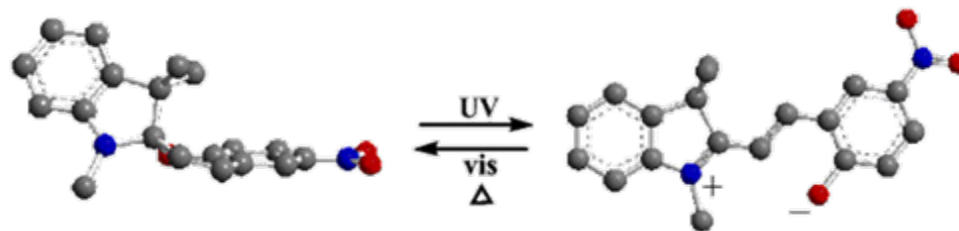


Incorporation of Photochromic Spiropyran Compounds and Spiropyran Modified Substrates into Flow Micro-systems

Silvia Scarmagnani and Zarah Walsh

Fernando Benito Lopez, Conor Slater, Mirek Macka,
Brett Paull and Dermot Diamond

Photochromism of Spiropyran



SPIROPYRAN

MEROCYANINE



POLARITY

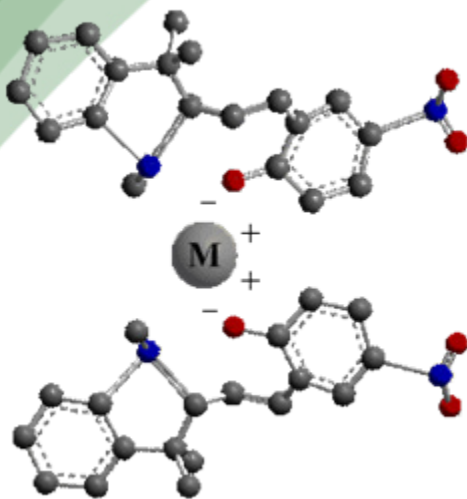
METAL BINDING



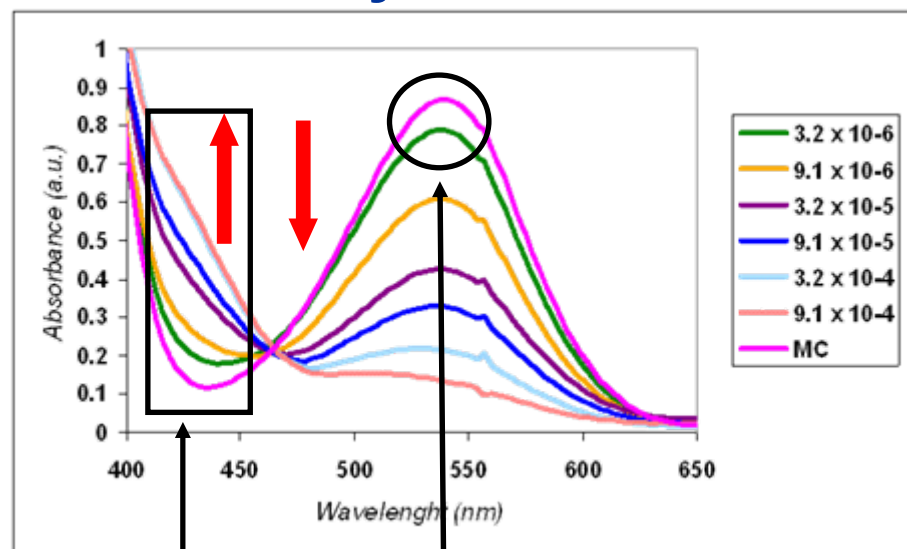
**Switchable electrosmotic
nanoflow**

**Switchable metal binding
stationary phases**

MEROCYANINE SOLUTION STUDIES ON MELAT BINDING

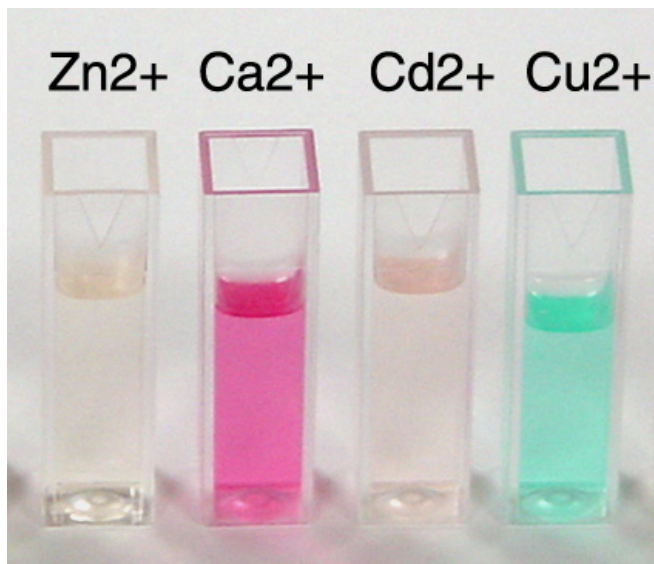


Merocyanine – Cu²⁺

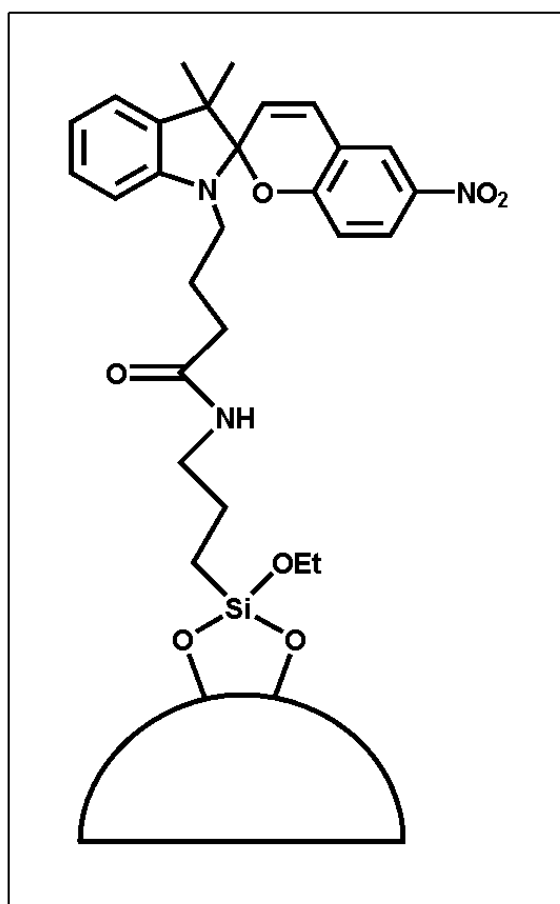


Decrease at 540 nm as free MC concentration decreases

Increase in absorbance below ~460 nm due to formation of MC-Cu²⁺ complex



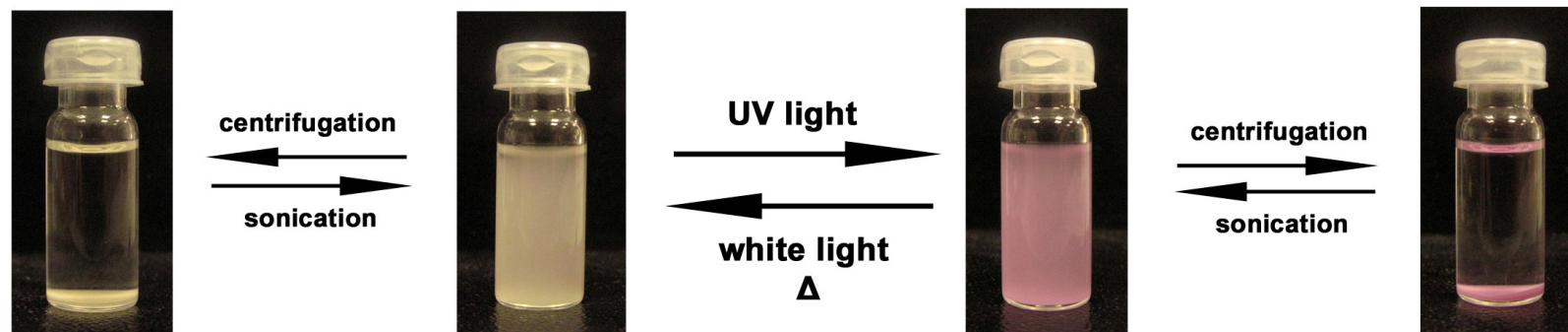
SPIROPYRAN MODIFIED SILICA MICROBEADS



Spiropyran Microspheres Functionalisation:

