



Schizophrenic Molecules and Materials with Multiple Personalities - How Materials Science could Revolutionise How we do Chemical Sensing.

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Schizophrenic Molecules and Materials with Multiple Personalities - How Materials Science could Revolutionise How we do Chemical Sensing.

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Abstract

Molecular photoswitches like spiropyrans derivatives offer exciting possibilities for the development of analytical platforms incorporating photo-responsive materials for functions such as light-activated guest uptake and release and optical reporting on status (passive form, free active form, guest bound to active form). In particular, these switchable materials hold tremendous promise for microflow-systems, in view of the fact that their behaviour can be controlled and interrogated remotely using light from LEDs, without the need for direct physical contact. We demonstrate the immobilisation of these materials on microbeads which can be incorporated into a microflow system to facilitate photoswitchable guest uptake and release. We also introduce novel hybrid materials based on spiropyrans derivatives grafted onto a polymer backbone which, in the presence of an ionic liquid, produces a gel-like material capable of significant photoactuation behaviour. We demonstrate how this material can be incorporated into microfluidic platforms to produce valve-like structures capable of controlling liquid movement using light.

Introduction

Chemical sensors are devices that provide information about binding events happening at the interface between a sensitive film/membrane and a sample phase. The function of the sensitive film/membrane is to ensure that the binding at this interface is as selective as possible usually by means of entrapped or covalently bound receptor sites. The binding event is further coupled with a transduction mechanism of some kind; such as a change in the colour or fluorescence of the film or a change in electrochemical potential. Clearly, these materials are 'active' as binding events must occur for them to be of any analytical use. However, it is self-evident that these sensitive interfaces will change over time, for example due to non-specific binding and biofouling in real samples that can lead to surface poisoning or occlusion, or leaching of active components into the sample phase. Consequently, the response characteristics of chemical sensors and biosensors will change with time, leading to gradual decrease in sensitivity, loss of selectivity and baseline drift. In practice, these effects are compensated for by regular calibration, until the device deterioration reaches some limiting level. In recent years, physical transducers have been increasingly deployed in sensor networks. However, for equivalent widely distributed chemical sensing to happen, there must be a revolution in the way chemical sensors/biosensors are employed, as conventional calibration is inappropriate for large-scale deployments due to the cost of ownership (particularly maintenance) of these rather complex devices. In this paper, we consider the use of materials that can be switched reversibly between two or more different 'personalities with radically

different characteristics. For example, materials that can exist in a passive form (non-binding) until a measurement is required, at which point the material is switched to an 'active' or binding form. Once a measurement is made, the material is switched back to the 'passive' form. This effect may have important potential applications in sensors, purification resins, separation science and drug delivery. We will also suggest how polymer actuators may provide routes to new active components in microfluidic manifolds, such as pumps and valves, that could form the basis of soft-polymer based circulation systems for handling samples, reagents, and standards in futuristic analytical devices that have a distinct biomimetic character.

Sensornets

'Sensornets' are large-scale distributed sensing networks comprised of many small sensing devices equipped with memory, processors, and short-range wireless communications capabilities.[1] These devices, known as 'Motes' can gather and share sensor data from multiple locations through in-built wireless communications capabilities. The vision of incorporating chemical and biological sensing dimensions into these platforms is very appealing, and the potential applications in areas critical to society are truly revolutionary.[2] For example, the 'environmental nervous system' concept likens the rapid access and response capabilities of widely distributed sensor networks to the human nervous system; i.e. it is able to detect and categorise events as they happen, and organise an appropriate response.[3] Sensors monitoring air and water quality will be able to provide early warning of pollution events arising at industrial plants, landfill sites, reservoirs, and water distribution systems at remote locations.

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 molecular world? Unfortunately, it would appear from the lack of field deployable devices in commercial production that attempts to integrate molecular sensing science into portable devices have failed to bear the fruits promised; this problem is what we call 'the chemo-/ bio-sensing paradox',[4] i.e. *'Chemo/bio-sensors **must have an 'active' or responsive surface incorporating sites that are pre-designed to bind with specific target species in order to generate the chemically or biologically inspired signal; at the same time, these surfaces should be passive, in that they should be resistant to effects that cause signal drift and loss of sensitivity.***

The interactions involved in these binding events can be very subtle, and even slight changes in the surface or bulk characteristics through processes like leaching, fouling, or decomposition, can have a significant effect on the output signal, and the overall performance of the device. This is in contrast to physical transducers, as they can function without having to make direct physical contact with the 'real world'. For example, thermistors are completely enclosed in a tough protective epoxy coating that enables heat to pass through from the real world, and light sensors, which are also completely enclosed, leaving a transparent window through which light can penetrate from the region under observation. When chemo/bio-sensors are exposed to the real world, their sensitive surfaces immediately begin to change, and hence they suffer from baseline drift and variations (usually reduction) in sensitivity, as well as cross-response to interferents that may be present in the sample.

In analytical science, we deal with this issue through regular calibration, meaning that the sensing surface is periodically removed from the sample and exposed to standards, the response characteristics checked, and any baseline drift or change in

sensitivity compensated. However, if this type of capability is to be provided to an autonomous chemo/bio-sensing platform, it requires that a liquid flow system is integrated, comprising pumps, valves, and interconnects. This drives up the complexity, price and power requirements of these platforms, and makes the realisation of small, autonomous, reliable, chemical sensing/biosensing devices impractical at present.

Therefore, the traditional vision of the ‘chemo/bio-sensor’ as a device with an active membrane attached to a pen-like probe is outdated, and needs to be completely rethought. In particular, the issue of how to predict and control surface characteristics at the interface between the device and the real world needs fresh thinking, as this is where the molecular interactions that generate the observed sensor signal happen. The key to progress will require breakthroughs arising from new concepts in fundamental materials science, such as the development of *adaptive* or *stimuli-responsive materials* that have externally or locally controllable characteristics. These materials could be regarded as having capability to switch between several completely different ‘personalities’ – schizophrenics at the molecular level!

In this paper, we shall show how certain photochromic molecules display intriguing switchable characteristics, and suggest ways in which this can be used to control the function and behaviour of sensing devices and platforms.

