Incorporation of acrylate based spiropyran monoliths in micro-fluidic devices for photo-controlled electroosmotic flow

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OBJECTIVES

Spiropyran photochromic compounds can be switched using light exposure between a non-polar spiro form(SP) and a zwitterionic merocyanine form (MC) that is subject to protonation (MC-H+). It has recently been demonstrated by Walsh et al. that, under acidic conditions, electroosmotic flow (EOF) generated in vinyl based spiropyran monoliths can be modulated using light irradiation [1]. We report the synthesis and characterisation of a new spiropyran-modified acrylate based monolith in terms of photo-controlled EOF,.

The ability to alter flow rates in micro-fluidic channels using light has very significant implications, as it could dramatically simplify the manner in which micro-flow systems are controlled.

METHODS

Synthesis of spiropyran acrylate monolith

- Pre-treatment of the PTFE coated fused silica capillaries with a silanising agent.
- Preparation of the pre-polymerisation mixture: EDMA, acrylated SP, AIBN and *t*-butanol.
- Filling of the PTFE capillaries with the pre-polymerisation mixture by capillary action and sealing of both ends using rubber septa.
- Placement of the PTFE capillaries on a water bath at 60°C for 90 minutes to initiate the *in-situ* polymerisation.
- Capillary washing with methanol in order to remove any un-reacted components.

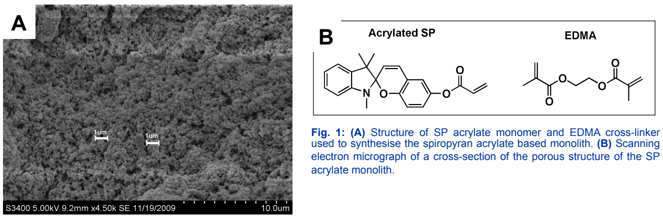

Fig. 1: (A) Structure of SP acrylate monomer and EDMA cross-linker used to synthesise the spiropyran acrylate based monolith. **(B)** Scanning electron micrograph of a cross-section of the porous structure of the SP acrylate monolith.

Micro-fluidic chip for EOF measurement

Incorporation of the spiropyran acrylate monoliths (8 mm x 0.4 mm) into a micro-fluidic chip (16 mm x 19 mm x 5 mm with channels 8 mm x 0.4 mm x 0.4) for EOF measurement.

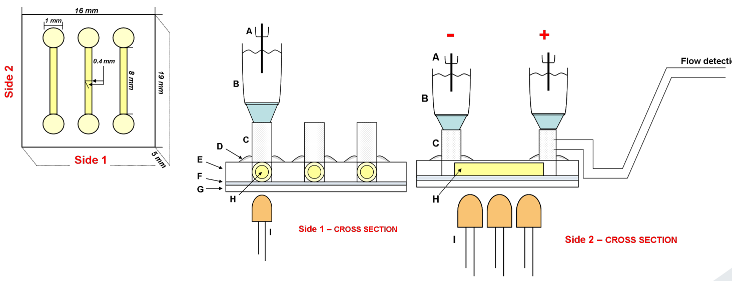

Fig. 2: Schematic representation of the cross section of the microchip side 1 and 2. A) Electrode; B) 1.5 ml 10^{-3} M HCl reservoir; C) PEEK tubing; D) epoxy glue; E) PMMA sheet 5 mm thickness; F) layer of PSA; G) second sheet of PMMA (0.5 mm thickness); H) SP acrylate monolith 8 mm length; I) white LEDs (430-760 nm) 3x3 square array of 9 LEDs.

RESULTS

The spiropyran acrylate monolith can be switched in the presence of acid (10^{-3} M HCl) between a MC-H⁺ form (with the appearance of a characteristic yellow colour) and an uncharged SP form *(Fig. 3)*.

