interactions



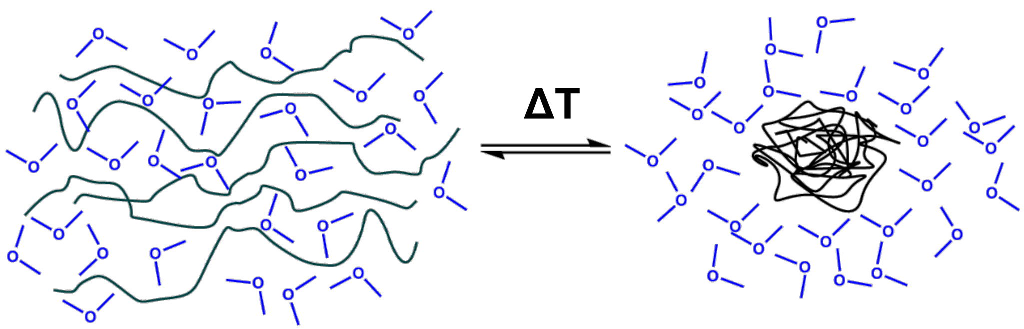
Poly(*N*-isopropylacrylamide)

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

pNIPAAM



Hydrophilic **Hydrophobic**



Hydrated Polymer Chains

Loss of bound water -> polymer collapse

Polymer based photoactuators based on pNIPAAm

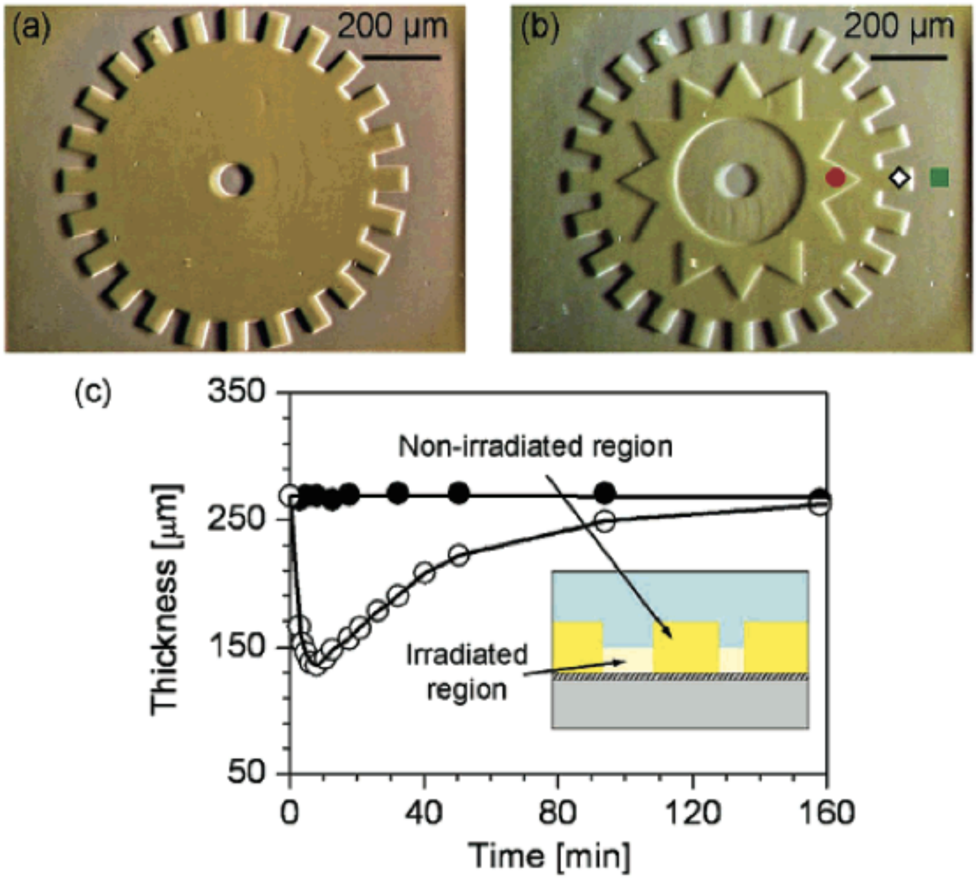
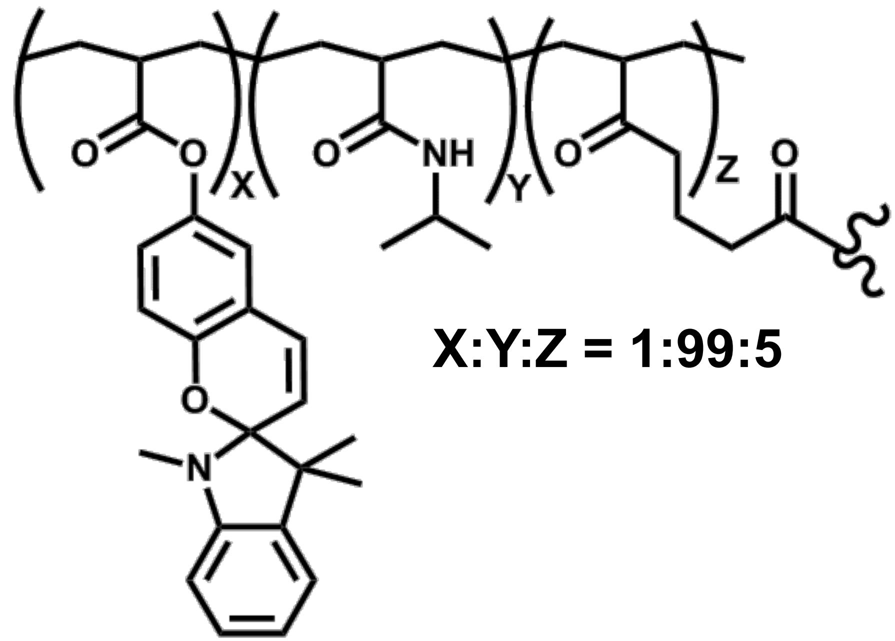


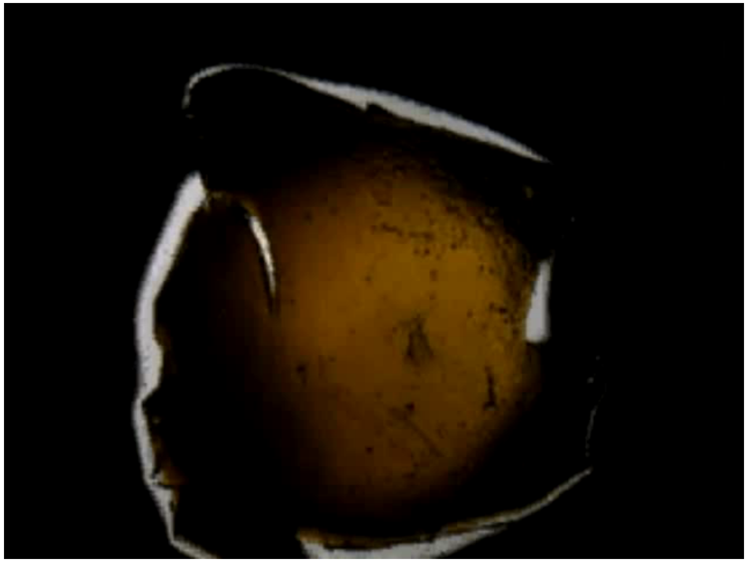
Figure 3. (a, b) Images of the pSPNIPAAm hydrogel layer just after the micropatterned light irradiation. Duration of irradiation was (●, red) 0, (◊) 1, and (■, green) 3 s. (c) Height change of the hydrogel layer in (●) non-irradiated and (○) irradiated region as a function of time after 3 s blue light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

