

Materials Science and the Sensor Revolution

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Introduction

For the past decade, we have been investigating strategies to develop ways to provide chemical sensing platforms capable of long-term deployment in remote locations.¹⁻³ This key objective has been driven by the emergence of ubiquitous digital communications and the associated potential for widely deployed wireless sensor networks (WSNs). Understandably, in these early days of WSNs, deployments have been based on very reliable sensors, such as thermistors, accelerometers, flow meters, photodetectors, and digital cameras. Biosensors and chemical sensors (bio/chemo-sensors) are largely missing from this rapidly developing field, despite the obvious value offered by an ability to measure molecular targets at multiple locations in real-time. Interestingly, while this paper is focused on the issues with respect to wide area sensing of the environment, the core challenge is essentially the same for long-term implantable bio/chemo-sensors,⁴ i.e.; *how to maintain the integrity of the analytical method at a remote, inaccessible location?*

The *analytical method* can be defined as the sequence of events that must take place in order to obtain a reliable measurement. Clearly there are many potentially limiting factors in any WSN deployment, including power management, communications strategy, and incorporation of a degree of local self-diagnostics or intelligence at the so-called sensing node. But these issues are common to all WSN deployments, and as scaled-up deployments based on physical transducers are now happening, they are not the limiting factor inhibiting equivalent deployments of bio/chemo-sensors. The core challenge for these devices, as mentioned above, is the ability to provide reliable data over extended periods of deployments (ideally years). So why after decades of research, and huge investments, are we still confounded by this challenge? The answer lies in failure of the integrity of the analytical method over time.⁵ In environmental water quality monitoring, the active sensing surfaces of bio/chemo-sensors that are directly exposed to the sample, change with time, due primarily to

biofouling, which causes the response characteristics (sensitivity, baseline, selectivity etc.) to change unpredictably, leading rapidly to device failure.⁶

One strategy that offers considerable scope for improving this situation is to separate the location of the analytical measurement from the sample through the use of a microfluidic platform into which the sample is drawn. We are convinced that microfluidic manifolds with capabilities that far surpass the current state-of-the-art can be realised, in terms of reliability, flexibility, compactness, ease of use, and low cost, without compromising analytical performance, but only through fundamental advances in materials science. The following are examples of exciting goals for materials science researchers, which, if achieved in a practically realistic manner, could revolutionise how we do chemical sensing;

- Biomimetic pumping and valving structures based on photochemical and electrochemical polymer actuators that can be fully integrated into fluidic manifolds;
- Controlling liquid flow rate using light, for example by modulation of surface charge to control electroosmotic pumping effectiveness, or to vary the local interfacial attractive force between a surface and a liquid;
- Controlling binding processes at surfaces using light to enable switching between active (binding) and passive (non-binding) states and facilitate processes like photoswitchable uptake and release of molecular guests;
- Integrating stimulus responsive behaviour with materials incorporating ionic liquids in order to improve platform long-term effectiveness, reliability and ruggedness.⁷⁻¹⁰

In the following sections, we will discuss the tremendous potential of switchable materials to provide critical advances that will underpin the next generation of functional molecular sensors.

Stimuli-Responsive Materials for Sensing

In recent years, we have investigated the concept of ‘adaptive’ or ‘stimuli responsive’ materials (i.e.; materials that can be switched between different isomers with widely differing property sets)¹¹⁻¹³ for sensing based on the following principles;

- The sensor surface should be in an inactive or passive state when a measurement is not being conducted

- The surface is converted into an active state under an external stimulus (optical in this case)
- The active surface binds with the target species and generates a signal that enables the analytical measurement to be made
- After the measurement is completed, the target species is expelled by an external stimulus (optical) and the surface returns to its inactive form.

In this way, it may be possible to maintain sensing surfaces in an inactive form that would remain relatively unchanged over time, potentially extending the sensor's useful lifetime by minimizing poisoning effects. It has been demonstrated that in principle we can optically switch on/off ion binding at a spiropyran-immobilized surface, and this process can be recycled. Spiropyran (SP) undergoes a photoinduced heterocyclic ring cleavage at the C–O spiro bond that results in the formation of a planar, zwitterionic and highly conjugated chromophore that absorbs strongly in the visible region, this being the merocyanine isomer (MC). Furthermore, the MC isomer has a phenolate anion site through which certain (d- and f-element) metal ions can bind, giving rise to a new absorption band in the visible spectrum, see Figure