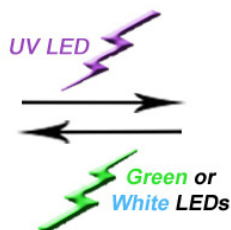
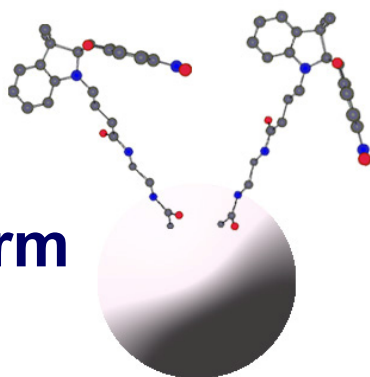
- NH_2 functionalisation of the silica surface
- Spiropyran (SP-COOH derivative) attaching *via* EDC coupling

Silica Beads – Switching -

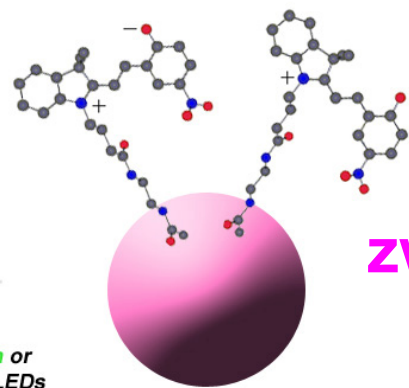


switching between

WHITE
spiro
uncharged form



PINK
mero
zwitterionic form

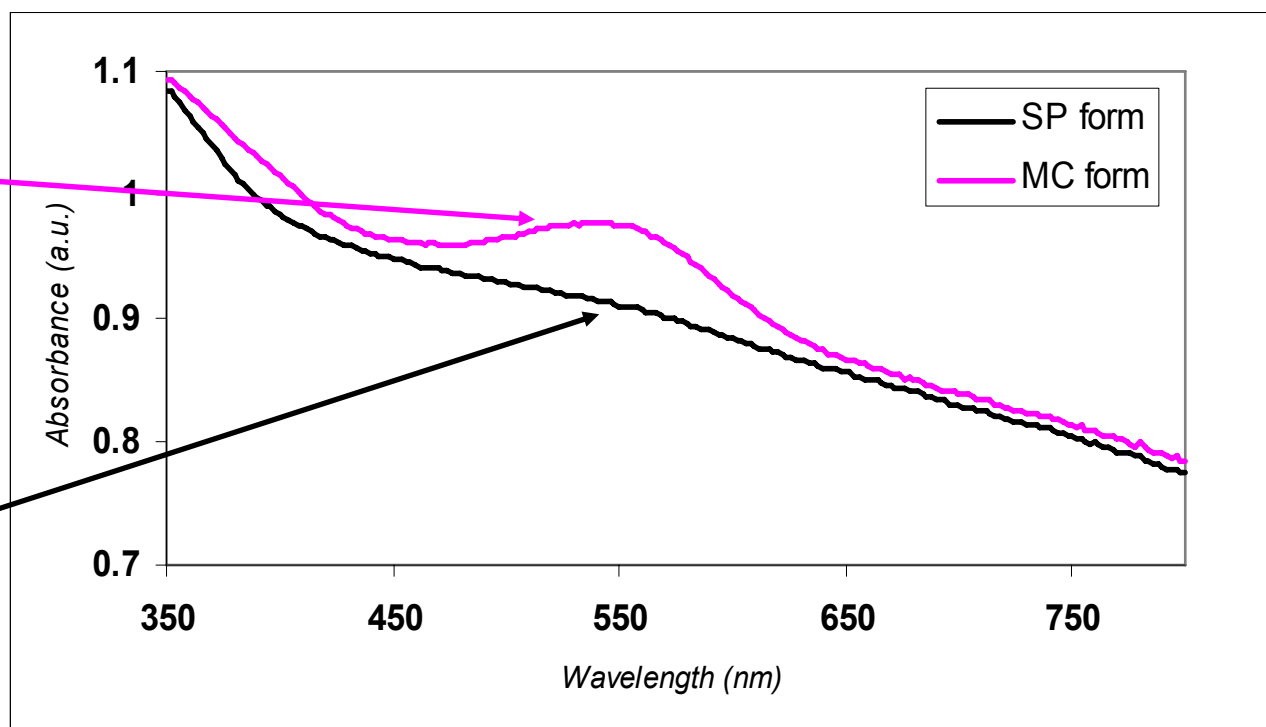


Spiropyran Switching on the Silica Bead

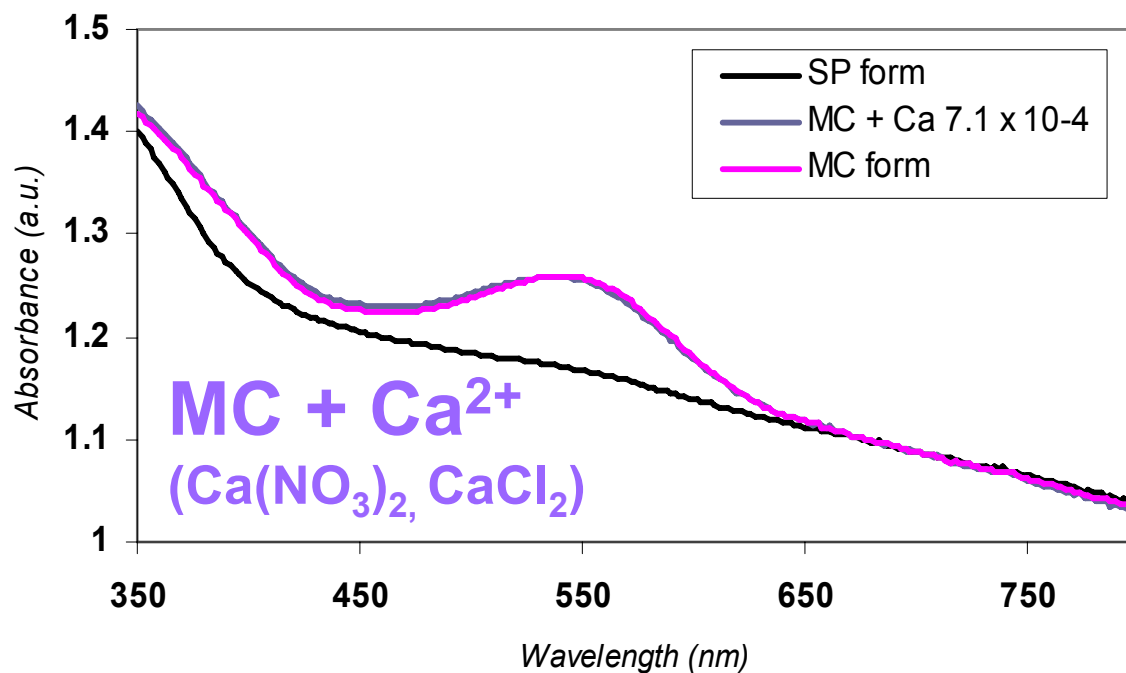
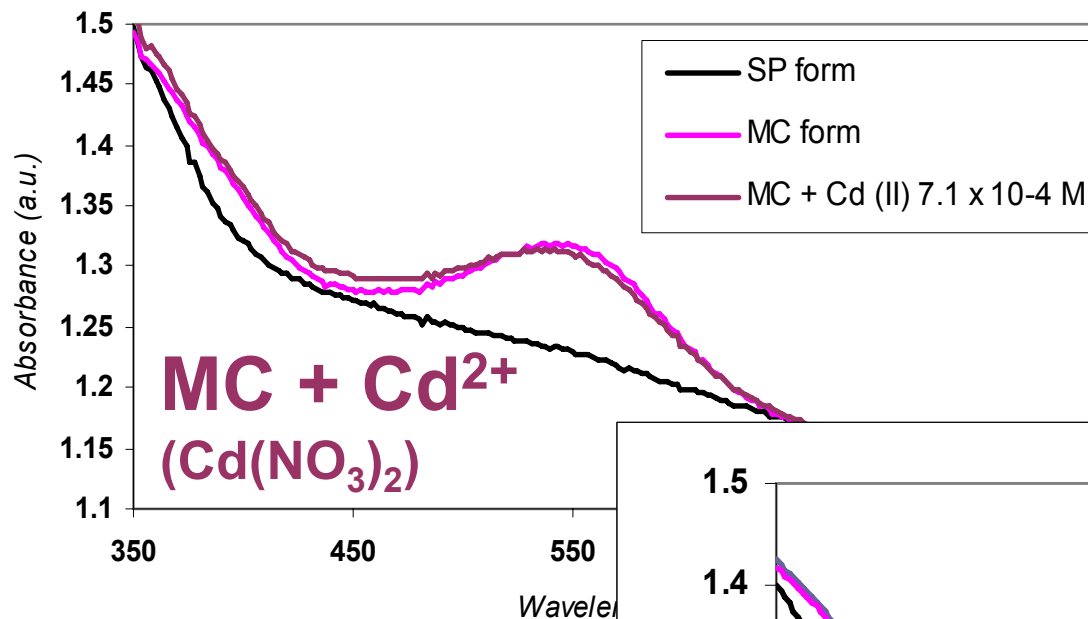
Silica MC $\lambda_{\max} = 558$ nm (EtOH suspension)