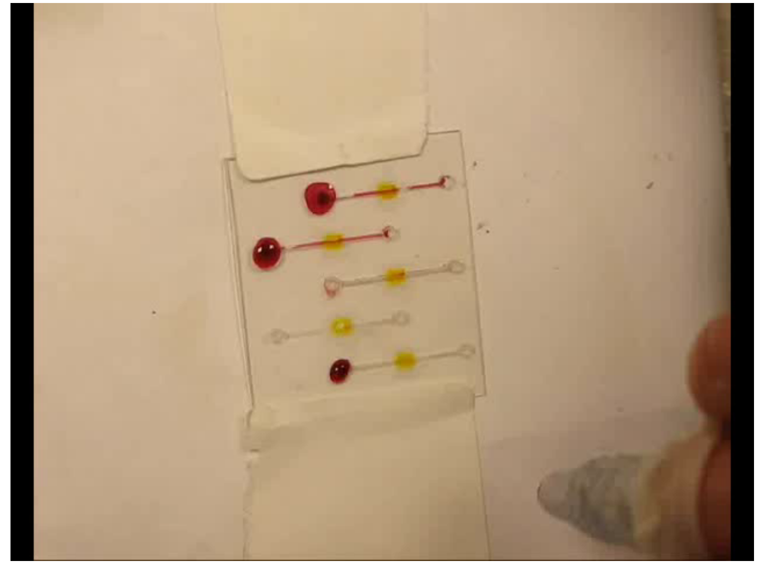


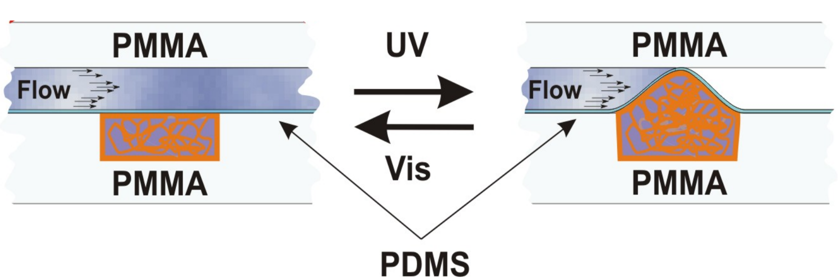
X:Y:Z = 1:99:5

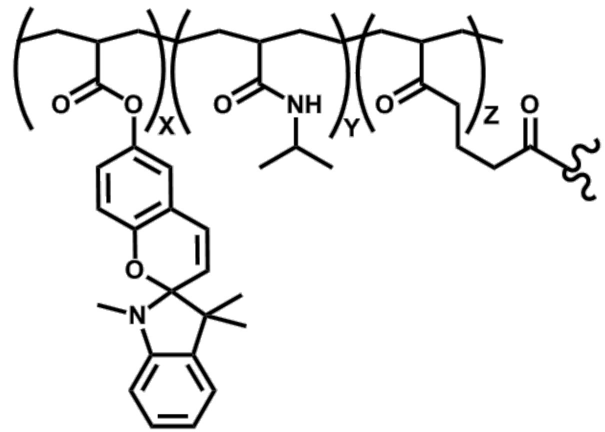
poly(N-isopropylacrylamide) (PNIPAAm)
Formulation as by Sumaru et al[1]
***1) Chem. Mater.,* 19 (11), 2730 -2732, 2007.**

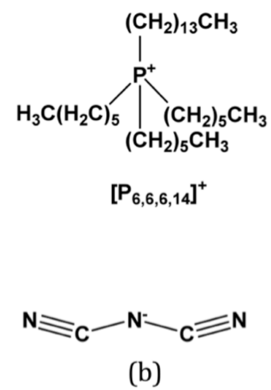
Photo-actuator polymers as microvalves in microfluidic systems