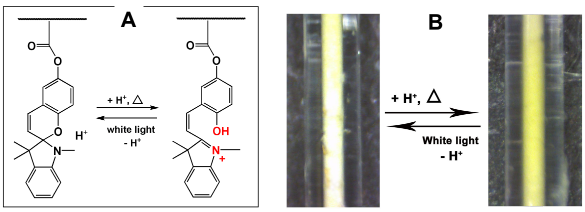

Fig. 3: (A) SP acrylate switching in acidic environment between the MC-H⁺ form (right) and the SP form (left) when irradiated with white light. **(B)** Picture of the spiropyran acrylate monolith flushed with HCl 10^{-3} M switched between the MC-H⁺ form, in the absence of light exposure and the SP form when irradiated with white light.

Micro-fluidic chip was filled with 10^{-3} M HCl and the working electrodes were placed inside the reservoirs. The EOF generated increases proportionally to the applied field *(Fig.4)* from ca. 0.7 µl/min (at 12.5 kV/m) to 1.6 µl/min (at 125 kV/m). When the same measurement is performed while exposing the monolith to white light (using a 3x3 square array of 9 white LEDs (430-760 nm), the EOF decreases by 15% on average. It reaches a maximum at 125 kV/m where a decrease of 20% is observed *(Table 1)*. The experiments were repeated in triplicate and the statistics shows reproducibility and a consistent decrease in the EOF when the monolith is exposed to white light irradiation.

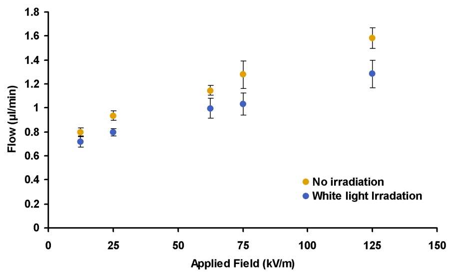

Fig. 4: Graph showing the EOF increase as an effect of the application of an increasing electric field both for the SP acrylate monolith in the MC-H⁺ form(no irradiation) and in the SP form (white light irradiation). Statistics shows that the EOF generated with or without white light irradiation is substantially different (n=3).

Flow rate variations when applying white light exposure and increasing electric field

Applied Field [kV/m]	No Irradiation (mean flow rate value) [µl/min]	White light Irradiation (mean flow rate value) [µl/min]	EOF DECREASE (%)
0	0	0	**0**
12.5	0.80 (± 0.03)	0.72 (± 0.04)	**10.0**
25	0.94 (± 0.04)	0.80 (± 0.02)	**14.9**
62.5	1.15 (± 0.04)	0.99 (± 0.08)	**13.9**
75	1.28 (± 0.11)	1.03 (± 0.09)	**19.5**
125	1.60 (± 0.08)	1.28 (± 0.10)	**20.0**

Table 1: Table showing the mean flow rate values (µl/min) recorded when increasing the applied field on the spiropyran functionalised monolith. The experiments were carried out exposing and not exposing the monoliths to white light irradiation. On the left the % of EOF decrease when the monolith is irradiated with white light irradiation is reported.

CONCLUSIONS

Acrylate based spiropyran monoliths have been synthesised and characterised in terms of photoswitchable EOF behaviour. Under acidic conditions, the SP monolith surface is preferentially in the MC-H⁺ form, which can be readily converted to the SP form through exposure to white light. When an external electric field is applied in the presence of 10^{-3} M HCl, EOF in the 0.7 µl/min to 1.6 µl/min range is generated. Under constant applied field, white light irradiation leads to a decrease in the EOF. Removal of the light source results in a flow increase. Clearly this spiropyran monolith can act as an electro-osmotic pump, in which the flow can be modulated through the presence or absence of light. This ability to profoundly alter such properties using light has very significant implications for science as it could lead to the development of micro-fluidic platforms where the liquid flow can be externally modulated using light irradiation.

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References

[1] Z. Walsh, S. Scarmagnani, F. Benito-Lopez, S. Abele, F.-Q. Nie, R. Byrne, C. Slater, D. Diamond, B. Paull, M. Macka, *Sensors and Actuators B: Chemical* **2010**, *In press.*