MC: 375 nm LED
irradiation

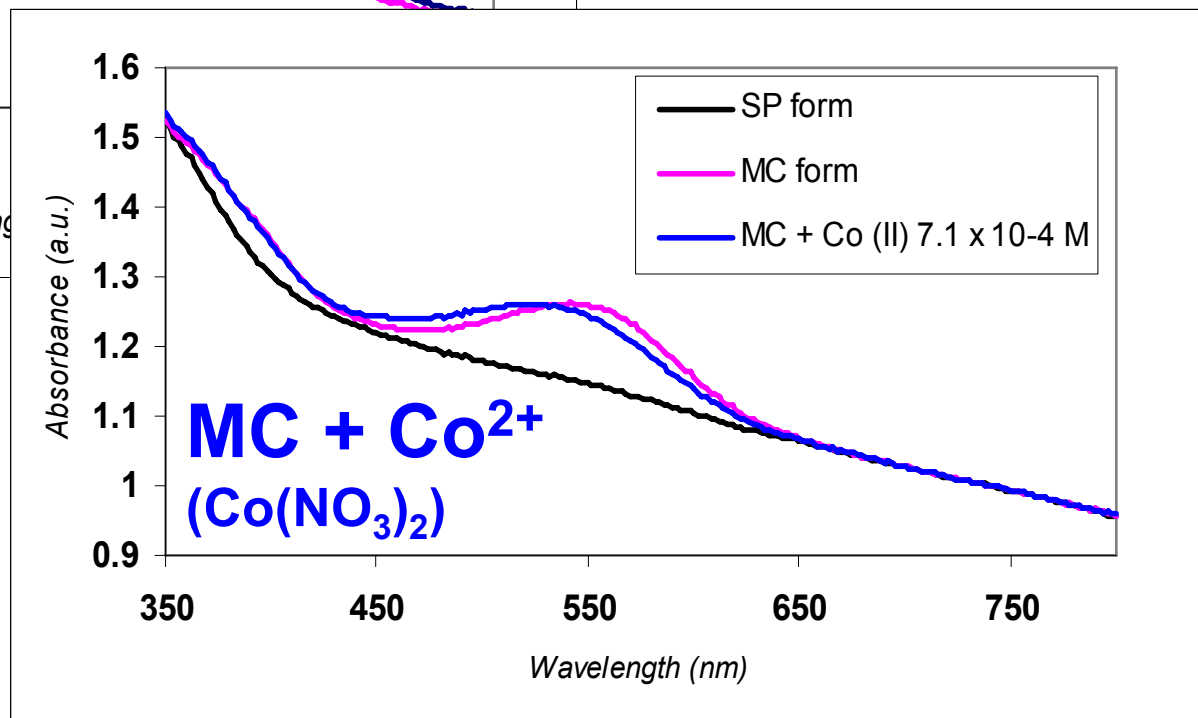
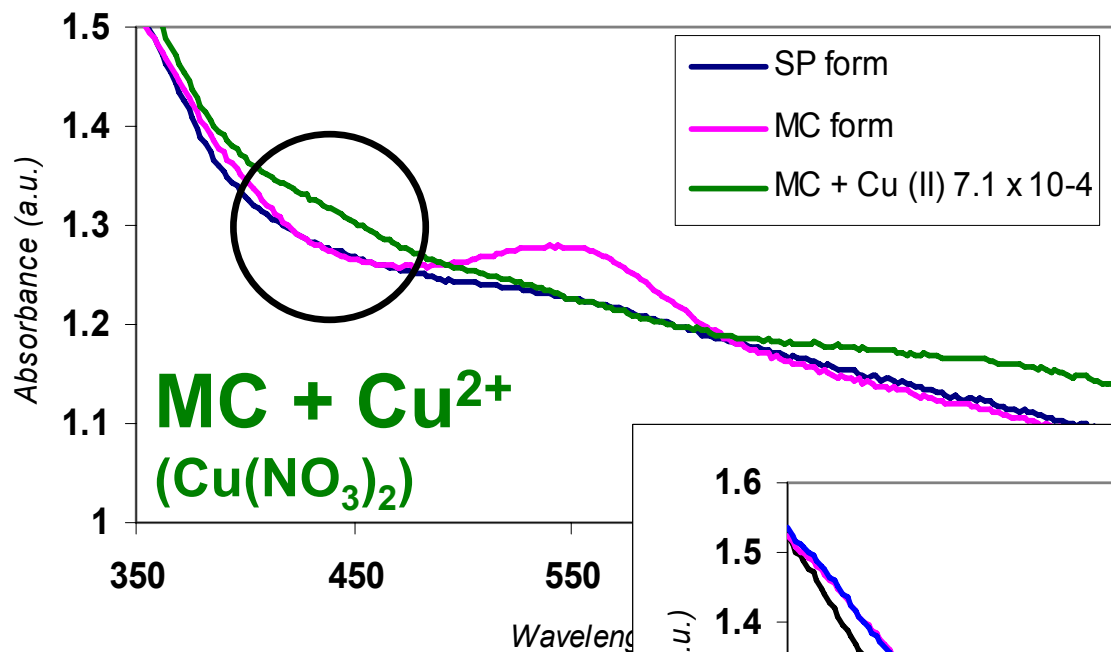
SP: 430-760 nm white
LED irradiation