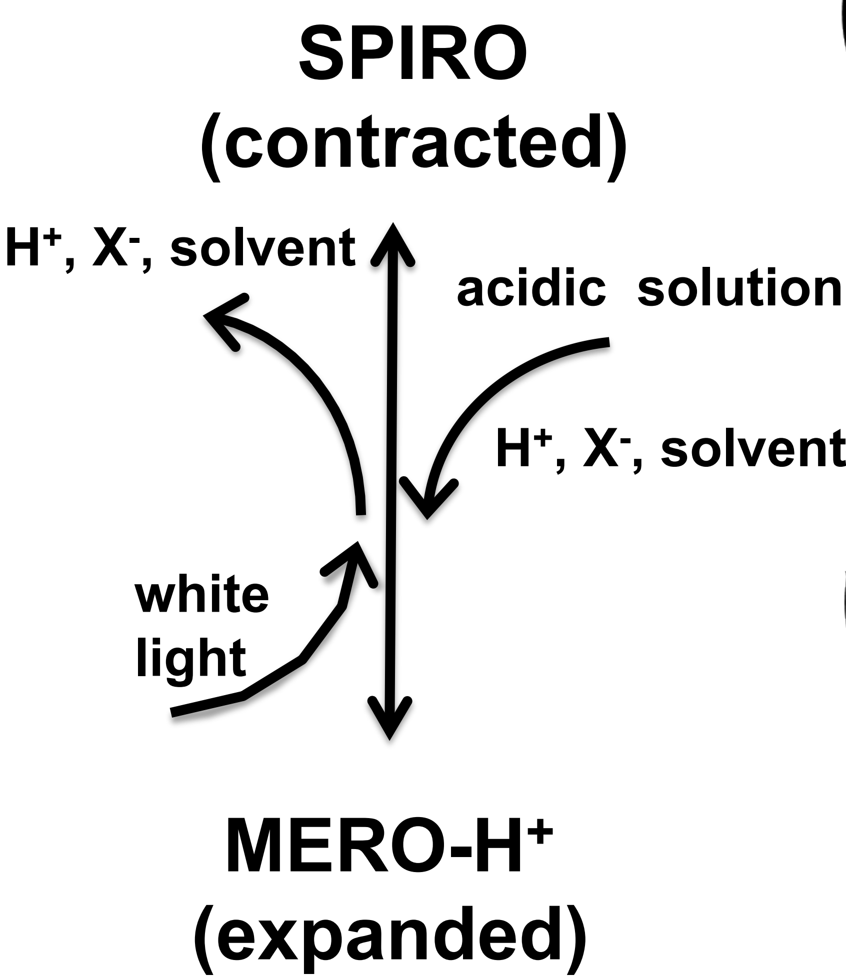


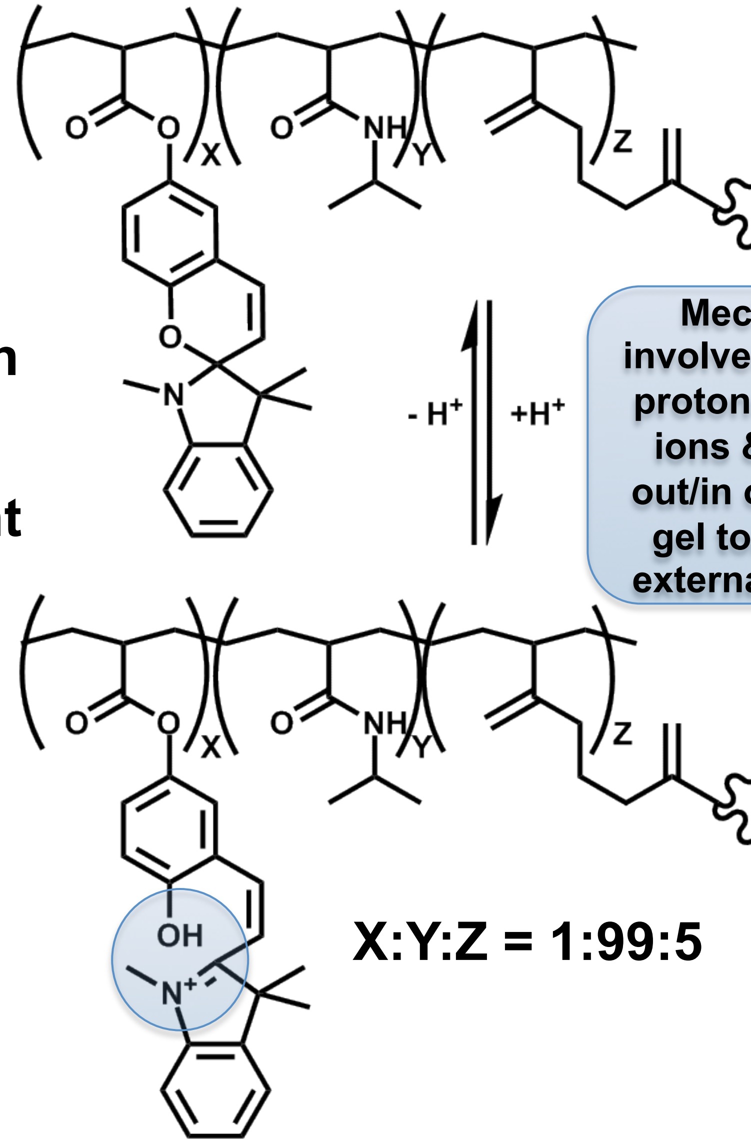


trihexyltetradecylphosphonium dicyanoamide $[P_{6,6,6,14}]^{+}[dca]^{-}$

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





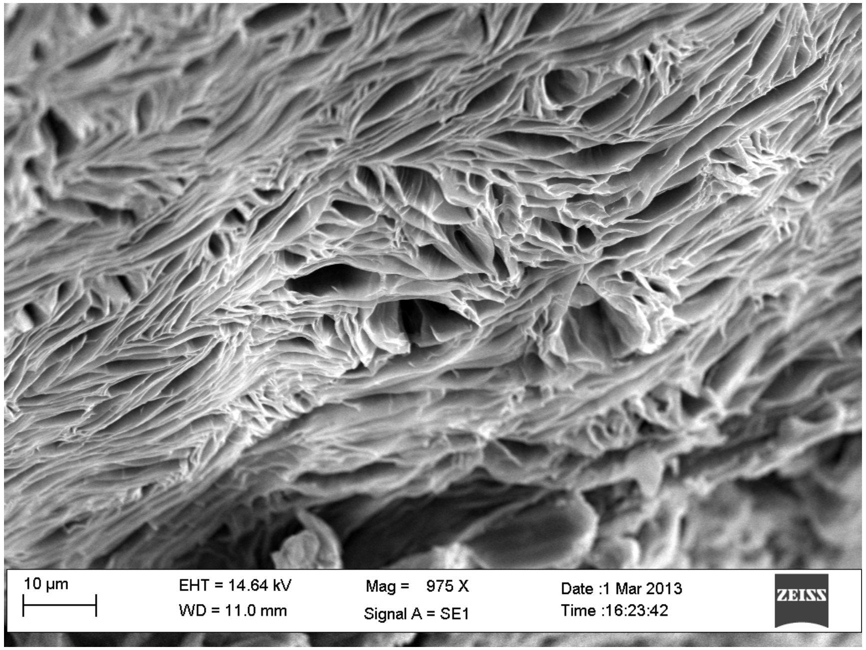
Mechanism involves diffusion protons, counter ions & solvent out/in of the bulk gel to/from the external solution

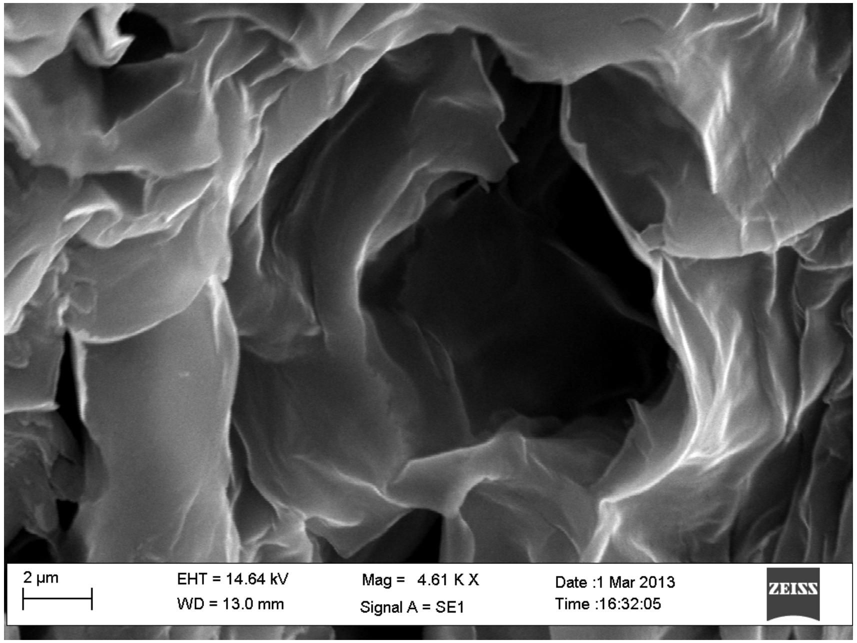
X:Y:Z = 1:99:5

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

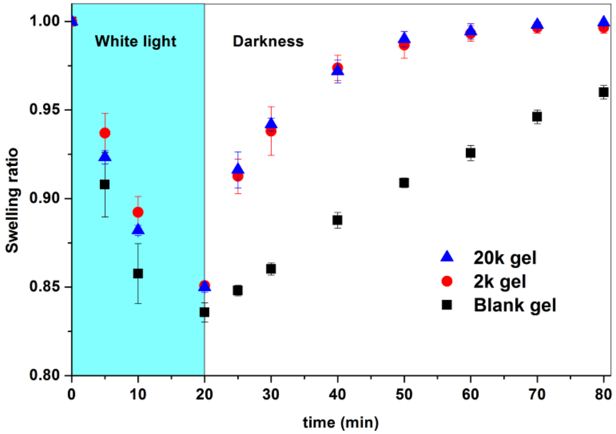
- Response time for re-swelling is slow - 10's of minutes due to diffusion mechanism
- Swelling requires protonation of the MC to $MC\text{-}H^+$ within the ionogel by the external bathing solution
- These issues more or less limit the applicability of the valves to single use

