Centre for
Data Analytics

Insight

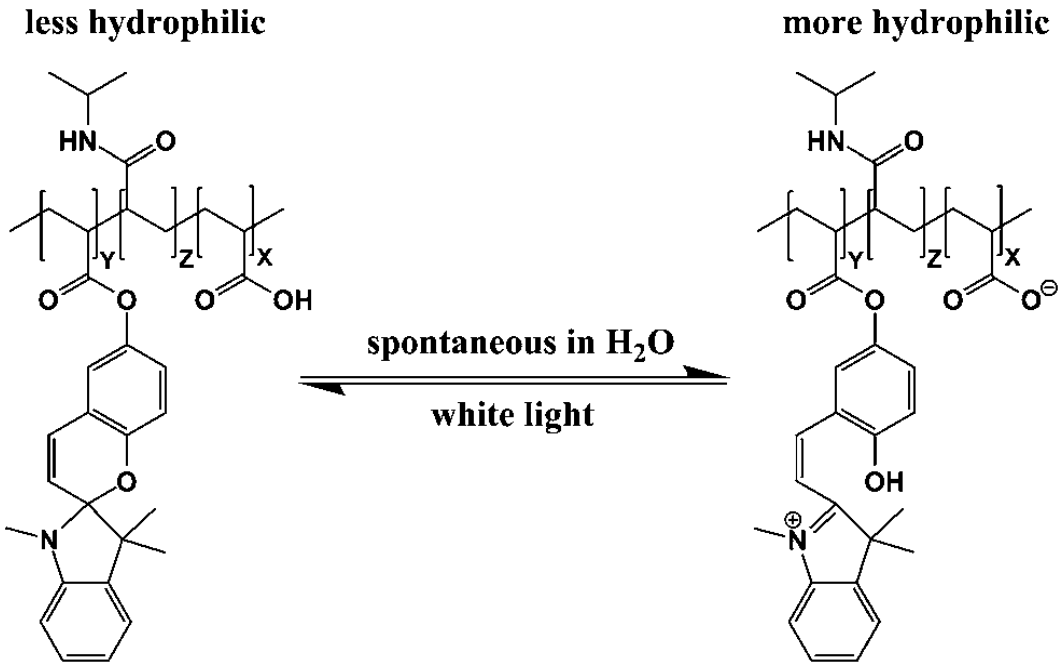
Photo-responsive materials
Capabilities and Perspectives

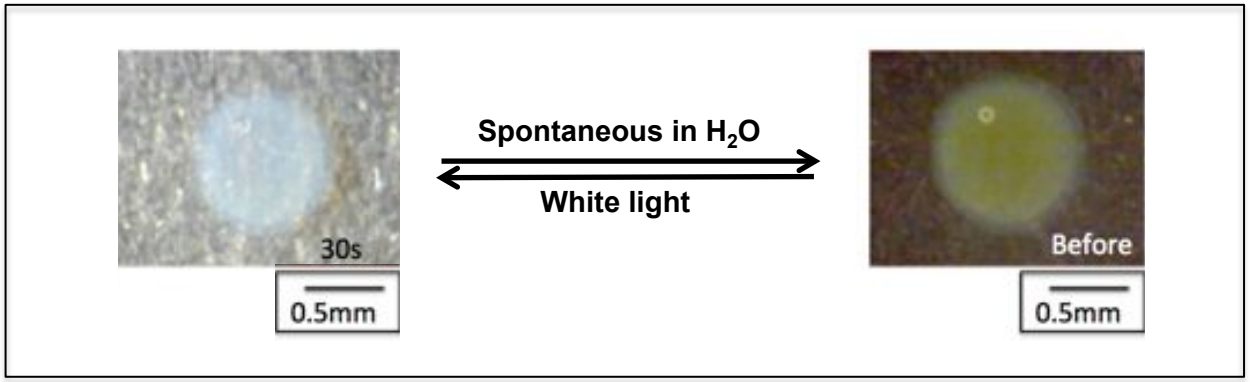
July 2014

Larisa Florea

DCU NUI Galway OÉ Gaillimh UCC sfi

Photo-responsive hydrogels

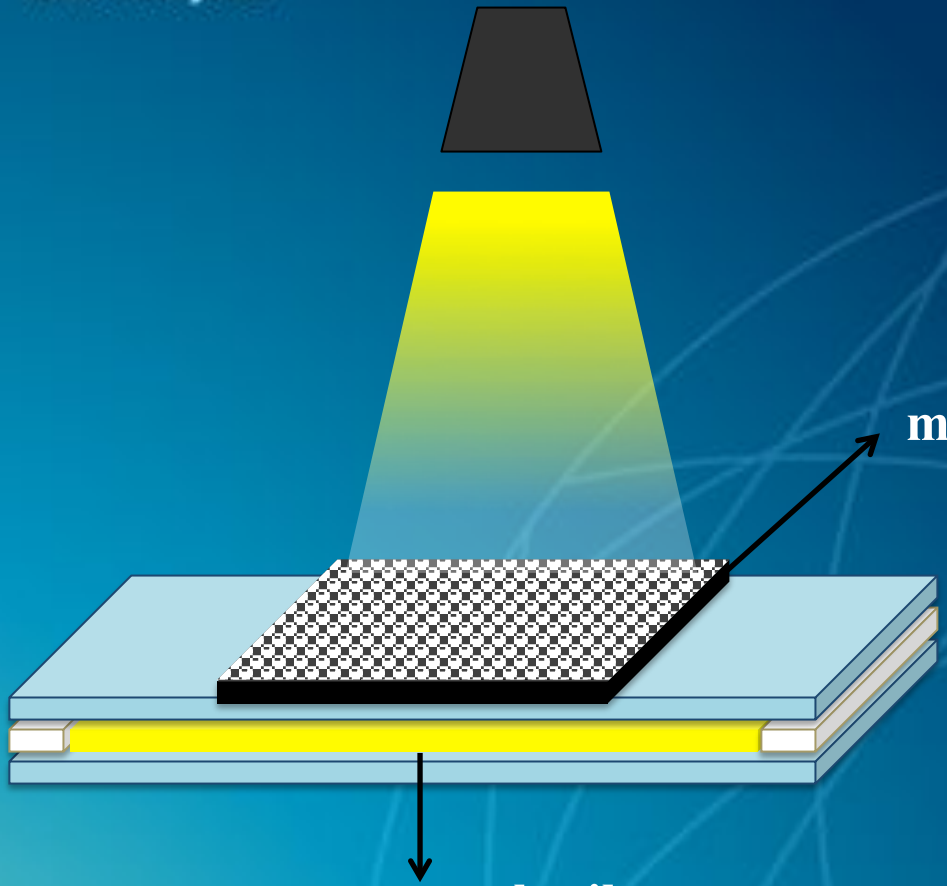




Microstructures preparation

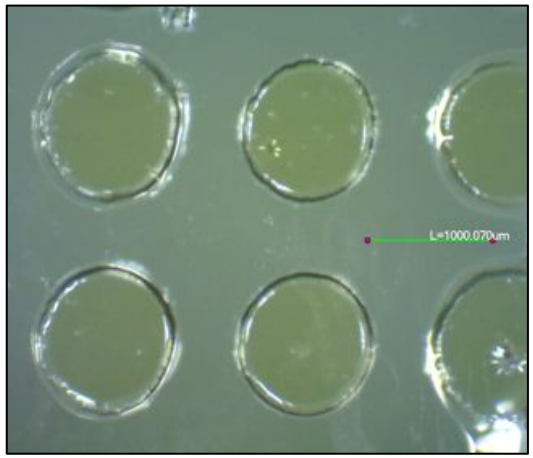
Centre for Data Analytics

Insight

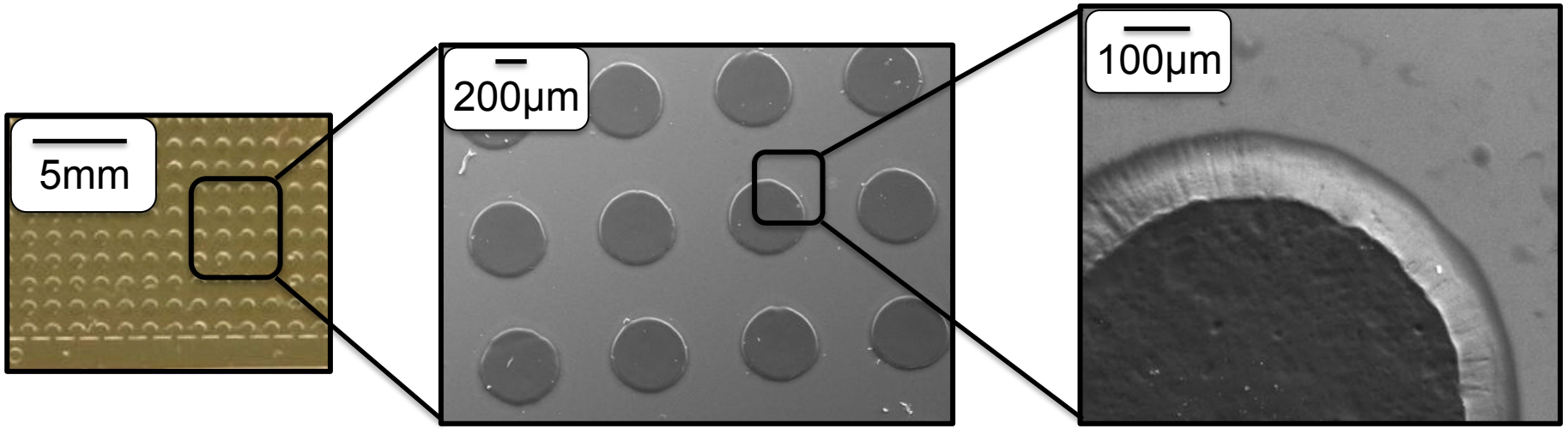


DCU UCC sfi

Hydrogels microstructures

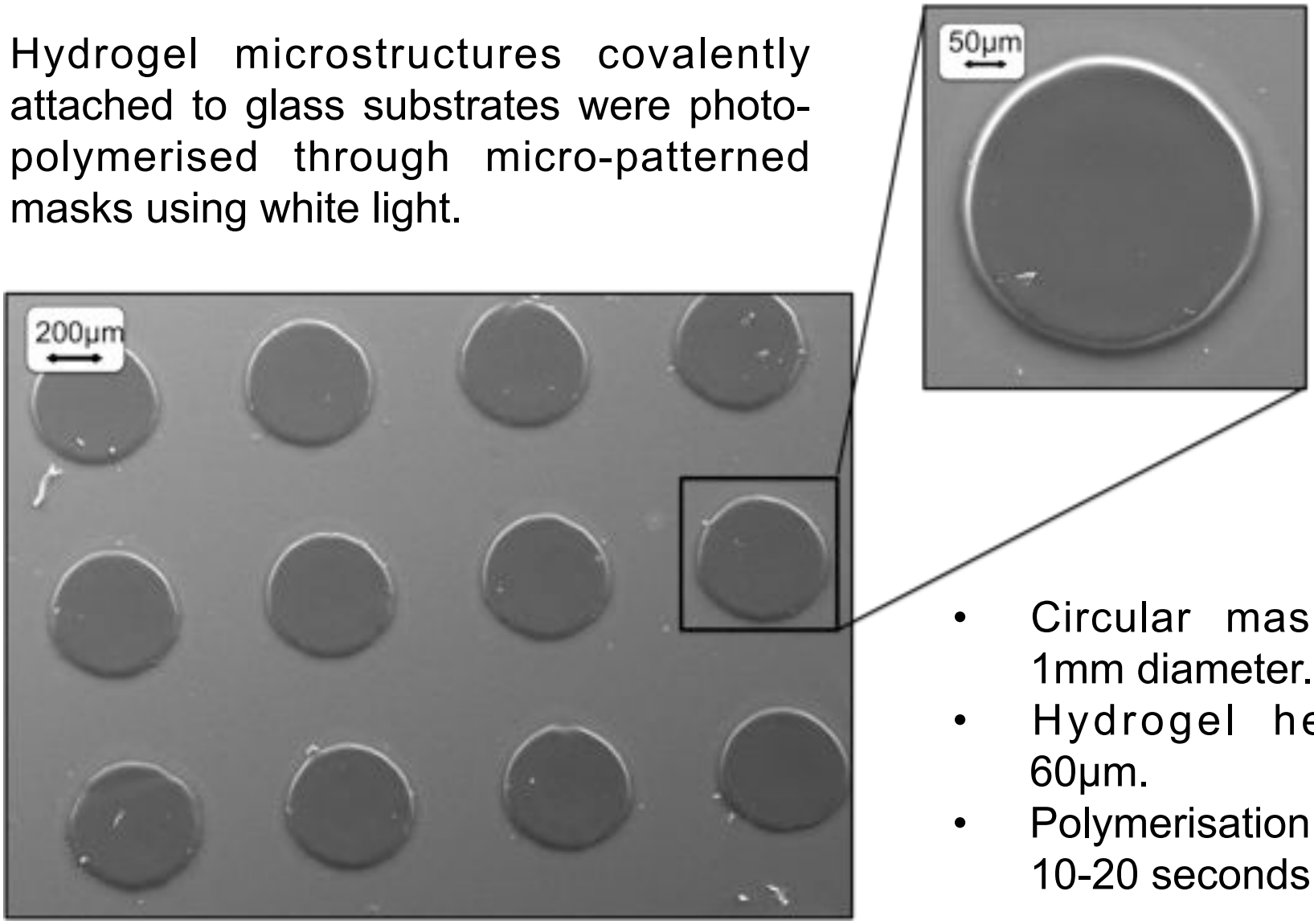


1 mol NIPAM
5% Acrylic acid
1% acrylated-Spiropyran
3% MBIS
1% PBPO
Polymerization solvent



Micro-patterned hydrogels

Hydrogel microstructures covalently attached to glass substrates were photo-polymerised through micro-patterned masks using white light.



- Circular masks of 1mm diameter.
- Hydrogel height: 60µm.
- Polymerisation time: 10-20 seconds.

Photo-responsive hydrogels

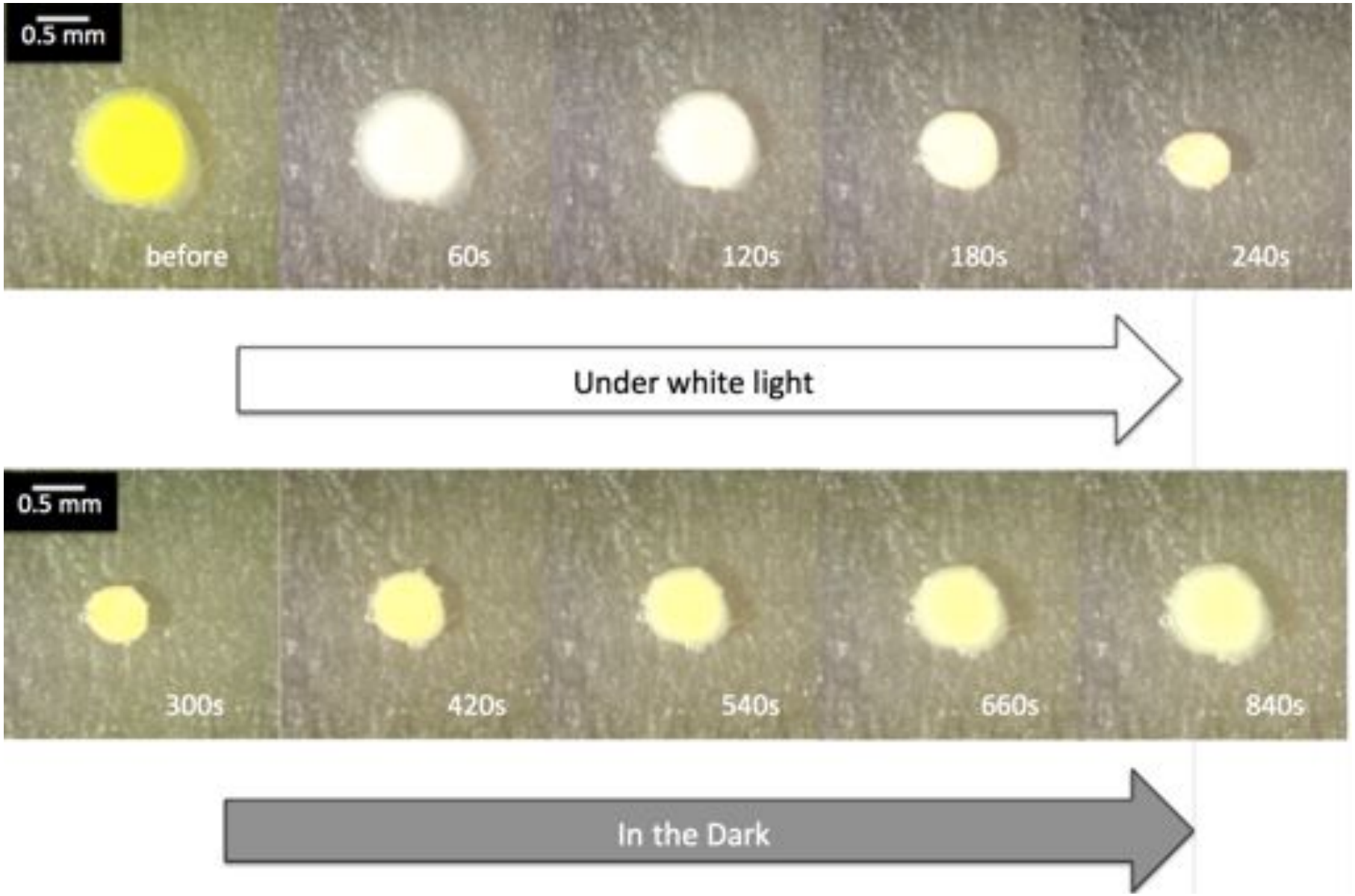
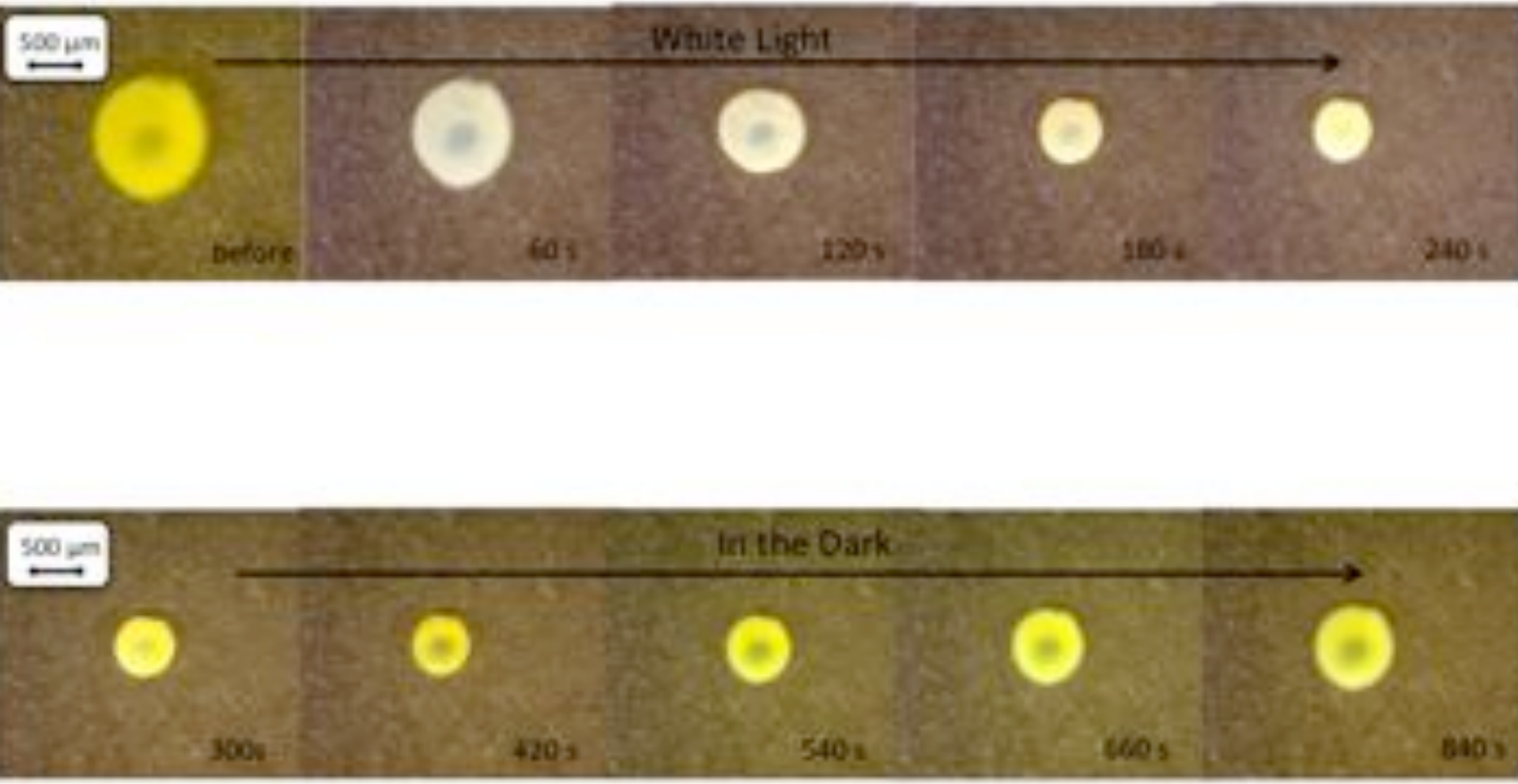
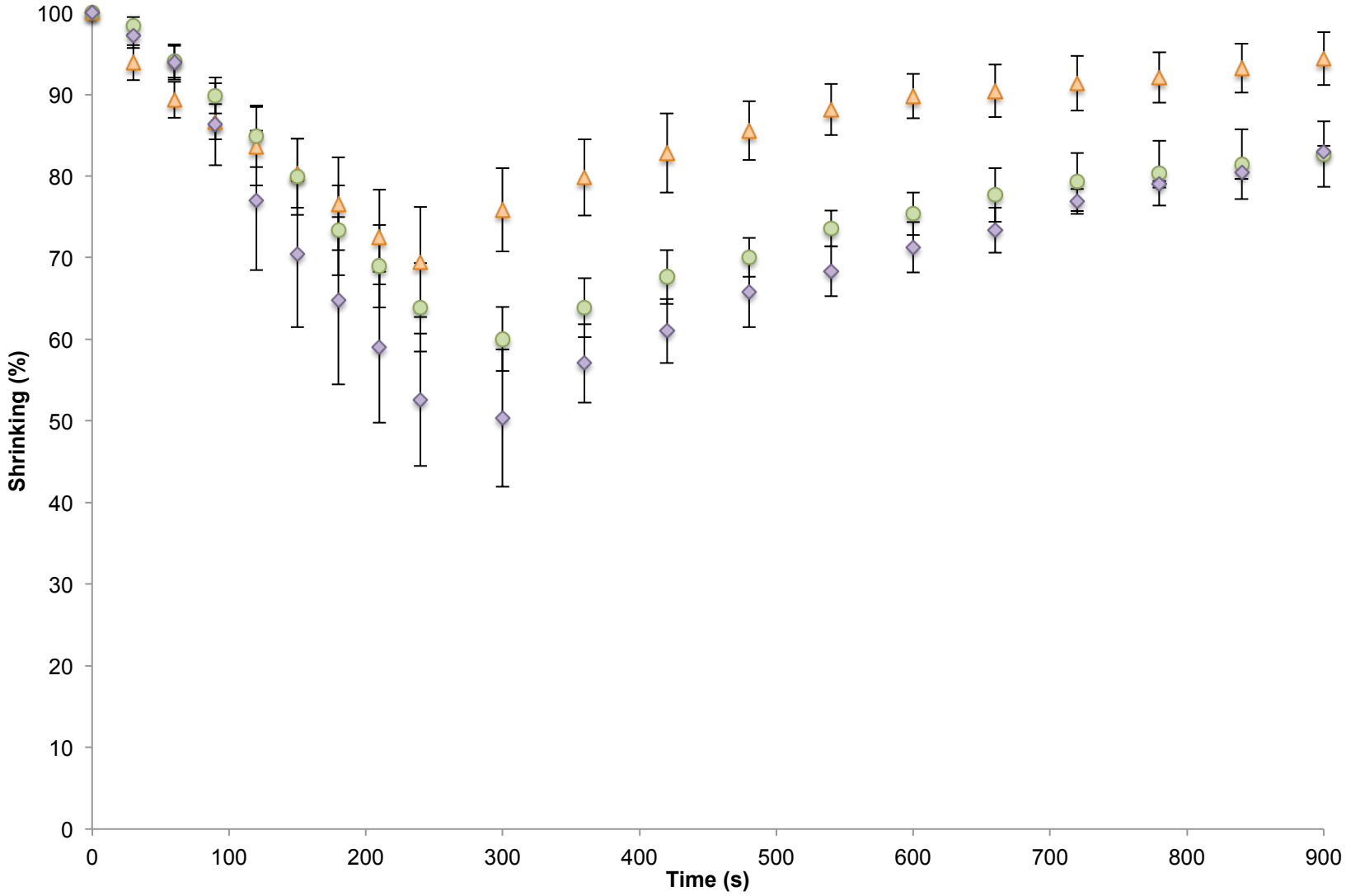