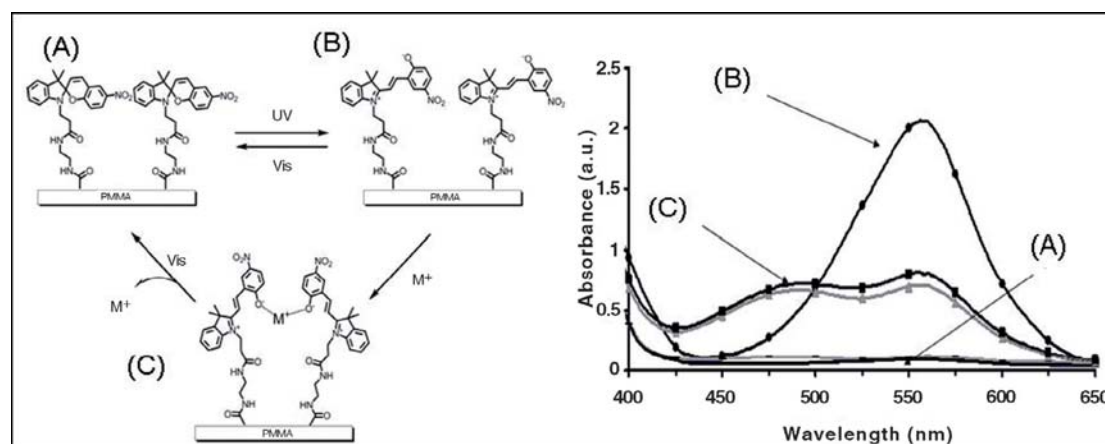


Figure 1.

Recent advances in light emitting diode technology now render them as very effective light sources for photoswitching between the two isomeric states of spiropyran, while simultaneously monitoring the colour of the surface (and hence the state of the system – passive, active, or active + bound metal ion) through reflectance colorimetry.^{14, 15} More recently, Fries et al have synthesized a series of spiropyran containing copolymers that were used as colorimetric sensors for divalent ions Cu^{2+} , Fe^{2+} , Zn^{2+} , Co^{2+} , and Ni^{2+} , and clearly the same approach could be extended to this series of target species.¹⁶

Hence this simple, low-cost, low-power LED-based experimental setup provides spatial and temporal control and monitoring of surface activation and guest uptake/release. This, coupled with low irradiance, is shown to generate significant improvement in fatigue resistance of SP-modified polymeric films, and may prove to be an important step towards more sophisticated materials capable of switching reversibly between active and passive forms, and simultaneously providing a number of transduction modes for gathering information about the molecular environment in the immediate vicinity of the binding site.¹⁵

Stimuli responsive materials for actuation

The development of fully integrated microfluidic devices is still hindered by the lack of robust fundamental building blocks for fluid control. Photo-controlled actuation is a particularly attractive option because the control stimulus is contactless and dynamically reconfigurable.

Smart functional materials have been developed to respond to a wide variety of stimuli, but their use in practical macro-scale devices has been hindered by slow response times arising mainly due to the diffusion processes that typically govern polymer swelling/contraction. The scaling-down to micro-fluidic devices should improve response times, due to the improved surface-to-bulk ratios of these actuators. At these dimensions, stimuli-responsive materials could dramatically enhance the capabilities of micro-fluidic systems by allowing self-regulated flow control.¹⁷

Usually, conventionally engineered micro-actuators based on electroosmotic, pressure, piezoelectric, thermoneumatic and electromagnetic effects require relatively complex procedures for integration into the micro-fluidic system. In most cases, actuation depends on external power supplies and micro-routing to provide physical contact for delivery of the actuation signal.¹⁸ Consequently, the vast majority of these concepts do not progress much further than research prototypes with limited practical applications. In the other hand, smart functional materials have advantages over conventionally engineered micro-fluidic actuators since they do not require an external power source to generate brusque volume changes in response to the surrounding.

pH Actuation

Beebe and co-workers have extensively studied functional hydrogel behaviour in micro-fluidic devices. The structures are photo-polymerised at the desired location by

flowing a mixture of monomers and a photo-initiator through the micro-channels and subsequent irradiation through a photomask. In Figure 2a, a pH-responsive hydrogel composed of acrylic acid and 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate was photo-polymerised around a prefabricated post. The dynamic response was characterised by measuring the step response of the hydrogel expansion. The conclusion was that the time response of the volume changed approximately with the square of the dimension as the hydrogel-based objects expand and contract according to the pH of the surrounding environment (Figure 2b).¹⁹ Later, the same group showed that a pair of photopolymerized hydrogel bistraps, with differing pH sensitivities, was capable of directional flow control in response to the local fluid environment in microfluidic channels in a manner similar to anatomic venous valves. Although the maximum pressure resistance of the valves was not very high at 12 psi, they had the ability to maintain a constant pressure drop over the flow-rate range 0.6-1.4 mL/min.²⁰ However, the use of pH as a control mechanism limits the number of independently controlled components that can be employed, and the components must also be stable over the required pH range.

