Beads, Boats and Switches: *Making things happen with Molecular Photoswitches*

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***Abstract*— In this paper we present recent results obtained with a stimulus-responsive materials based on the photo-switchable behaviour exhibited by spiro-cyclic derivatives. Our results suggest that these highly novel materials offer unique capabilities hitherto inaccessible using conventional materials. In particular, we will focus on photocontrolled guest binding and release, inherent signalling of status, photo-actuation and solvent driven motion of small structures as examples of the fascinating behaviour of these exceptional materials.**

Keywords-component; stimuli-responsive materials, photo-switching, benzospiropyran.

I. *INTRODUCTION*

Despite the tremendous advances in nanotechnology which now enable us to manipulate and characterize materials to a level unimaginable to previous generations of sensor scientists, our ability to perform even relatively simple chemical and biological measurements at remote locations is still severely hampered. For example, truly implantable devices capable of long-term (years) chemo/bio-sensing are still unknown, and remote sensing of important chemical and biological targets in the environment is still heavily dependent on platforms that adhere more to the 'coffee-machine' configuration than to the small, autonomous, low-cost devices that could provide dynamic information about the status of our environment at multiple locations.[1]

The fundamental problem is that these devices often employ a sensitive sensing surface to generate the chemo/bio-selective signal, and the surface response characteristics are inherently affected by any process that affects the state of the surface sample interface, such as leaching of receptor molecules (active binding sites), occlusion of the surface (e.g. through bioflouling), or the presence of interferents in the sample. Therefore, this sensitive surface begins to change as soon as it is exposed to the real world, and the response characteristics (slope, selectivity, baseline, response time etc.) also begin to change.[2] Traditionally, analytical scientists have tackled this problem through regular recalibration with standards of known concentration. However, this means that the device must be capable of sophisticated fluid handling, and must therefore incorporate pumps, valves, reservoirs and conduits for handling of samples and standards. This dramatically pushes up the cost and complexity of the platform, and makes dense deployments of environmental sensors, and long-term implantable sensors fundamentally unrealizable, at least in their present form. It is clear that we need to reach into materials science to find radically new approaches to solving issues like control of surface binding processes and liquid movement, non-contact interrogation of device status, and utilisation of local energy sources for long-term autonomous operation. [3]

Making Use of Molecular Photoswitches

Controlling Binding Behaviour at Surfaces

Spiropyrans and related spirocyclic compounds like spirooxazines can be reversibly switched between two forms, the spiro (SP) form, and the merocyanine form (MC), that exhibit dramatically different properties.[4, 5] For example, the MC form is highly charged (zwitterionic), strongly colored (purple, λmax ca. 560 nm), and capable of binding metal ions, amino acids and DNA. In contrast, the SP form is uncharged, colorless and does not bind molecular guests. Switching between the two forms can be readily achieved using UV light (SP to MC) and white/green light (MC to SP). SP-derivatised polymer surfaces can be generated using a variety of standard synthetic procedures, leading to solid materials whose surfaces can be activated (using UV light), deactivated (using white/green light). Furthermore, the activated surface changes color when certain metal ions are bound, and exposure to white light releases the guest and restores the passive surface. Hence the entire system is self-indicating in terms of status (passive, active-free, active-bound), and easily switched using simple low power sources like LEDs.[6, 7] We have SP functionalised the surface of microbeads, both silica and polystyrene, and demonstrated this switchable behaviour happening under phonic control.[8] Immobilisation of these beads in microcolumns opens the way to phonically controlled separations, and the use of SP-functionalised beads to pick up, transport and release molecular guests to pre-selected locations. Key to effective switching of the SP-MC system is the length of the molecular tether used to attach the SP groups. These need to be at least eight methylene units long to provide the flexibility required for molecular reorganisation that accompanies switching between the two forms, and for formation of guest complexes. This photo-controlled binding behaviour has been shown to extend to other classes of molecular guests like amino acids,[9] organic ions[10] and

DNA.[11]

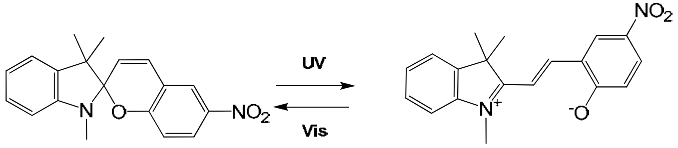


Figure 1. Photo-isomerisation of nitro-benzospiropyran (SP), left, to its merocyanine (MC) isomer, right.