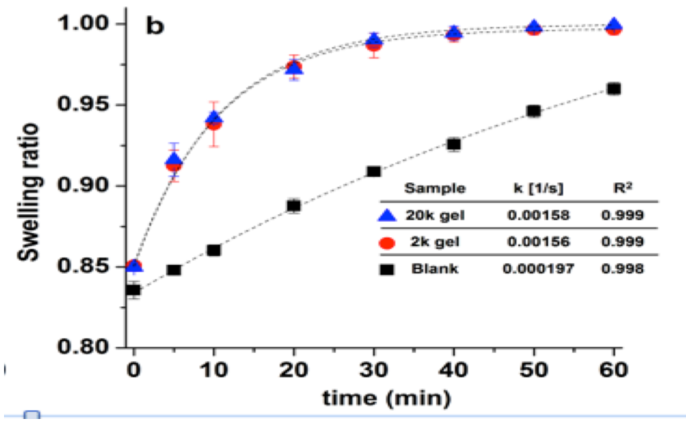
Porous Gels





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

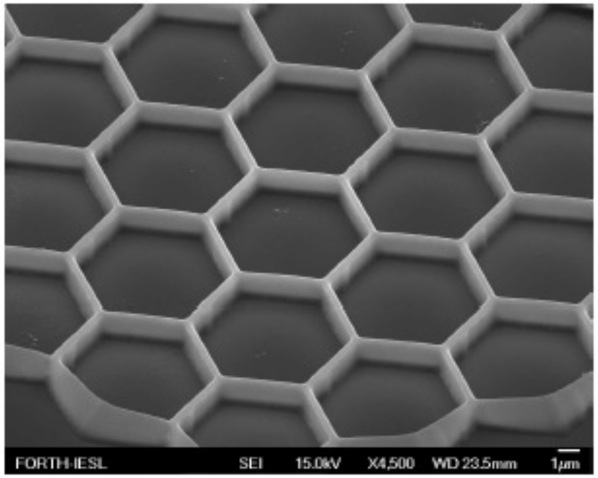




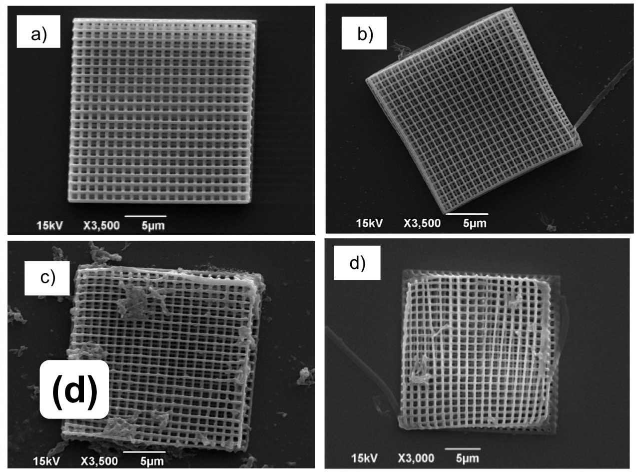
On the re-swelling side; highly porous gels now recover ca. an order of magnitude faster;

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

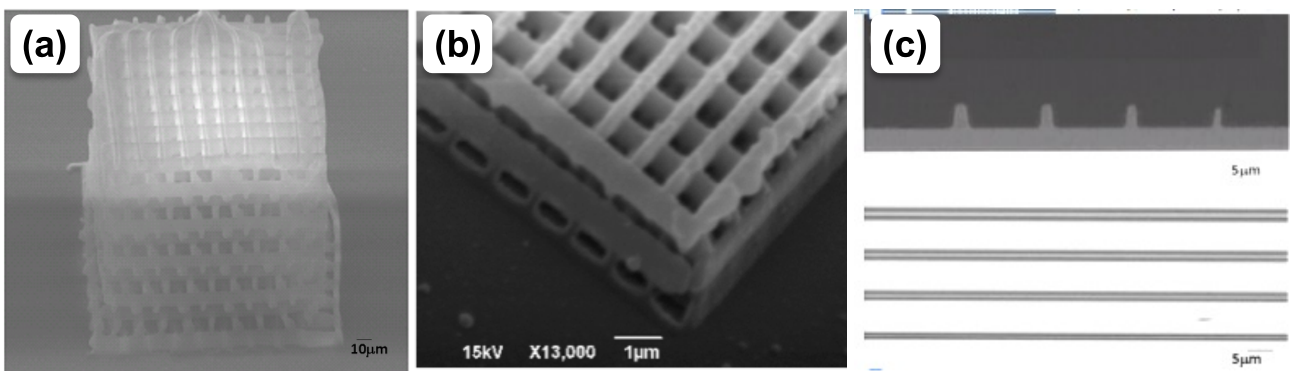
Reduce scale – increase response time
3-d Spiro-doped sol-ionogels