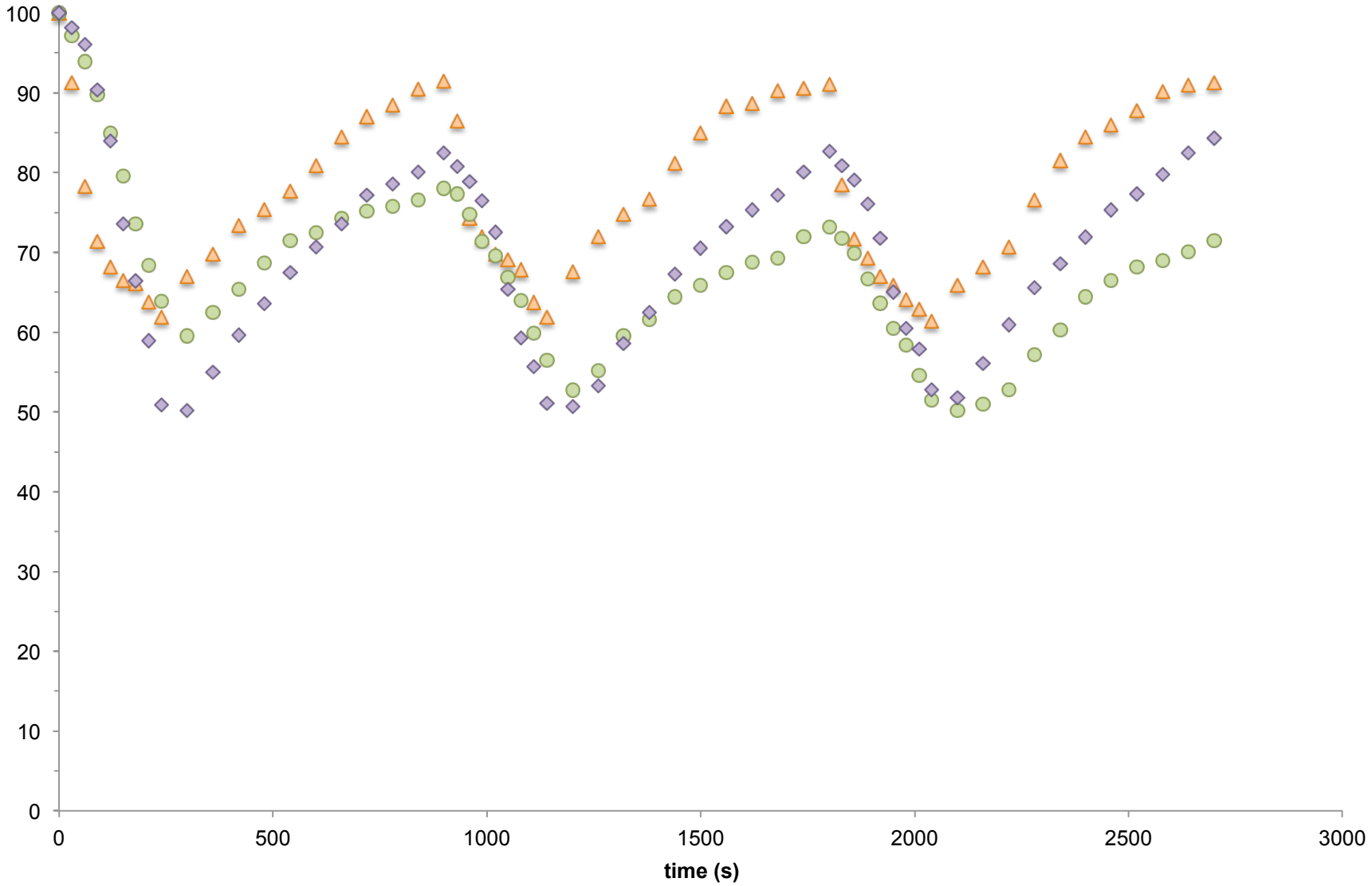
Photo-responsive hydrogels



1st Irradiation Cycle

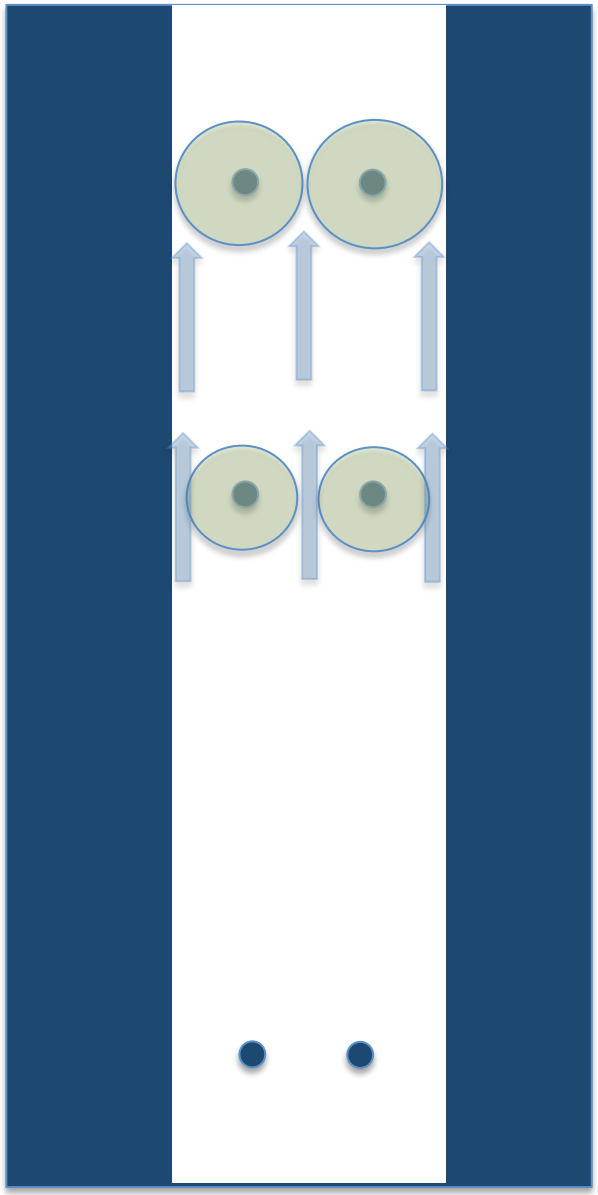


Multiple Irradiation Cycles

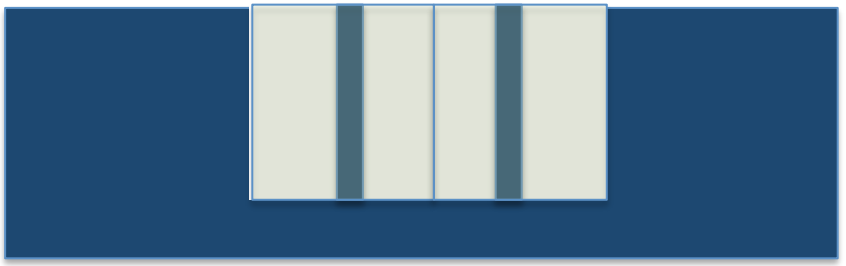


Valve applications

Micro-valve fabrication and working principle

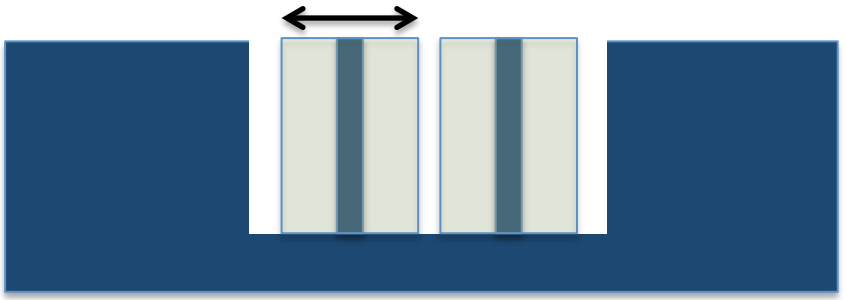


3

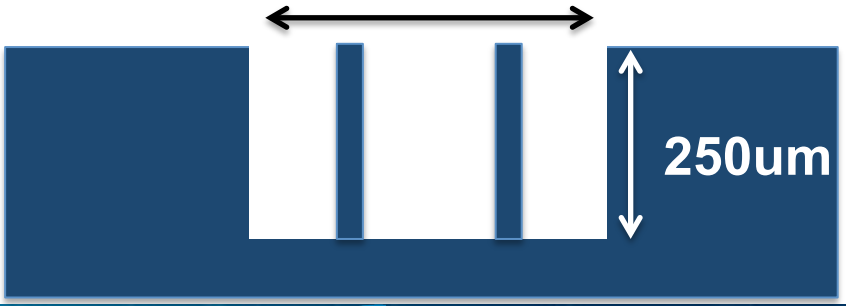


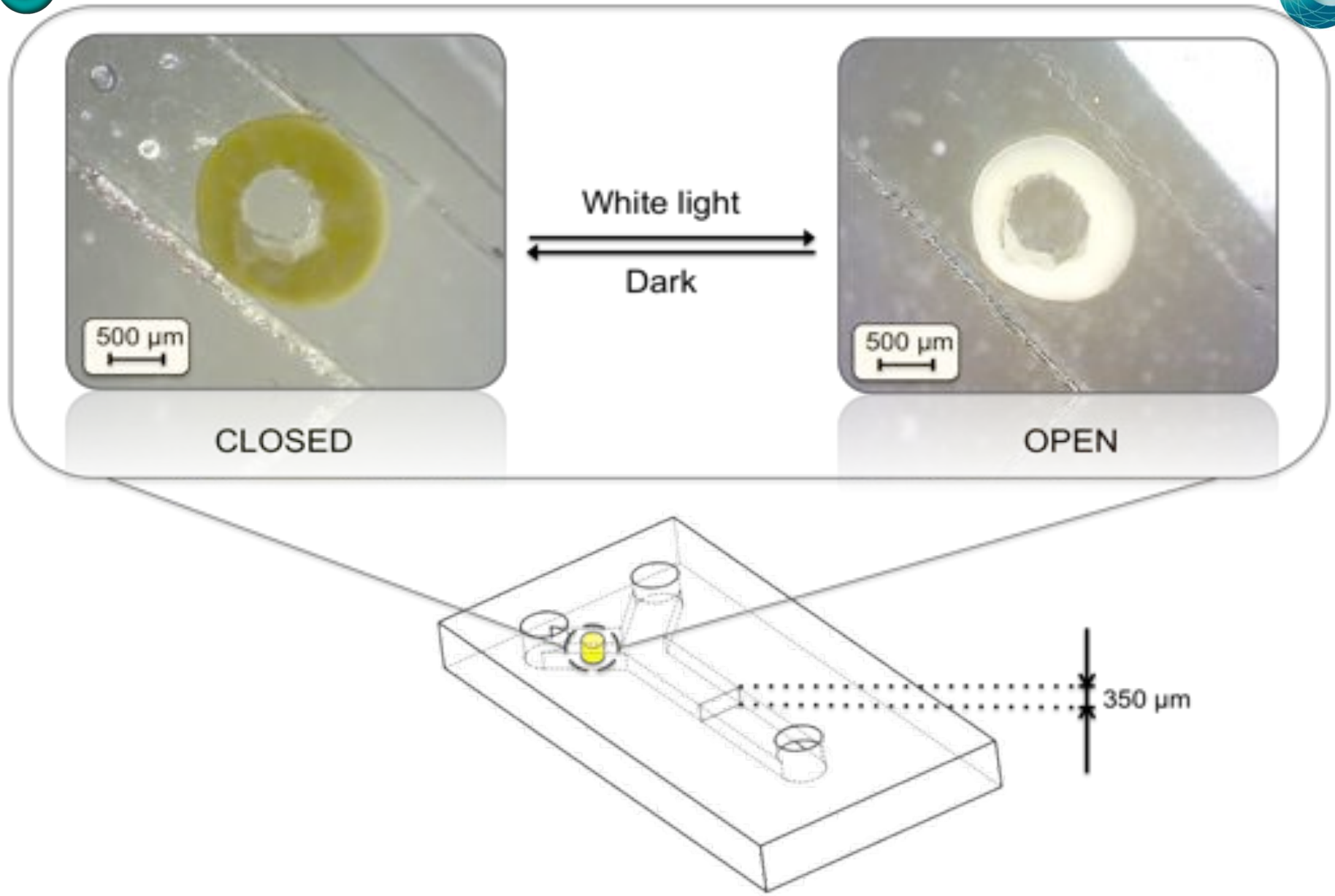
250um gel disks polymerised around pillar using mask