Experimental

Materials and instruments

(1'-(3-carboxypropyl)-3',3'-dimethyl-6-nitrospiro(2H-1)benzopyran-2, 2'-(2H)-indole) (SPCOOH, Figure 1) was synthesized as reported elsewhere [5]. Polybead carboxylate microbeads 2.035 μm diameter, 2.79% solid contents, were purchased from PolySciences Inc. Plain silica microspheres ($5 \pm 0.35 \mu\text{m}$ diameter, 5 % solid contents), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC hydrochloride), (3-Aminopropyl)triethoxysilane (APTES), 2-(N-morpholino)ethanesulfonic acid hydrate (MES hydrate), 1,8-diaminooctane, calcium nitrate hydrate, copper(II) nitrate trihydrate and zinc chloride were purchased from Sigma Aldrich (Ireland). Ammonia solution 25% was purchased from Sharlau Chemie (Spain). Homogeneous suspensions of microbeads were generated using a Bransonic Ultrasonic Cleaner 5510 from Branson Ultrasonics Corporation, USA. UV (375 nm), white (430-760 nm), blue (430 nm), green (525 nm), red (630 nm) LEDs were purchased from Roithner Laser Technik, Austria. The UV light source used for the solution studies was a BONDwand UV-365nm obtained from Electrolyte Corporation, USA. Sample spinning was carried out using a ROTOFIX 32 centrifuge (Global Medical Instrumentation, Inc., USA.). Absorbance spectra were recorded using a Well Plate Spectrometer (Medical Supply Co., Ireland). Reflectance spectra were recorded using a miniature diode array spectrophotometer (S2000[®]) combined with an FCR-7UV200-2 reflection probe (7 X 200 micron cores) and a DH-2000-FSH deuterium halogen light source (215-1700 nm, Ocean Optics Inc., Eerbeek, Netherlands). A white reflectance standard WS-1-SL was used to standardise the measurements at 100% reflectance (Ocean Optics Inc., Eerbeek, Netherlands).

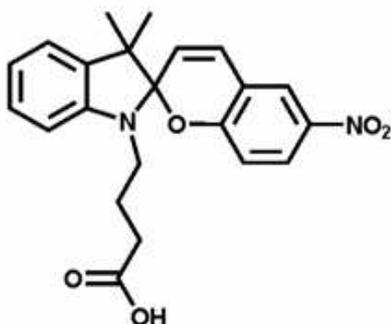


Figure 1. 1'-(3-carboxypropyl)-3',3'-dimethyl-6-nitrospiro(2H-1)benzopyran-2, 2'-(2H)-indole (SPCOOH).

Covalent immobilisation of spiropyran on the surface of silica microspheres

1) Amino groups coating of the silica microsphere surface

A sample of a suspension of silica microspheres (0.1 g in 2 ml of water) was diluted with 22.5 ml ethanol. 2.5 ml of ammonia solution 25% and 2 ml of APTES were added and the mixture stirred under reflux for 48 hours. The microspheres suspension was then cooled, separated from the reaction mixture by centrifugation, suspended in 4 ml of ethanol and washed 6 times with fresh ethanol. The washing procedure consists of a four step process:

1. Centrifugation of the suspension for 3 minutes at 4000 rpm.
2. Removal of the supernatant, addition of 4 ml of fresh solvent.
3. Sonication of the suspension for 5 minutes.
4. Subsequent further centrifugation.

2) Covalent immobilization of Spiropyran on the surface of amino groups functionalised silica microbeads

3 ml of a 15 mg ml⁻¹ solution of SPCOOH in ethanol was added to 2 ml of an 11 mg ml⁻¹ solution of EDC in ethanol. The reaction mixture was stirred for half an hour at room temperature in the dark. A 1 ml suspension of 0.1 g of the amino functionalised microspheres in ethanol was added to the spiropyran/EDC solution and the reaction mixture stirred for 72 hours at room temperature in the dark. Finally, the spiropyran functionalised microbeads were profusely washed 10 times with ethanol following the above procedure and stored at 4 °C in the dark.

Evaluation of metal interactions with SP-coated microspheres

Spiropyran coated silica and polystyrene microspheres suspended in ethanol were exposed to the same concentrations (10⁻⁴ M) of ethanolic solutions of Ca²⁺ and Cu²⁺ (polystyrene microspheres) and Ca²⁺, Cu²⁺ and Zn²⁺ (silica microspheres) in order to evaluate the complex formation at the bead surface.

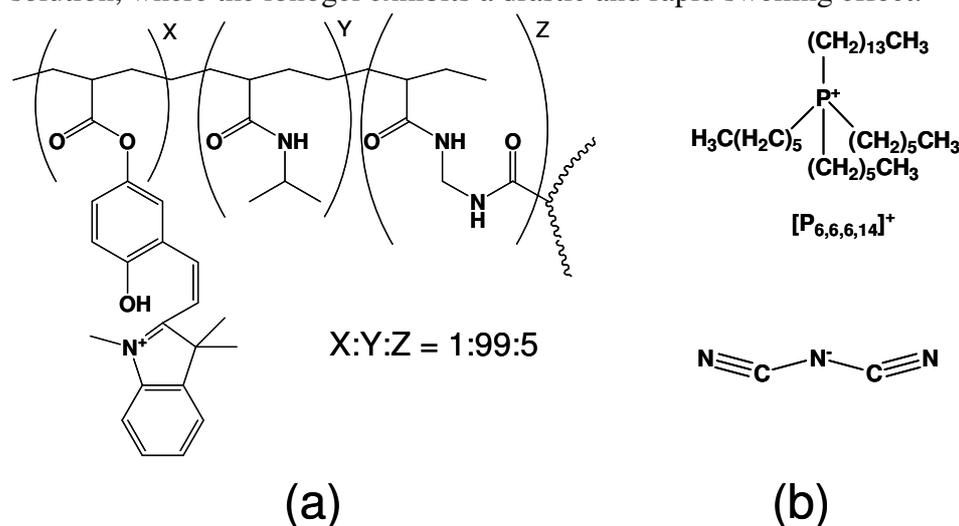
Each experiment was carried out using the following procedure:

1. Exposure of the microspheres to a white LED for 1 minute (promotes MC conversion to the SP form)
2. Recording of the spectrum of the colourless SP form.
3. Exposure of the microspheres to a UV LED for 1 minute (promotes SP conversion to the MC form).
4. Recording of the spectrum of the coloured MC form.
5. Addition of 10⁻⁴ M metal solution in ethanol to the microspheres.
6. Recording of the spectrum.