Controlling Movement

Interestingly, SP-modified polymers also exhibit photoactuation behavior, due to changes in overall charge and solvent uptake/release that accompany switching. The actuation behaviour can be enhanced by using an ionic liquid medium to produce ionomer gels. We have integrated these hybrid materials into microfluidic valve structures, and demonstrated very effective photonic control of liquid flow using low-power, low-cost LEDs.[12] In addition to valve based control, we have also recently demonstrated the use of SP-coatings on microcapillaries to control electro-osmotic pumping. In this case, the SP-coating on the capillary wall is protonated to give an overall positive charge that leads to the formation of the charged double layer necessary for effective generation of electro-osmotic force (EOF). Switching of the coating using UV light generates the zwitterionic MC form, which disrupts the double layer and reduces the EOF-based flow,[13] and hence the flow rate of the system can be controlled using light. Very recently, a surprising degree of movement has been demonstrated using lithographically structured poly-N- isopropylacrylamide (pNIPAAm) gels. The gels were soaked in ethanol and then transferred to water, where they moved spontaneously through expulsion of the ethanol from the gel.[14] We have demonstrated similar effects using solvent loaded ionogels incorporated into small floating structures (mm dimensioned 'boats'!).

II. RESULTS AND DISCUSSION

Controlling Binding Behaviour at Surfaces

Recently polystyrene and silica microspheres were covalently functionalised with SP derivatives. Their behaviour have been characterised in terms of UV-vis and reflectance spectroscopy[8]. In order to further investigate the surface property of the microspheres, single association force measurement using atomic force microscopy (AFM) and contact angle measurements were carried out. Kado reported the single association force measurement between a gold cantilever tip and a gold surface both functionalised with SP derivatives.[15] We report the photoresponsive behaviour of SP using single association force measurements between SP functionalised silica microspheres (5 μm diameter) that have been immobilised on a gold AFM tip and a SP functionalised glass surface.

Figure 2 shows an example of single association force measurement curve. Red lines represent the extend curves (the cantilever is pushed against the surface). Blue lines represent retract curves (the cantilever is retract from the surface). When the cantilever approaches the surface van der Waals attractions (which produce a negative peak very close to the surface) or repulsions (when no negative peak is present) can occur. Then when the cantilever is moved away from the surface, if attractions between the surface and the cantilever are present, an adhesion peak appear on the graph, which is bigger than the van der Waals peak, as it has to overcome this force to move from the surface. If no attraction is occurring, no adhesion peak is present. Figure 2 also shows the single association force measurement curve obtained for SP modified bead and SP functionalised glass slide. It can be clearly seen that the tip experiences a stronger force than van der Waals interactions.

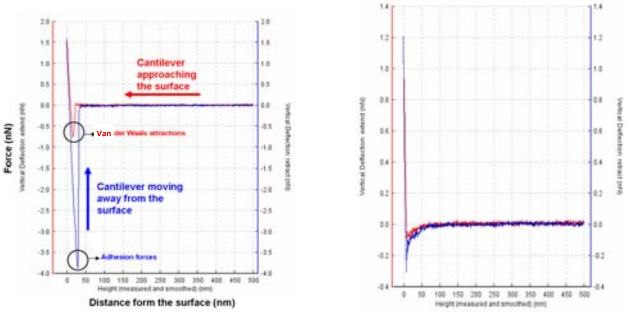


Figure 2. Single association force measurement curve showing typical van der Waals attractions and adhesion forces, left. Single association force measurement curve showing experimental result for SP modified bead and SP functionalised glass slide, right.