2



1

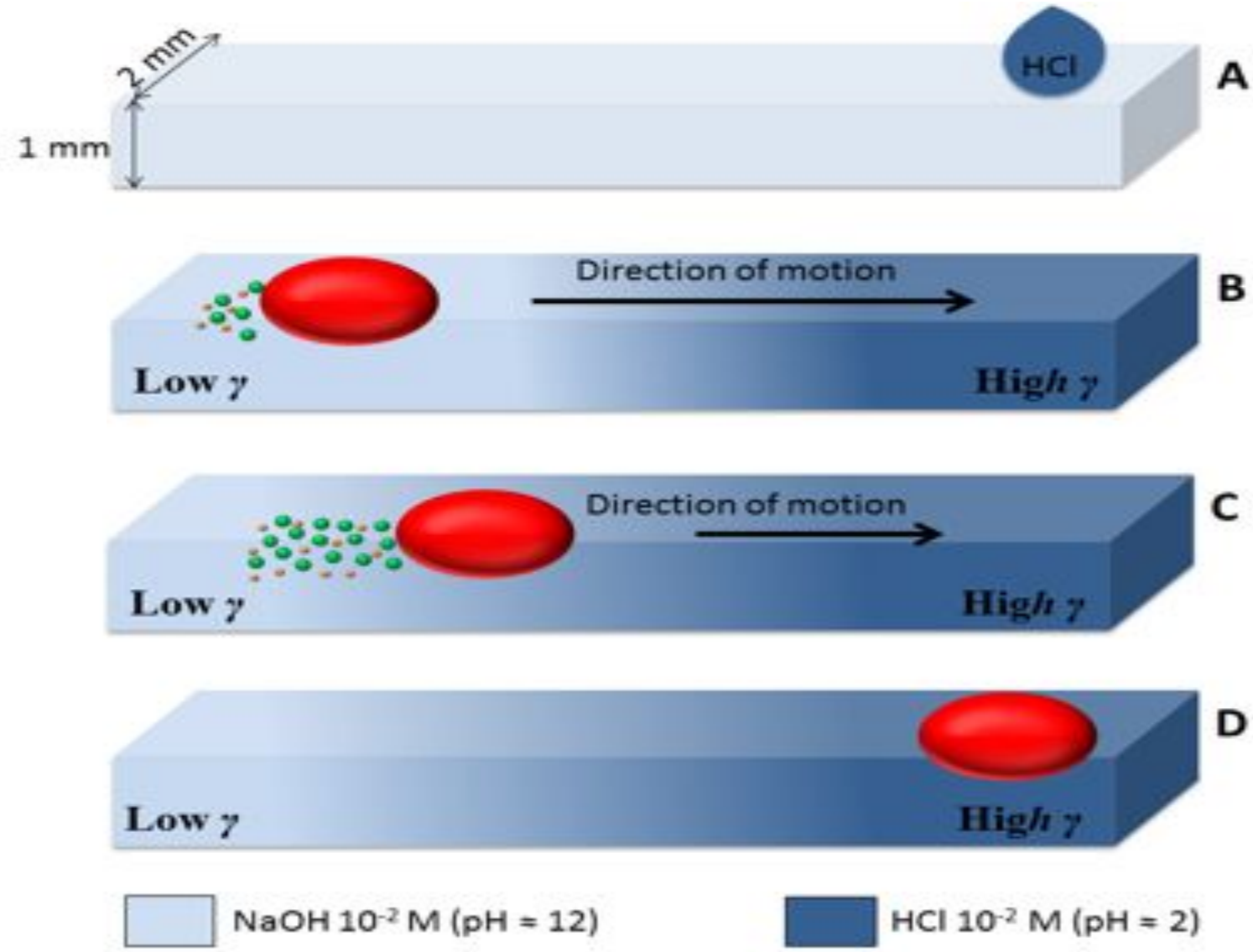



500 µm
White light
Dark
500 µm
CLOSED
OPEN
350 µm

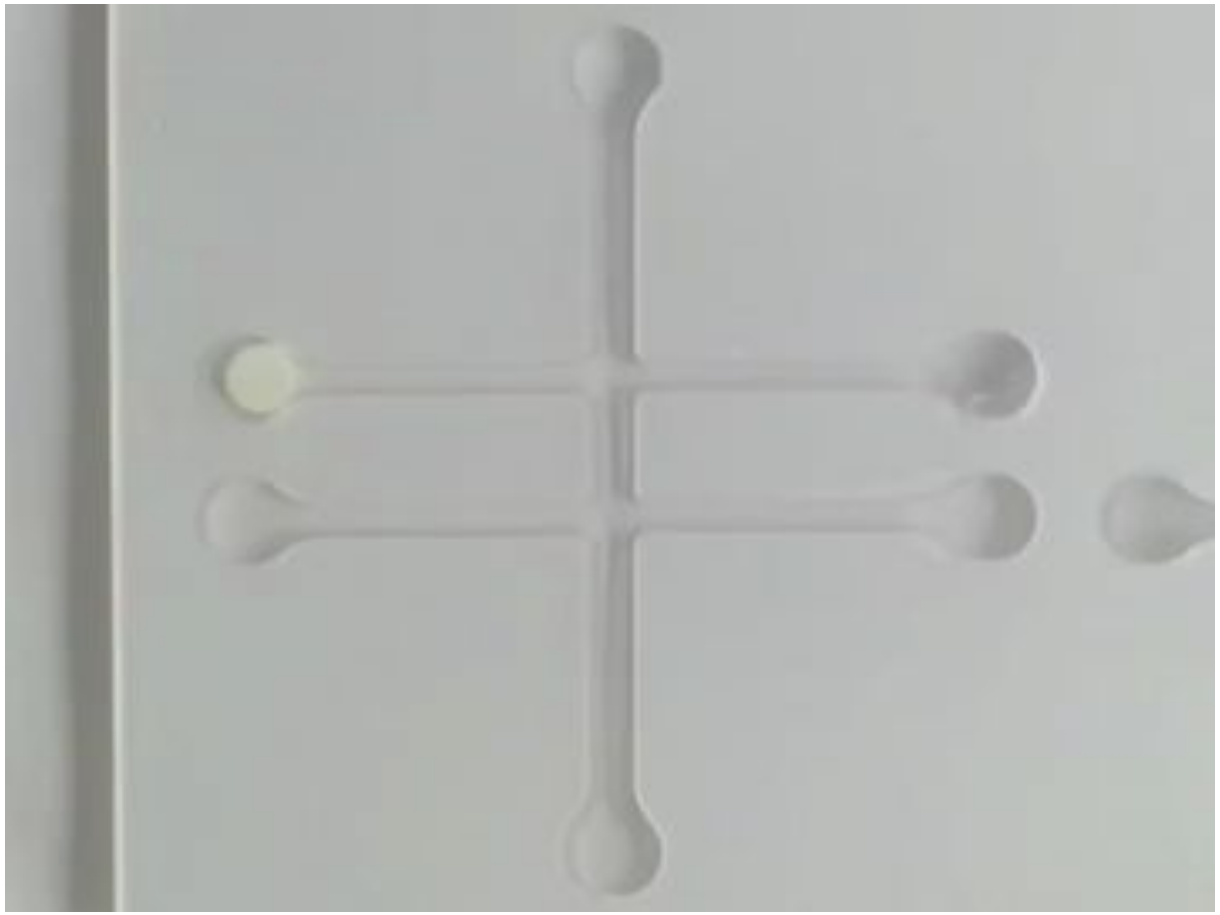
Surfactant-driven vehicles

Chemotactic Droplets

Controlled-release of surfactants

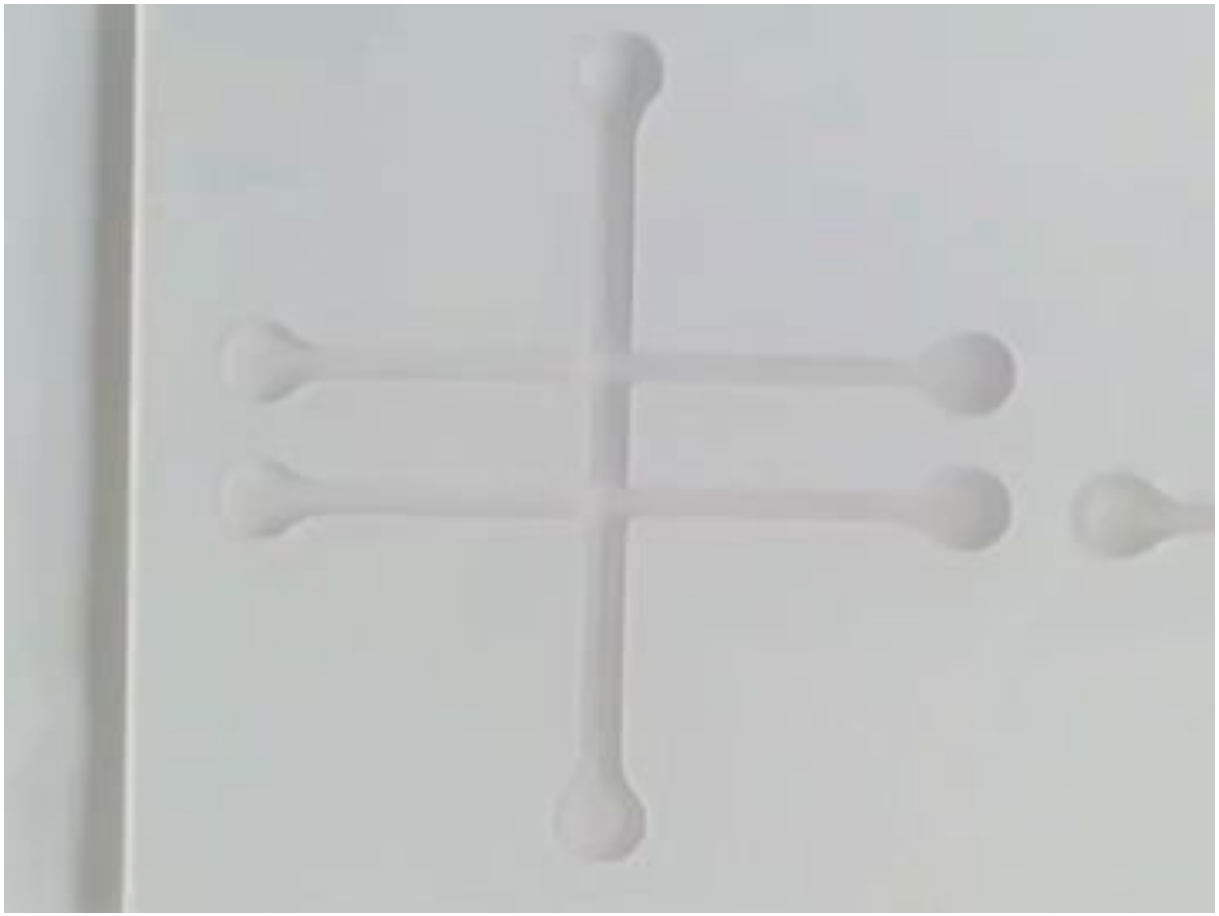


Video 1



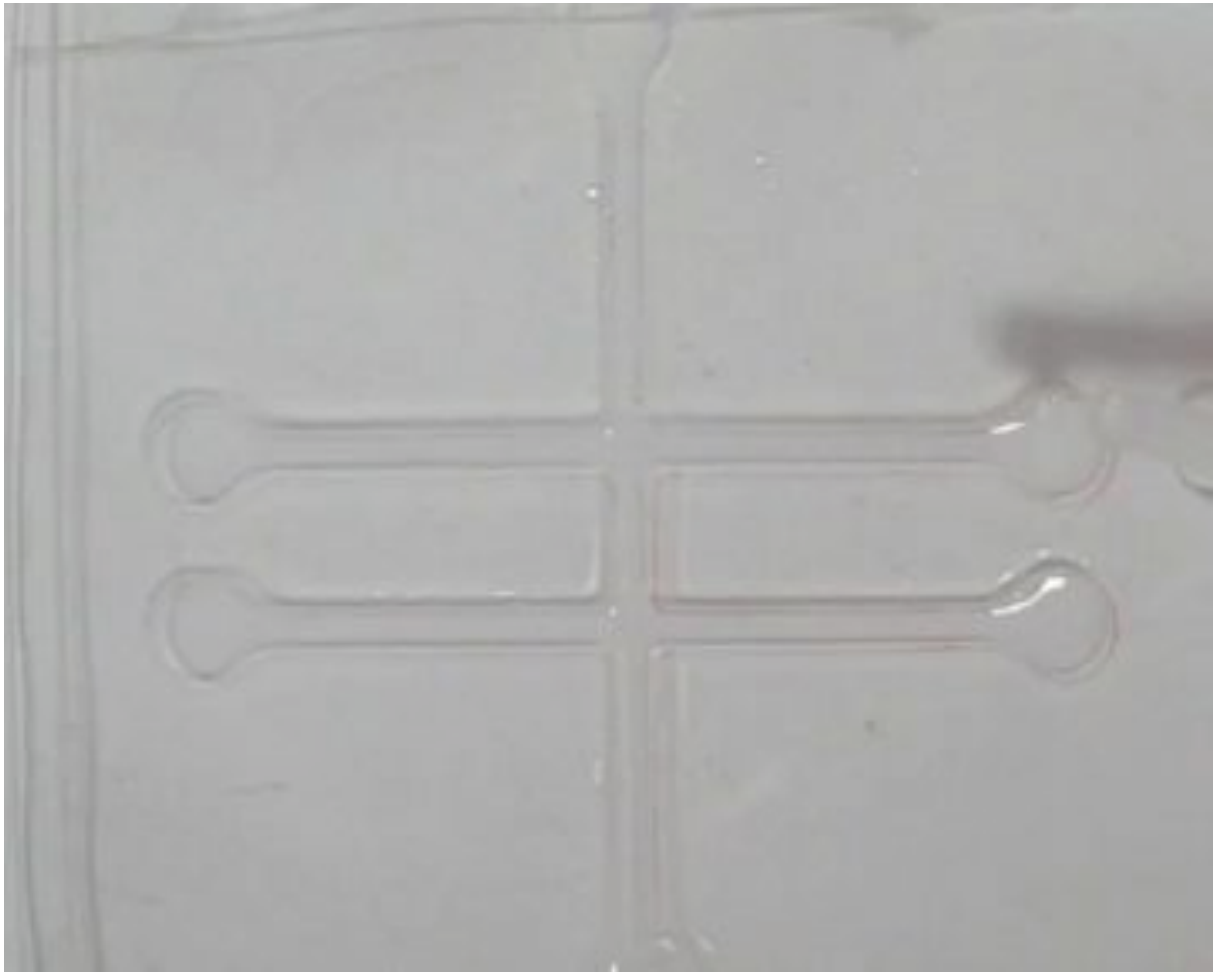
Speed X 4

Video 2:



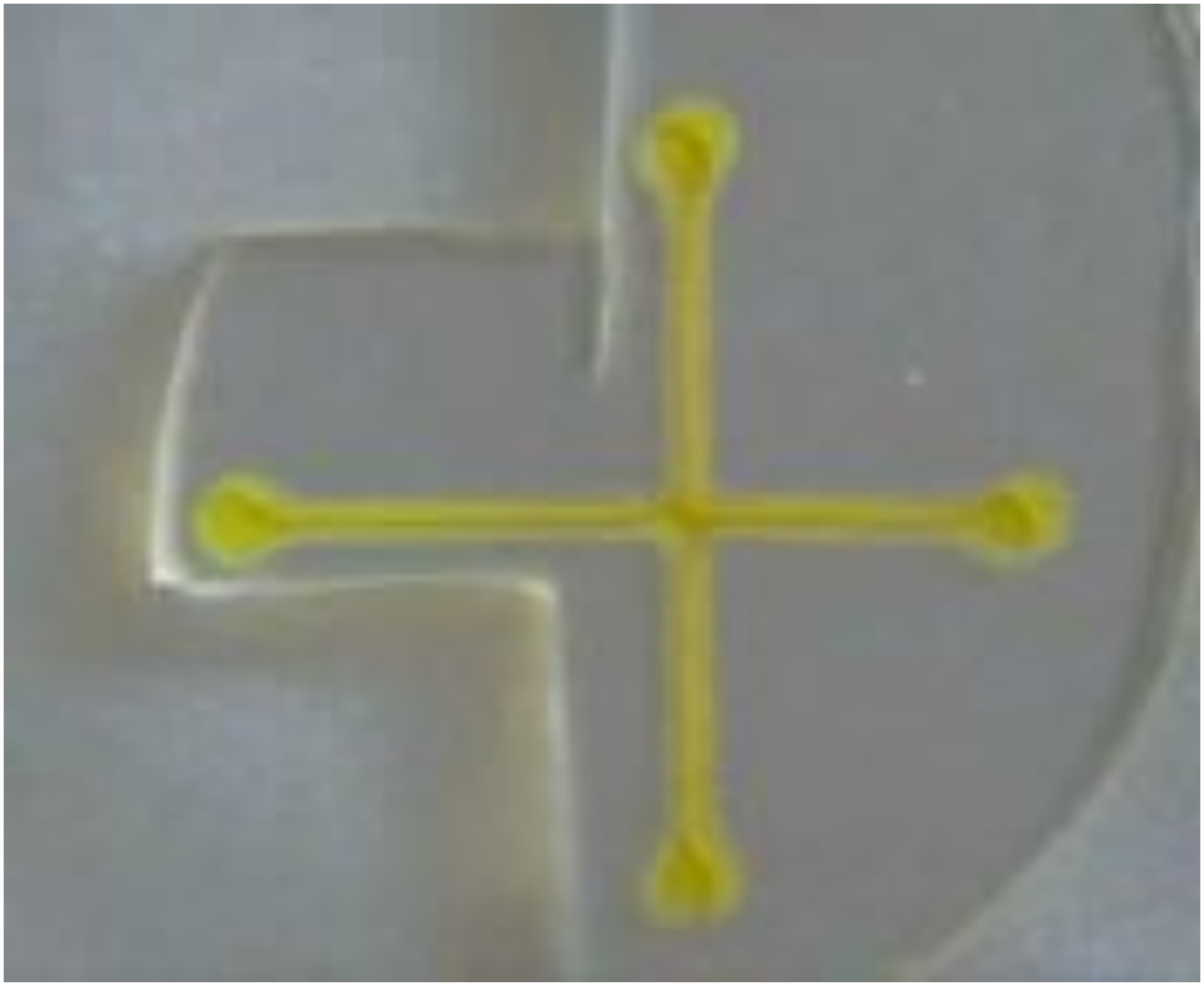
Speed X 2

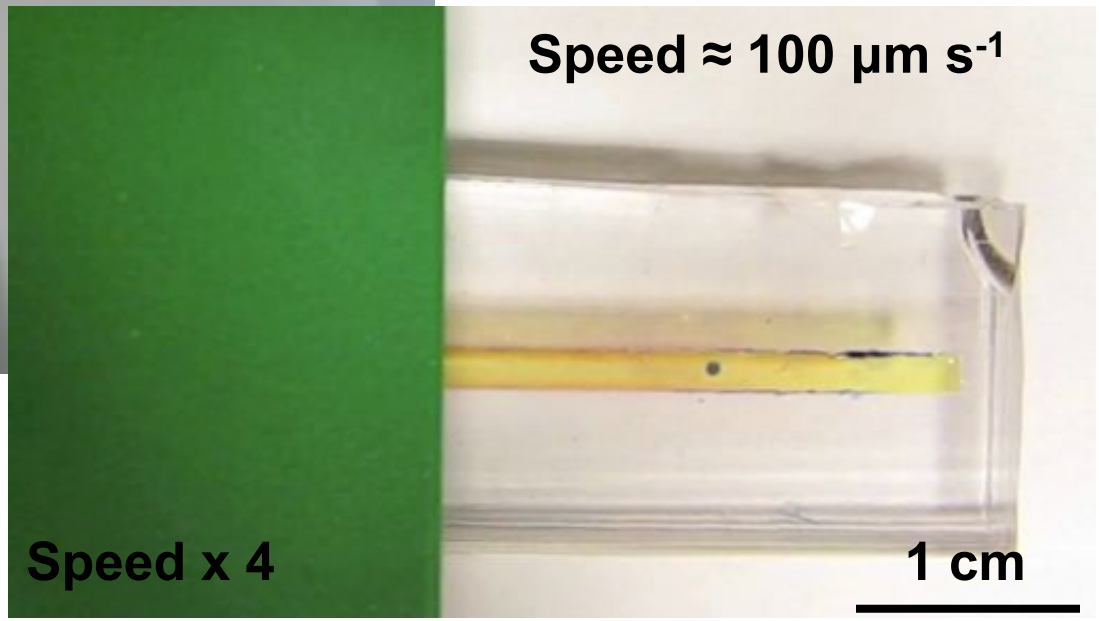
Multiple Chemotactic Droplets



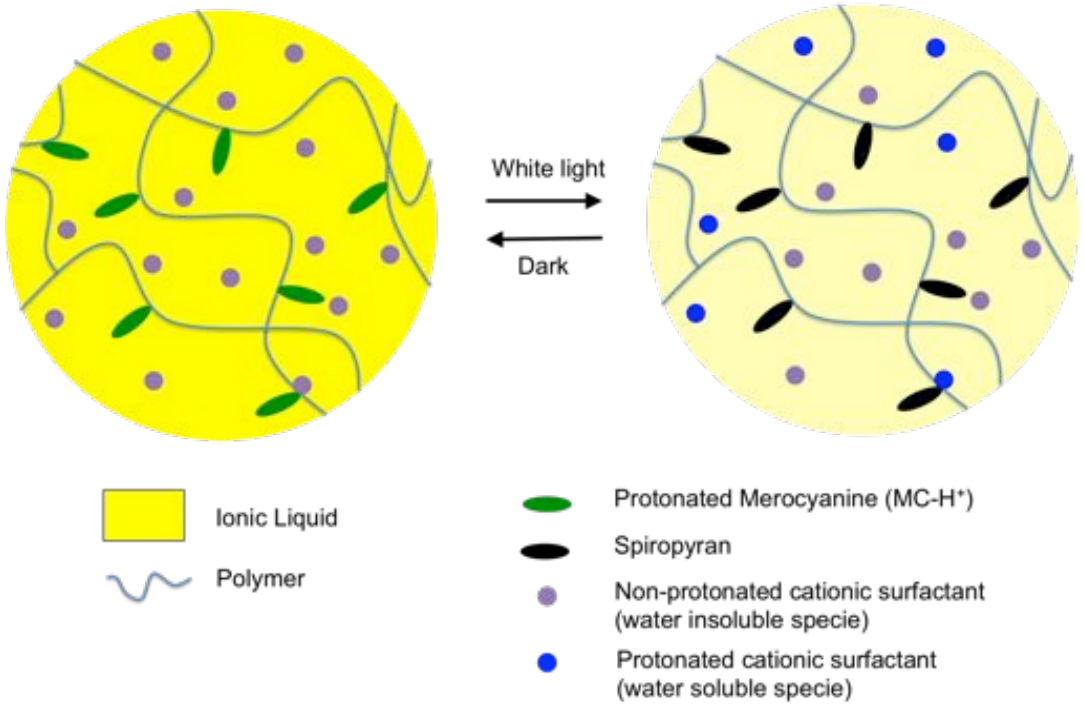
Speed X 2

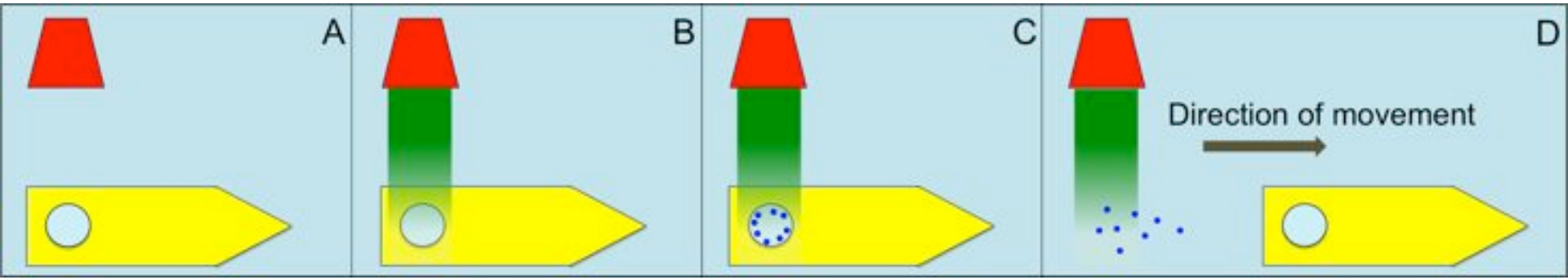
Photo-activated chemopropulsion



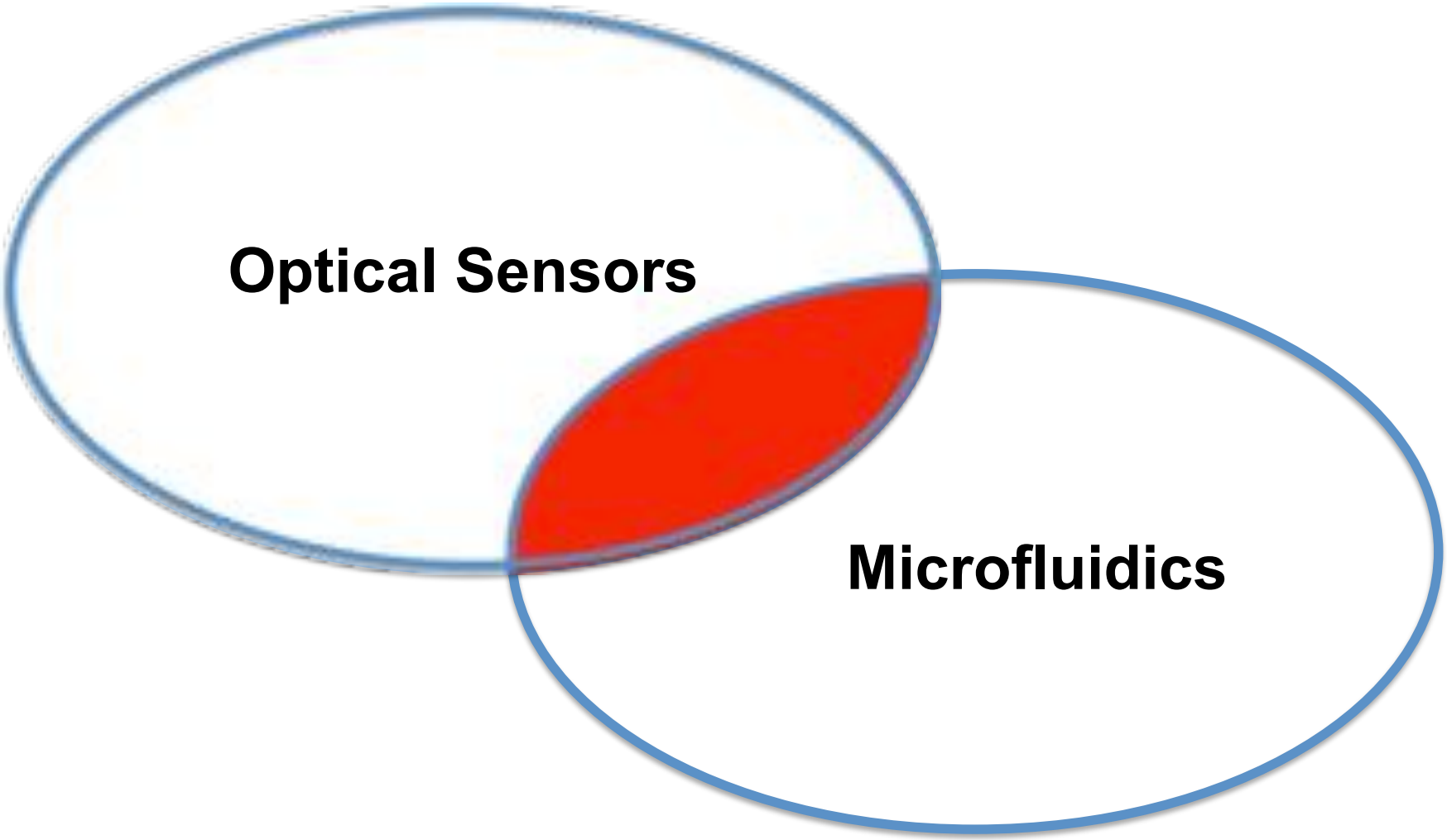

Speed ≈ 100 μm s-1
Speed x 4
1 cm

Perspectives



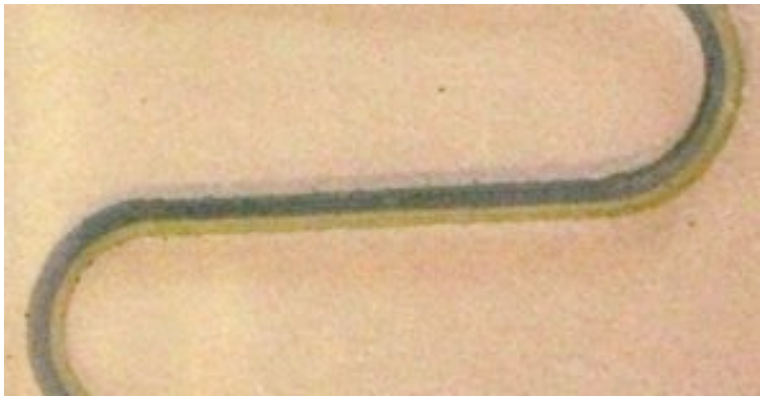


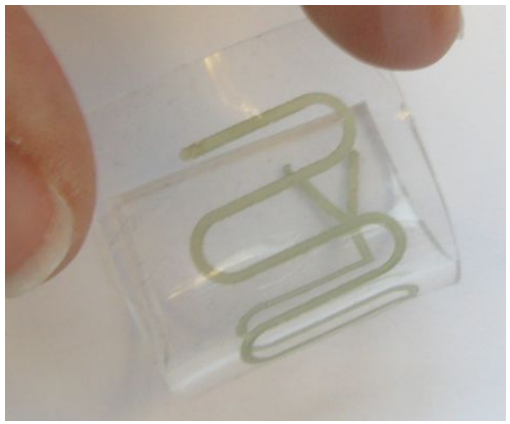
Optical Sensors in Microfluidics



Polyaniline functionalised micro-capillaries and micro-fluidic channels

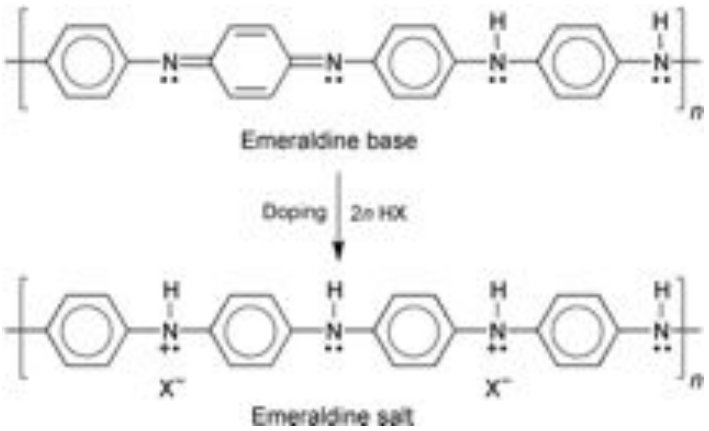
- pH sensing
- ammonia sensing
- diffusion study





Polyaniline Nanofibres

- low cost, easy synthesis
- reversible acid-base doping-dedoping chemistry
- environmental stability

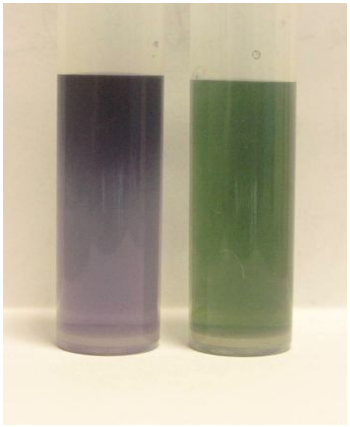


Insulating State

Blue/Violet Colour

Conducting State

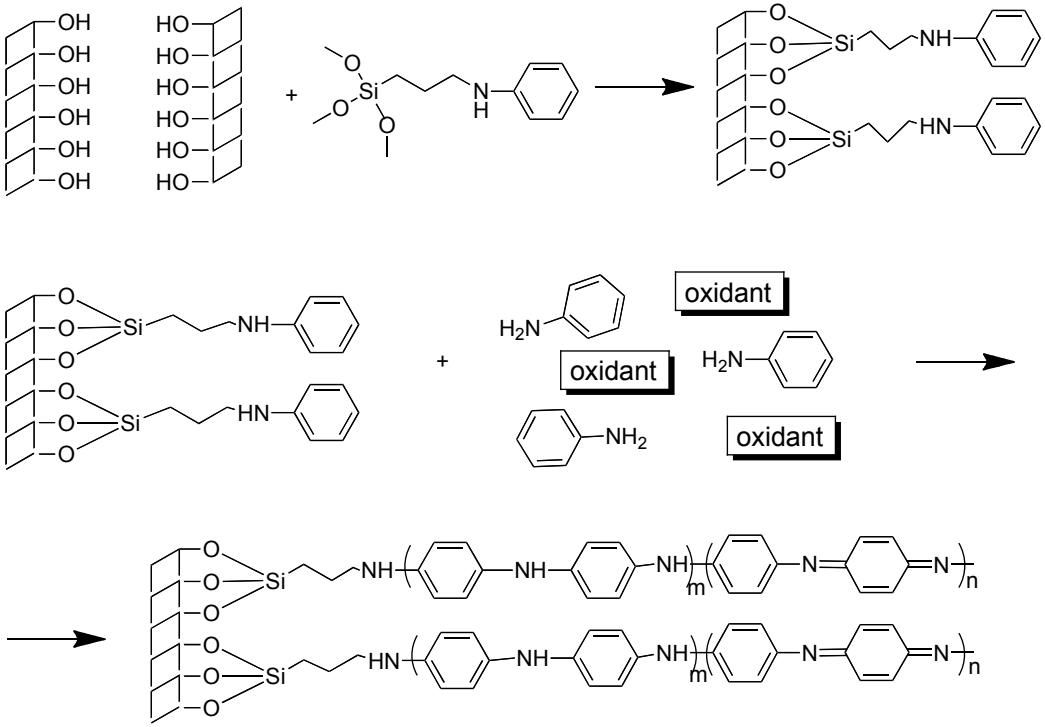
Green



J.X. Huang, S. Viril, B.H. Weller, R.B. Kaner / J.Am.Chem.Soc. 125 (2003), 314-315

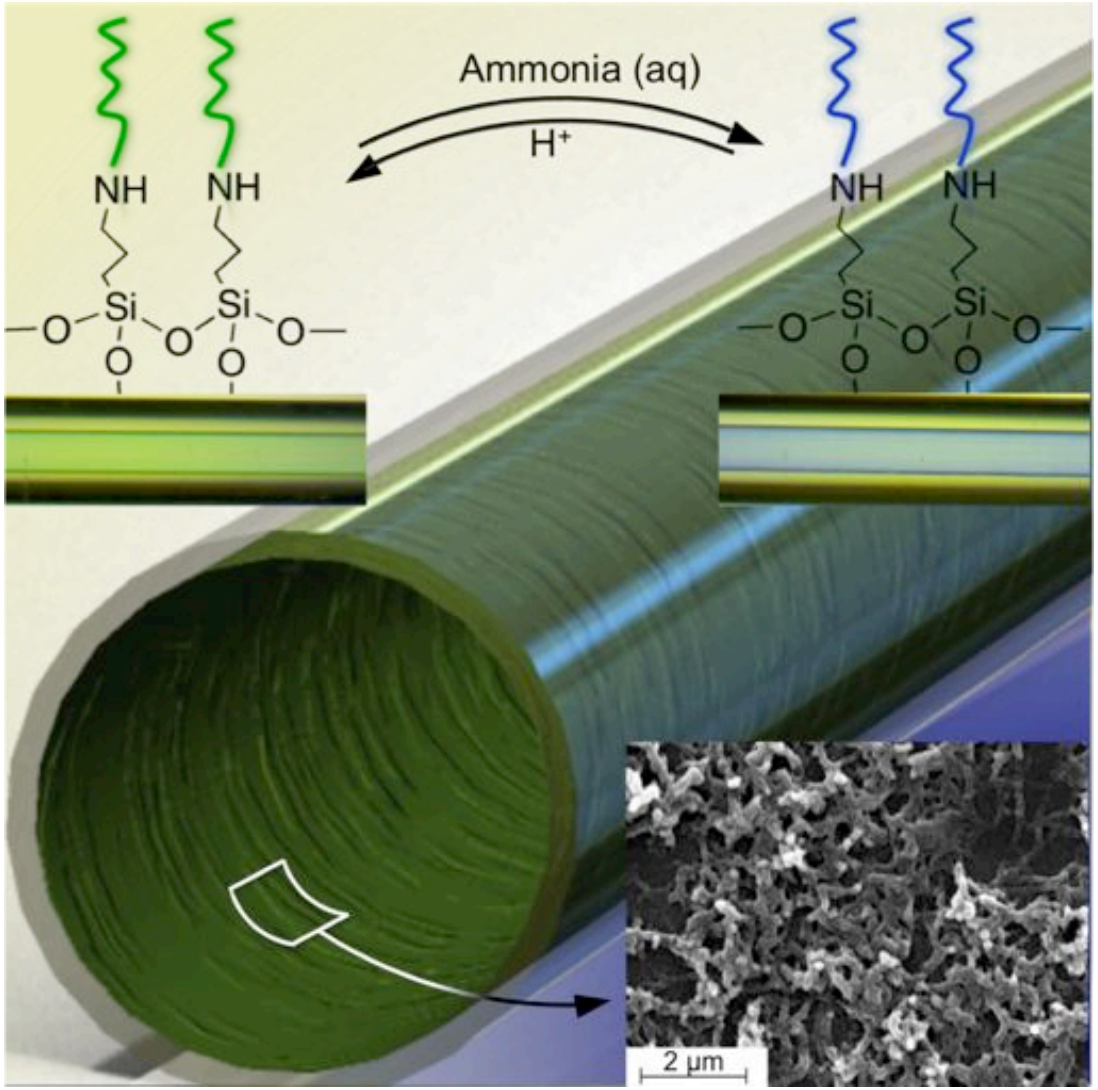
Polyaniline-coated micro-capillaries for ammonia sensing

➢ Micro-capillary functionalisation

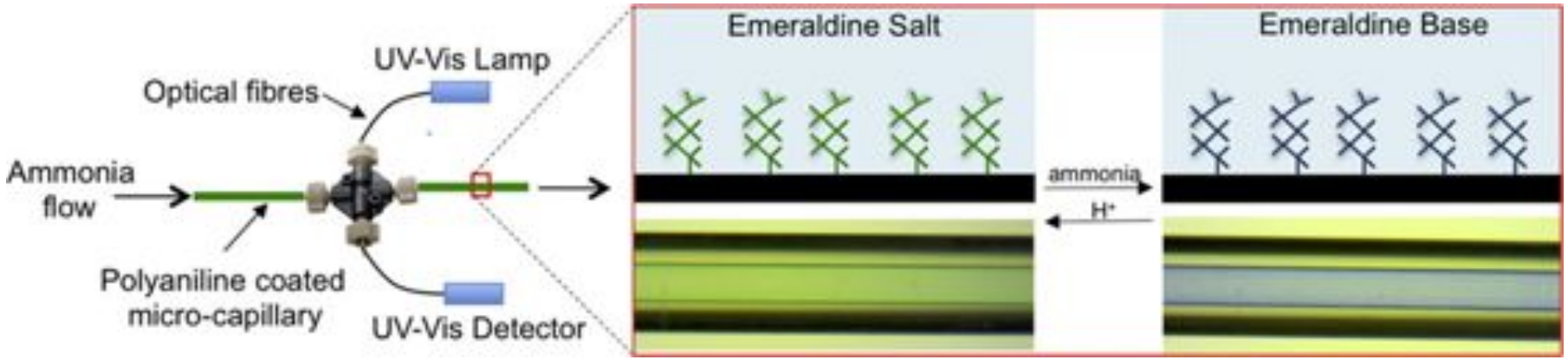


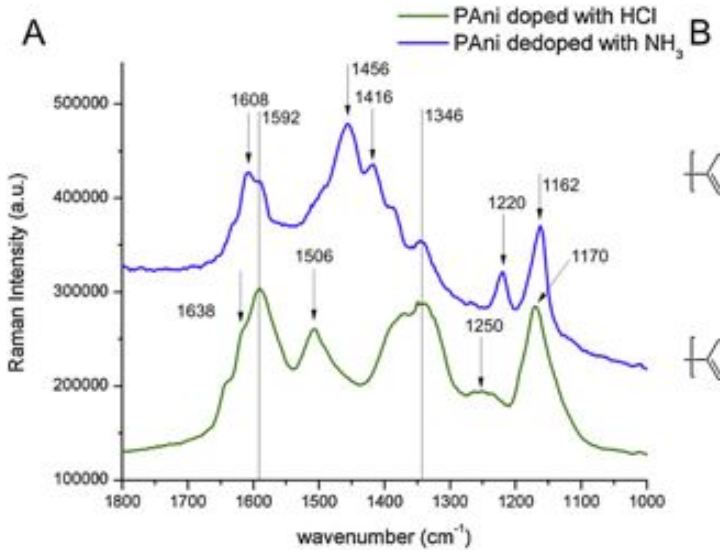
L. Florea, D. Diamond and F. Benito-Lopez, *Anal. Chim. Acta*, 2013, 759, 1-7

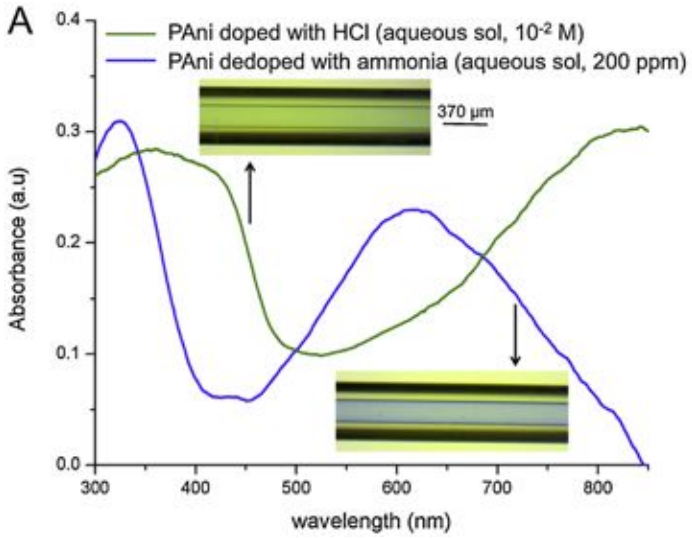
Polyaniline-coated micro-capillaries for ammonia sensing