7. Exposure of the microspheres to a white LED for 1 minute (promotes metal expulsion and MC conversion to the SP form)
8. Recording of the spectrum of the colourless SP form.

Preparation of photo-responsive phosphonium based ionogel

The ionogel consists of three monomeric units; *N*-isopropylacrylamide (NIPAAm), *N,N*-methylene-bis(acrylamide) (MBAAm) and acrylated benzospiroopyran in the ratio 100:5:1, respectively (Scheme 1). The acrylated benzospiroopyran is synthesised as described elsewhere [6]. A reaction mixture solution placed in the micro-fluidic reservoir was prepared by dissolving the NIPAAm monomer (452 mg, 4.0 mmol), the MBAAm (10.8 mg, 0.07 mmol), acrylated spirobenzopyran monomer (14.0 mg, 0.04 mmol), and the photo-initiator dimethoxy-phenylacetophenone (DMPA) (10.2 mg, 0.04 mmol) into 1-butanol (1.0 mL). These monomers were photo-polymerised within an ionic liquid matrix. For this example, the ionic liquid matrix used was trihexyltetradecylphosphonium dicyanoamide [$P_{6,6,6,14}$][dca]. UV irradiation source for polymerization (365 nm) was placed 8 cm far from the monomers. When the polymerization was completed, the gels were washed with ethanol and 0.1 mM HCl aqueous solution for 10 min to remove the unpolymerised liquid and the excess of ionic liquid. Finally the ionogels were kept for two hours in 0.1 mM HCl aqueous solution, where the ionogel exhibits a drastic and rapid swelling effect.



Scheme 1. a) Photo-responsive polymer poly(*N*-isopropylacrylamide), *N,N*-methylene-bis(acrylamide) and acrylated benzospiroopyran in the ratio 100:5:1, respectively. b) trihexyltetradecylphosphonium dicyanoamide [$P_{6,6,6,14}$][dca] ionic liquid.

Micro-fluidic device fabrication

The micro-fluidic device shown in Figure 2 (4 x 4 cm) was easily fabricated in poly(methyl methacrylate) (PMMA) and pressure-sensitive adhesive (PSA) in four layers using CO₂ ablation laser and it consists of five independent micro-channels. The ionogel valve is placed in a square reservoir (300 × 300 μm), fabricated using the CO₂ laser, within the PMMA 125 μm and the PSA 80 μm thickness layers. It is important to mention here that micro-valves can be easily relocated simply by varying the layer layout. A second PSA layer with the channel structures (80 μm deep, 150 μm width, and 20 mm length) was fabricated using the CO₂ laser and terminally glued to the

previous PSA layer to generate the micro-fluidic structure. Finally the upper PMMA layer, which contains the inlets and outlets, closes the micro-fluidic structure.

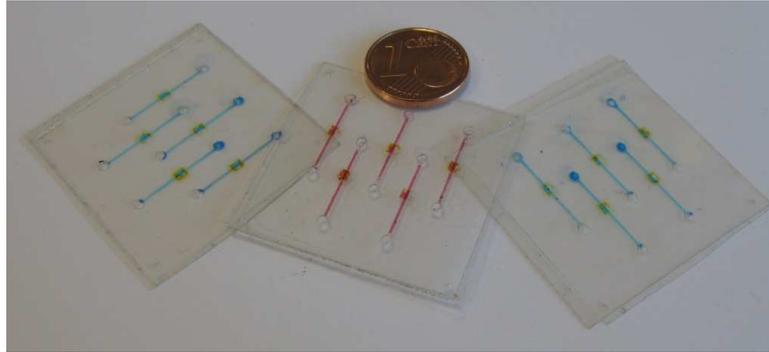


Figure 2. Picture of three micro-fluidic devices fabricated in PMMA:PSA polymer by CO₂ ablation laser system. Channels were filled with different dyes to improve channel visualization.

Characterization of the photo-responsive phosphonium based ionogel

Volume phase transition behaviour of the photo-responsive phosphonium based ionogel was investigated using visible light irradiation. The physical shrinking by photo-induced dehydration of the ionogel was measured on-line by contact profilometer experiments when visible light is applied, Figure 3, and by visual observation using a PARISS: "Prism and Reflector Imaging Spectroscopy System" equipped with a CCD camera.

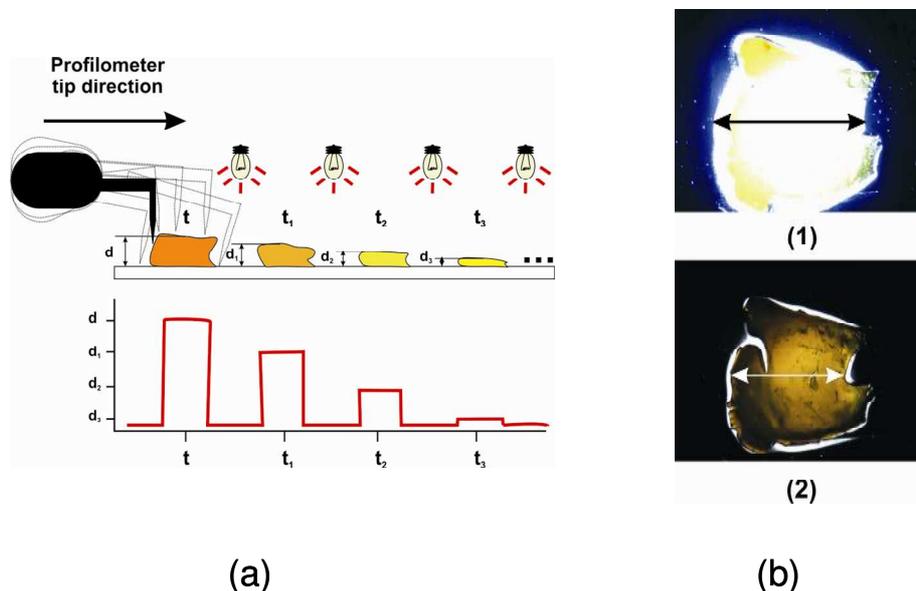


Figure 3. a) Schematic representation of the set-up used for the profilometer measurements. b) Ionogel shrinking process: 1- during white light irradiation, 2- two seconds after white light irradiation, size decrease 29 % in volume.