Contact angle measurements were also performed to prove the presence of SP on the surface of the glass slide. It was demonstrated that surface energy could be modulated using light to isomerise between the unpolar SP form and the polar MC. For the glass slide treated with the piranha solution, the slide presents a contact angle of 13°. The functionalisation of this slide with SP induces an increase of the contact angle of 50° when the slide is in the SP form. After UV irradiation (356nm) of the SP glass slide there is a decrease in the contact angle of an average value of 7-8° due to the increased polarity of the MC form, see Figure 3. The change is small, probably because of the low concentration of covalently bound SP, but it indicates that the surface polarity is changing by light irradiation.

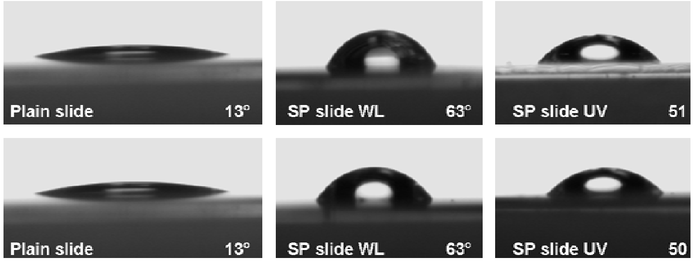
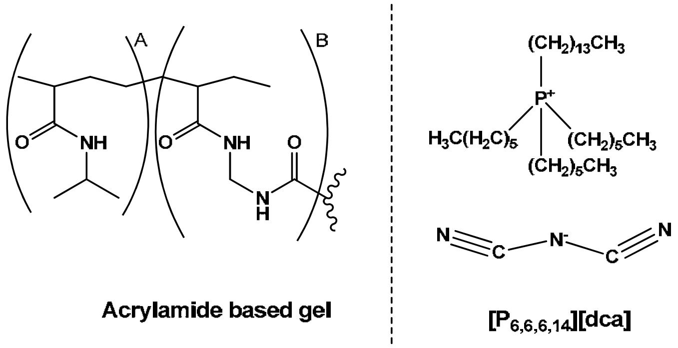


Figure 3. Changes in contact angle measurements observed due to immobilisation of SP, photo-induced contact angle observed due to photo-isomerisation of the non-polar SP to the polar MC isomer.

Controlling Movement

We have recently published work on polymeric materials containing ionic liquids. Ionic liquids (ILs) are a class of novel solvents with very interesting properties which are attracting the attention of a growing number of researchers.[16] ILs are organic salts composed of anions and cations that are in the liquid state at ambient conditions and many show negligible volatility and non-flammability.[17] They have also been labelled as ‘designer solvents [18], because it is possible to tailor anions and/or cations for specific functions such as catalysis, solubility and viscosity. Incorporating ILs into polymer gels is also attractive as it may generate materials with the inherent advantages of ILs within a solid or semi-solid gel-type structure.[19] This could lead a new era in polymer gels in ILs since the actuation behavior can be monitored in an open environment without the need to consider solvent evaporation. Bassik *et al* investigated the solvent driven motion of poly-*N*-isopropylacrylamide (PNIPAm) gels.[14] The gels were soaked in ethanol and then transferred to water, where they moved spontaneously. This movement is driven by the expulsion of the ethanol from the gel and subsequent ethanol spreading at the air-water interface. We are using PNIPAm gels containing phosphonium based ILs, see Figure 4, to investigate these solvent driven motions for actuation of objects in aqueous media.



Acrylamide based gel

$[P_{6,6,6,14}][dca]$

Figure 4. Poly-*N*-isopropylacrylamide cross-linked gel consisting of (A) 95 wt% isopropyl acrylamide and (B) 5 wt% *N,N'*-methylene bisacrylamide, left. Tetradecyl(trihexy) phosphonium dicyanamide $[P_{6,6,6,14}]$[dca], ionic liquid used in ionogel, right.