Doping dedoping properties

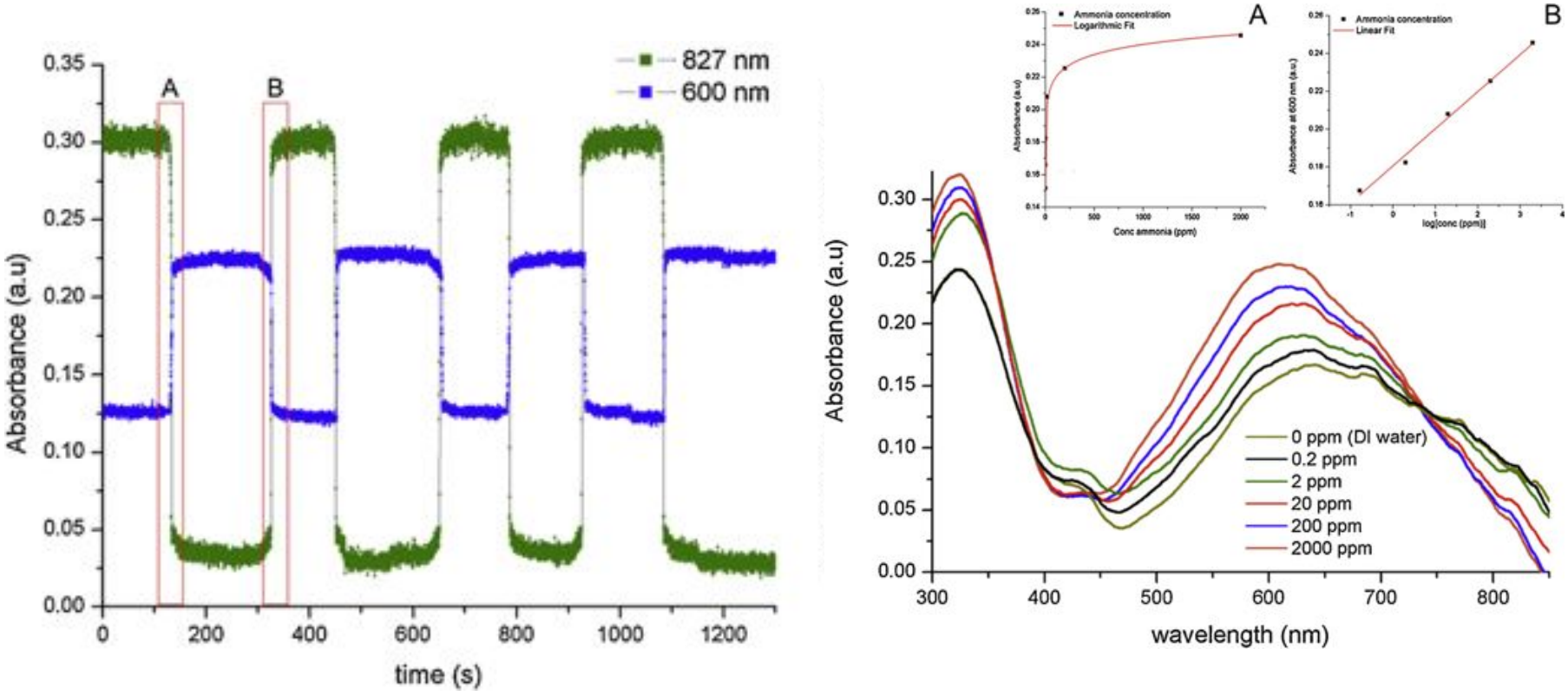






L. Florea, D. Diamond and F. Benito-Lopez, *Anal. Chim. Acta*, 2013, 759, 1-7

Ammonia sensing



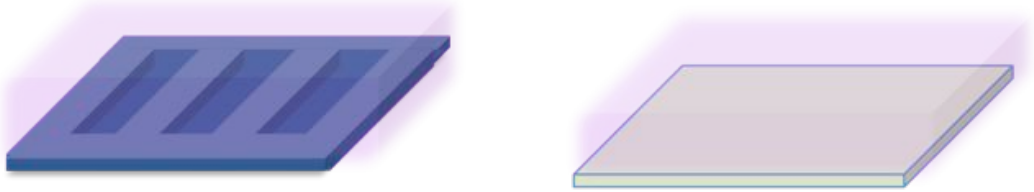
L. Florea, D. Diamond and F. Benito-Lopez, *Anal. Chim. Acta*, 2013, 759, 1-7

From micro-capillaries to micro-channels

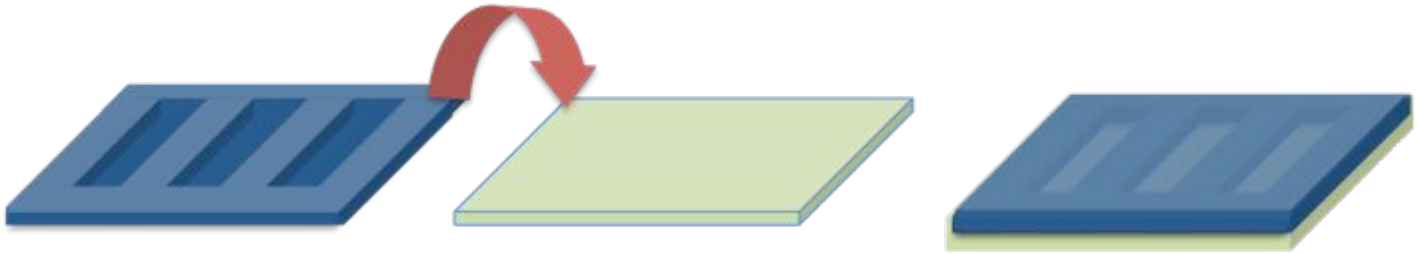
Micro-chip fabrication

✓PDMS is poured onto master mold, cured at 80°C for 1 h and removed from mold.

✓PDMS and glass slide are treated with oxygen plasma.



✓PDMS and glass slide are brought together.

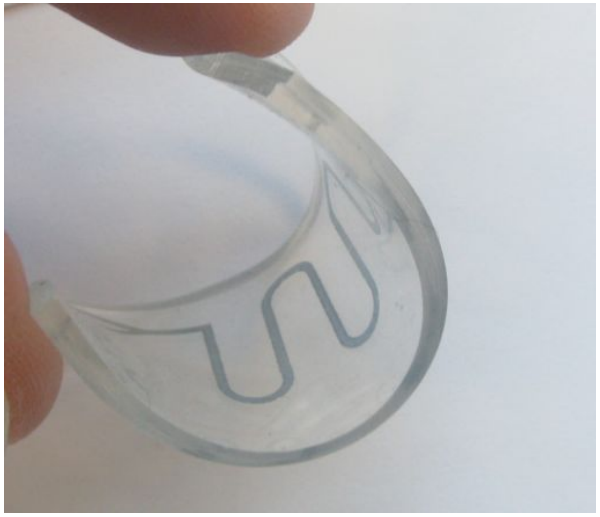


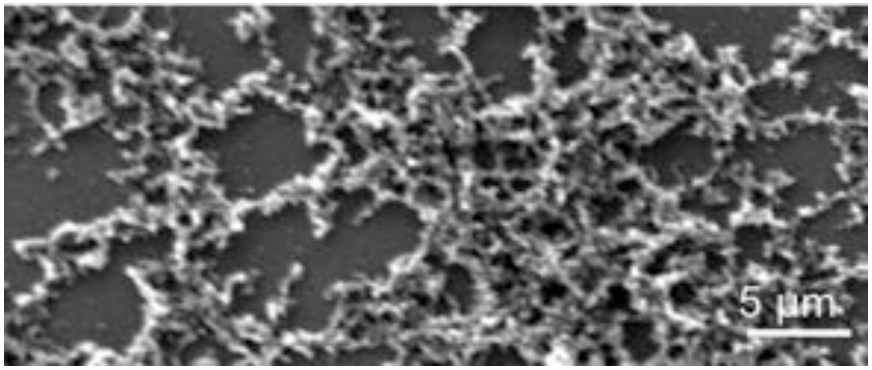
L. Yu, C.M. Li, Y. Liu *et al.* / Lab Chip, 9 (2009), 1243–1247.

Micro-channels

500µm x 1000µm

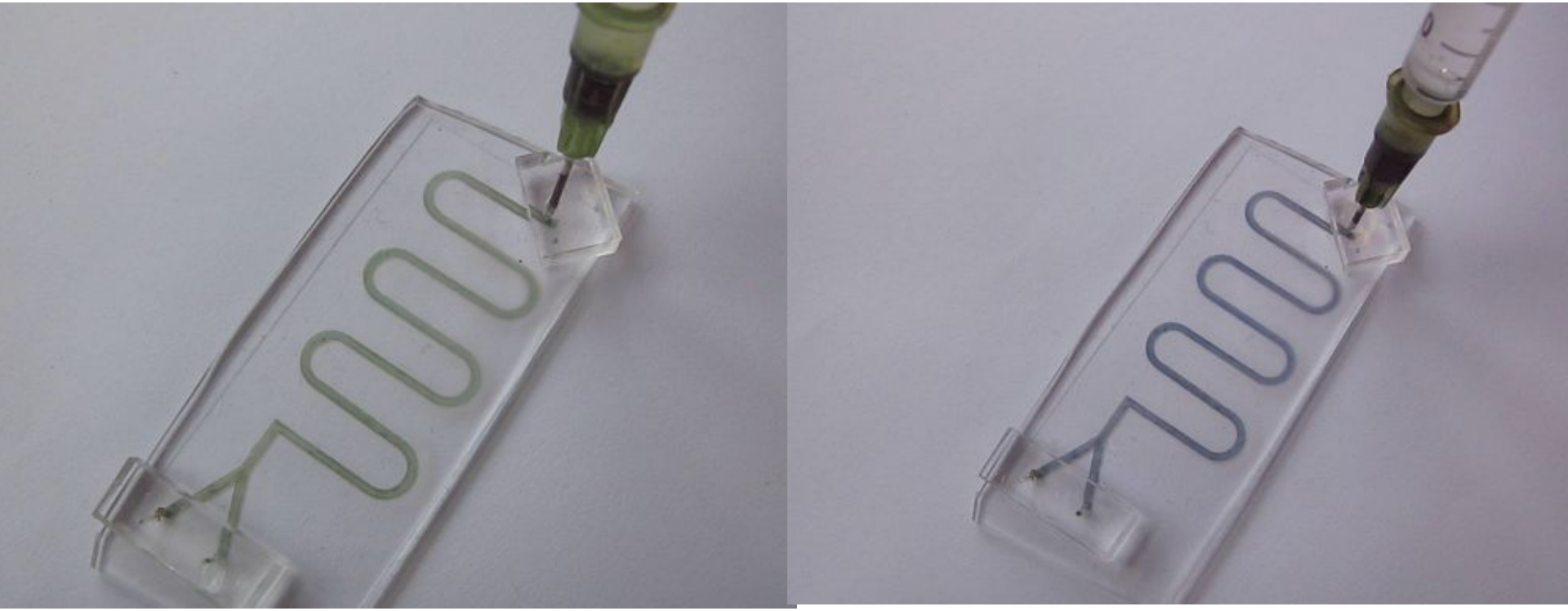
1000µm x 100µm





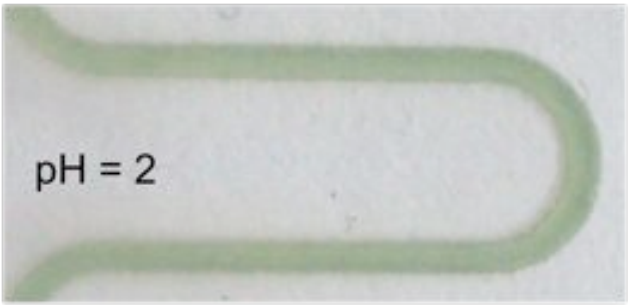
45µm x 50µm

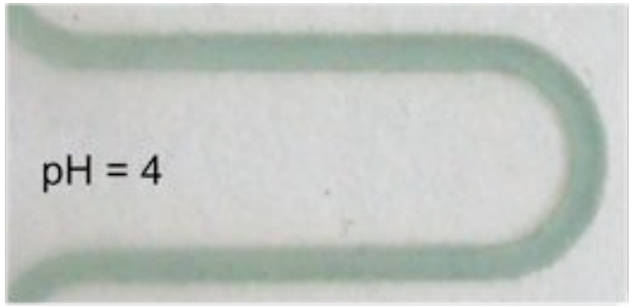
Fast Response

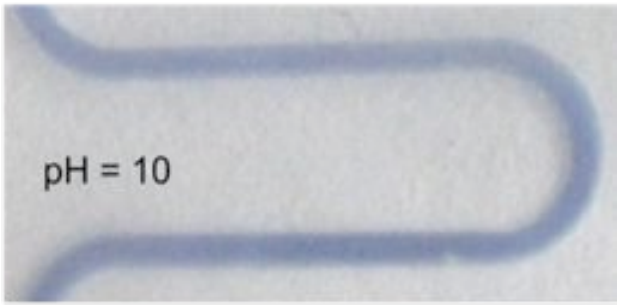


L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.

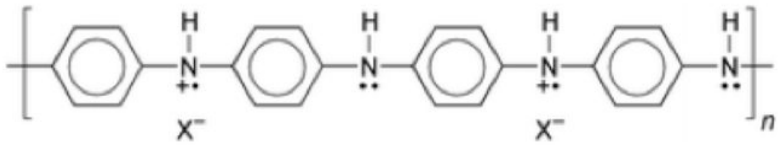
pH sensing in continous flow



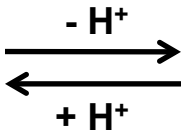


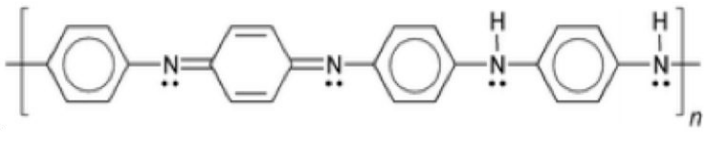


Dedoping process



Emeraldine Salt (ES)

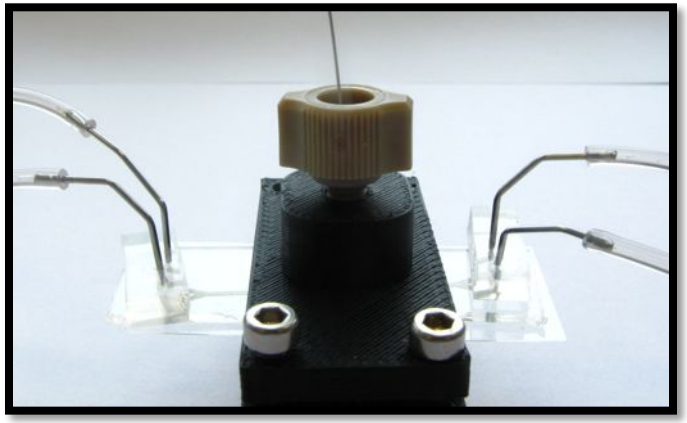


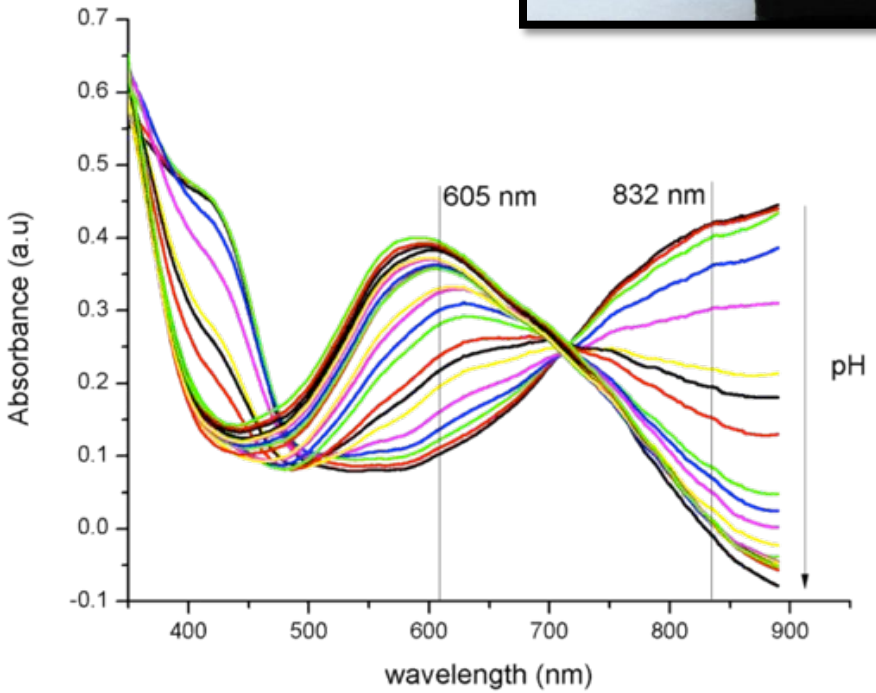


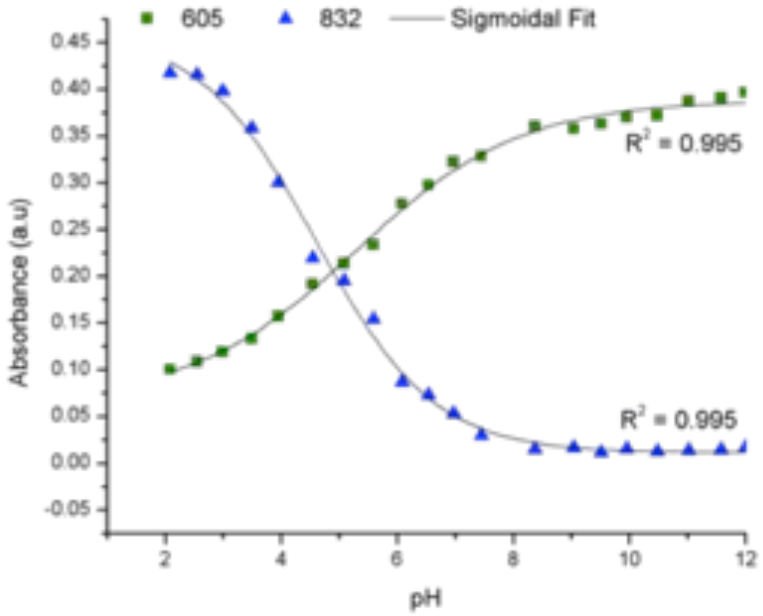
Emeraldine Base (EB)

L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.