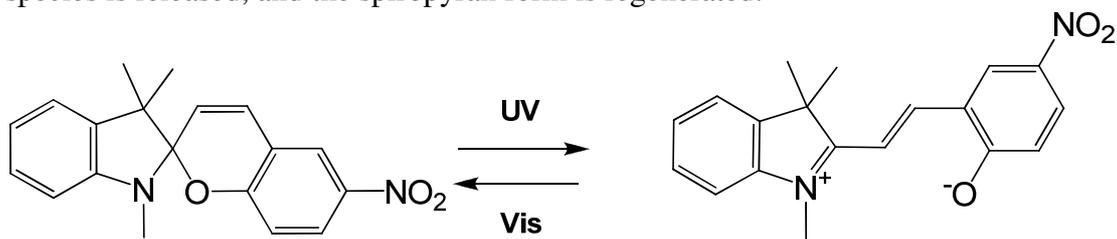
Evaluation of micro-valve function

In order to evaluate the function of the ionogel micro-valves fabricated on the micro-fluidic device, a red dye, B₁₂ vitamin 1 μ M concentration in water was placed into the inlet reservoir. In the outlet, a constant vacuum was applied as the driving force.

Visible light irradiation was carried out at 5 mm separation from the valve. When light is applied the polymer decreases in volume and the valve opens, letting the coloured liquid pass through the channel. The liquid movement was observed with a CCD camera.

Results and Discussion

There is considerable interest in spiropyrans and similar photochromic molecules due to their potential applications in areas such as light-sensitive eyewear,[7] information recording and processing,[8] optical memory,[9] and molecular devices.[10] We are interested in their optical sensing applications [11-14] and in particular their potential for playing multiple roles within a chemical sensor (photoswitch, ligand, transducer). Utilizing photo-switchable molecules such as spiropyrans, which can be switched between active or passive forms, may enable such behaviour to be realised. Upon exposure to UV light, the colourless spiropyran (SP) molecule undergoes a heterocyclic ring cleavage that results in the formation of the merocyanine (MC) form (Scheme 2), which has a deep purple colour as it is a planar, highly conjugated chromophore with a strong absorbance in the visible spectrum. It is well known that, after removal of UV light, the predominant MC form generated will thermally isomerize back to its equilibrium state; and this decay in absorbance typically follows first-order kinetics. [15] Furthermore, the MC isomer has a phenolate anion site to which ions, protons and amino acids can bind, giving rise to new absorption bands in the visible spectrum. [16-18] By shining white light on the colored complex, the guest species is released, and the spiropyran form is regenerated.



Scheme 2. Structures of nitrobenzospiryran (SP), left, and merocyanine (MC), right.

Therefore these photoswitchable molecules possess some of the characteristics we are interested in employing in next generation analytical platforms. However, it is a significant challenge to manifest these characteristics in a materials format that is compatible with the microfluidic platforms we employ. In order to achieve this, we need to incorporate the switchable moiety within a polymeric matrix through a range of approaches such as physical entrapment within bulk polymers,[19] grafting to monomers,[5] or standard surface immobilisation chemistries like EDC coupling.[20] We are particularly interested in bringing addition innovation to this process, for example, by generating novel hybrid materials such as photoswitchable ionogels (see below).

Computational analysis

In order to assist with this research, and to better understand the molecular basis for observed characteristics, we have recently employed computational analysis techniques to aid in the design of innovative hybrid materials comprising of spiropyran derivatives and ionic liquids. Standard *ab initio* molecular orbital theory and density functional theory (DFT) calculations were carried out using GAUSSIAN

03 [21], which enabled excitation energies of the MC isomer to be computed at CIS(D)/6-31+G(d,p) level. All molecular orbitals were plotted using the HF/6-31+G(d,p) electron density. The molecular orbitals on the MC isomer are shown in Figure 4. The first excitation arising from the HOMO has an energy of 569 nm, and as this excitation is allowed by symmetry, it is clearly evident in the visible spectrum.

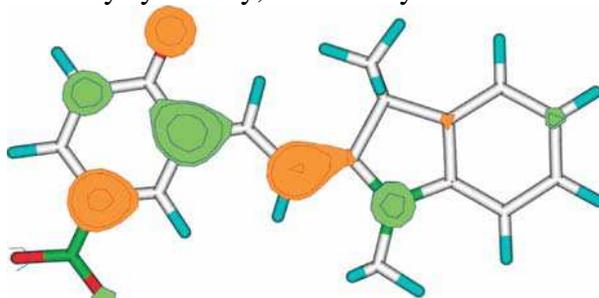


Figure 4. HOMO-1 molecular orbital of the MC isomer.

We have also studied the interactions of organic cations and anions with the MC isomer, such as imidazolium [emim]⁺ and dicyanoamine [dca]⁻. For [emim]⁺, we found that the [emim]⁺ cation appears to interact predominantly via the C2 carbon which resides only 2.92 Å (the C---O distance, Figure 5a) away from the phenolate oxygen. The sum of the van der Waals radii of the carbon and oxygen atoms is 3.22 Å and hence, the C---O separation appears to be considerably shorter than a normal close contact. This C2 hydrogen is in fact known to be quite acidic.[22] The C2 hydrogen atom sits in between the carbon and oxygen atoms (CHO bond angle close to linear) introducing a very short/strong hydrogen bond of just 1.865 Å (H---O distance). As a comparison, a strong hydrogen bond, e.g. O---H---O, is slightly longer in length, around 1.9 Å.[23] Moreover, such a close proximity of the two ions results in a through-space orbital interaction, with molecular orbitals on both oxygen and carbon atoms overlapping, and forming a strong interaction between the two molecules. Due to the through-space interaction, the species formed is likely to be quite stable and will thus hinder conversion of the MC form back to the aplanar SP isomer.[24] The optimised structures of MC with the [dca]⁻ anion are shown in Figure 5b. This suggests that the two conjugated systems are tilted away from one another, a feature which will also inhibit the thermal relaxation of MC back to SP state, as the two conjugated systems have a much lower degree of interaction. These calculations have led us to prepare similar systems and investigate these materials experimentally, as described below.