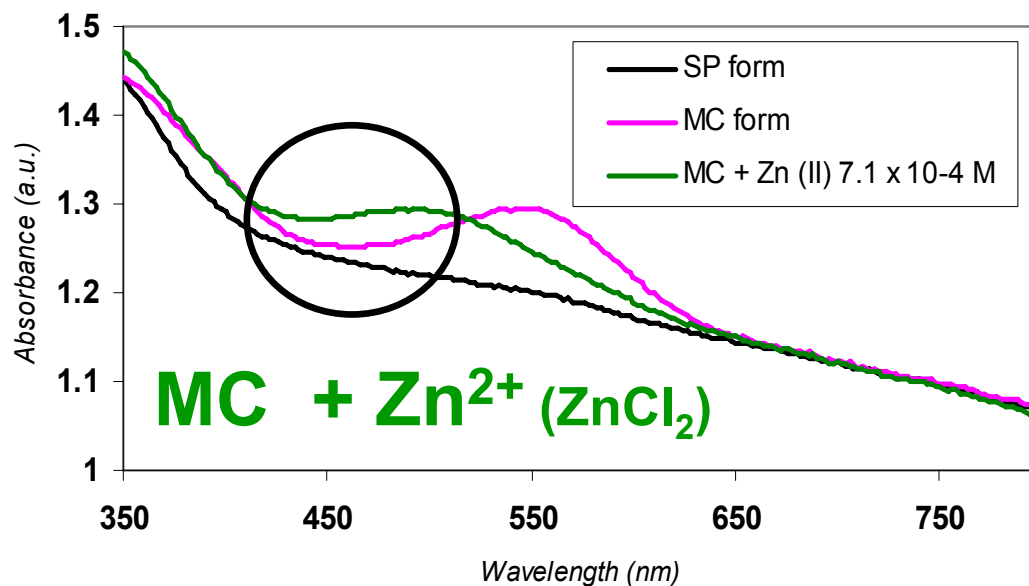
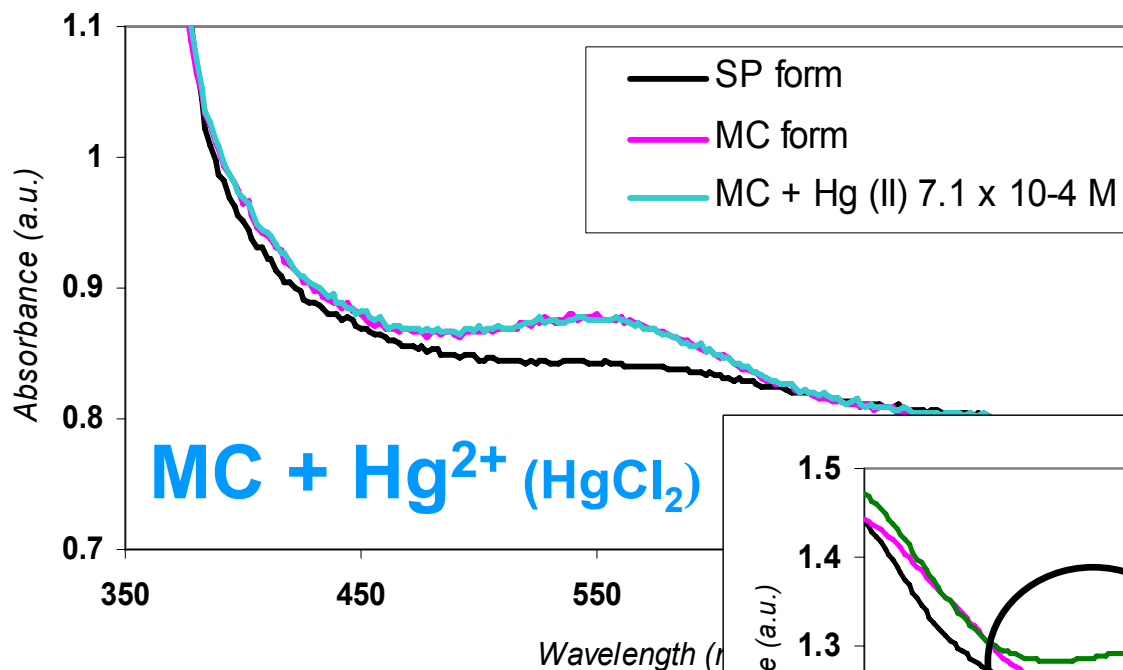
Beads in the presence of Metal Ions