pH sensing in continous flow







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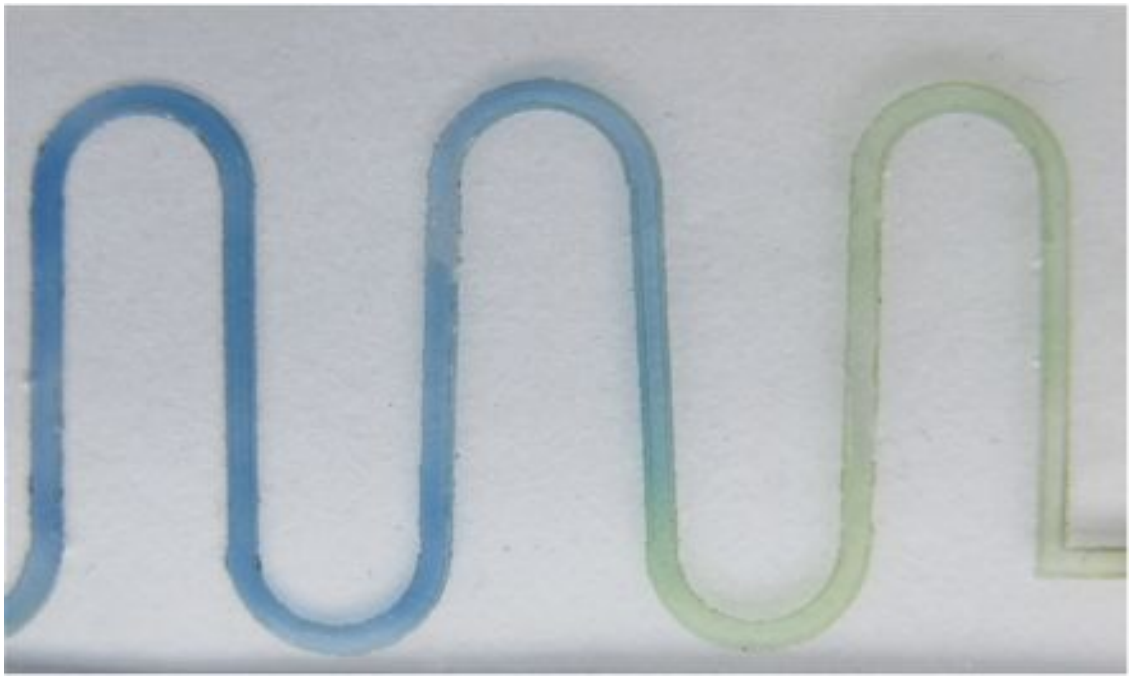
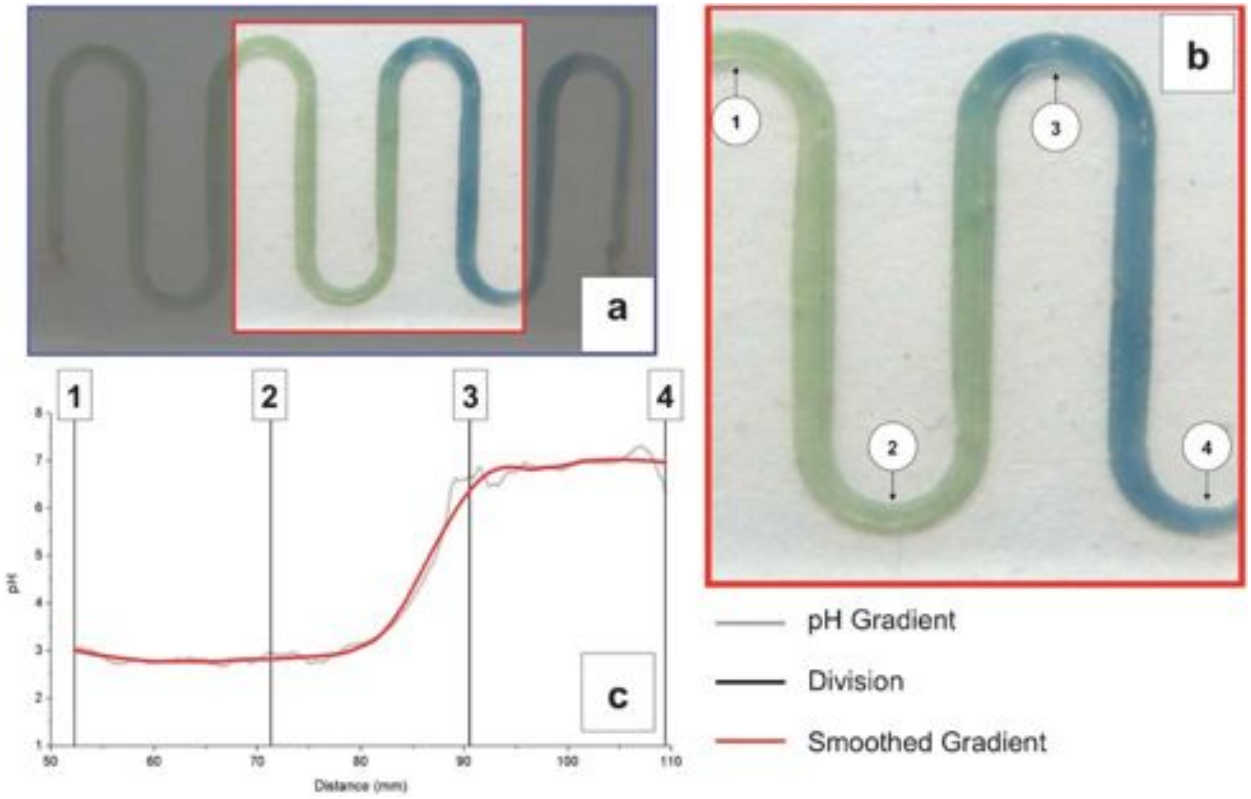
Dynamic pH sensing

NaOH 10^{-2} M



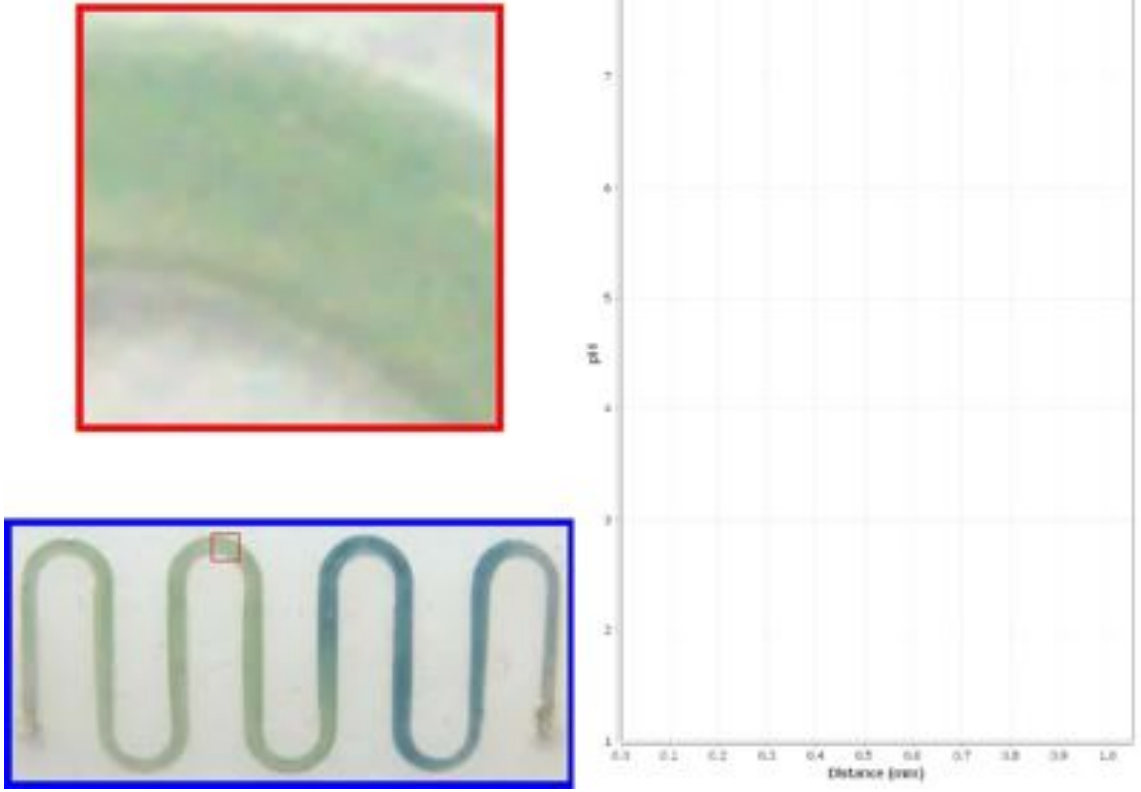
HCl 10^{-2} M

pH gradient sensing



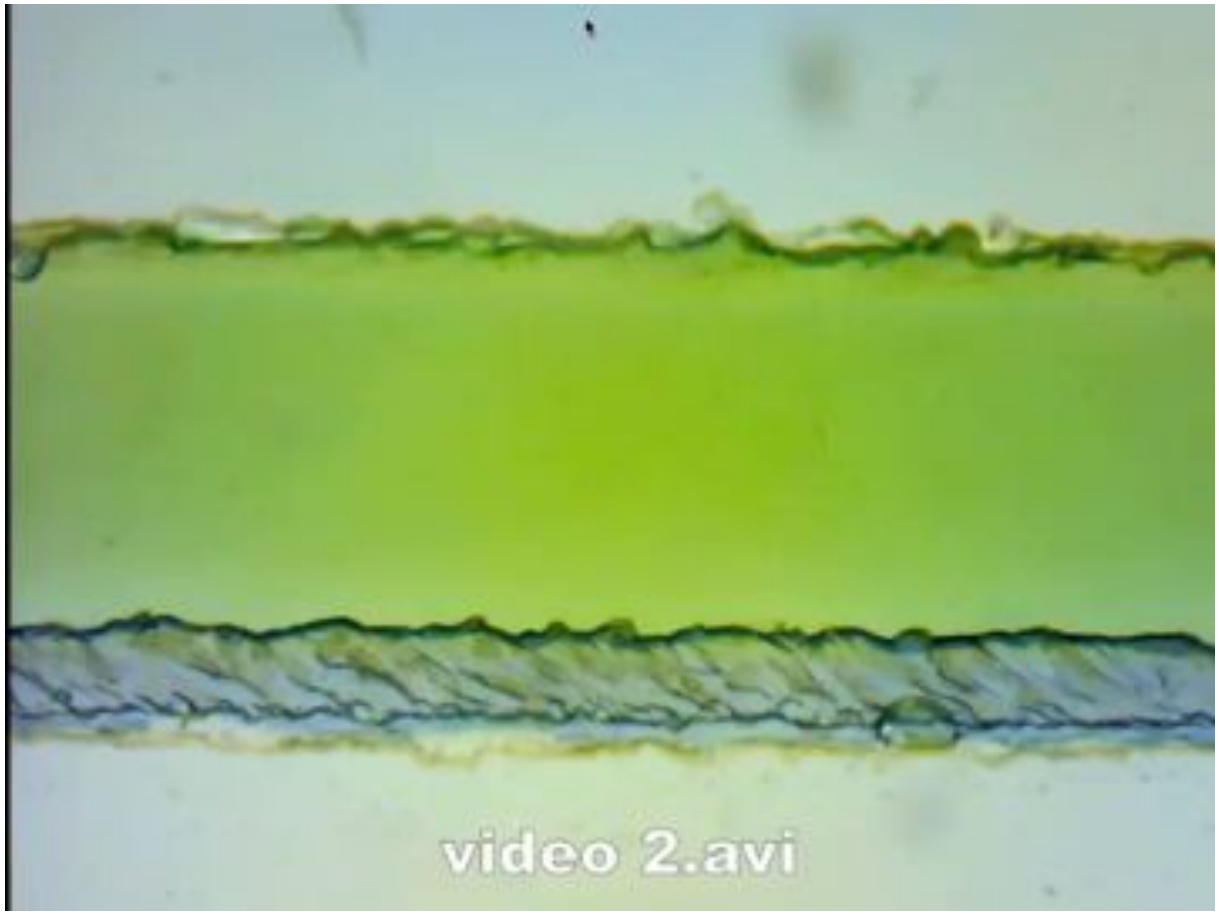
L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.

pH gradient sensing



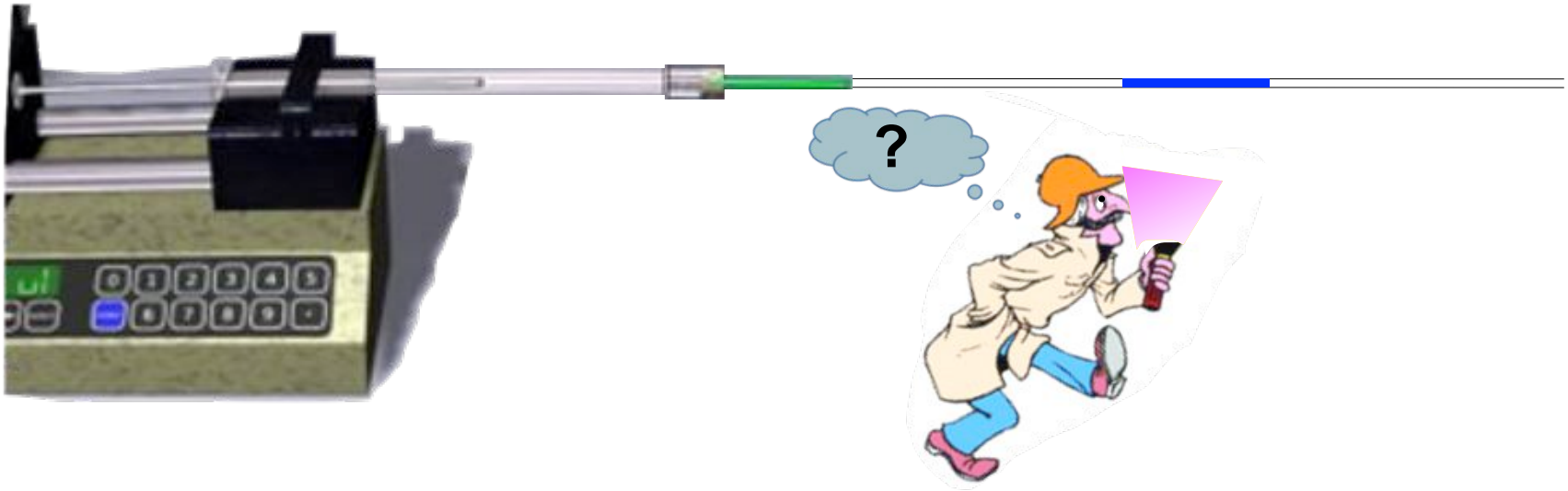
L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.

Study of diffusion process

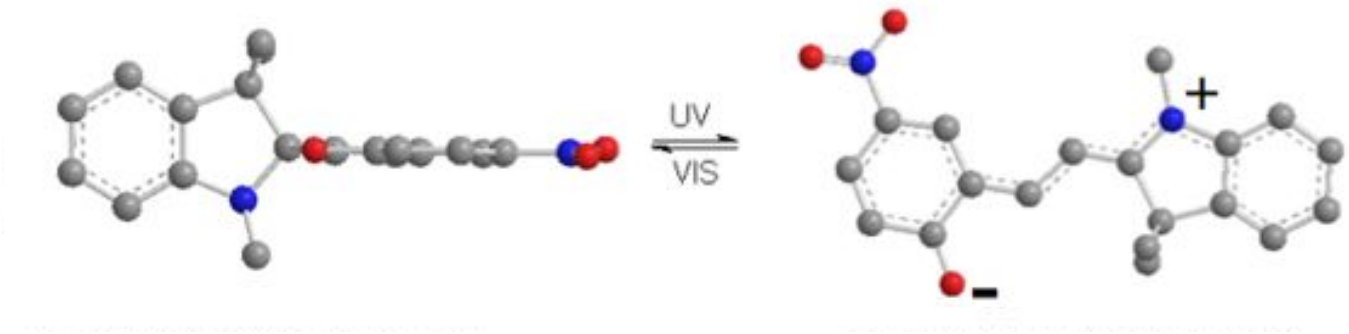


Spiropyran polymeric brushes functionalised micro-capillaries

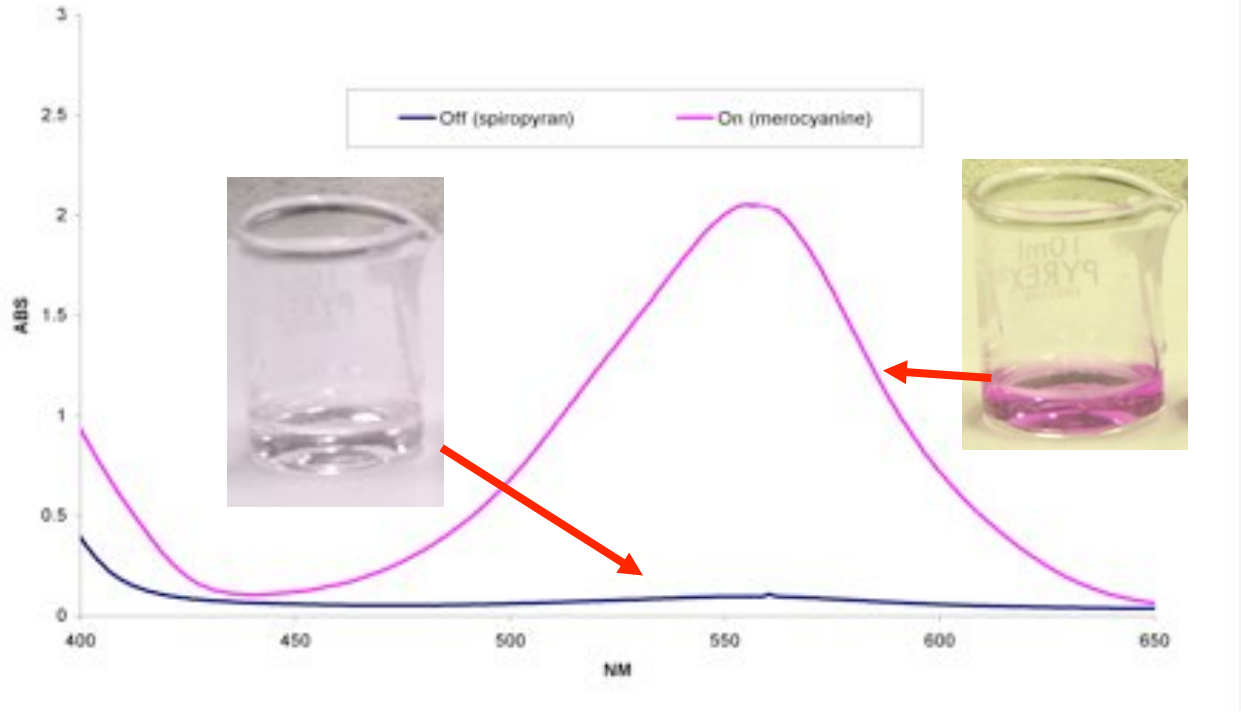
- ON/OFF sensing
- solvent sensing
- metal ion sensing



Spiropyran

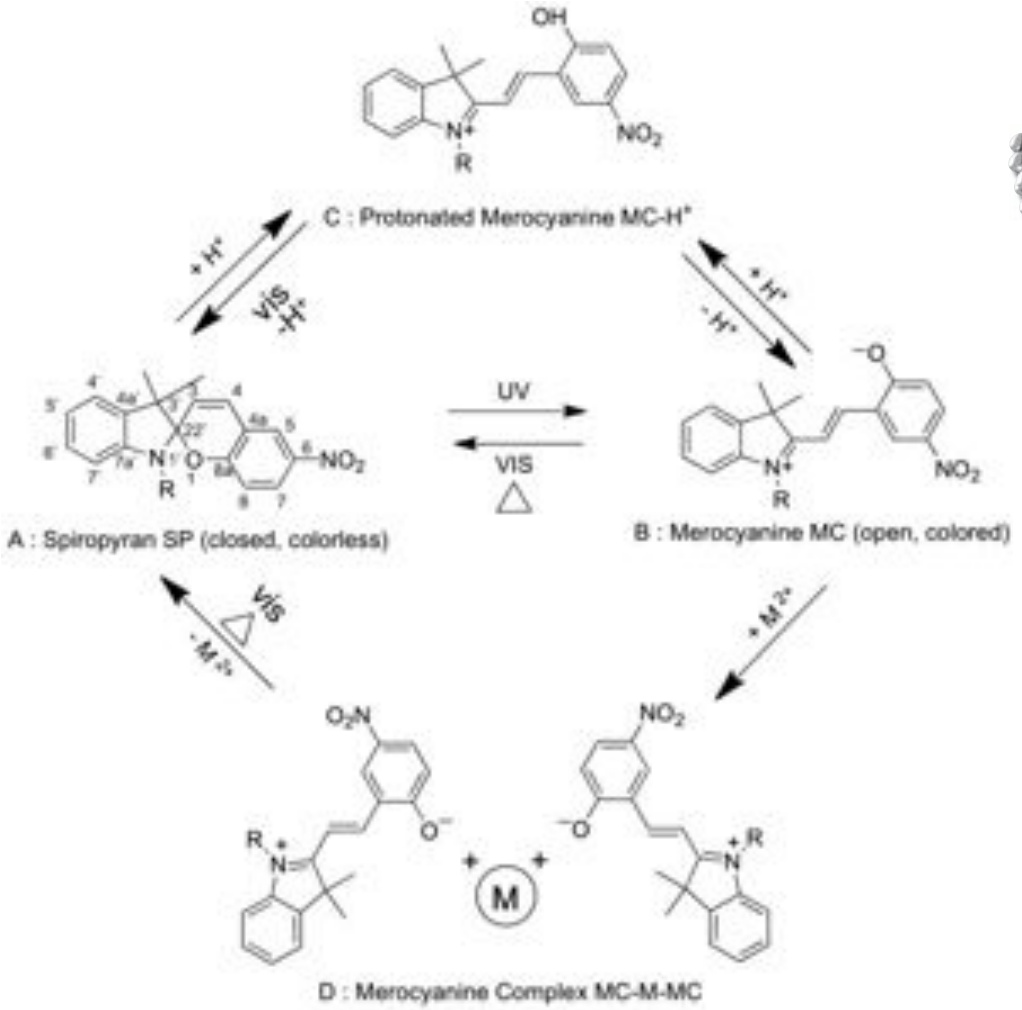


A : Spiropyran SP (closed, colorless) **B : Merocyanine MC (open, colored)**

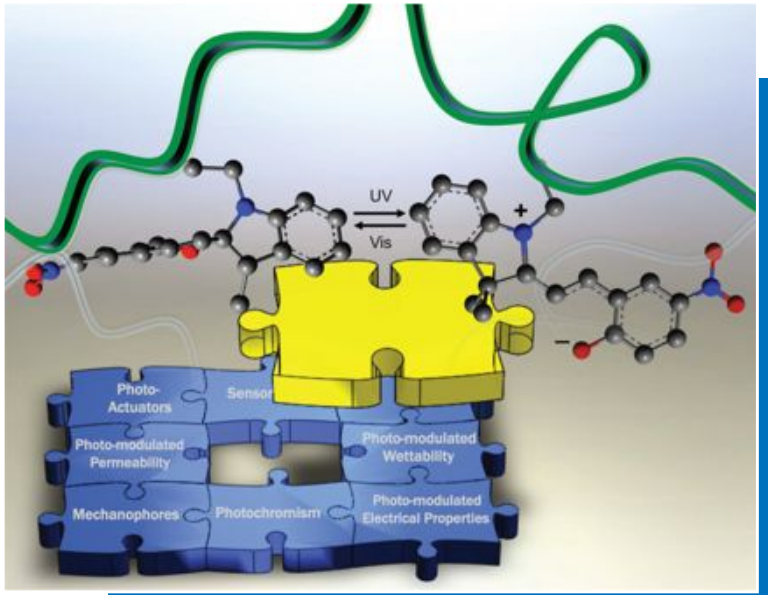


Spiropyran

ISSN 1438-7492 · MMENFA 297 (12) 1129–1236 (2012) · Vol. 297 · No. 12 · December 2012 D 51047