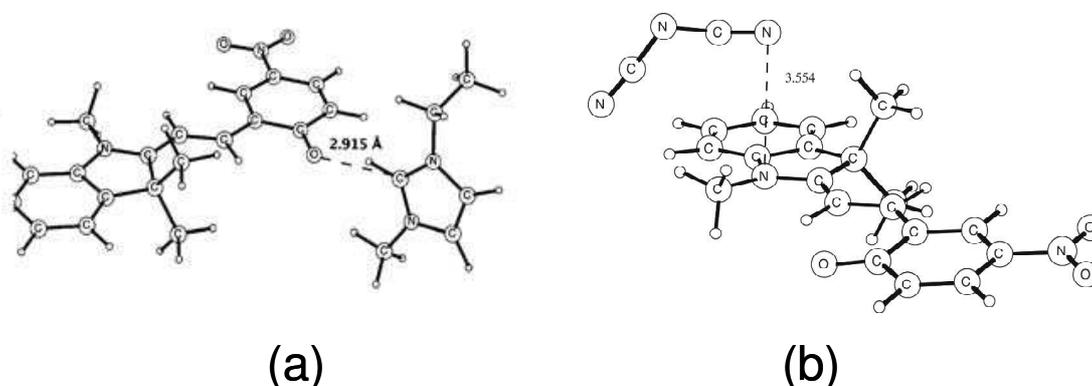


Figure 5. Optimized structures of MC isomer with the (a) [emim]⁺ and (b) [dca]⁻ at B3LYP/6-31+G(d).

Chemical Sensing utilizing bead technology

In the past we have utilized polymeric supports for photo-regenerable chemical sensing applications. [20, 25] Bead based systems are particularly interesting from the chemical sensing perspective as they have higher surface area compared to flat surfaces, which can enhance kinetics compared to conventional surfaces.[26] In addition beads can be moved like a fluid but are easily separated from the liquid phase and hence their incorporation into flow systems for separation science holds many advantages.[27, 28] Recently spiropyran has been covalently immobilised on the surface of silica and polystyrene microspheres and their light-modulated characteristics including ion-binding capability have been investigated.[29] Covalent functionalisation involves the use of a carboxylated spiropyran derivative (Figure 1) which is attached to the bead surface via EDC coupling chemistry.[20] The resulting SP-functionalised microspheres can be switched back and forth between a pink coloured MC form and a colourless SP form using a 375 nm UV-LED (SP \Rightarrow MC switching) and a 430-760nm white LED (MC \Rightarrow SP switching) (Figure 6).

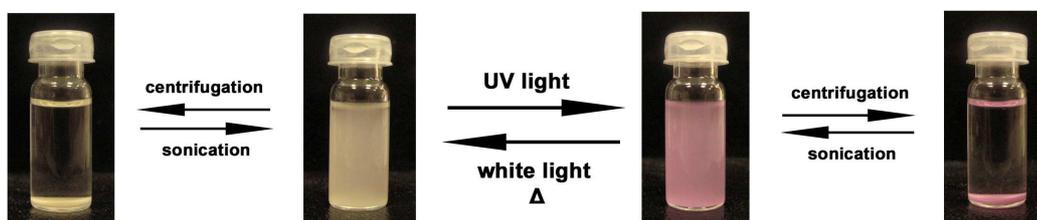


Figure 6. Spiropyran switching between the colourless SP and the pink MC form on the surface of the silica functionalised microspheres.

The colour changes have been detected using reflectance spectroscopy (in the case of polystyrene microspheres, due to their high scattering effect) and absorbance spectroscopy (in the case of silica microspheres, due to their higher transparency). Upon irradiation with UV-LED for 1 minute, the pink MC form is generated on the microsphere surface, and the characteristic 560 nm band appears, further exposure of the MC-microspheres to a white LED for 1 minute causes reconversion to the colourless SP form and the disappearance of the characteristic MC band, as seen in Figure 7. When the MC-microspheres are exposed to certain metal ion solutions, they undergo further spectral and visible colour changes, due to the formation of MC₂-M²⁺ complexes. Subsequently exposure of the beads to illumination with a white LED causes the metal-ion guest to be expelled and the SP form is restored, ready for another ion-binding event. In the case of the silica microspheres the greatest ion binding effects were observed in the presence of Zn²⁺ and Cu²⁺ ions (Figure 7). Under exposure of the MC-microspheres to Zn²⁺, a clear visual colour change from purple (MC) to light pink (MC₂-Zn²⁺) can be observed. This is caused by a decrease in the MC absorbance band around 560 nm and the emergence of a new absorbance band centred around 525 nm arising from the MC-metal ion complex, consistent with the replacement of free MC by the ion-complex on the microsphere surface.