Recently, a theoretical model has been proposed to explain the acid-base behaviour of covalently cross-linked polymers bearing acidic groups in equilibrium with an aqueous solution which could assist in the rational optimisation of micro-fluidic hydrogel valve performance.²¹ It is proposed that inhomogeneous swelling of polymer actuators is governed to the pH and salinity of the external solution, and by the physical constraints arising from the device design. It is claimed that this approach will enable other researchers to model complex phenomena in pH-sensitive hydrogels more rigorously.

Kim *et al.*²² demonstrated that the swelling characteristics of hydrogels vary depending on hydrogel shape and size. Their results suggest that for optimal actuator function, hydrogels with a bar/rod shape have faster swelling times compared to circular equivalents. These shapes are useful for the fabrication of novel reconfigurable microfluidic components, such as active channel walls and polymer-pump pistons.

Light Actuation

Light-based stimulation of actuators is a very flexible and universal method since light can be applied locally and instantaneously in a non-contact manner to an object present within the micro-fluid structure.

Light irradiation can change the volume of hydrogel structures to control fluid motion through the micro-valves^{23, 24} using a light-to-heat energy conversion mechanism. A localised temperature increase is caused by light irradiation inducing volume changes of the hydrogel's "heat mode". Similar approaches are used to melt embedded paraffin plugs,^{25, 26} wherein the temperature increase caused by light irradiation induces phase changes in the paraffin (solid to liquid), and the valve opens.

Effective flow control in a cyclic olefin copolymer (COC) micro-chip was achieved using a quartz halogen illuminator with tungsten filament by light-actuation of a monolithic micro-valve based on a thermo-responsive polymer, poly(*N*-isopropylacrylamide) (PNIPAAm). Pressure-tolerance was tuned by changing the mechanical strength of the polymer monolith inside the micro-channel, through varying the relative amounts of monomer and crosslinker. Moreover, the response time and pressure resistance of the valve was further optimized by the amount of tetrahydrofuran in the polymerization mixture. The micro-valves resisted pressures up to 1350 psi, with a opening and closing response time of 4.0 and 6.2 s respectively.²⁷

Independent optical control of microfluidic valves formed from optomechanically responsive nanocomposite hydrogels (poly-[*N*-isopropylacrylamide-*co*-acrylamide]) was achieved using strongly absorbing gold nanoparticles or nanoshells embedded in the actuator polymer. This approach has the advantage of allowing independent control of valves formed from composites with different nanoparticles through changing the illumination wavelength.²⁸

A novel optically addressable microactuator array (microfluidic "flash memory") with latched operation has been proposed by Hue and co-workers. It consists of individual phase-change based actuators addressed by localized heating through focused light patterns provided by a modified projector or high power laser pointer. After the initial light "writing" during which the phase is temporarily changed to a liquid form, the actuated status is self-maintained by the solid phase of the actuator without power and pressure inputs, Figure 3. The microfluidic flash memory can be re-configured by a new light illumination pattern and common pressure signal providing a flexible,

energy-efficient, and low cost multiplexing solution for microfluidic applications based on physical displacements.²⁹

In contrast, photoresponsive hydrogels undergo volume changes by photo-isomerization of a photoresponsive chromophore; this mode of change is known as “photon mode”.^{26, 30} Spirobenzopyran-functionalized poly(N-isopropylacrylamide) pSPNIPAAm hydrogels using as micro-valves. Blue light irradiation induces isomerization of the spirobenzopyran chromophore from a protonated open-ring structure to a closed-ring structure. This isomerization causes dehydration of the polymer chain, resulting in shrinkage of the gel in aqueous solution.³¹

Using the same principle of actuation it is possible to generate on-demand micro-channels with arbitrary pathways by simply micro-patterned light irradiation of a sheet composed of the photoresponsive hydrogel with a computer-controlled maskless micro-pattern projection unit Figure 4. This fluid control method enables the formation of arbitrary micro-channels and the opening of targeted micro-valves at desired times.³²

It is possible to disrupt flows in a micro-fluidic channel with two-phase flows using optical radiation pressure and the formation of liquid jets. Using this approach, a ‘total-optical-lab-on-a-chip’ system was investigated and tested by Delville *et al.* to explore fluid actuation by light. Optical radiation pressure of a laser wave was able to induce large scale flows, to create soft channels for guiding these flows and to drive optical streaming of fluid interfaces and droplet shedding. The method showed appealing prospects to form valves, samplers, switchers, sorters, mergers and mixers, and to even develop further these actuators and to couple them.³³

