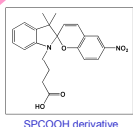


OF PHOTOCROMIC SPIROPYRAN DYES IN POLYMERIC SUBSTRATES FOR METAL ION SENSING AND MICRO-FLUIDICS

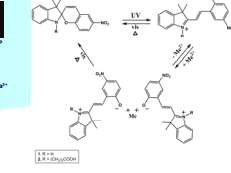
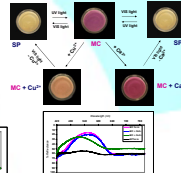
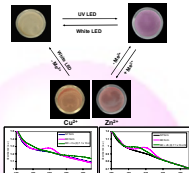
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SPIROPYRAN FUNCTIONALISED MICROBEADS FOR PHOTODYNAMIC SEPARATION



Polystyrene and silica microbeads (2 and 5 μm respectively) have been recently successfully functionalised with a modified spiropryan derivative (SPCOOH) and their photochromic properties have been investigated using reflectance and absorbance spectroscopy.

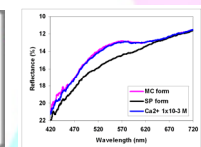
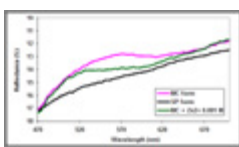
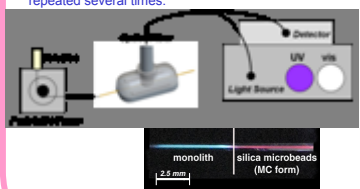


The microbeads can be switched using low power light sources such as light emitting diodes (LEDs) from a colourless and binding-inactive spiro form (SP) by irradiation with a white LED (430-760 nm) to a purple, ion-binding active merocyanine form (MC) by exposure to a UV LED (375 nm). When in the merocyanine active state, in the presence of transition metal ions such as Cu²⁺ and Zn²⁺, the microbeads undergoes a further spectral and colour changes that varies according to the metal. Subsequent irradiation with white LED caused reformation of the spiro form and release of the metal ion. Alkaline earth metal such as Ca²⁺ doesn't cause any appreciable spectral of colour change. This processes have been cycled and repeated several times.

Spiropryan silica microbeads in the presence of Cu²⁺ and Zn²⁺ ions

Spiropryan polystyrene microbeads in the presence of Cu²⁺ and Ca²⁺ ions

The MC form can bind metal ions through the phenolate anionic site. The guests can be subsequently expelled by irradiation with visible light and the spiropryan reverts to the SP form

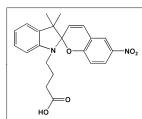


On the basis of these behaviours the spiropryan functionalised silica microbeads have been packed on a polytetrafluoroethylene coated fused silica UV transparent capillary (100 μm diameter) by adapting a monolithic frit (pore size <2 μm), to create new photoswitchable stationary phases. When packed into the capillary, reflectance measurements were carried out while flushing Ca²⁺ and Zn²⁺ into the column. Ca²⁺ doesn't cause any appreciable spectral change while the presence of Zn²⁺ could be detected by a reflectance spectral shifts. When the column was then irradiated with white light, the SP form is restored, the metal ions released and upon further UV irradiation the MC form is reformed ready for another cycle... The resulting column is an example of photodynamic system for retention, detection and release of metal ions passing through the capillary.

Using light it is possible to modulate the column behaviour towards the binding of metal ions: irradiation of the column with a UV LED converts the column to the active (MC) state which binds metal ions. Irradiation with white or green light reverses this effect, and the guest ions are released, and the beads reconverted to the original inactive form. This system can be used in principle as a self-indicating photodynamic separation platform.

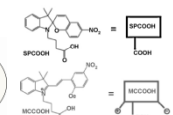
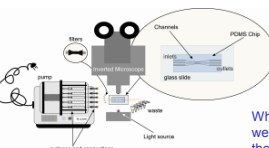
a) Scarmagnani, S. et al. *e-Journal of Surface Science and Nanotechnology* 2009, 7, 649 – 652; b) Scarmagnani, S. et al. *Journal of Materials Chemistry* 2008, 18, 5063-5071; c) Scarmagnani, S. et al. *International Journal of Nanomanufacturing* 2009, accepted.

SPIROPYRAN MODIFIED MICROFLUIDIC CHIP CHANNELS FOR PHOTONICALLY CONTROLLED SENSOR ARRAY DETECTION OF METAL IONS



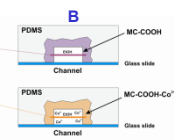
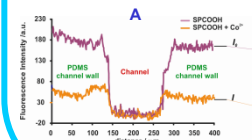
The microfluidic device consists of five independent 94 μm depth, 150 μm width channels fabricated in polydimethylsiloxane. SP-COOH is immobilized / physisorbed directly on ozone plasma activated PDMS microchannel walls.

The results presented here show that an array of microchannels in a PDMS chip can be fabricated and subsequently functionalised with photochromic spiropryan (SP-COOH). Upon exposure to appropriate stimuli, this platform displays photo-controlled uptake and release of certain metal ions, and examination of fluorescence emission can provide evidence of which ions are present. This behaviour is fully reversible through multiple cycles. In addition, the platform is inexpensive, and can be made using relatively simple equipment.