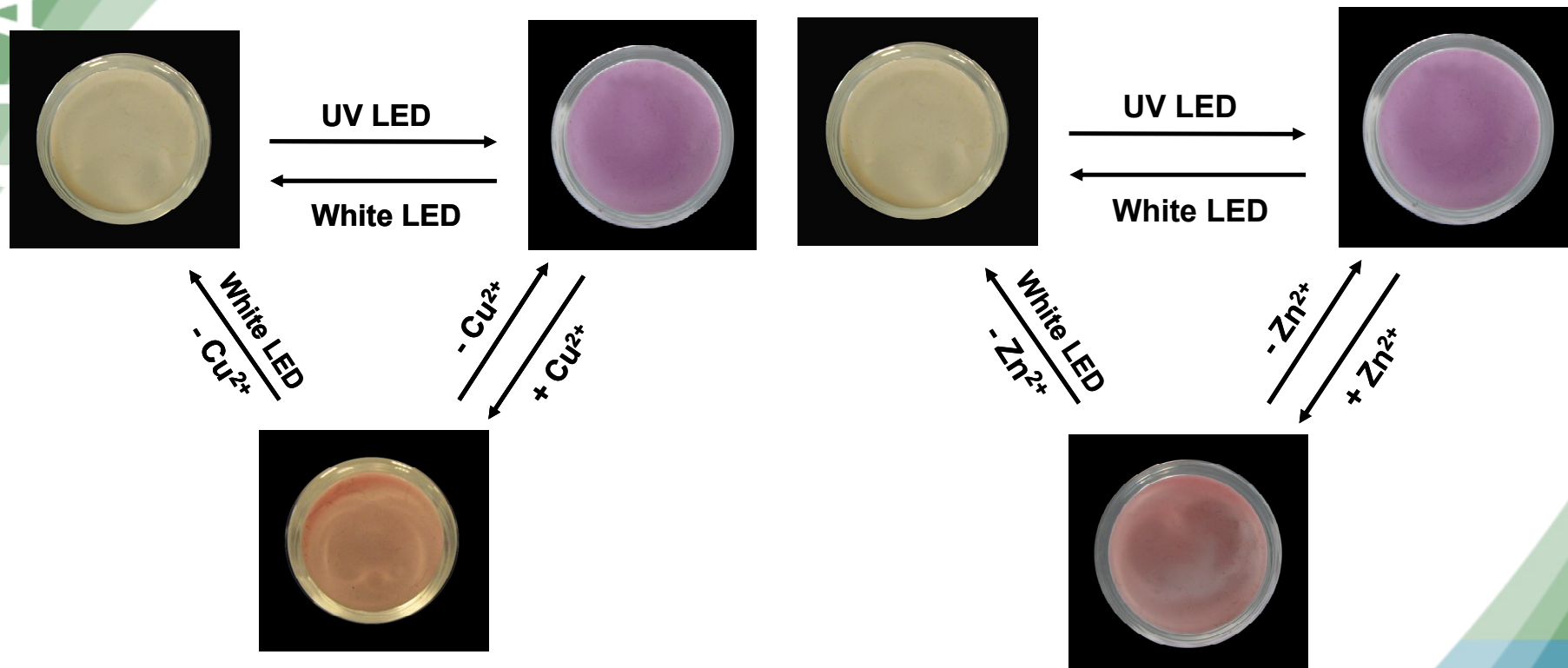
Beads in the presence of Metal Ions



Beads in the presence of Metal Ions



Colour change in the presence of Cu^{2+} and Zn^{2+}

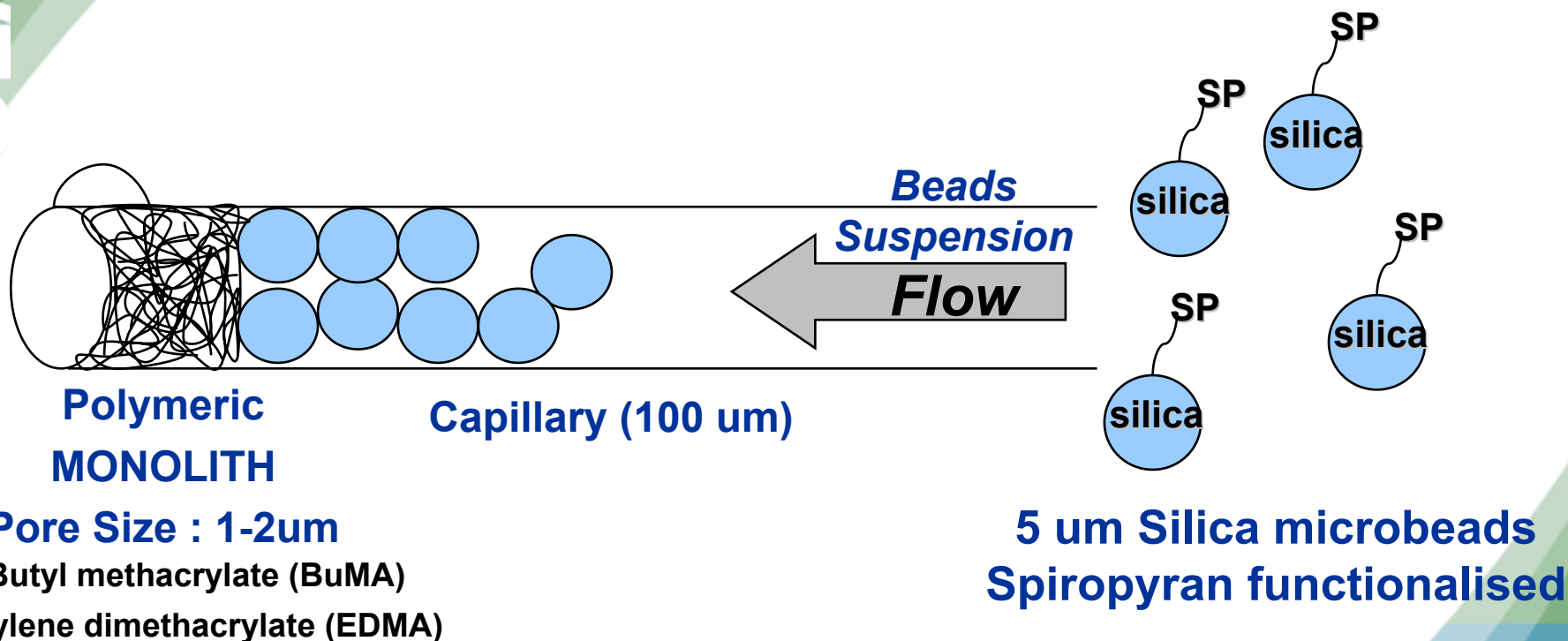


MC + Cu^{2+} ($\text{Cu}(\text{NO}_3)_2$)

MC + Zn^{2+} (ZnCl_2)

SILICA SPIROPYRAN-modified MICROBEADS

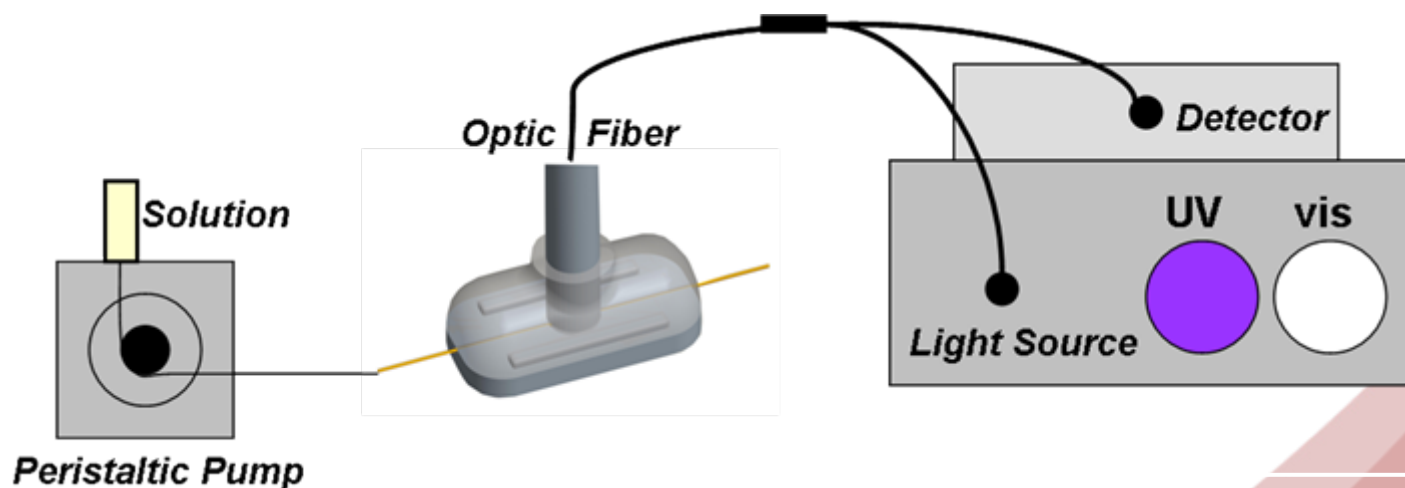
- CAPILLARY PACKING -



SILICA SPIROPYRAN-modified MICROBEADS

Capillary REFLECTANCE DETECTION

- Capillary FLUSHING with ethanolic solution for 30 min
- IRRADIATION with vis-light for 3 minutes (beads in the SP form)
- REFLECTANCE recording
- IRRADIATION with UV-light for 3 minutes (beads in the MC or MC+Me form)
- REFLECTANCE recording