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

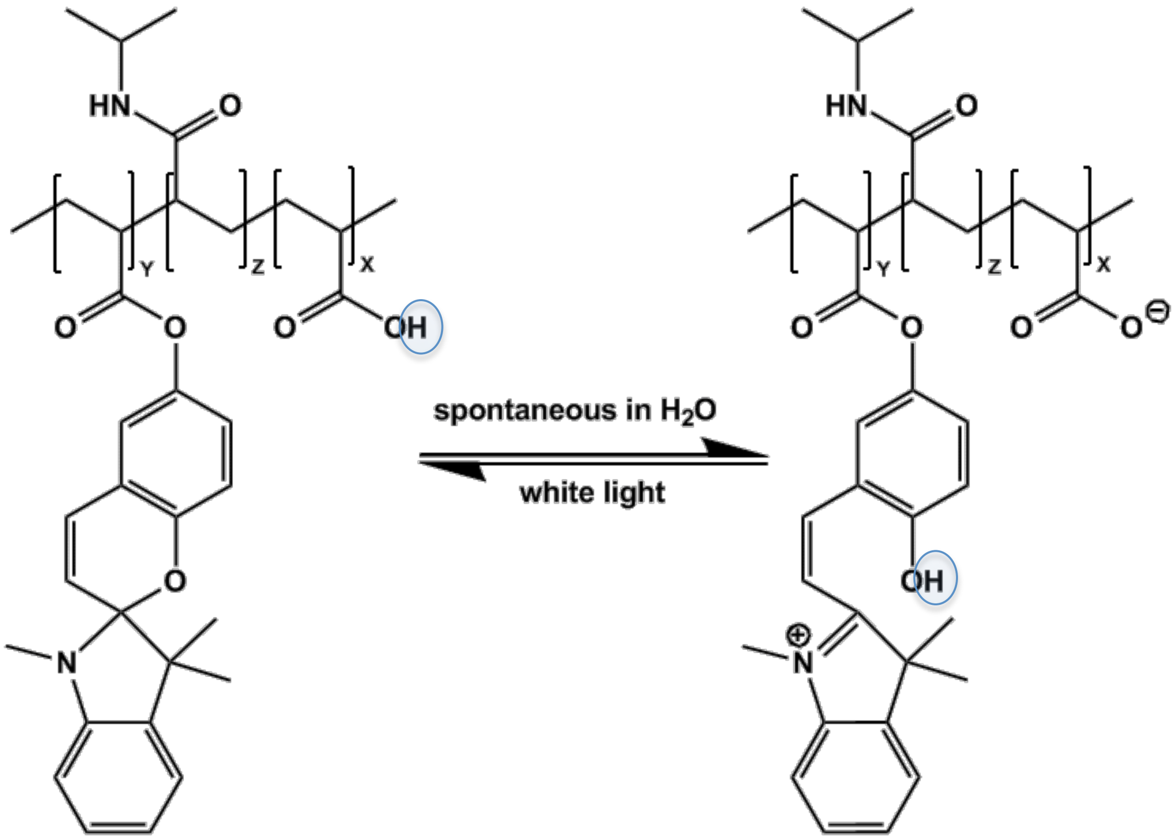


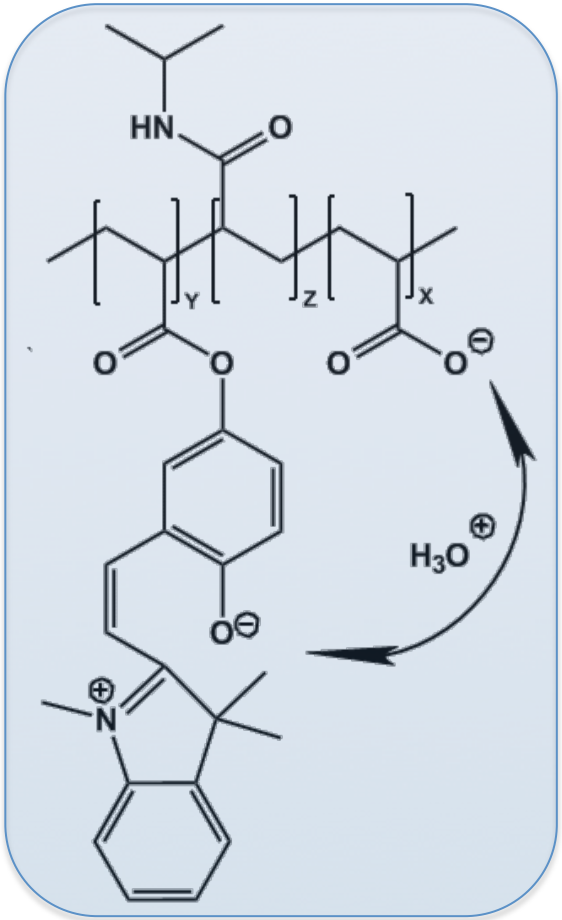
Two photon polymerised (2PP), patterned ionogels (a) and (b), and (c) feature resolution down to 150 nm or less; (d) spiropyran co-polymerised in a gel 'woodpile' structure.

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

Removing the need to 'prime' re-swelling in acidic media: 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

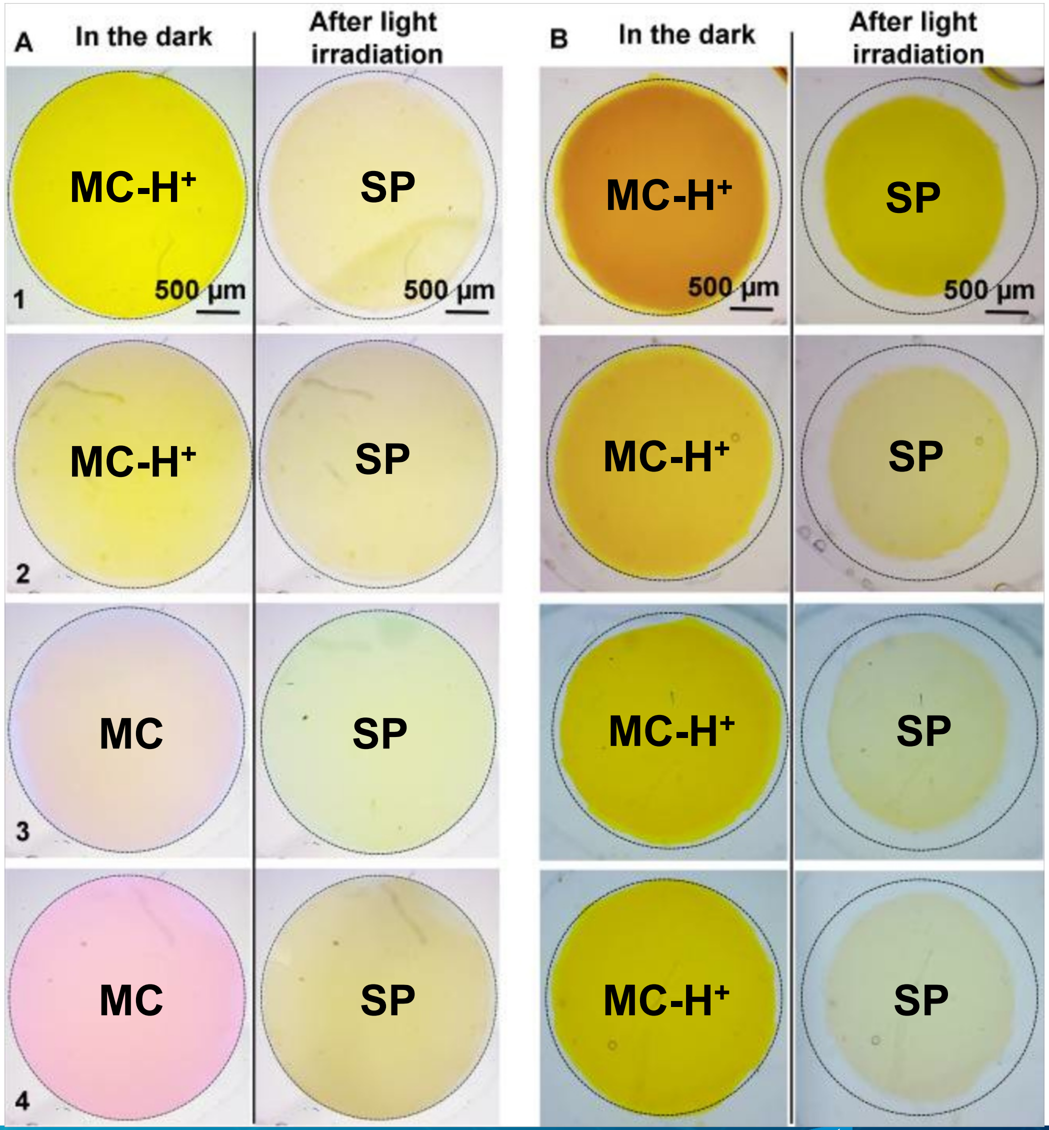
Switching changes from primarily

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

to

MC -> SP

Gel actuation stops



Gel with 5 % AA

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

Switching stays primarily as

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

Gel actuation continues

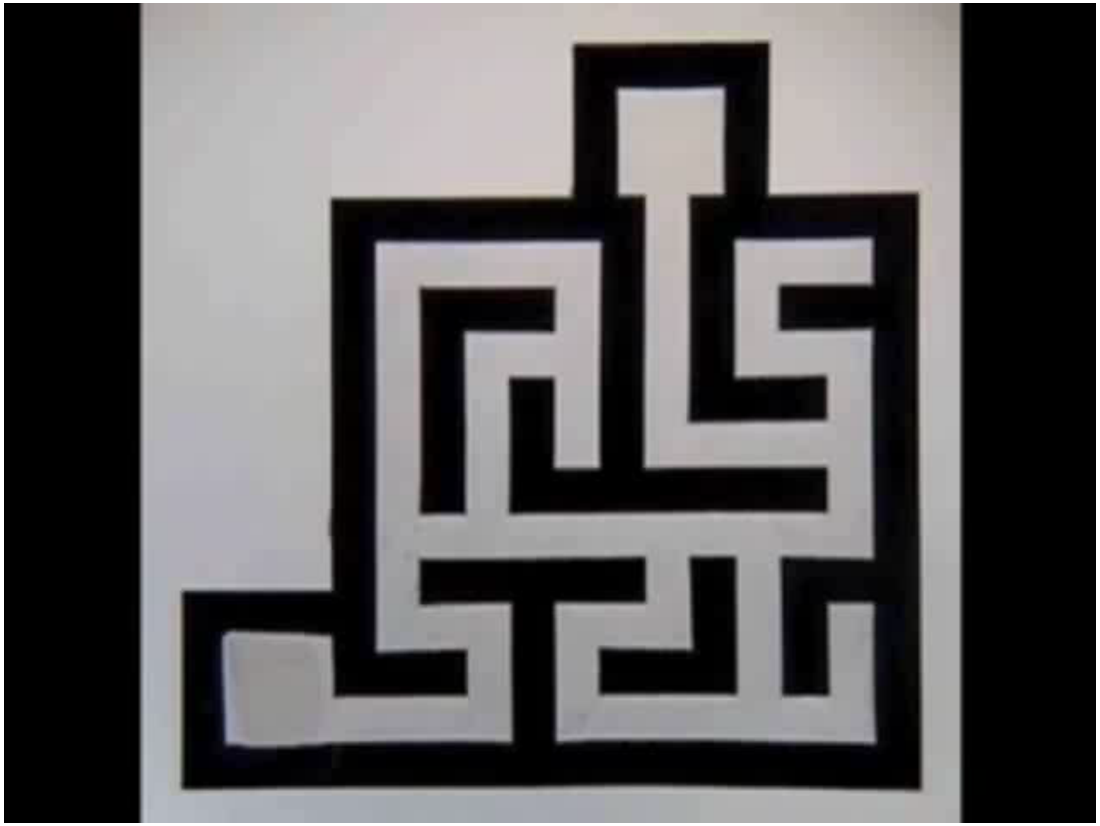
Why move the solvent at all?

