

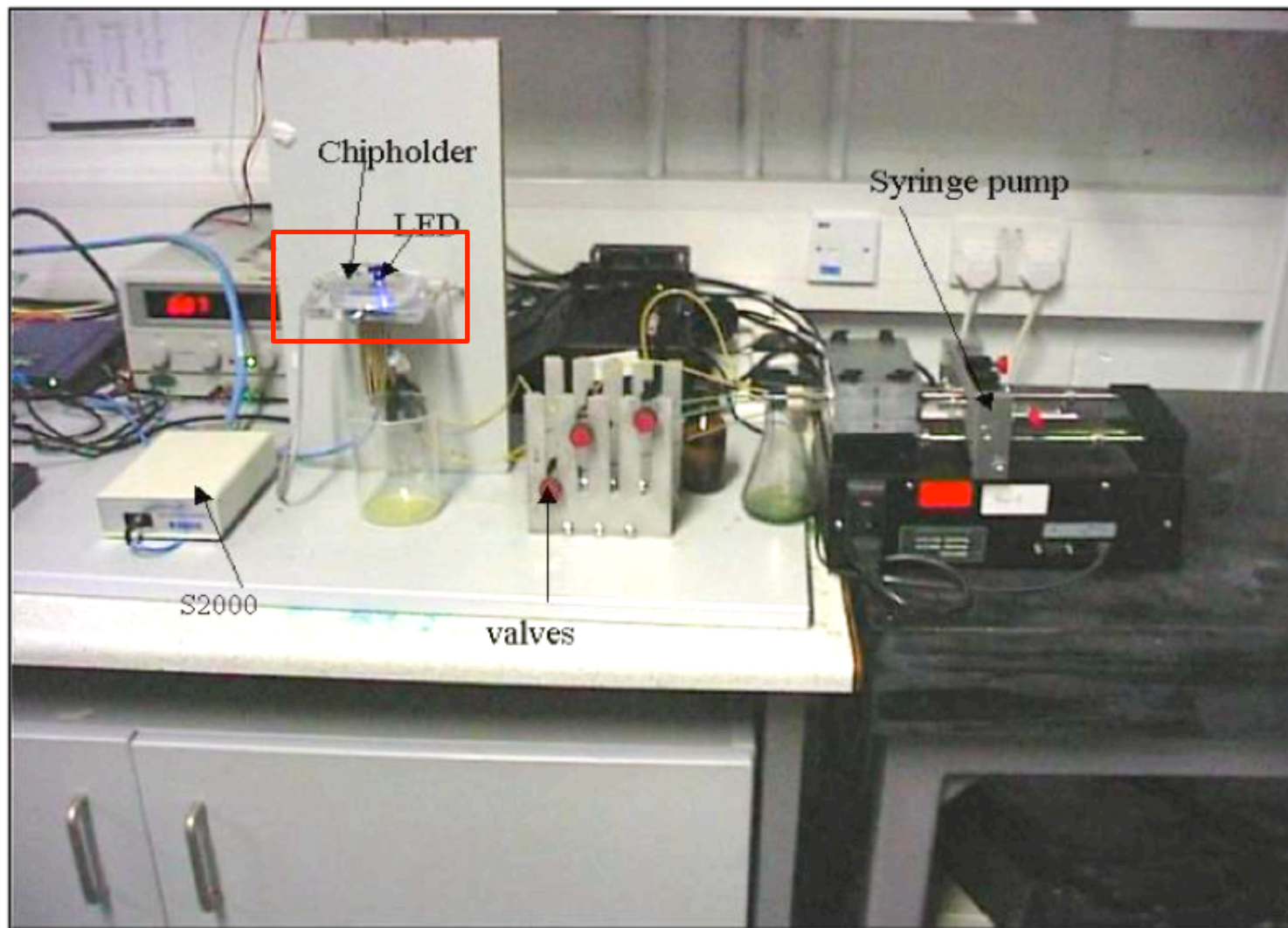


# Stimuli-responsive Materials for Self-reporting Micro-fluidic Devices

Dr. Larisa Florea, Aishling Dunne, Wayne Francis,  
Danielle Bruen, Alexandru Tudor, Dermot Diamond