In our laboratories we have used four novel ionic liquid polymer gels (ionogels) as photo-actuated valves incorporated into micro-fluidic manifolds, Figure 5. The ionogels incorporate benzospiropyran units and phosphonium-based ionic liquids. The valves were actuated by simply applying localised white light irradiation. Through variation of the composition of the ionogels, each of the micro-valves can be tuned to open at different times under similar illumination conditions. Therefore, flows through the manifold were independently controlled by a single light source.³⁴

Van Oosten *et al.* elegantly demonstrated the fabrication of polymer micro-devices using inkjet printing technology in combination with self-organizing liquid-crystal network actuators. Using the self-assembling properties of the liquid crystals large

strain gradients were created. Light-driven actuation was chosen to allow simple and remote addressing. Moreover, by simply changing the wavelength of the light micro-actuators fabricated using different subunits selectively actuation was possible, Figure 6. These actuators mimic the motion of natural cilia having the potential to create flow and mixing in wet environments such as lab-on-a-chip. A great advantage of this methodology is that the process is easily adapted for roll-to-roll fabrication, allowing for large-scale and low-cost production of miniaturized active polymer systems.³⁵

Mimicking natural systems, sidorenko *et al.* developed dynamic actuation systems by integrating high-aspect-ratio silicon nanocolumns, either free-standing or substrate-attached, with a hydrogel layer. The nanocolumns were put in motion by the “muscle” of the hydrogel, which swells or contracts depending on the humidity level. This actuation resulted in a fast reversible reorientation of the nanocolumns from tilted to perpendicular to the surface. The dynamic control of the surface nanofeatures have exciting applications in actuators, microfluidics, or responsive materials.³⁶

Magnetic control

Magnetic force has become a promising tool for fluid manipulation in micro-fluidic devices, because it can work under a non-contact mode without the limitations of the surface property of microchannels and the composition of working solutions, especially for capturing, sorting and manipulation of cells, virus and even single molecules.³⁷

Remote controlled flow regulation in a microfluidic device was performed using a hydrogel nanocomposite valve with magnetic nano-particles dispersed in temperature-responsive *N*-isopropylacrylamide hydrogels. The swelling and collapse of the resultant nano-composite was remotely controlled by application of an alternating magnetic field (AMF), figure 7. The valve was integrated into a ceramic microfluidic device with Y-junction channels. AMF of frequencies of 293 kHz were applied for an ON–OFF control on the flow.³⁸ Although the response of the valve is in the minute scale, it can be precisely controlled by the nano-composite composition and geometry making them very attractive as actuators in micro-devices.

Ferromagnetic nanoparticles (Fe_3O_4) embedded in cylindrical hydrogel materials (poly(*N*-isopropylacrylamide)) were used as a flow regulator via thermo-mechanical gating within micro-fluidic channels. By an oscillating magnetic field (100–1000

kHz) that induces heat, the valving actuation was controlled. This methodology might be ideal for many biomedical applications, including synergistic application of heat and sustained releasing capability of chemotherapeutic agents.³⁹

Fluid manipulation was achieved using magnetic polymeric artificial cilia on the walls of a microfluidic channel. Cilia of 300 μm were fabricated from a ferromagnetic polymer made from iron nano-particles and polydimethylsiloxane (PDMS) and the actuation was generated with a homogeneous rotating magnetic field ($\mu_0 H < 50 \text{ mT}$) generated with a compact external electromagnet. The use of magnetic actuation makes the artificial cilia particularly suited for lab-on-a-chip applications because of the absence of perturbation of magnetic fields by (bio)chemical fluids.⁴⁰

Valve actuation was carried out using the flexibility of the PDMS walls of a microfluidic device when pressed together by the aid of a permanent magnet and a small metal bar (NdFeB) lying below the channel of interest. The operation of the valve is dependent on the thickness of the PDMS layer, the height of the channel, the gap between the chip and the magnet.⁴¹ Although it is a relatively unsophisticated approach, the magnetically controlled valve is sufficient for injection and fluid manipulation in portable micro-devices. In addition, since the magnetic valve operates externally and chips are made from PDMS the whole structure can be manufactured at low cost and can be disposable.

Precise low-power control of fluid flow at the micro-scale is crucial for the successful development of lab-on-a-chip and portable systems. An autonomous micro-pump was actuated by gel dehydration, evaporation, and subsequent gel absorption. Simple micro-pumps structures were fabricated using microfabrication techniques with glass, silicone polymer, and agarose or polyacrylamide gel with a homogeneous flow actuation in the picolitre per second range for several hours.⁴²

