Using Molecular Photoswitches to Build Functionality for Microfluidic Systems

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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)

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

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

UV

VIS, Δ

Switching 'On-Off'

Off (spiropyran)  On (merocyanine)

-abs

ABS

Model: Off (spiropyran)  On (merocyanine)
Non-specific (BSP) and specific (MC) Interactions

Charged species
Poly(\(N\text{-isopropylacrylamide}\))

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

\[
\text{Hydrated Polymer Chains} \quad \leftrightarrow \quad \Delta T \quad \text{Loss of bound water} \quad \rightarrow \quad \text{polymer collapse}
\]
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.

poly(N-isopropylacrylamide) (PNIPAAm)
Formulation as by Sumaru et al\textsuperscript{1}
Photo-actuator polymers as microvalves in microfluidic systems

Actuation Mechanism

SPIRO (contracted)

H⁺, X⁻, solvent

acidic solution

H⁺, X⁻, solvent

white light

MERO-H⁺ (expanded)

X:Y:Z = 1:99:5

Mechanism involves diffusion protons, counter ions & solvent out/in of the bulk gel to/from the external solution
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
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. \[ 2.0 \times 10^{-4} \text{ S}^{-1} \]
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

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

Ziolkowski et al., Soft Matter, 2013, 9, 8754–8760
Spontaneous Reformation of Acidified Merocyanine during Actuation Cycling in non-acidified water

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

Gel with 0 % AA

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

Switching changes from primarily

MC-H⁺ -> 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-H⁺ -> SP+H⁺

Gel actuation continues
Why move the solvent at all?

<table>
<thead>
<tr>
<th>[sample] / mol l⁻¹</th>
<th>Ratio H₂O/Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0x10⁻⁶</td>
<td>5.56x10⁷</td>
</tr>
<tr>
<td>1.0x10⁻⁹</td>
<td>5.56x10¹⁰</td>
</tr>
<tr>
<td>1.0x10⁻¹²</td>
<td>5.56x10¹³</td>
</tr>
</tbody>
</table>

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
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); \( \text{HDA} \leftrightarrow \text{H}^+ + \text{DA} \).

**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*

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

Free protons generated by exposure of aqueous SP-SO$_3$H to white light; pH changes from ca. 6.0 to 4.0
Mechanism of Photo-Stimulated Droplet Movement

(with David Officer, UOW)

A

1. Decreasing pH

2. \( \uparrow H^+ \)

3. Decreasing pH

4. Direction of motion

B

DCM droplet

Aqueous boundary region

Bulk aqueous region

Droplet region

Aqueous solution

HDA

\( \text{Cl-H}^+ \)

\( \text{DA}^- \)
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