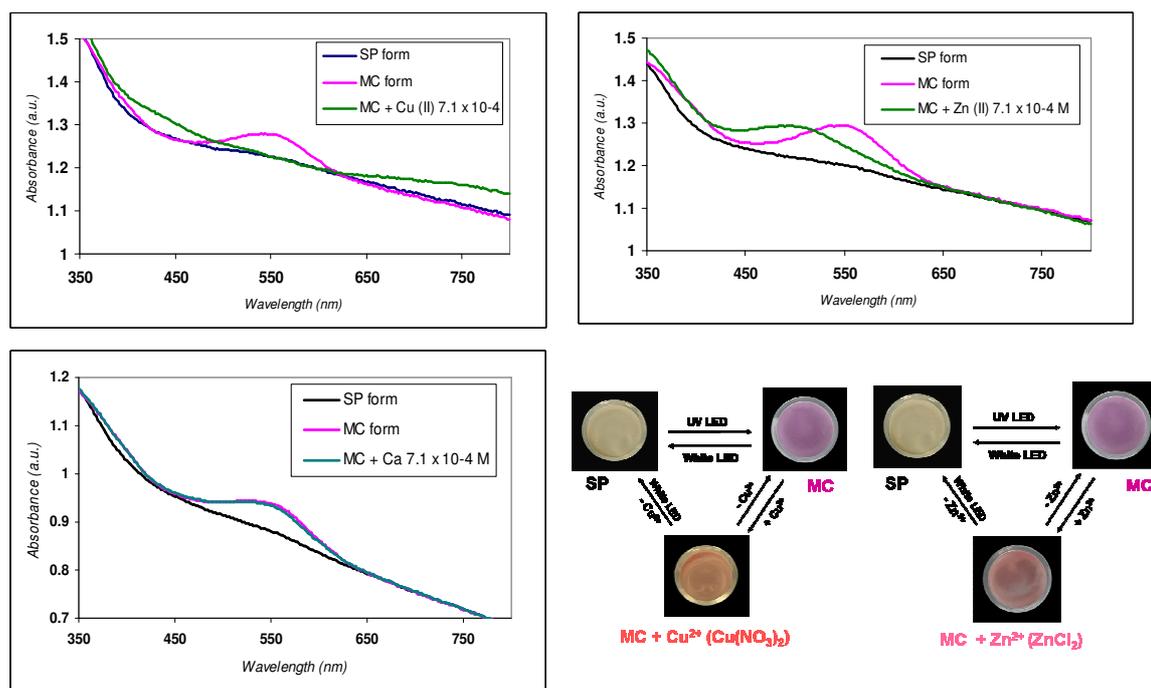


Figure 7. Absorbance spectra and visual colour changes on the surface of silica microspheres in the presence of the MC and SP form and after exposure of the MC form to metal ions (Cu^{2+} , Zn^{2+} and Ca^{2+}).

Similarly, the addition of Cu^{2+} ions to the MC-microsphere sample results in a colour shift from purple to orange (formation of $\text{MC}_2\text{-Cu}^{2+}$ complex), which arises from the disappearance of the 560 nm MC peak and the simultaneous appearance of two new absorbance bands at 440 nm and 750 nm. In both cases, after the formation of the MC-metal ion complex, replacement of the metal ion solution with clean ethanol, followed by irradiation of the microbeads for 4 minutes with a white LED, leads to expulsion of the bound Cu^{2+} ions and complete reformation of the SP form on the beads. Following this, irradiation of the microspheres for 2 minutes with the UV-LED converts the SP back to the MC form, ready for another metal ion uptake and release cycle. This light-modulated ion retention and release behaviour, coupled with visible indication of the bead state, opens the possibility of developing photocontrolled stationary phases that can be activated and deactivated using light. These results show that spiropyran modified beads can be used for the photo-controlled selective accumulation and release of ions. Furthermore, the system is inherently self-indicating, as each form (SP, MC, $\text{MC}_2\text{-M}^{2+}$ complex) has a different colour and UV-vis spectrum. Clearly, this behaviour could have many interesting applications in selective pre-concentration on certain ions, transport of bound ions to remote locations, and controlled release of bound ions, using light as the external controlling stimulus. Figure 8 shows functionalised polystyrene microspheres packed into an optically transparent silica capillary being switched between the two forms (SP and MC). In this form, the beads can clearly be applied to photocontrolled metal-ion uptake and release in a capillary flow system.

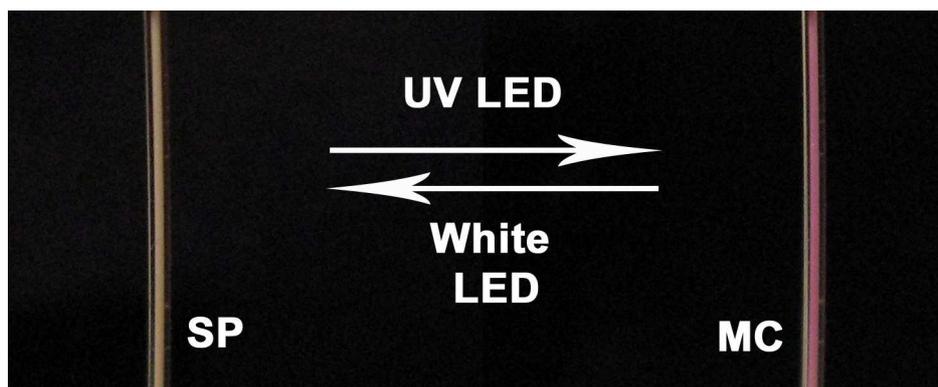


Figure 8. Switching of SP-modified polystyrene microspheres between the SP and MC forms in a silica microcapillary using UV and white LEDs.

Polymeric Actuation using light- Applications in Microvalve Technology.

Even with their impressive physical changes, electro-actuators employing soft polymer materials like conducting polymers have not solved the micro-actuator problem within the field of microfluidics. This is due to the complex fabrication schemes required to incorporate these materials into microfluidic manifolds. Therefore, controlling physical properties with temperature,[6, 30] photon irradiation,[31, 32] or specific chemical (pH, ionic strength)[33, 34] stimuli would be of great benefit for rapid prototyping.