Chemotactic Materials for Advanced Delivery Functions

Chemotaxis is the phenomenon in which body cells, bacteria, and other single-cell or multicellular organisms direct their movements according to certain chemicals in their environment. This process is important for bacteria to locate food (for example, glucose) by 'swimming' towards the highest concentration of food molecules, or to flee from poisons (for example, phenol). Chemotaxis research has been primarily focused in the field of biological sciences. More recently, the Grzybowski group have reported the use of chemotactic droplets in maze solving applications.⁴³ The droplets

are powered by a combination of acid/base chemistry and surface tension effects. When subjected to a pH gradient within a maze, these droplets move toward regions of low pH (at a rate of $\sim 10 \text{ mm s}^{-1}$) and find the simplest route through the maze structure (over several centimetres), see Figure 8. Chemotactic droplets were made up of a combination of hexyldecanoic acid (HDA) and a solvent immiscible with water (mineral oil or dichloromethane). The mechanism of droplet motion can be explained by surface tension effects stemming from HDA deprotonating as it diffuses from the droplet. More protonated HDA is found in the direction facing the source of acid. This asymmetric distribution translates into a gradient of surface tension, giving rise to convective flows, which is responsible for droplet motion. We believe that this work could form the basis of new delivery vehicles for more advanced analytical functions. This approach has exciting possibilities, as in principle it allows programmed movement of molecules throughout a complex fluidic system without the need for pumps and valves, which could lead to very simple yet powerful ways to deliver reagents to particular locations.

Conclusions

The role of materials science has never been more critical. It is evident that the technologies of the near-future, and consequently, the way society functions, will depend on the work of talented researchers working many fascinating materials concepts. In the area of microfluidics, polymer actuators will become fully integrated into functioning platforms that will be much more biomimetic in character than current technologies. Photoswitchable actuators are particularly interesting in that no direct physical contact is required to deliver the actuation signal, which simplifies fabrication processes. Chemically-based stimulation is also an exciting concept as in this case, either through spontaneous movement of molecules within channels or through chemically sensitive actuators. However, the real proof of these new concepts and emerging materials will be in the realisation of complete functioning prototypes that perform a useful task in a manner that has convincing advantages over existing approaches.

Acknowledgements

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Figure

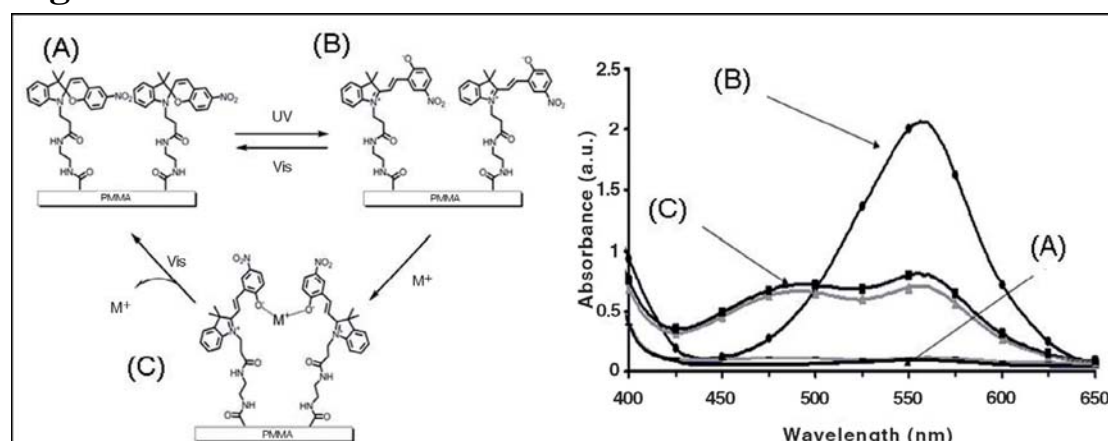


Figure 1. Representation (left) and corresponding UV-Vis spectrum (right) of photo-controlled ion-binding at a SP-modified surface. (A) – Colorless SP-immobilized surface. (B) – Upon illumination with UV light, the surface becomes active and bright purple (574 nm) due to the photoisomerization of SP to MC. Illumination of this surface with visible light switches MC back to SP. (C) – Exposure of activated surface to a solution of divalent metal ions leads to formation of the complex MC₂-M²⁺ and further colour change of the surface (in this case MC₂-Co²⁺ complex = 482 nm). Irradiation of this surface with green light leads to transformation of MC₂-M²⁺ back to the original passive, colourless SP, with simultaneous release of the bound M²⁺ ions.