Ionogels dimensions play a very important role in the actuation of the boat. For instance, big pieces of ionogel (> 2 mm length) cause slow actuation. The boat moves slowly in the water but the control of the direction can be carried out more easily. In the other hand, small pieces of ionogel (< 1 mm length) cause fast actuation but poorer control in the boat direction. The weight and dimensions of the object subjected to movement is also crucial. For instance, in the case of small boats (2x smaller than the one presented in Figure 5) the same amount of ionogel causes very fast actuation but no control in the boat direction. Speed is as fast as 50 mm s^{-1}. In the case of a bigger boat, half size of the one presented in figure 1 the speed is reduced to 35 mm s^{-1} but the direction control is also poor. In the case of the boat of Figure 6 the speed is reduced to 10 mm s^{-1} and the direction of the boat can be easily control by changing the position of the ionogel, Figure 5a.

Figure 5b shows a series of snapshots of the performance of the ionogel. The boat with the ionogel is floating in basified water (0.01 M NaOH). A solution of bromocresol green in ethanol is placed in the boat reservoir (photograph 2-3). The ethanol is strongly absorbed by the ionogel (colour of the ionogel changes from yellow to blue due to the dye) and the actuation start to take place (photo 4). The ethanol is expelled out of the ionogel by replacement of the ethanol molecules by water molecules in the ionogel matrix. The interchange of solvent molecules generates micro-movement of the ionogel which generate the blue dye clouds of dye in the water. The high surface tension energy release between ethanol and water in the ionogel interface cause the movement of the whole structure. In this particular case the position of the ionogel determines that the boat moves in a quasi-circular trajectory as it is drawn in Figure 5a. Once all the ethanol present in the reservoir has passed through and has been expelled out of the ionogel the boat stops. The same procedure can be carried out continuously without any indication of polymer degradation.

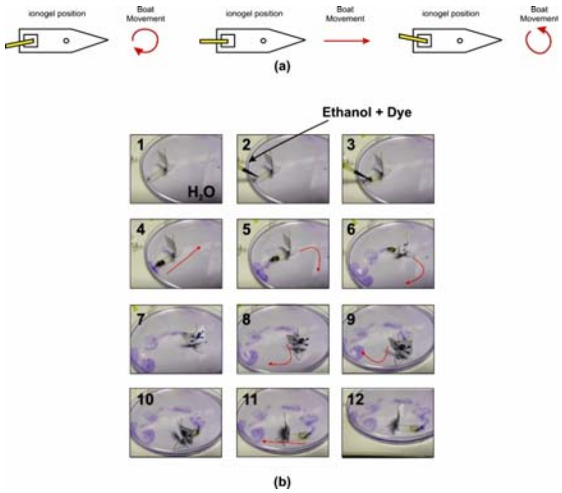
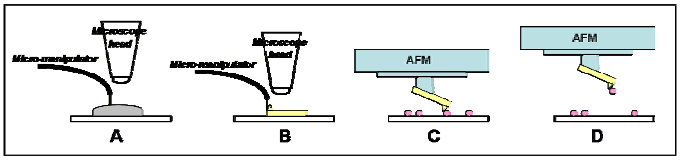


Figure 5. (a) Schematic representation of the boat movement according to ionogel position. (b) Snapshots of the boat actuation in the presence of ethanol.

III. EXPERIMENTAL

Microsphere attachment to the AFM cantilever

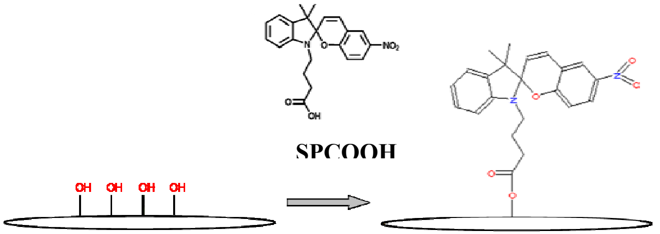
Epoxy-glue is deposited on a glass slide and using a microscope combined with a micromanipulator a small amount of glue is up taken with the tip of the micromanipulator arm, as depicted in Scheme 1. The micromanipulator tip carrying the glue is placed in contact with the side of the cantilever tip in order to deposit some of the glue on the cantilever tip. The cantilever tip placed on the AFM is pushed in contact with one bead deposited on atomically smooth mica surfaces. When the cantilever is released from the surface the attachment of the bead to the side of the cantilever tip can be verified using the microscope present below the AFM head. The epoxy-glue which holds the bead on the cantilever tip is left to cure overnight.