July 2016

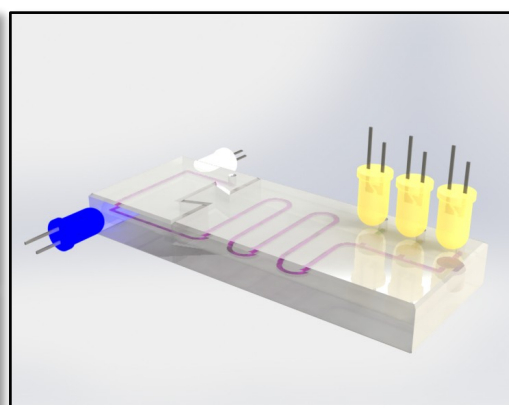
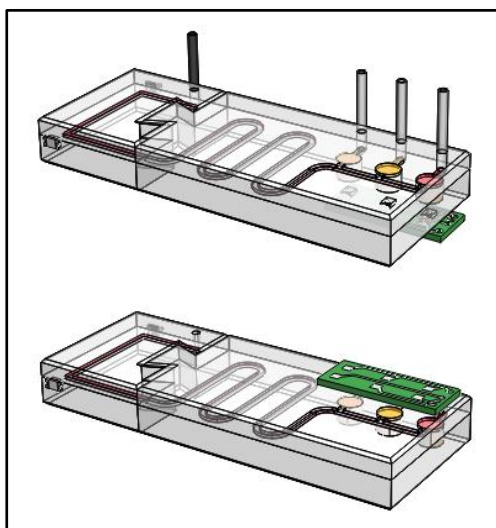
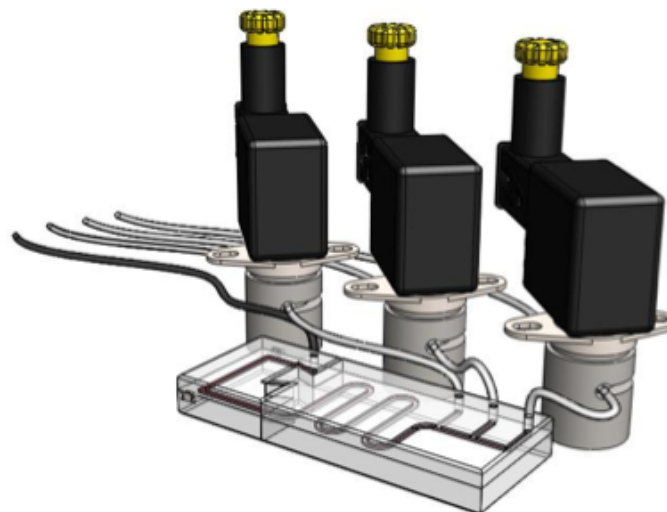
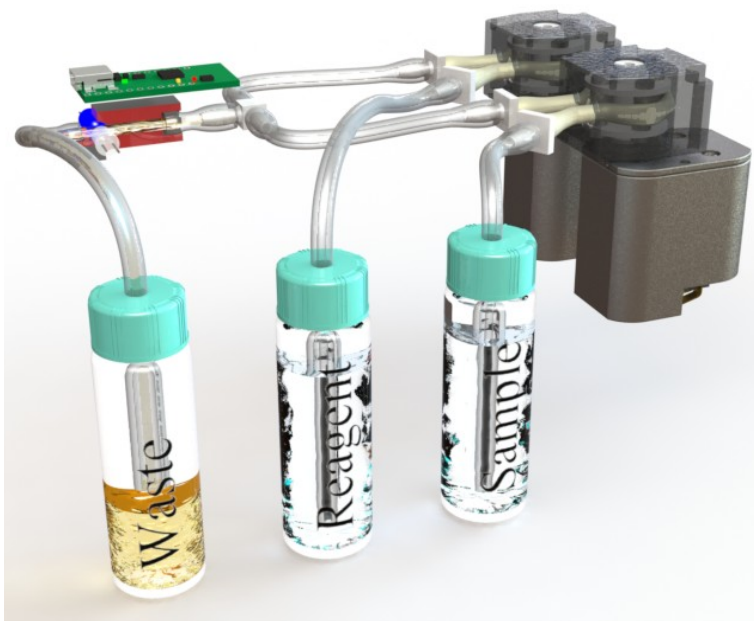


**Chemical Sensing using an Integrated uFluidic System based on Colorimetrics: A Comparative Kinetic Study of the Bertholet Reaction for Ammonia Determination in Microfluidic and Spectrophotometric Systems, A Daridon, M Sequiera, G. Pennarun-Thomas, J Lichtenberg, E Verpoorte, D Diamond and NF de Rooij, Sensors and Actuators B, 76/1-3, (2001) 235-243.**