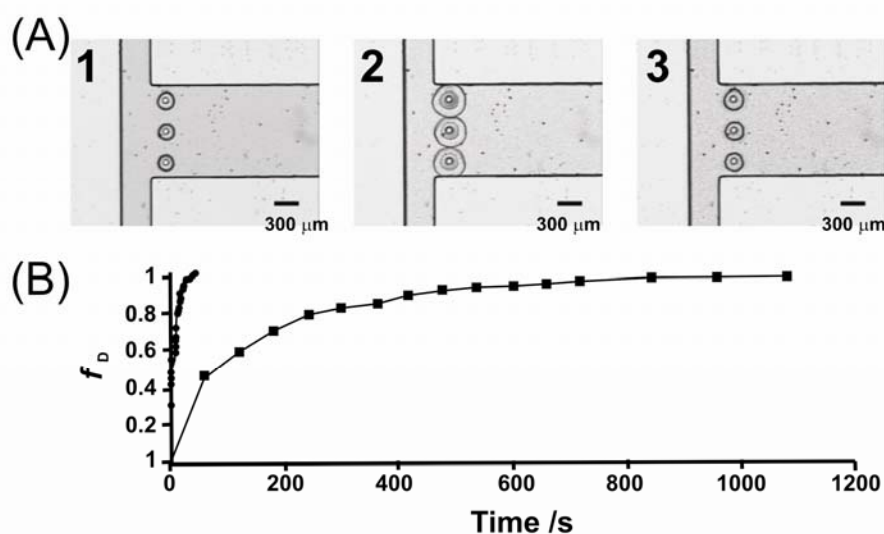


Figure 2: (A) 1-Device after polymerization of the hydrogel. 2-The hydrogel blocks the channel in its expanded state. 3- The contracted hydrogel allow fluid to flow. (B) The improvement in time response of the hydrogel design (circles) versus an alternative design that uses a single larger cylindrical structure in the same size channel (squares). f_D is the fractional change in diameter. Reproduced with permission from ref. 35. Copyright 2000 Nature Publishing Group.

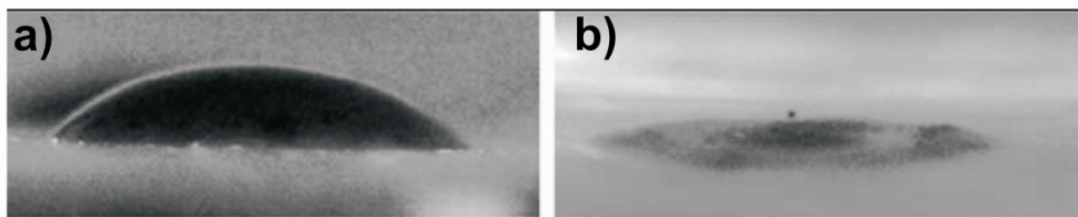


Figure 3: Side view of single actuator operation by a projector. **a)** Large membrane deflection upon light illumination and universal bus pressure; **b)** deflection erased by a second light illumination (no pressure applied). Reproduced with permission from ref. 29. Copyright 2008 The Royal Society of Chemistry.

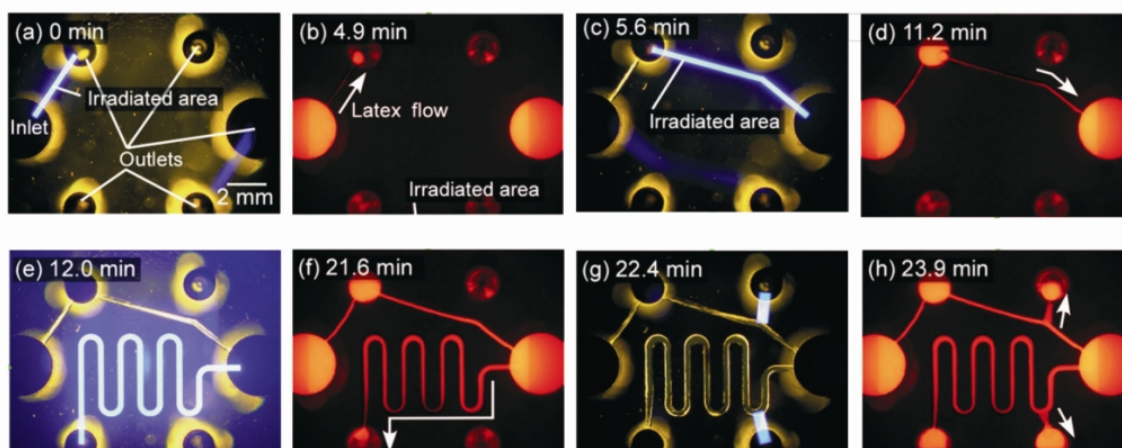


Figure 4: micro-channels fabrication on demand using micro-patterned light irradiation. White arrows indicate the flow direction of a fluorescently labeled latex bead suspension. **a)** Micro-channel formation by micro-patterned light irradiation of the pSPNIPAAm hydrogel sheet. **b)** Latex bead suspension flow through the microchannel after irradiation. Flow of the red colored latex bead suspension from the inlet to the upper-left-side outlet is slightly visible. **c)-h)** Three consecutive sequences of micro-patterned light irradiation and microchannel formation. Reproduced with permission from ref. 34. Copyright 2009 The Royal Society of Chemistry.