We have developed a photo-responsive microvalve from a hybrid material (ionogel), see Scheme 1. In an acidic aqueous system in the dark, the ionogel (MC-H⁺) is in a protonated open-ring form. When irradiated by blue light, the MC-H⁺ isomerizes immediately to a closed-ring form (SP), dissociating protons and losing positive charges. When the light is turned off, the chromophore returns spontaneously to the protonated open-ring form, which is more thermodynamically stable in the dark than the closed-ring form. The photoisomerization affects the hydration of the ionogel significantly. Under dark conditions, the MC-H⁺ form (hydrophilic) ionogel is yellow. When the ionogel is irradiated with blue light, the ionogel decolorizes, indicating the SP form (hydrophobic) is present. Simultaneously, the gel reduces in size due to loss of charge, and associated induced dehydration of water from the polymer. This photo-induced dehydration results in a physical shrinkage of the ionogel, as seen in the images within Figure 3b. Our results indicate that the photo-induced ionogel shrinkage proceeds through two distinct steps; at first, the isomerization of the MC-H⁺ to closed-ring SP (uncharged) form take place under white light irradiation for 3 s, calculated experimentally to be $2.5 \times 10^{-2} \text{ s}^{-1}$. The resultant hydrophobic isomer induces the dehydration of polymer main chain. After 150 seconds of exposure to visible light, there is a 73 % decrease in the ionogel height, Figure 3a, as monitored using a physical contact profilometer. The rate constant for the slower (shrinkage) stage was experimentally calculated to be 0.457 s^{-1} . [35] Optical control of a microvalve structure built into a microfluidic channel was demonstrated as shown in Figure 9. A drop of a solution containing a red dye was placed in the inlet of the channel while at the outlet a vacuum was applied (Figure 9a). The microvalve was irradiated with white light as shown in Figure 9b, and the micro-valve opened after 3 s, allowing liquid to pass through the channel to the outlet, Figure 9c-e. The light intensity necessary to control the ionogel micro-valve is not particularly intense, for example, a simple white LED ca. 1 mW cm^{-2} [19] can be used to actuate the valve.

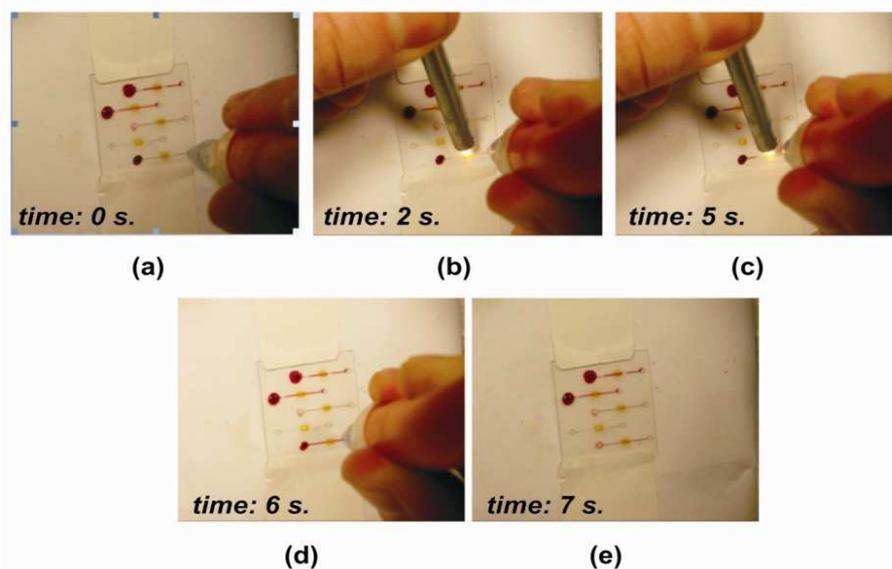


Figure 9. Performance of the ionogel micro-fluidic valve. a) Micro-valve is closed; vacuum is unable to draw the red dye through the micro-channel. b) White light is applied opening the micro-valve. c-e) The red dye moves along the micro-channel.

The isomerization of the MC-H⁺ induced by white light irradiation is a reversible phenomenon. The closed-ring form returns spontaneously to the protonated open-ring form, which induces the swelling of the ionogel. Therefore, it is possible to reuse the micro-valves repeatedly, although the ionogel in its present form requires more than 30 min to swell again and block the whole channel. Nevertheless, a large number of micro-valves can be fabricated simultaneously using the same process described above and therefore, the method is suitable for large-scale integration of micro-valves on microfluidic manifolds. The micro-valve control by light irradiation provides non-contact operation and independent manipulation of multiple fluids on microfluidic devices, as well as parallel control of multiple micro-valves. It is expected that such photoresponsive polymer gel micro-valves will be an advantageous technique for integrated multifunctional micro-fluidic devices.[36]

Conclusions

The key to many new technologies lies in the development of materials that exhibit stimulus-responsive behaviour. This area has undergone rapid growth in recent years, as the science and technology of molecular and nano-scale control and characterization of materials continues to develop. The range of materials that can be switched between dramatically different modes of behaviour is expanding rapidly, and in this paper, we have only been able to provide an introduction into some of the exciting possibilities that can arise from materials containing spiropyran derivatives. Even within the limits of this particular paper, it is clear that these materials could revolutionise the capabilities of analytical platforms, facilitating light modulated uptake and release of molecular guests on channel surfaces and beads, transport of bound species to other locations on beads, photo-switchable separation of sample components, light-actuated valves and pumps to control liquid flow, which, if integrated with simple optical detection, could provide a route to low-cost analytical platforms with whose characteristics are completely controlled using light. And

beyond the analytical world, these materials have the potential to be incorporated into a wide range of specialist and consumer products within the next 5 years that could dramatically impact on society. Furnishings and clothes that change colour, textiles that can sense and communicate, chemical sensors whose surface binding activity can be turned on/off, and materials with light switchable hydrophobicity/permeability. All in all, it seems clear that there are exciting times ahead in sensor science aligned with adaptive or stimuli-responsive materials!