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

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

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

Chemotactic Systems



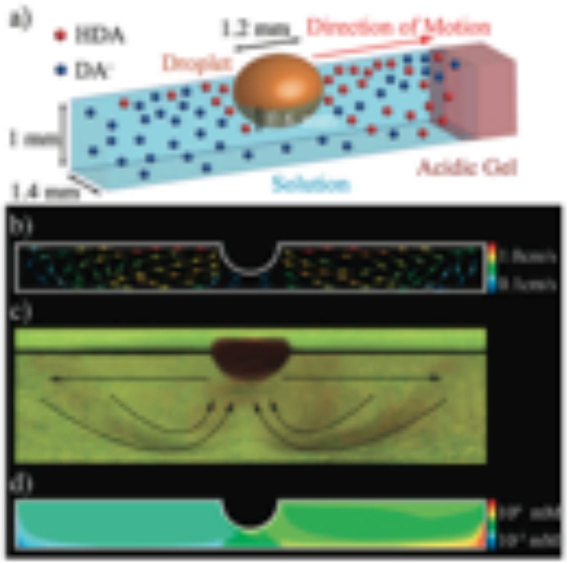


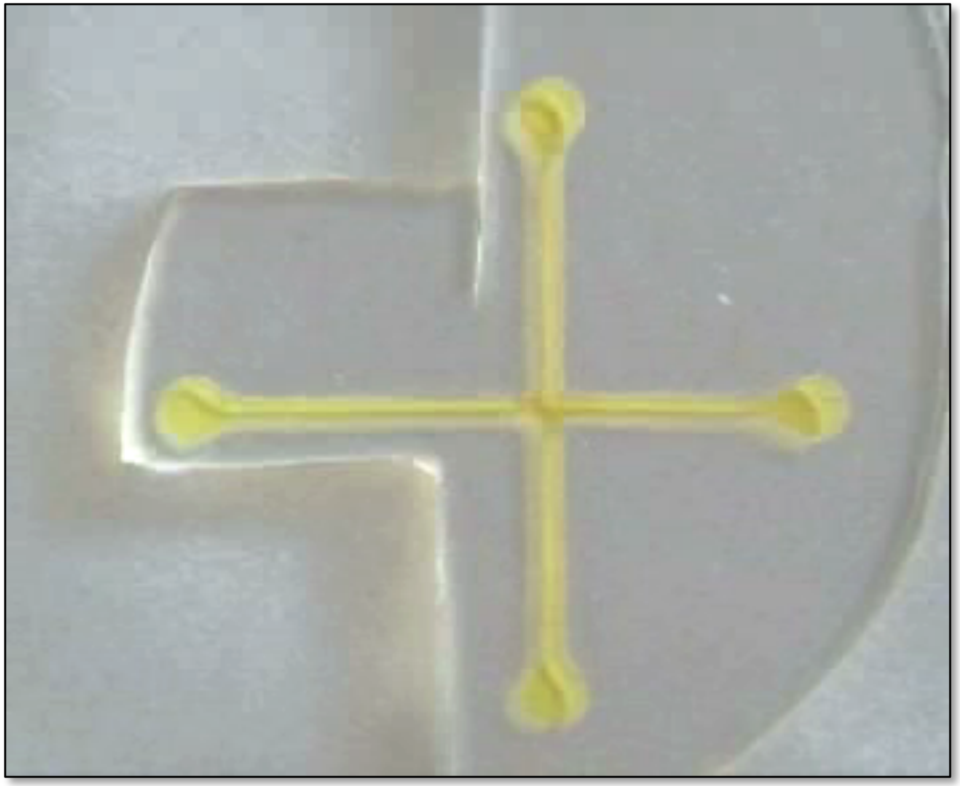
Figure 2. (a) Scheme of a droplet in a channel. The presence of HDA at the liquid−air interface gives rise to convective flows. Since more HDA is present in the direction facing the source of acid, the flows and forces are asymmetric. (b) Velocity field based on the theoretical model described in the main text (calculated using the Fluent computational fluid dynamics package from Ansys). (c) Experimental image of the convection rolls visualized using Neutral Red indicator (see also video 3 in the SI). (d)

Published on Web 11/01/2010 (speed ~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 HAD at droplet-air interface (greater concentration of HAD towards lower pH side); **HDA <-> H^+ + 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***

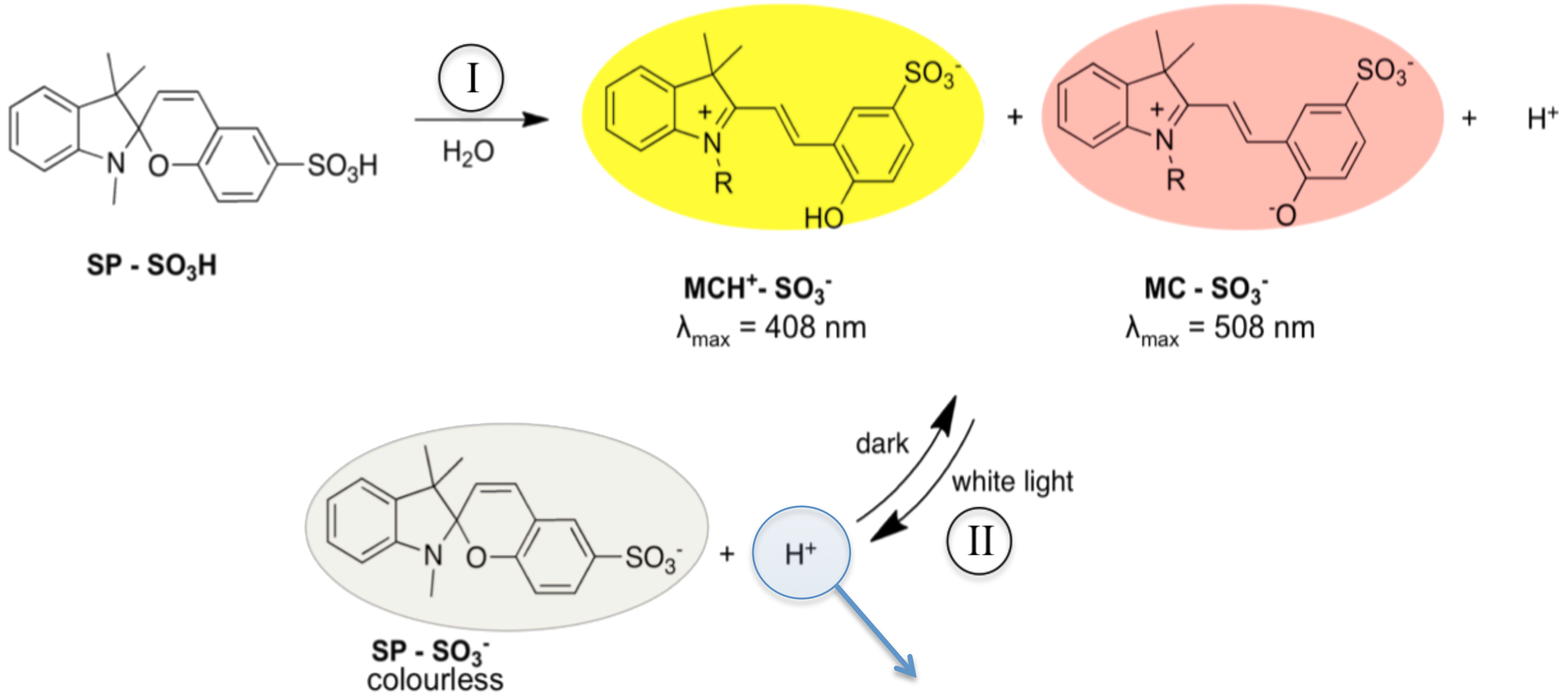
Fuerstman, M. J.; Deschatelets, P.; Kane, R.; Schwartz, A.; Kenis, P. J. A.;Deutch, J. M.; Whitesides, G. M. *Langmuir 2003, 19, 4714.*