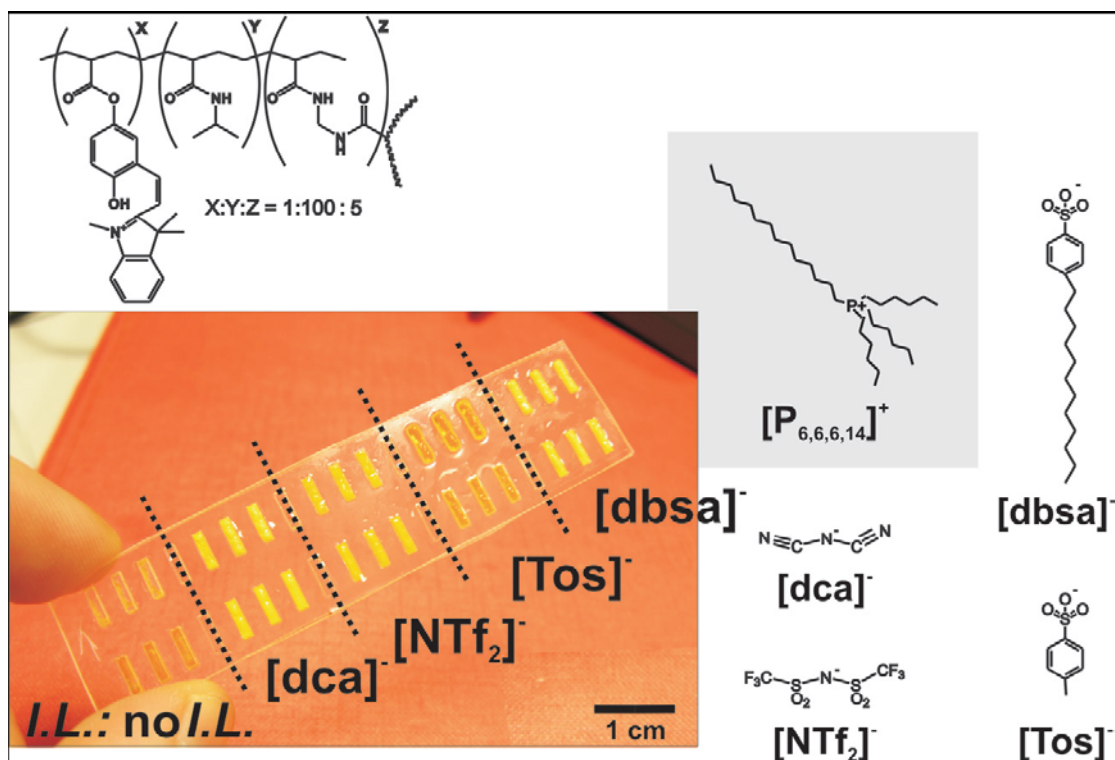


Figure 5: a) Chemical structure of the photo-responsive ionogel (top left) and four ionogels polymerised in a PMMA mould. b) Trihexyltetradecylphosphonium-based ionic liquid chemical structures. Reproduced with permission from ref. 34. Copyright 2010 The Royal Society of Chemistry.

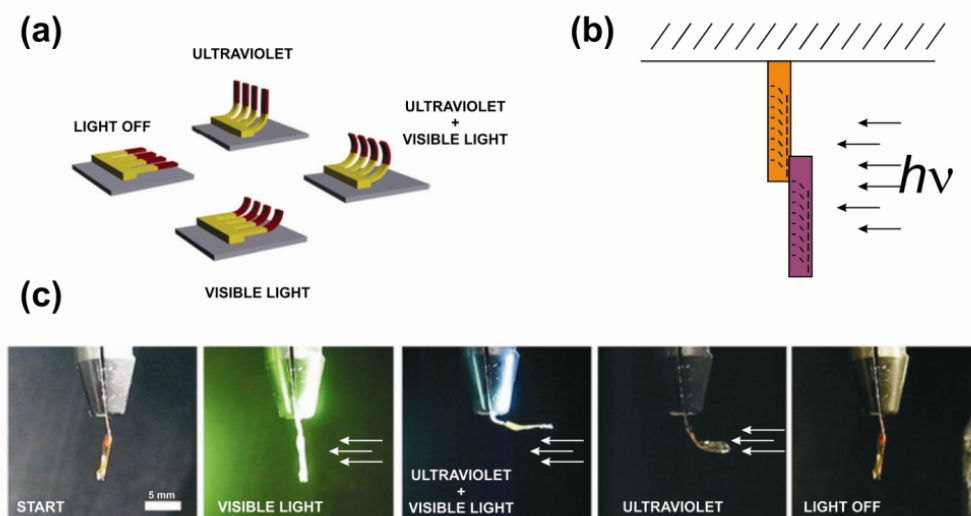


Figure 6: Artificial cilia and their motions. a) Artificial, light-driven cilia produce an asymmetric motion controlled by the spectral composition of the light. b) Schematic representation of the macroscopic set-up, showing the orientation of the molecules. c) Steady-state responses of a 10 μm thick, 3 mm wide and 10 mm-long modular liquid-crystal network actuator to different colours of light. Reproduced with permission from ref. 35. Copyright 2009 Nature Publishing Group.