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References

1. Shenker S, et al., ACM SIGCOMM Computer Communication Review, 2003. **33**(1): p. 137-142.
2. Diamond, D., *Internet-scale sensing*. Analytical Chemistry, 2004. **76**(15): p. 278A-286A.
3. Diamond, D., *Internet-scale chemical sensing: is it more than a vision?* NATO Security through Science, Series A: Chemistry and Biology, 2006. **2**(Advances in Sensing with Security Applications): p. 121-146.
4. Byrne, R. and D. Diamond, *Chemo/bio-sensor networks*. Nature Materials, 2006. **5**(6): p. 421-424.
5. Rosario, R., et al., *Photon-Modulated Wettability Changes on Spiropyran-Coated Surfaces*. Langmuir, 2002. **18**(21): p. 8062-8069.
6. Szilagyi, A., et al., *Rewritable Microrelief Formation on Photoresponsive Hydrogel Layers*. Chemistry of Materials, 2007. **19**(11): p. 2730-2732.
7. Crano, J.C., et al., *Photochromic compounds: chemistry and application in ophthalmic lenses*. Pure and Applied Chemistry, 1996. **68**(7): p. 1395-1398.
8. Guglielmetti, R., *Spiroyrans and related compounds [applications]*. Studies in Organic Chemistry (Amsterdam), 1990. **40**(Photochromism: Mol. Syst.): p. 855-78.
9. Dvornikov, A.S. and P.M. Rentzepis, *Accessing 3D memory information by means of nonlinear absorption*. Optics Communications, 1995. **119**(3,4): p. 341-6.
10. Willner, I., et al., *Reversible light-stimulated activation and deactivation of *a*-chymotrypsin by its immobilization in photoisomerizable copolymers*. Journal of the American Chemical Society, 1993. **115**(19): p. 8690-4.
11. Collins, G.E., et al., *Photoinduced switching of metal complexation by quinolinospiropyranindolines in polar solvents*. Chemical Communications (Cambridge), 1999(4): p. 321-322.
12. Collins, G.E., et al., *Spectrophotometric Detection of Trace Copper Levels in Jet Fuel*. Energy & Fuels, 2002. **16**(5): p. 1054-1058.

13. Winkler, J.D., C.M. Bowen, and V. Michelet, *Photodynamic Fluorescent Metal Ion Sensors with Parts per Billion Sensitivity*. Journal of the American Chemical Society, 1998. **120**(13): p. 3237-3242.
14. Suzuki, T., et al., *Photo-reversible Pb²⁺-complexation of insoluble poly(spiropyran methacrylate-co-perfluorohydroxy methacrylate) in polar solvents*. Chemical Communications (Cambridge, United Kingdom), 2003(16): p. 2004-2005.
15. Gorner, H., *Photochromism of nitrospiropyrans: effects of structure, solvent and temperature*. Physical Chemistry Chemical Physics, 2001. **3**(3): p. 416-423.
16. Gorner, H. and A.K. Chibisov, *Complexes of spiropyran-derived merocyanines with metal ions - Thermally activated and light-induced processes*. Journal of the Chemical Society-Faraday Transactions, 1998. **94**(17): p. 2557-2564.
17. Evans, L., III, et al., *Selective Metals Determination with a Photoreversible Spirobenzopyran*. Analytical Chemistry, 1999. **71**(23): p. 5322-5327.
18. Ipe, B.I., S. Mahima, and K.G. Thomas, *Light-Induced Modulation of Self-Assembly on Spiropyran-Capped Gold Nanoparticles: A Potential System for the Controlled Release of Amino Acid Derivatives*. Journal of the American Chemical Society, 2003. **125**(24): p. 7174-7175.
19. Stitzel, S., R. Byrne, and D. Diamond, *LED switching of spiropyran-doped polymer films*. Journal of Materials Science, 2006. **41**(18): p. 5841-5844.
20. Byrne, R.J., S.E. Stitzel, and D. Diamond, *Photoregenerable surface with potential for optical sensing*. Journal of Materials Chemistry, 2006. **16**(14): p. 1332-1337.
21. Frisch, M.J.T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A., *GAUSSIAN 03*. 2004, Gaussian Inc: Wallingford CT.
22. MacFarlane, D.R., et al., *Lewis base ionic liquids*. Chemical Communications (Cambridge, United Kingdom), 2006(18): p. 1905-1917.
23. Modig, K., B.G. Pfrommer, and B. Halle, *Temperature-Dependent Hydrogen-Bond Geometry in Liquid Water*. Physical Review Letters, 2003. **90**(7): p. 075502.
24. Byrne, R., et al., *Photo- and solvatochromic properties of nitrobenzospiropyran in ionic liquids containing the [NTf₂]⁻ anion*. Physical Chemistry Chemical Physics, 2008. **10**(38): p. 5919-5924.

25. Radu, A., et al., *Photonic modulation of surface properties: a novel concept in chemical sensing*. Journal of Physics D: Applied Physics, 2007. **40**(23): p. 7238-7244.
26. M.-S. Kim, et al., Transducers, 2003.
27. Adam, T., Lüdtke S., and K. K. Unger, *Application of 0.5- μ m porous silanized silica beads in electrochromatography* Journal of Chromatography A, 1997. **786**(2): p. 229-235.
28. Adam, T., Lüdtke S., and K. K. Unger, *Packing and stationary phase design for capillary electroendosmotic chromatography (CEC)*. Chromatographia, 1999. **49**: p. S49-S55.
29. Silvia Scarmagnani, et al., *Polystyrene bead-based system for optical sensing using spiropyran photoswitches*. Journal of Materials Chemistry, 2008. **18**: p. 5063-5071.
30. Reber, N., et al., *Transport properties of thermo-responsive ion track membranes*. Journal of Membrane Science, 2001. **193**(1): p. 49-58.
31. Sugiura, S., et al., *Photoresponsive polymer gel microvalves controlled by local light irradiation*. Sensors and Actuators, A: Physical, 2007. **A140**(2): p. 176-184.
32. Kameda, M., et al., *Photoresponse gas permeability of azobenzene-functionalized glassy polymer films*. Journal of Applied Polymer Science, 2003. **88**(8): p. 2068-2072.
33. Kim, S.J., et al., *Surprising shrinkage of expanding gels under an external load*. Nature Materials, 2006. **5**(1): p. 48-51.
34. Eddington, D.T., et al., *An organic self-regulating microfluidic system*. Lab on a Chip, 2001. **1**(2): p. 96-99.
35. Sugiura, S., et al., *Photoresponsive polymer gel microvalves controlled by local light irradiation*. Sens. Actuators, A FIELD Full Journal Title:Sensors and Actuators, A: Physical, 2007. **A140**(2): p. 176-184.
36. Sugiura, S., et al., *On-demand microfluidic control by micropatterned light irradiation of a photoresponsive hydrogel sheet*. Lab Chip, 2009. **9**: p. 196-198.