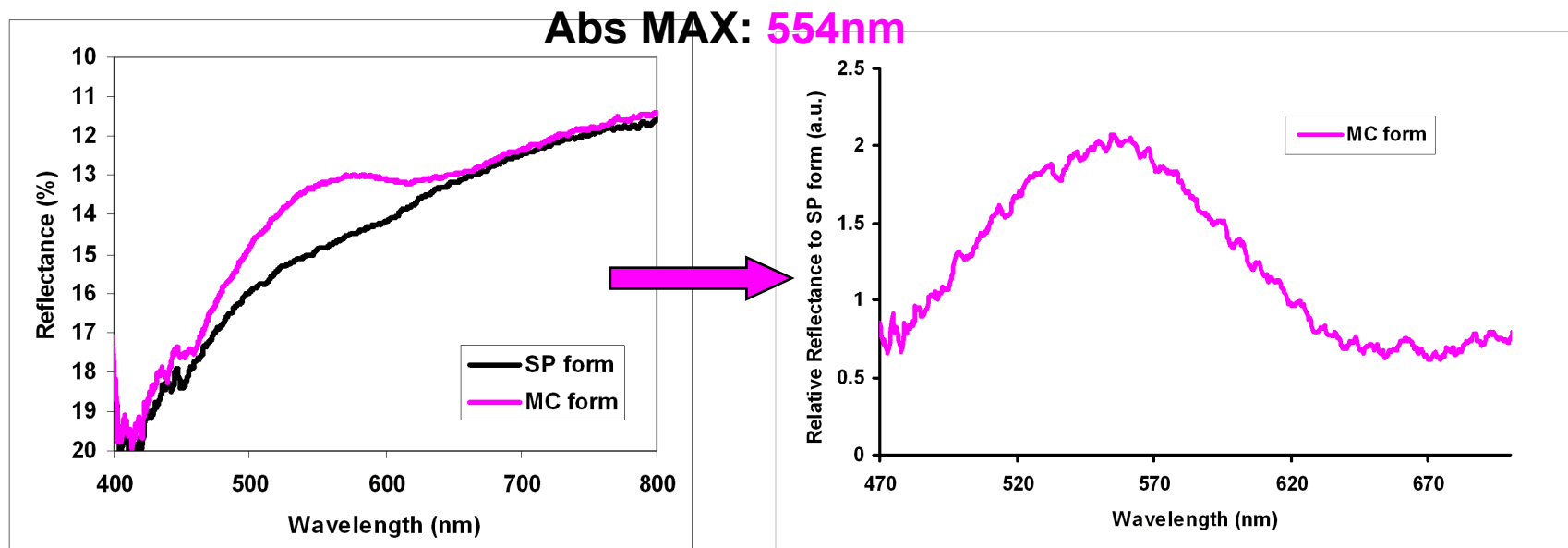


SILICA SPIROPYRAN-modified MICROBEADS - SWITCHING -



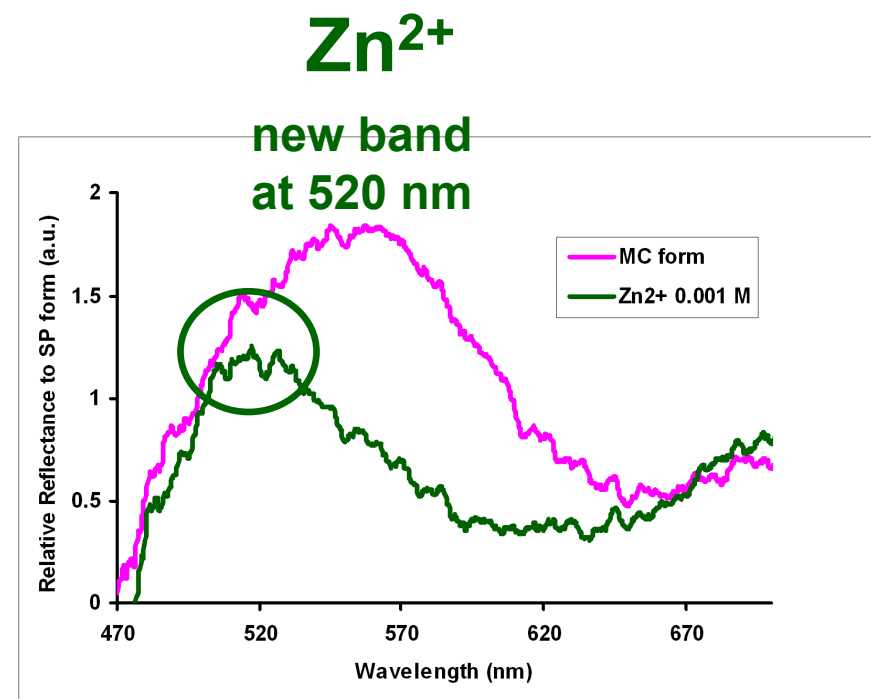
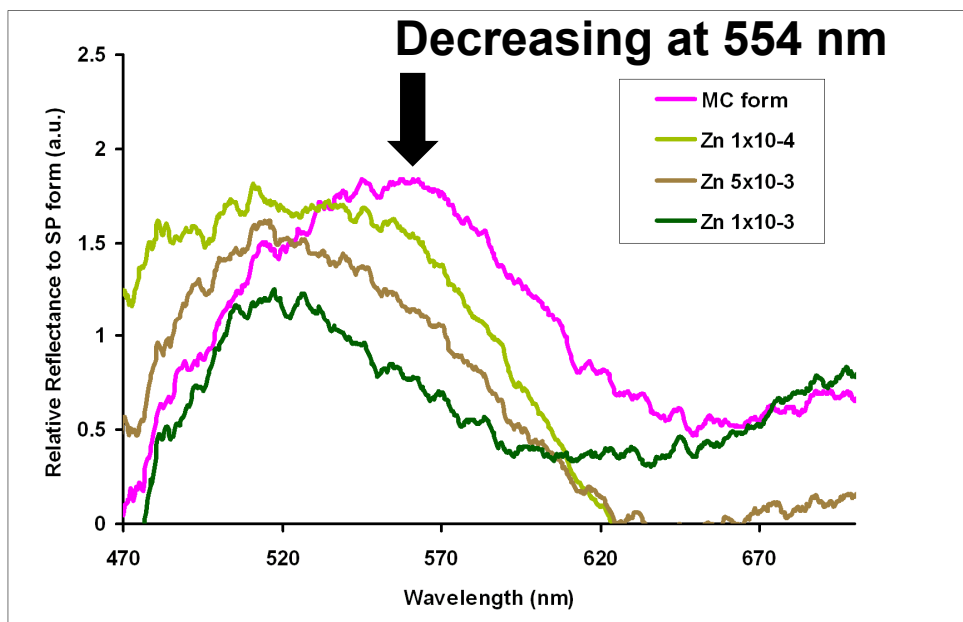
← under UV irradiation

← after removal of the light source



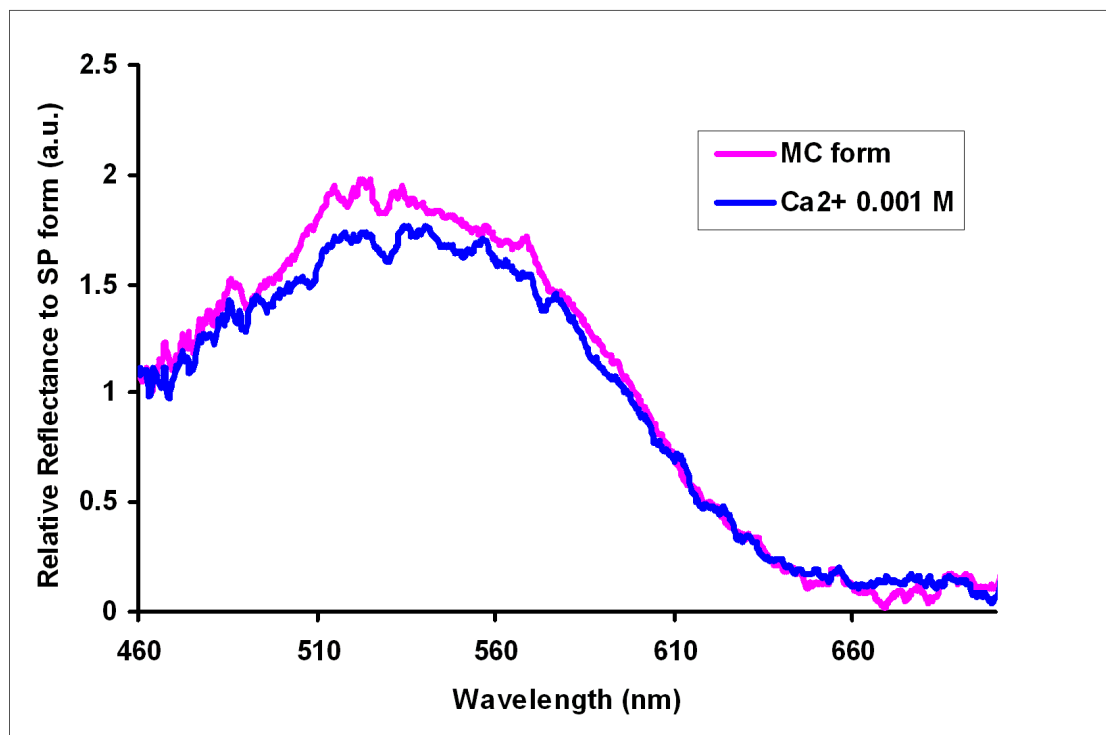
SILICA SPIROPYRAN-modified MICROBEADS

- METAL DETECTION -



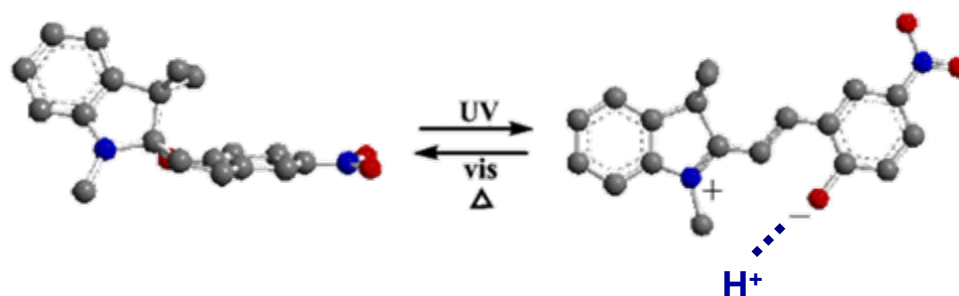
SILICA SPIROPYRAN-modified MICROBEADS - METAL DETECTION -

Ca^{2+} NO SPECTRAL CHANGE



Switchable Electromotive Nanoflow - Spiropyran Monolithic stationary phase -

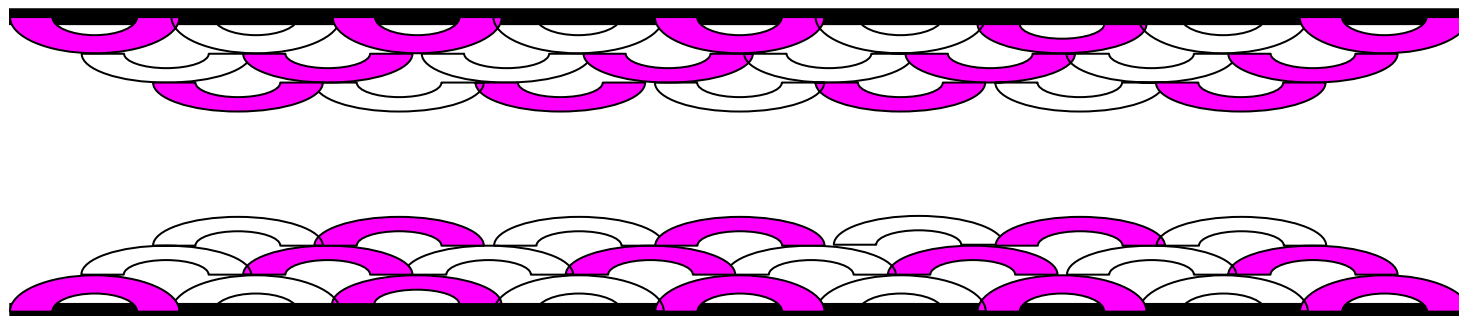
Zarah Walsh



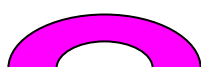
- Possibility of protonation of the merocyanine form
- Strong change in the surface polarity
- Light switchable electromotive nanoflow