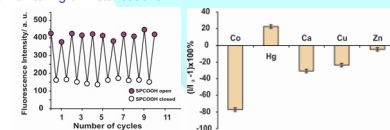


When the colourless, inactive, spiropryan coating absorbs UV light it switches to the highly coloured merocyanine form, which also has an active binding site for certain metal ions. Therefore metal ion uptake can be triggered using UV light and subsequently reversed on demand by shining white light on the colored complex, which regenerates the inactive spiropryan form, and releases the metal ion.

When stock solutions of several metal ions (Ca²⁺, Zn²⁺, Hg²⁺, Cu²⁺, Co²⁺) are pumped independently through the five channels, different optical responses were observed for each metal (i.e. complex formation with metal ions is associated with characteristic shifts in the visible spectrum), and the platform can therefore be regarded as a microstructured device for online multicomponent monitoring of metal cations.



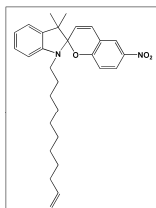
Fluorescence intensity of the MC-COOH form adsorbed in the PDMS channel walls in the presence of 10⁻³ M cobalt (II) metal ion solution in ethanol, (I) and fluorescence intensity of the MC-COOH form adsorbed in the PDMS channel walls in the presence of 10⁻³ M metal ion solutions in ethanol. The experiment has been repeated three times and the fluorescence intensity error is in the range of ± 10 a.u. (B) Schematic representation of a chip channel showing the MC-COOH form physisorbed inside the PDMS channel walls; lines represent the location where experiments were carried out.



Fluorescence Emission Measurements Associated with SP-COOH Modified PDMS Channel Walls in the Presence of Metal Ions.

d) Benito-Lopez, F. et al. *Sensors and Actuators B: Chemical* 2009, 140, (1), 295-303.

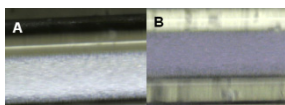
SPIROPYRAN BASED MONOLITHIC MATERIALS FOR USE AS PHOTO-CONTROLLABLE ELECTROOSMOTIC PUMPS



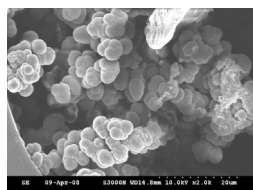
To our knowledge we report the first photo-dynamically controllable electroosmotic pump for micro-fluidic devices based on photochromic spiropryan polymer monoliths. These scaffolds have a photochromic ligand incorporated in the bulk of the monolith by copolymerisation.

The aim of this work is to encase the photochromic monoliths within micro-fluidic chips and apply a voltage across the channel while the monolith is in each of its two forms. This will show that there is a difference in flow rate between the two forms and that it is possible to modulate the flow rate using light irradiation.

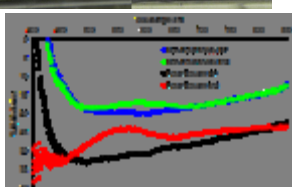
The spiropryan photochrome contains a long vinyl chain which allows it to be copolymerised with a divinylbenzene cross-linker. Upon irradiation of the monolith can be switched from a colourless, uncharged form (SP) to an intensely coloured, zwitterionic form (MC), however, there is no net charge. Flushing the monolith with dilute HCl produces a net positive charge in both forms, allowing electroosmotic flow to be produced. The difference in the charge density (highest on the SP form), and not the charge itself, causes the difference in flow rate between the two forms of the monolith. White light produces the SP form and an increase in the flow rate while UV light produces the merocyanine and a decrease in the flow rate.



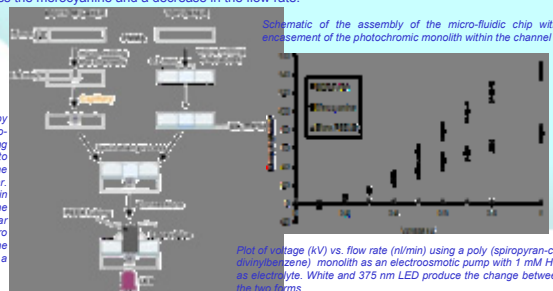
Optical micrographs of the poly (spiropryan-co-divinylbenzene) monolith showing the colour change between the spiropryan form (A) and the merocyanine form (B).



Scanning electron microscope image of the poly (spiropryan-co-divinylbenzene) monolith



Reflective absorbance spectroscopy of the poly (spiropryan-co-divinylbenzene) monolith showing the response of the monolith to changes in irradiation when the environment is polar or non-polar. The blue line shows spiro form in non-polar matrix, the green line shows merocyanine in non-polar matrix, the black line shows spiro form in polar solvent and the red line shows the merocyanine form in a polar solvent



Schematic of the assembly of the micro-fluidic chip with placement of the photochromic monolith within the channel

Plot of voltage (kV) vs. flow rate (nl/min) using a poly (spiropryan-co-divinylbenzene) monolith as an electroosmotic pump with 1 mM HCl as electrolyte. White and 375 nm LED produce the change between the two forms