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

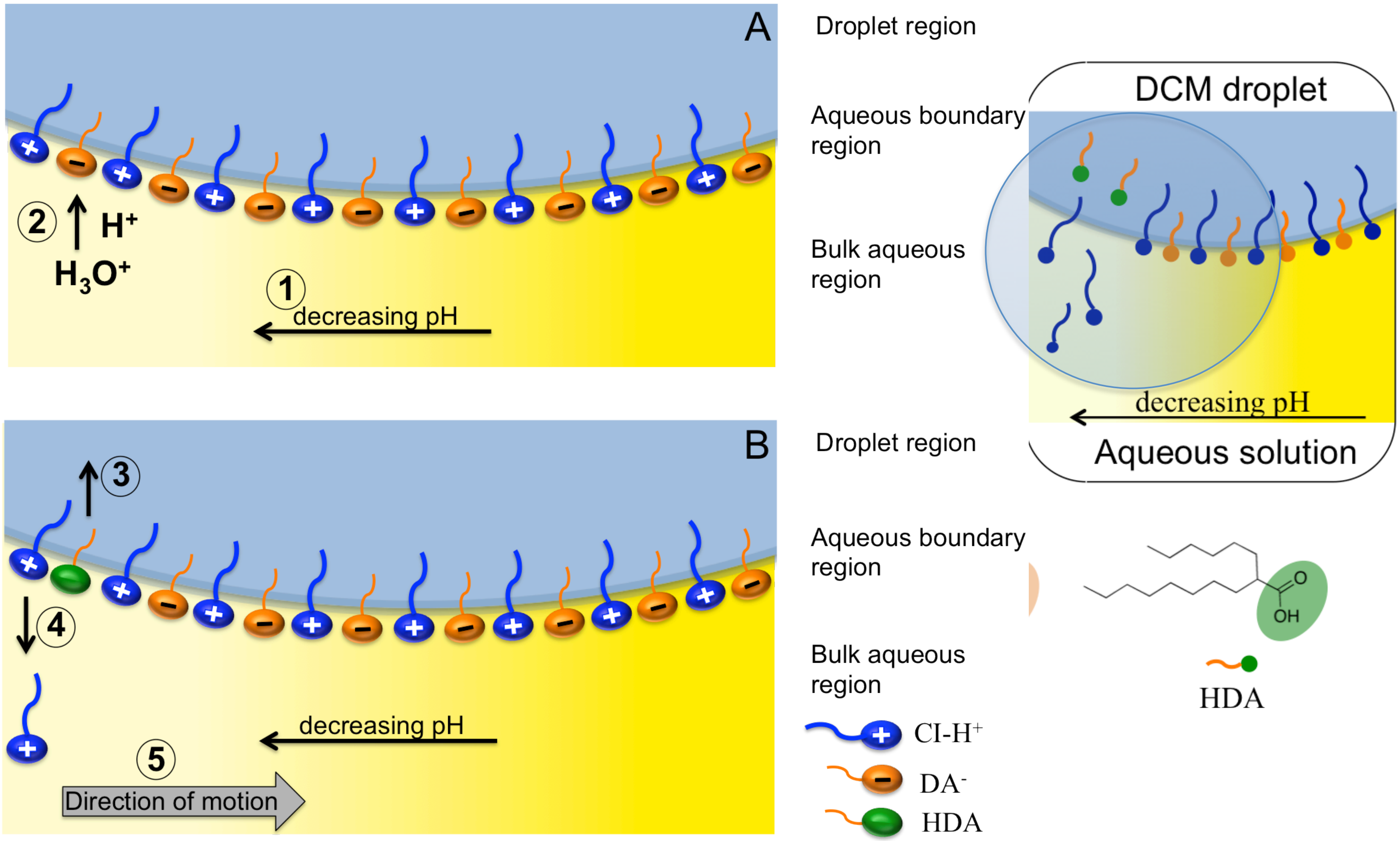
Photo-generation of pH gradients



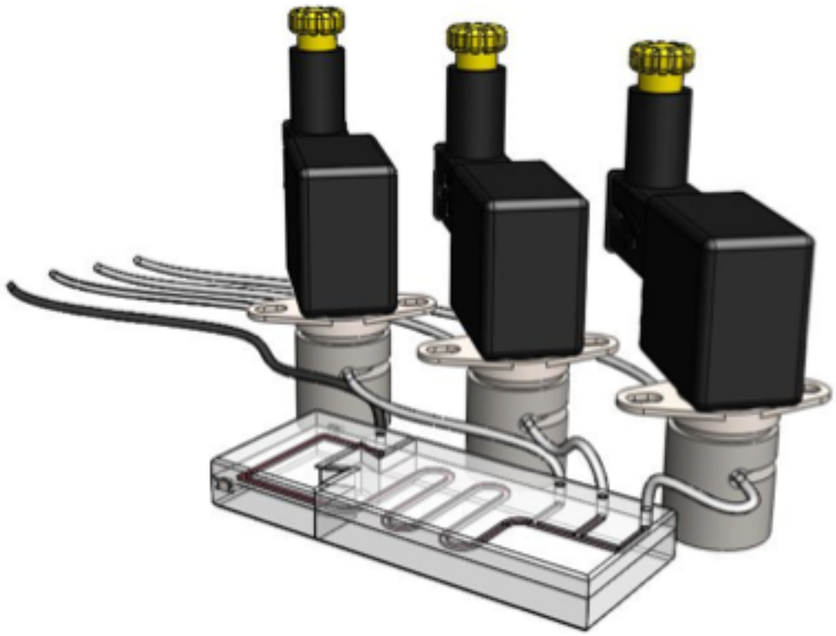
$$MCH^{+}\text{-}SO_3^{-} \Leftrightarrow SP\text{-}SO_3^{-} + H^{+}$$