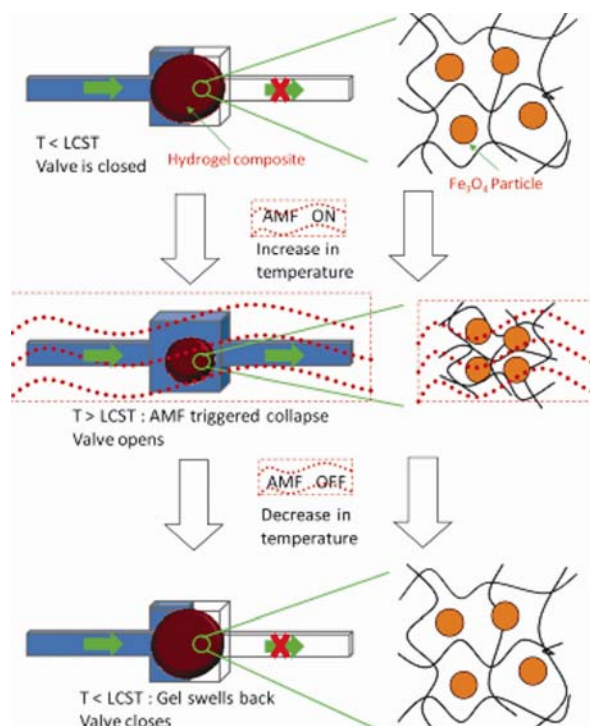


Figure 7: Schematic of the concept of remote controlled hydrogel nanocomposite valves with an alternating magnetic field (AMF). Application of the AMF results in collapse of the hydrogel, leading to opening of the valve. Reproduced with permission from ref. 38. Copyright 2009 The Royal Society of Chemistry.

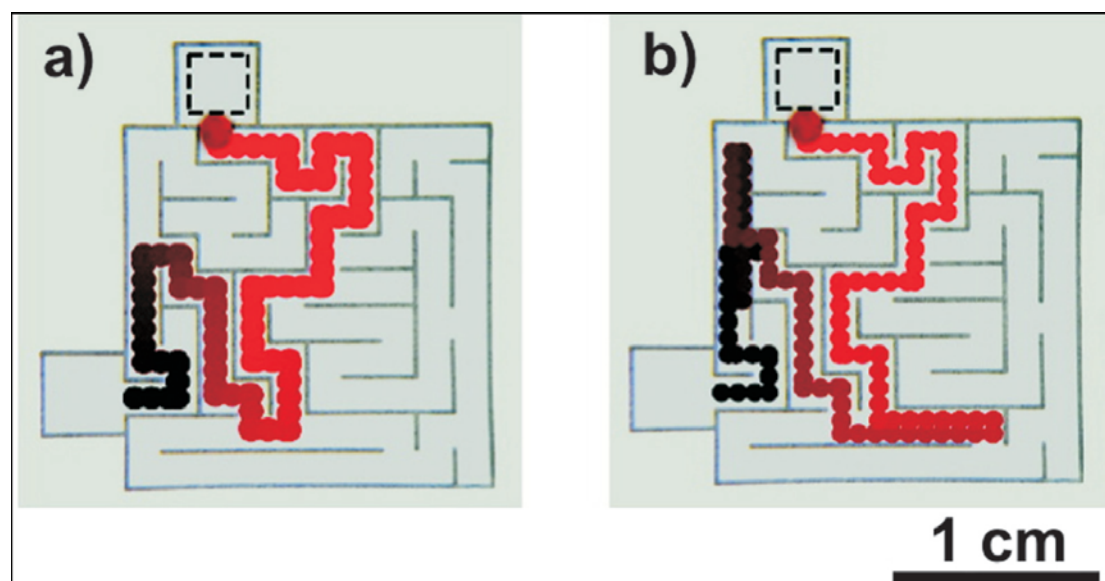


Figure 8: Maze solving by chemotactic droplets. In (a), the droplet moved straight to the exit along the shortest path. In (b), the droplet went astray at two locations but corrected its trajectory and ultimately found the shortest path. Reproduced with permission from ref. 42. Copyright 2010 American Chemical Society.

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