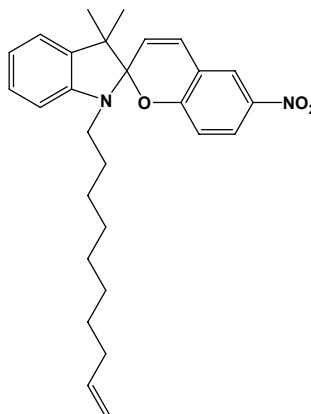
Switchable Electromotive Nanoflow - Spiropyran Monolithic stationary phase -

SP-co-DVB



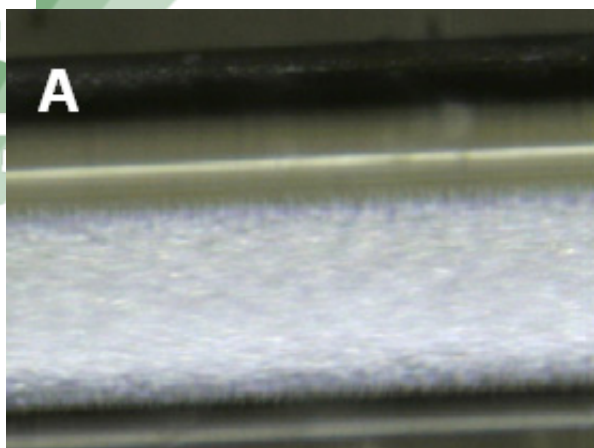
 = DVB monomer (divinylbenzene)

 = SP monomer

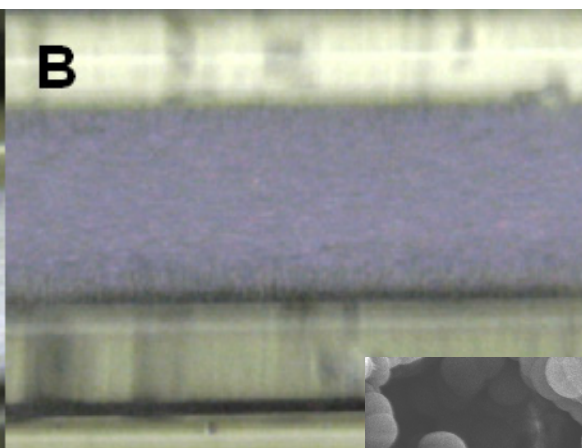


**Thermal
polymerisation
60 ° C for 5 days**

SP-DVB Monolith imaging Microscopy and SEM analysis

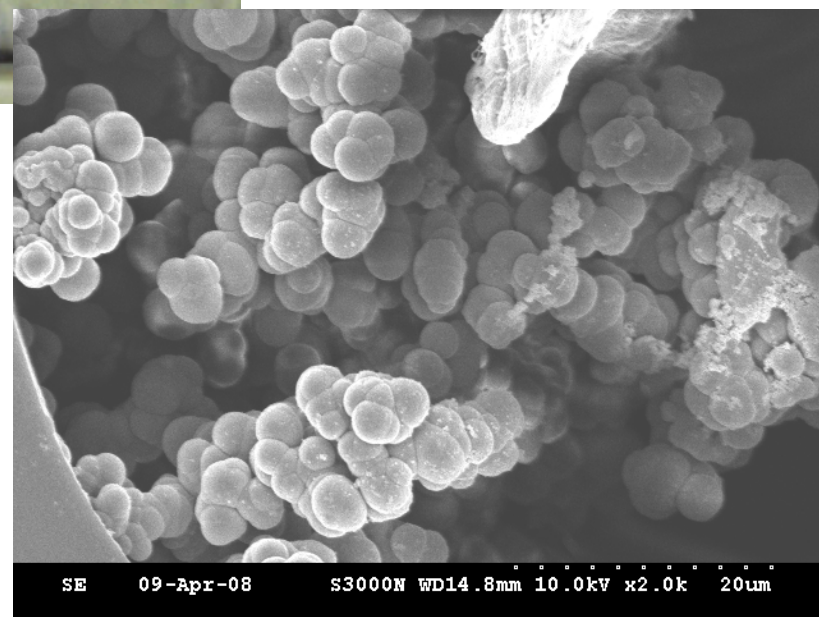


SP form

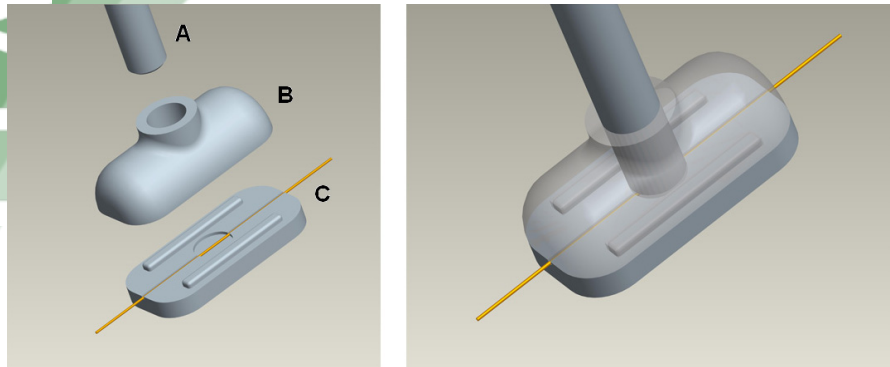


MC form

**SEM image of the
spiropyran monolith**

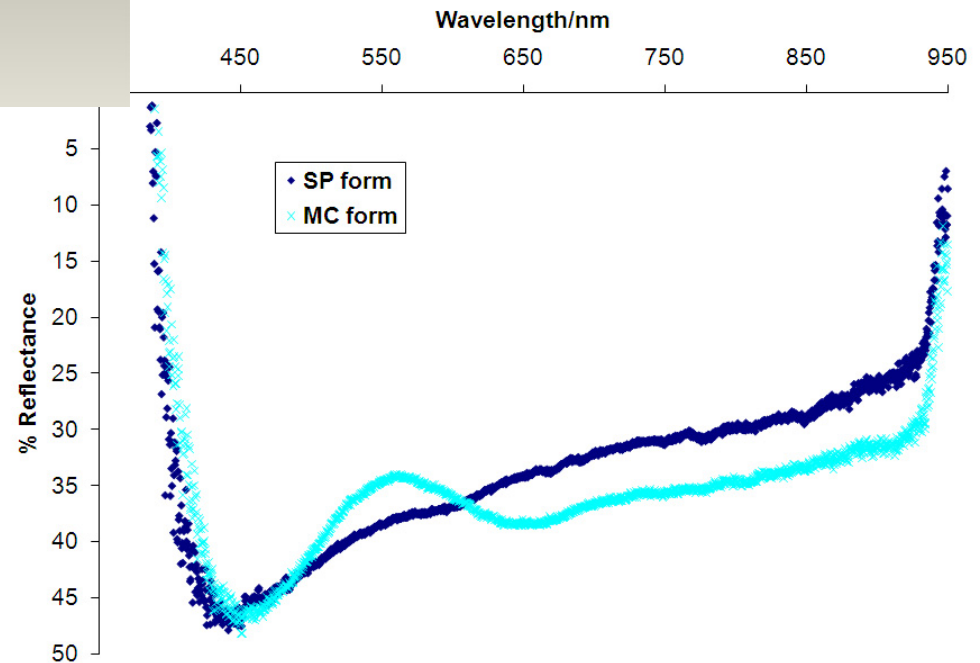


Reflectance measurement of UV-vis changes due to spiropyran-merocyanine conversion