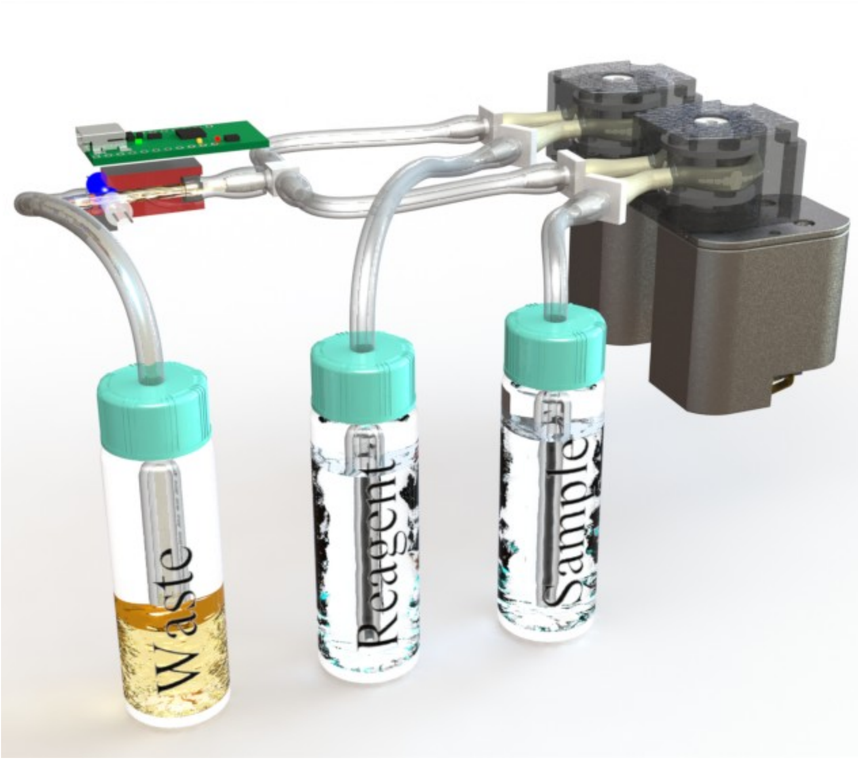
Free protons generated by exposure of aqueous SP-SO_3H to white light; pH changes from ca. 6.0 to 4.0

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

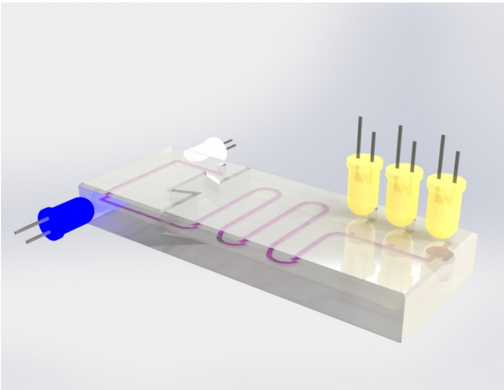


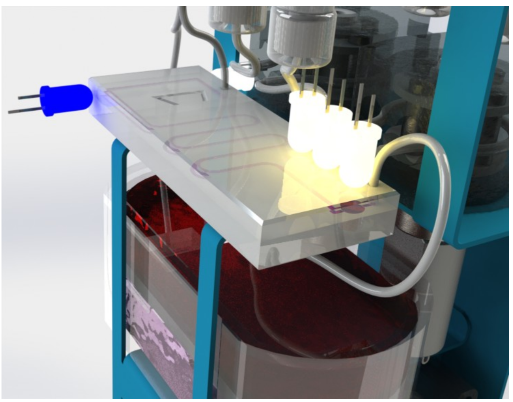
Can we go from this:

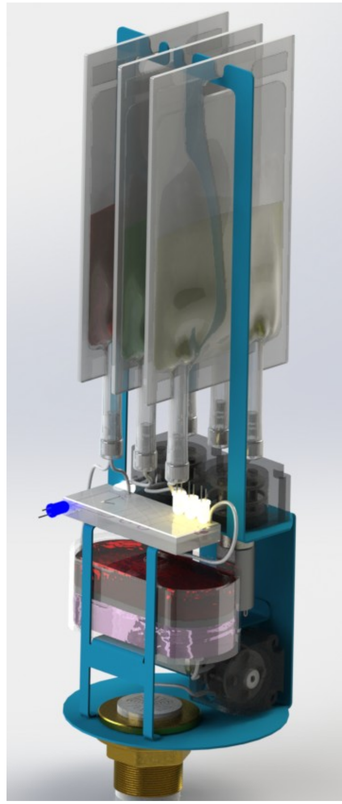


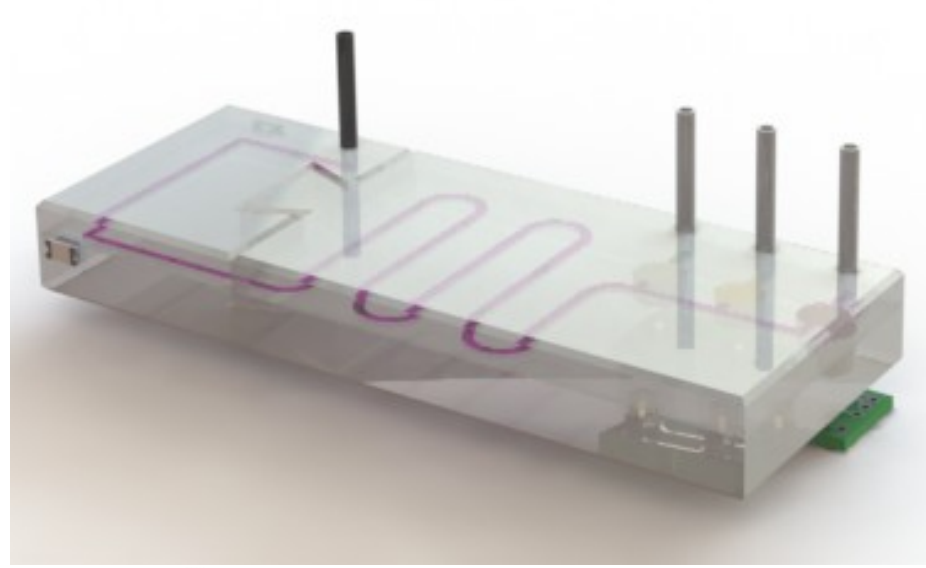


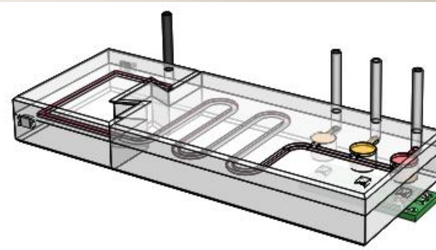
Towards Multifunctional Photo-Fluidics

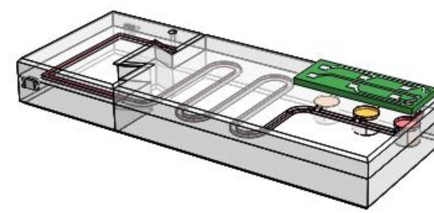












- Fluidic handling completely integrated into the microfluidic chip
- Valves actuated remotely using light (LEDs)
- Detection is via LED colorimetric measurements
- Integrate micro-droplet/vehicle controlled movement
- Integrate photo-controlled sequestration and release of molecular targets

Questions?

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

www.ncsr.ie