Scheme 1. Microsphere attachment to the AFM cantilever

Spiropyran glass slide modification

Glass slide was immersed in piranha solution (3:1 H_2SO_4:H_2O_2 (30% solution)) for 30 minutes at 50 °C. Then the slide was profusely washed with deionised water and subsequently with acetonitrile and dried under nitrogen. The glass slide was then immersed in a solution containing 2.5 mg of SPCOOH, 1.3 mg of N,N'-dicyclohexylcarbodimide (DCC) and 0.07 mg of 4-dimethylaminopyridine (DMAP) in acetonitrile, as shown in Scheme 2. This was allowed to stir overnight at room temperature in the dark.



Scheme 2. Immobilisation of SPCOOH to glass slide via DCC coupling chemistry.

Preparation of Ionogel

N-isopropylacrylamide (NIPAAm, Sigma Aldrich) was purified by recrystallization in a mixed solution of hexane and toluene. N,N-methylene-bis(acrylamide) (MBAAm, Sigma Aldrich), 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Sigma Aldrich). Tetradecyl(trihexy) phosphonium dicyanamide $[P_{6,6,6,14}]$[dca] (obtained compliments of Cytec Industries). Depending on size of ionogel required, concentration of components altered. 1 g of NIPAAm and 0.05g of MBAAm dissolved in 2mls of $[P_{6,6,6,14}]$[dca], to this 0.01g of DMPA was added and placed in sonicator at 50^{o}C for 30 mins. Solution then irradiated with 365 nm light for 20 mins to generate ionogel. Sample immersed in ethanol to remove unreacted monomers and DMPA. Sample dried in oven at 50^{o}C for 24 hrs before use.

Boat fabrication

The boat shown in Figure 6 (20 x 5 mm x 280 µm) was easily fabricated in poly(methyl methacrylate) and pressure-sensitive adhesive in three layers using CO_2 ablation laser and it consist of a waterborne structure and a small square reservoir of 2 x 4 mm where dyed ethanol is placed for ionogel actuation. The sail-pole is a 5 mm long 360 µm external diameter silica capillary with a 4 x 4 paper sail glued to the main boat by blue-tak. The overall boat weight is 4.7 g while the ionogel is less than 2 mg weight and 900 µm length, 300 µm width and 5 µm of thickness. The ionogel is placed in between the two solvents: water, where the boat floats and ethanol, that it is placed in the boat reservoir.

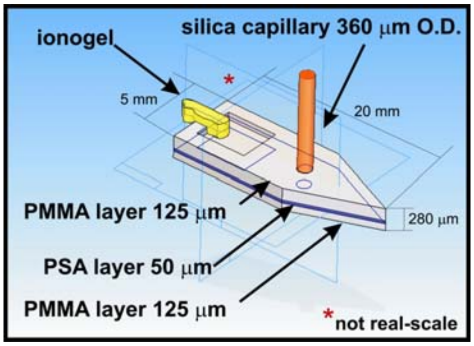


Figure 6. Schematic representation of boat.

IV. CONCLUSIONS

Clearly, these stimuli-responsive materials offer fascinating possibilities for highly innovative approaches to chemo/biosensing devices and platforms, for example, through optically controlled microfluidic manifolds in which liquid movement can be controlled using light. Coupled with photo-controlled uptake and release of molecular guests this could provide the basis for flexible control of molecular processes occurring within fluidic manifolds, without the need for a physical link between the controlling stimuli and the manifold. Such capabilities have the potential to completely revolutionise how we perform analytical measurements - what we need now is to couple creativity and imagination with materials science and engineering, to produce exemplars of these futuristic analytical platforms and convincingly demonstrate their practical application to specific problems.

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