Macromolecular Materials and Engineering



Special Issue:
Advances in Actively Moving Polymers

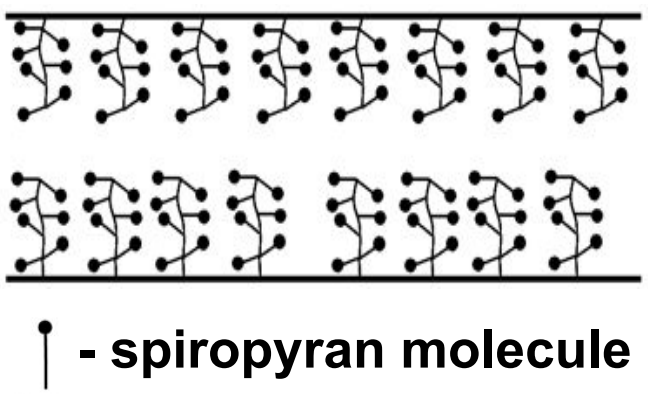
Guest-edited by Andreas Lendlein

12/2012

WILEY-VCH

L. Florea, D. Diamond and F. Benito-Lopez, ***Macromolecular Materials and Engineering***, 2012, 297, 1148-1159.

Our Approach



- spiropyran molecule

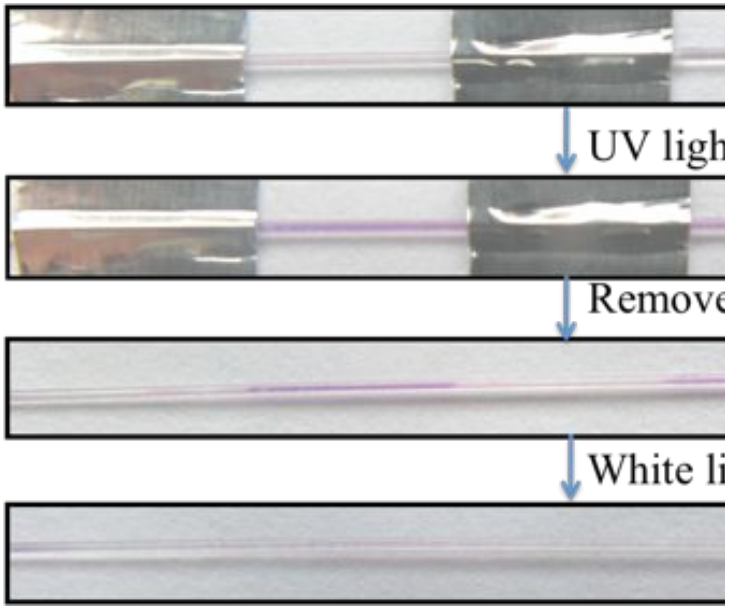
- polymer brushes
- high loading of spiropyran molecule
- 3D arrangement

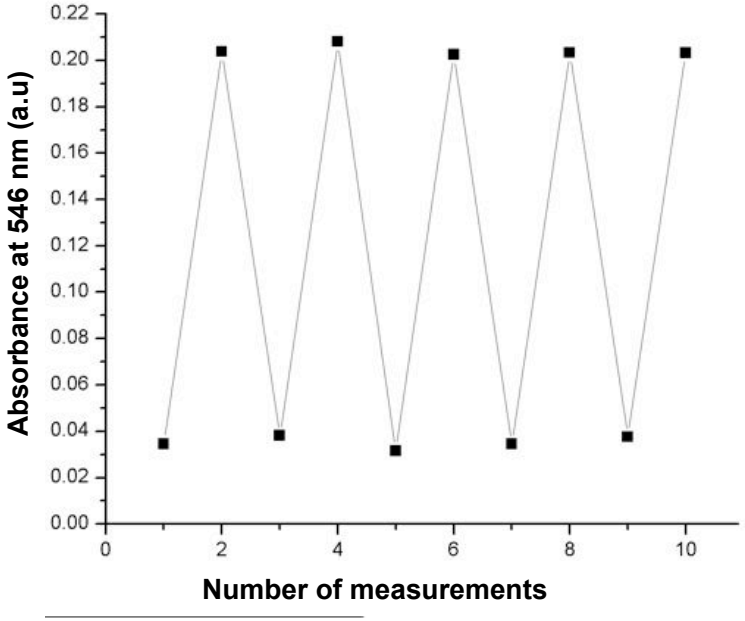
Micro-capillary : Convenient platform for rapid analysis and detection

Advantages

- act as a mechanical support for the optically sensitive layer
- represents an optical waveguide structure
- suitable for real-time continuous flow analysis
- requires very small volume of analyte

Characterisation

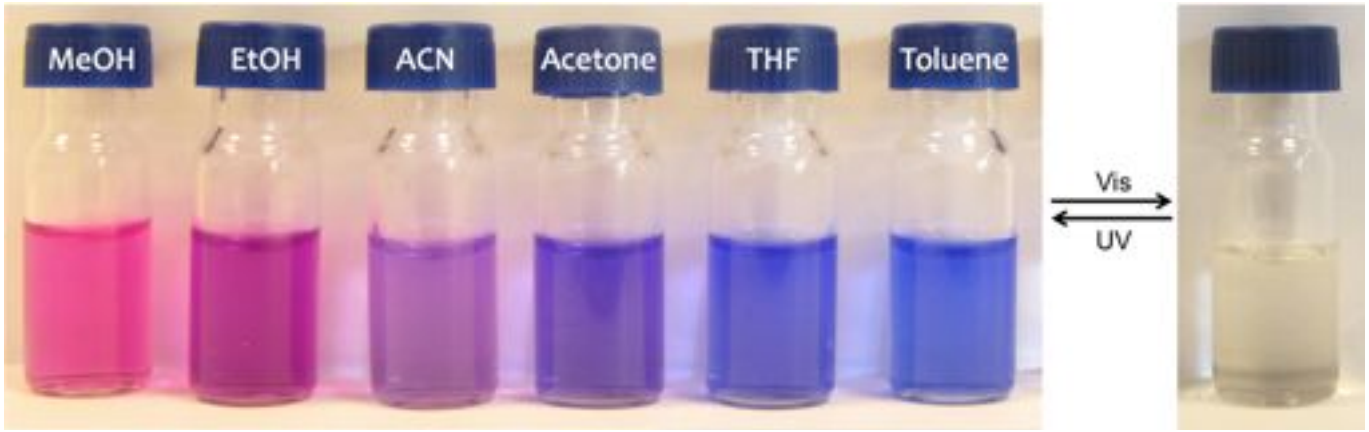




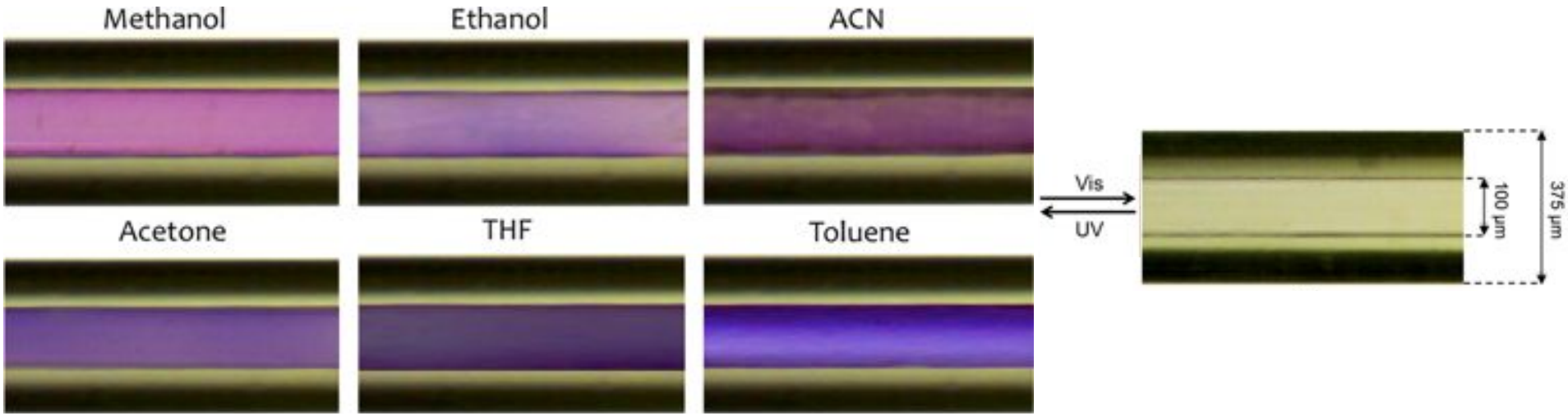
L. Florea, A. Hennart, D. Diamond and F. Benito-Lopez, *Sens. Actuators B: Chem.*, 2012, 175, 92-99.