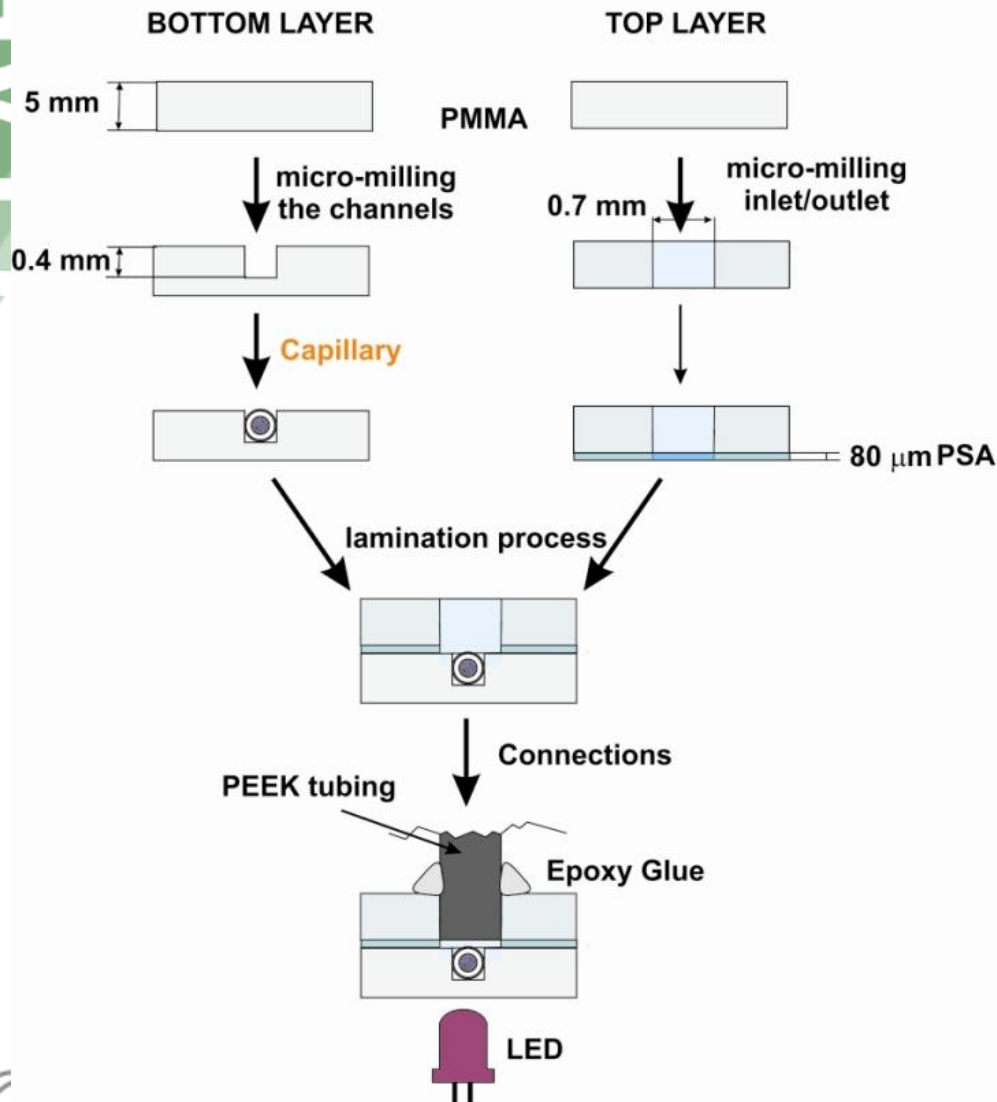
Reflectance set-up

Reflectance measurements
of the SP and the MC form
of the SP-DVB during
ethanol flushing

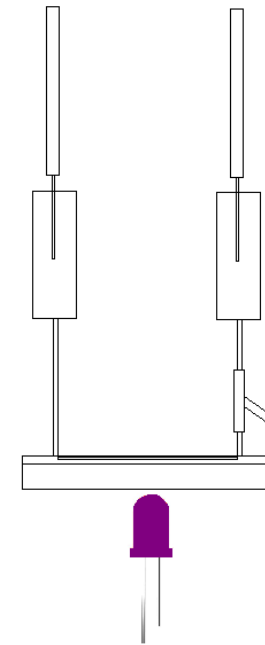


Light-Tunable Electromotive Nanoflow

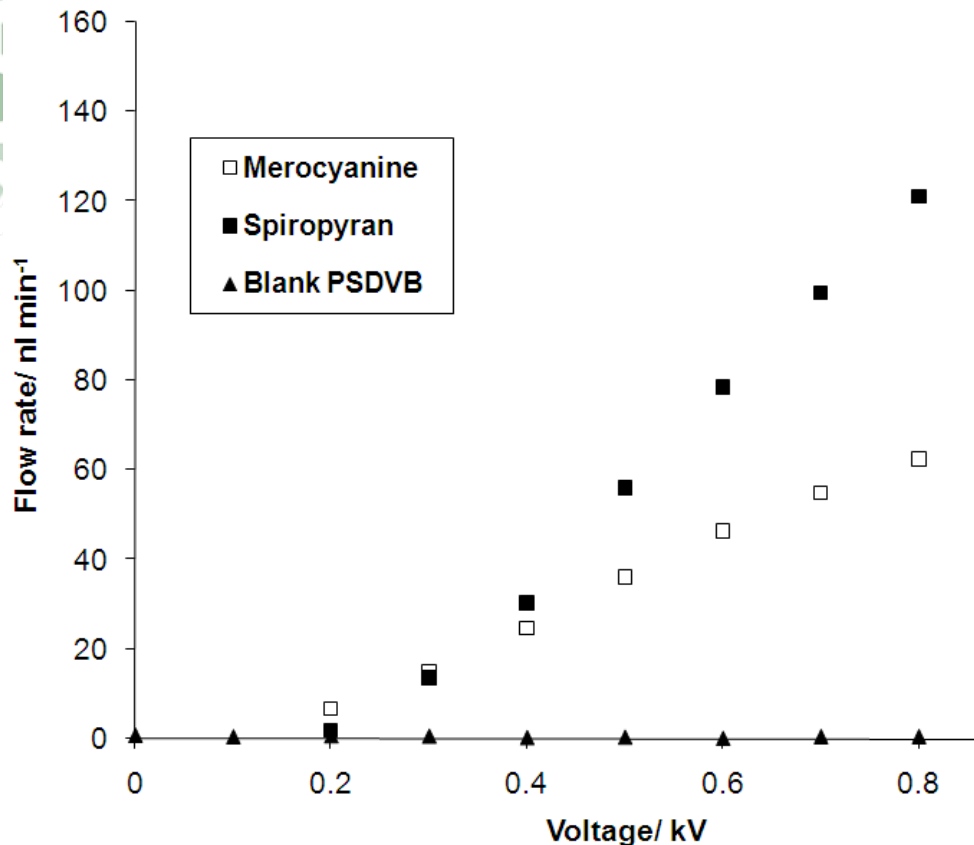
Experimental set-up



**Constant Irradiation
during the measurement
using LEDs**



Light-Tunable Electrosmotic Nanoflow



- HCl solution 1mM
- 7 increasing applied voltage steps were measured
- Light tunable SP-DVB monolith compared to DVB without SP

Future Direction

Incorporation of the light-induced reversible metal binding effect and tunable EOF pump on a microchip device

Acknowledgements

People

- Prof. Dermot Diamond, Prof. Brett Paull, Dr. Mirek Macka
- Zarah Walsh, Dr. Fernando Benito Lopez, Dr. Nameer Alhashimy, Conor Slater, Dr. Robert Byrne
- Clarity group

Funding Sources

- Science Foundation Ireland
SFI 03/IN3/1361, 07/CE/I1147, 07/RPF/MASF812
- Marie Curie Excellence Grant and Funding (MEXT-CT-2004-014361)