Solvatochromic Behaviour

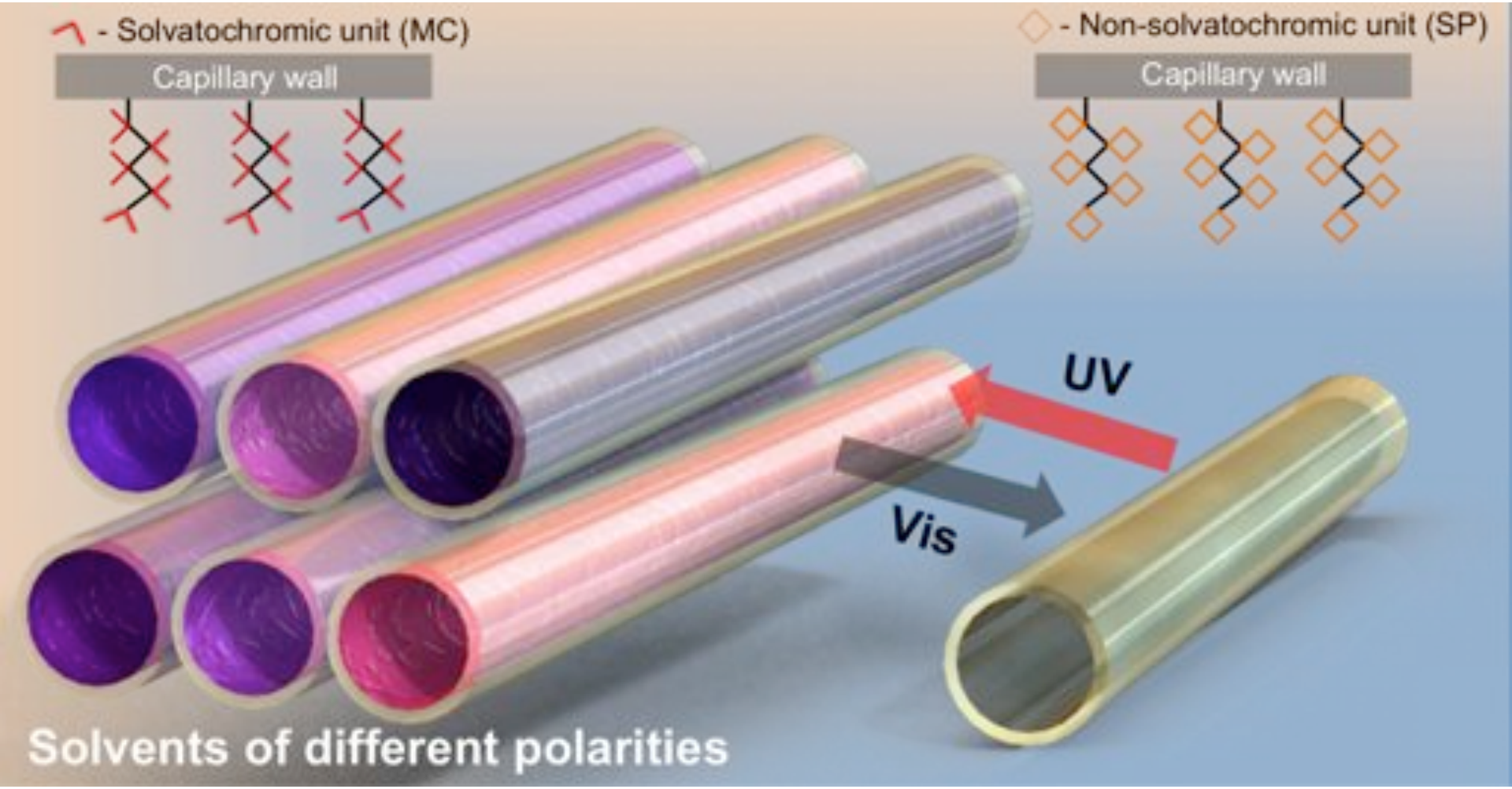
➢ In solution



➢ Polymeric brushes

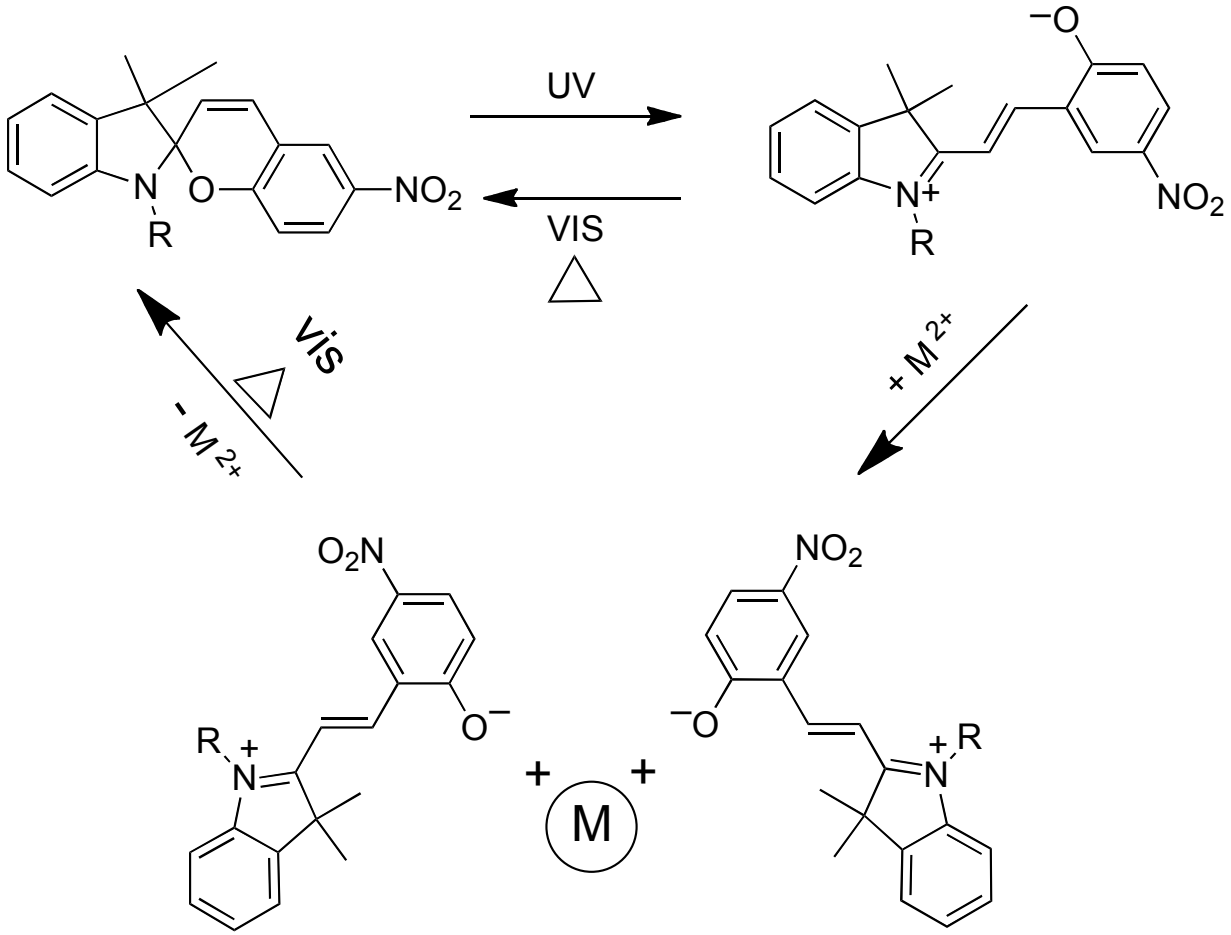


Solvatochromic Behaviour



L. Florea, A. McKeon, D. Diamond and F. Benito-Lopez, *Langmuir*, 2013, 29, 2790-2797.

Metal ions sensing, binding and releasing

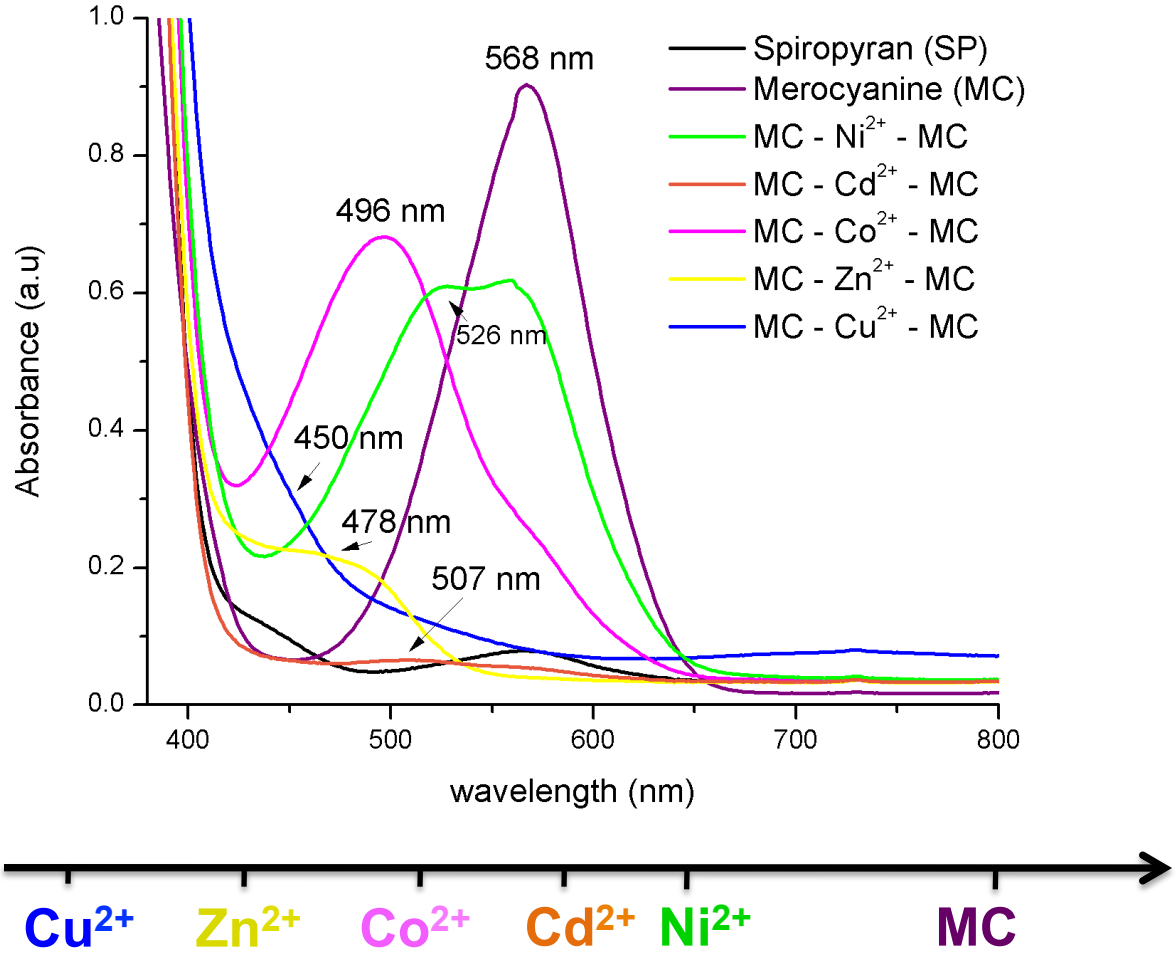


Metal ions sensing binding and releasing

I. Solution studies

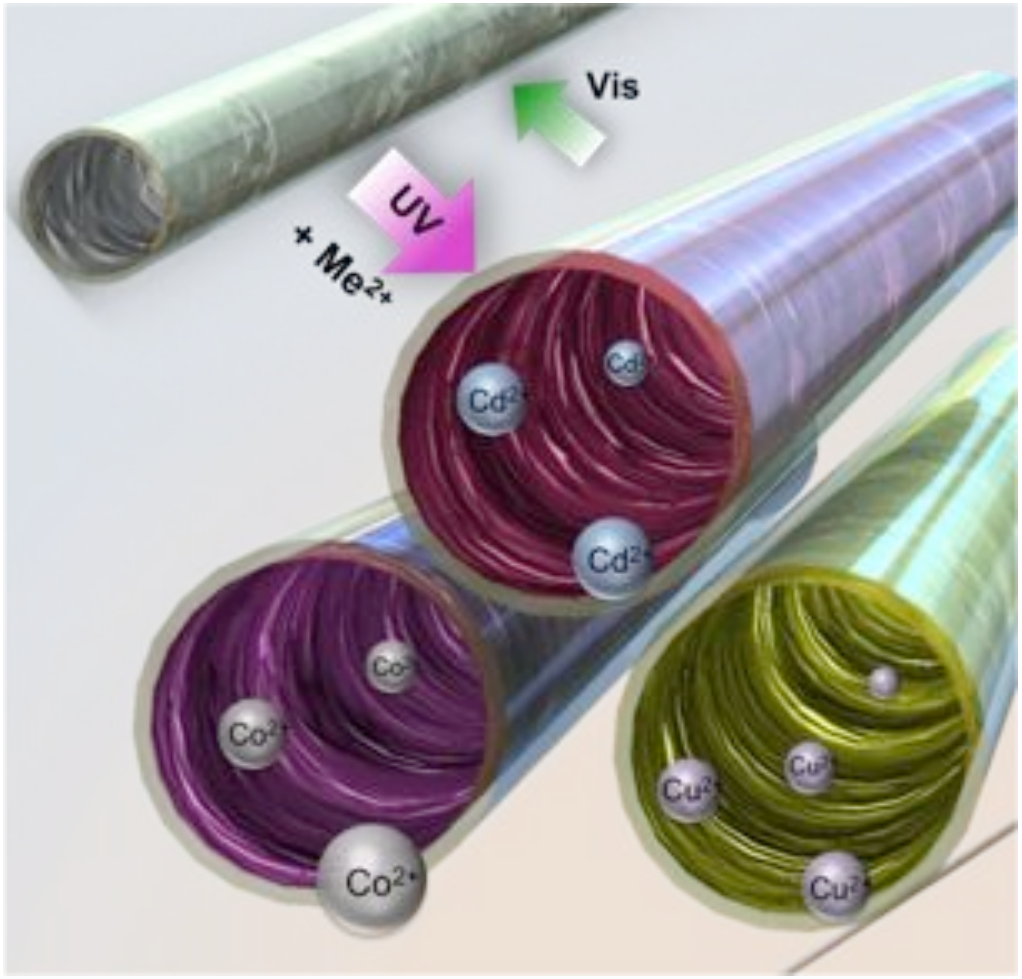
Metal ions sensing binding and releasing

I. Solution studies



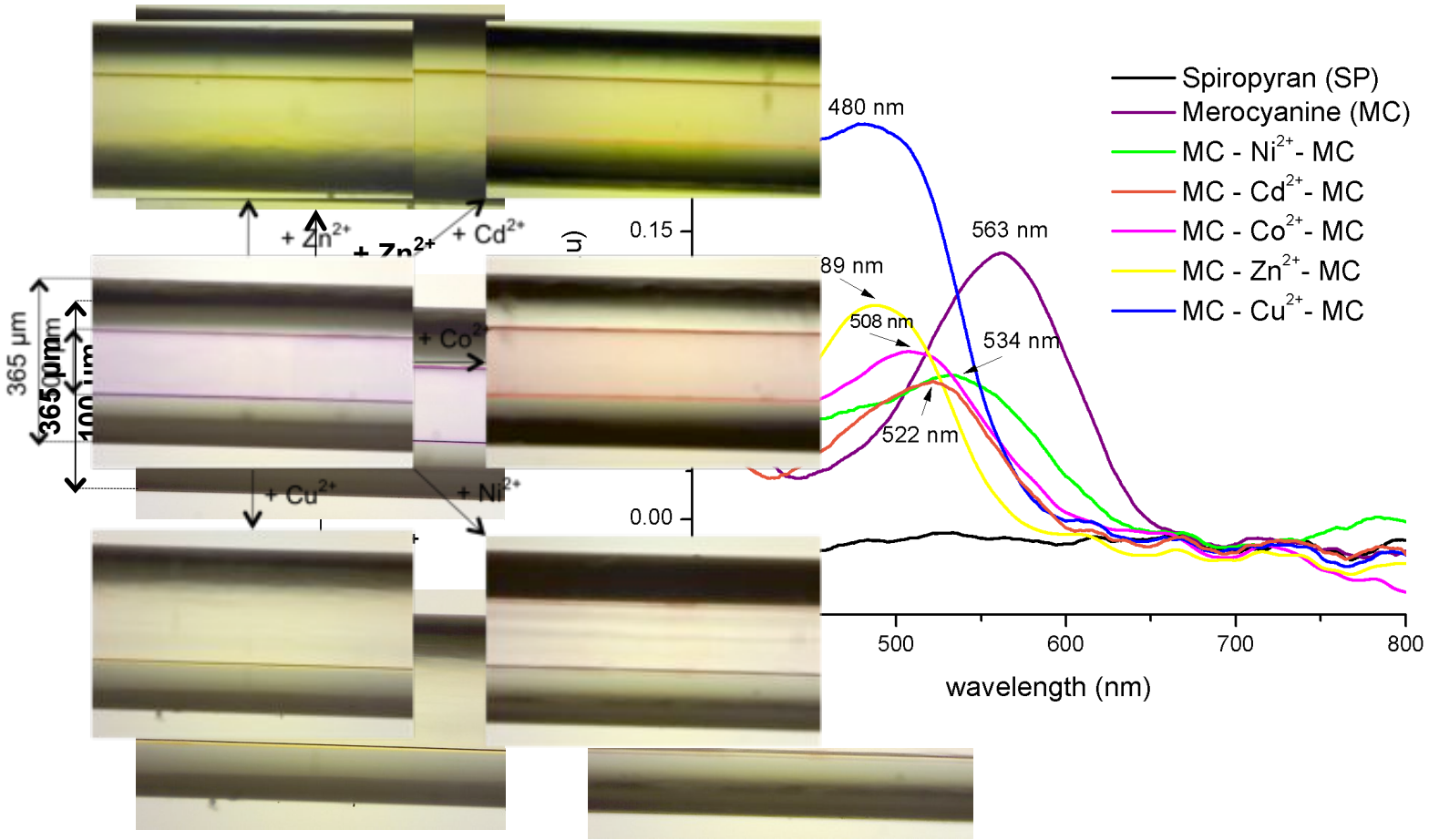
	Wavelength (nm)
MC	568
MC-Ni^{2+}	526
MC-Cd^{2+}	507
MC-Co^{2+}	496
MC-Zn^{2+}	478
MC-Cu^{2+}	450

Metal ions sensing, binding and releasing



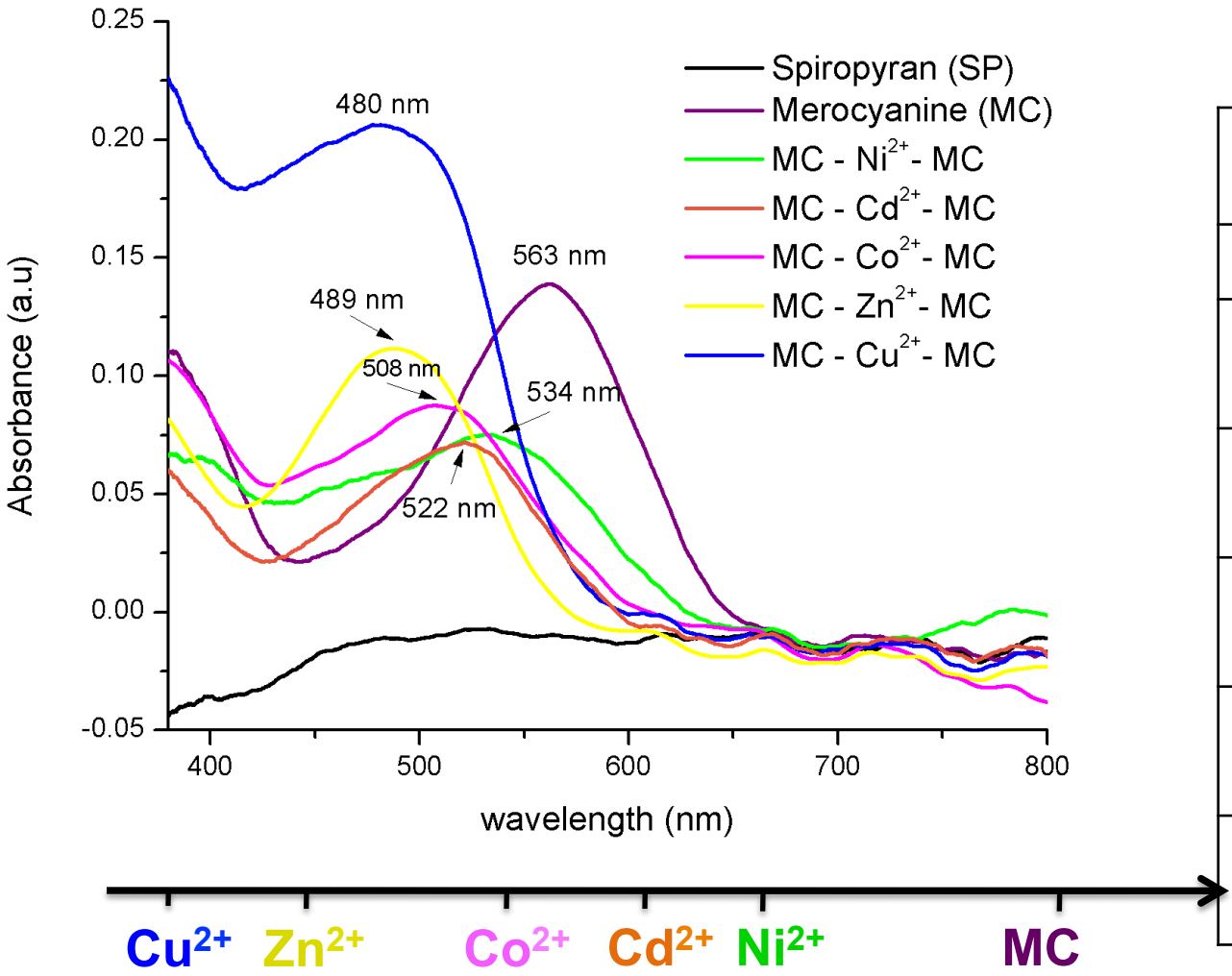
Metal ions sensing binding and releasing

II. Capillary coatings



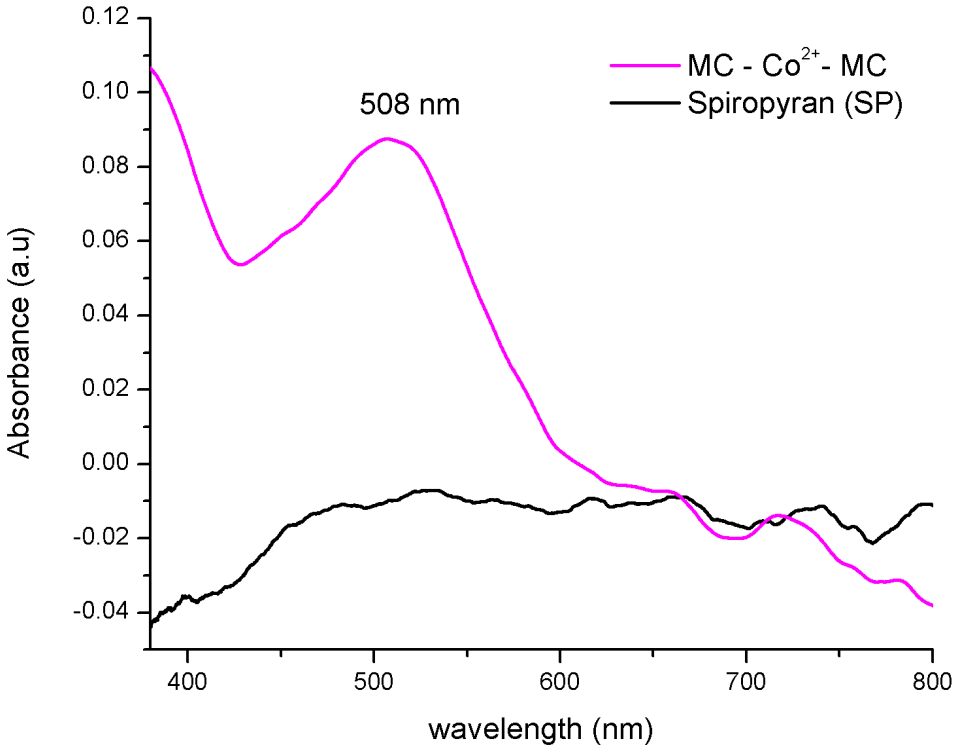
Metal ions sensing binding and releasing

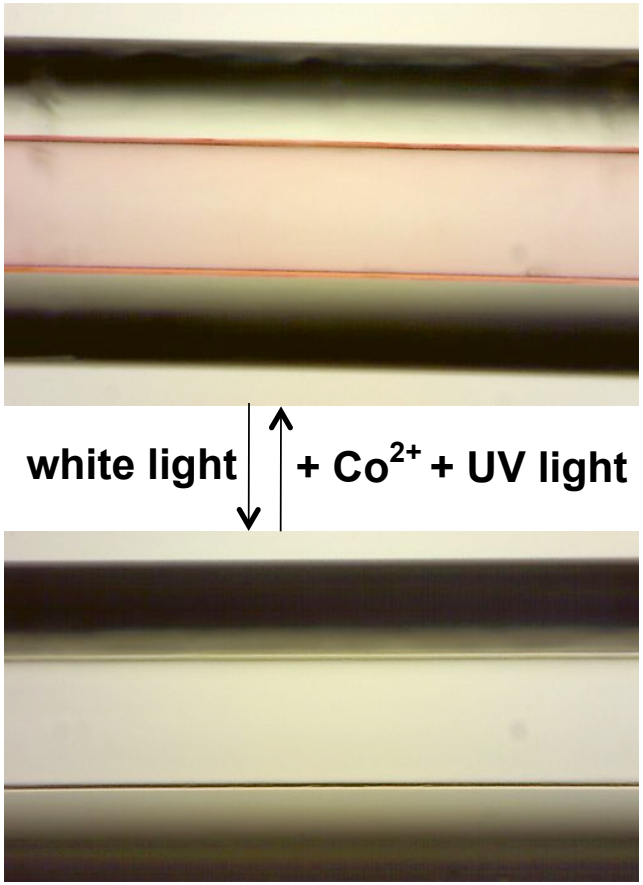
II. Capillary coatings



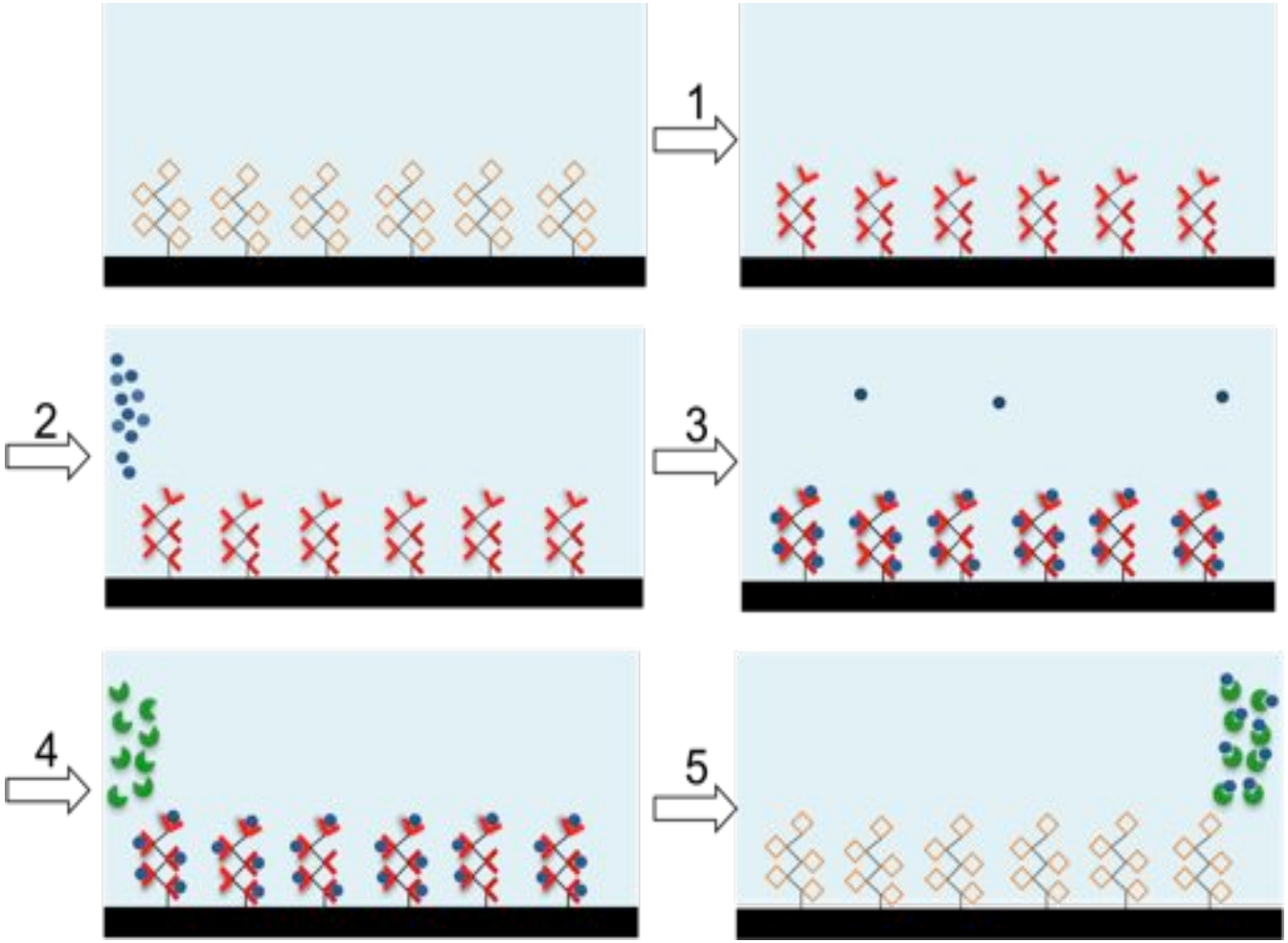
	Wavelength (nm)
MC	563
MC-Ni^{2+}	534
MC-Cd^{2+}	522
MC-Co^{2+}	508
MC-Zn^{2+}	489
MC-Cu^{2+}	480

Metal ions binding and releasing





Quantitative binding



Non binding form

Binding form

Cu^{2+}

PADAP

Binding capacity: ~$7x10^{-8}$ Cu^{2+} mole/ mm^3 coating.

- **Self-diagnostic for continuous flow device**
- **Solvent detection and divalent metal ion detection in micro-capillaries**
- **Sensing behaviour can be switched on/off remotely using light**

Acknowledgments

- Dr. Cormac Fay
- Wayne Francis
- Aishling Dunne
- Dr. Fernando Benito-Lopez
- Prof. Gordon Wallace
- Prof. Dermot Diamond
- Adaptive Sensors Group
- Insight SFI award

Thank you!