# Can we go from this:



- Fluidic handling completely integrated into the microfluidic chip





# Stimuli-responsive Materials

**Materials whose characteristics can be changed using an external stimulus**

**Thermal**

**Mechano**

**Photo**

**pH**

**Chemo**





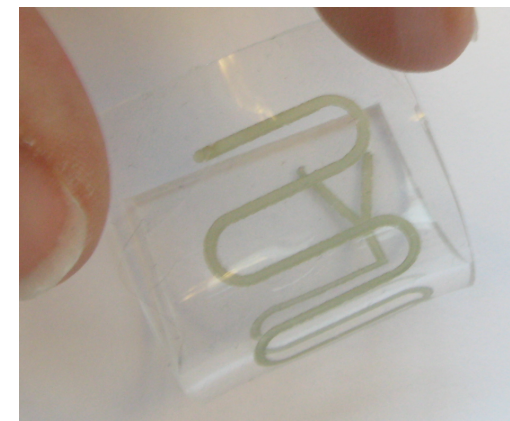
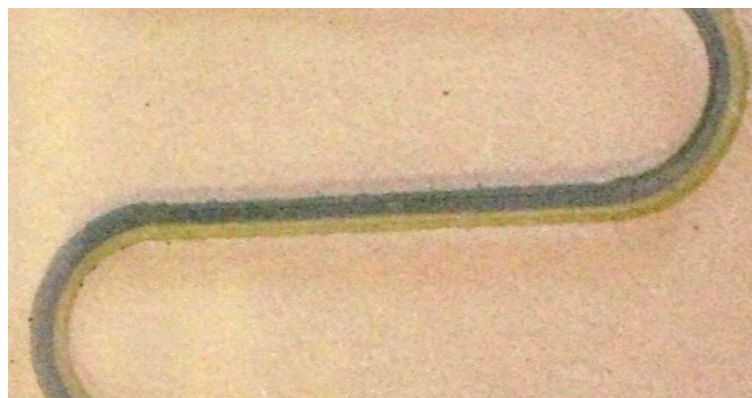
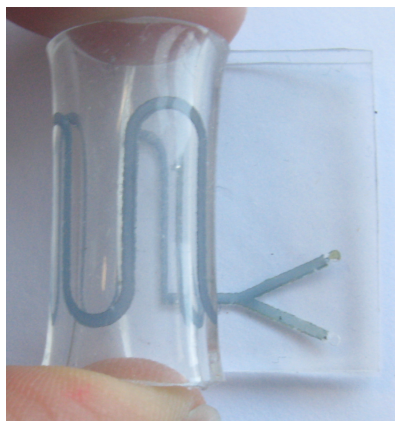
# Stimuli-responsive Materials in Microfluidics

- **smart coatings**
- **photo-modulated surfaces**
- **photo-actuated valves**
- **photo-generated micro-channels**



# 1. Polyaniline functionalised micro-capillaries and micro-fluidic channels

- pH sensing
- ammonia sensing
- diffusion study

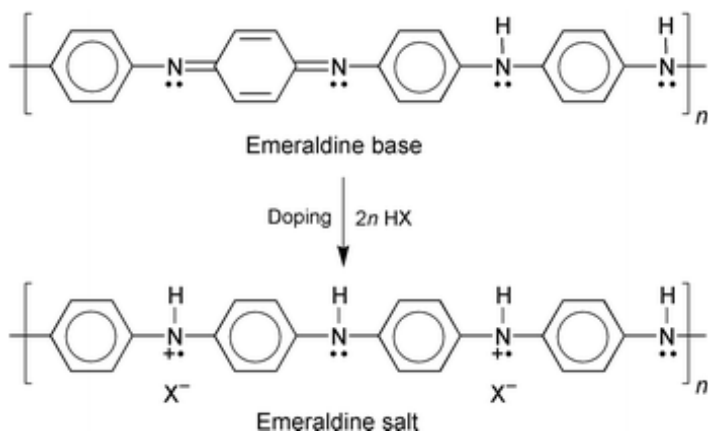






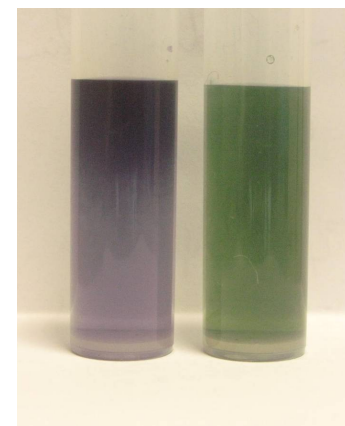
# Polyaniline Nanofibres

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



Insulating State  
Blue/Violet Colour

Conducting State  
Green

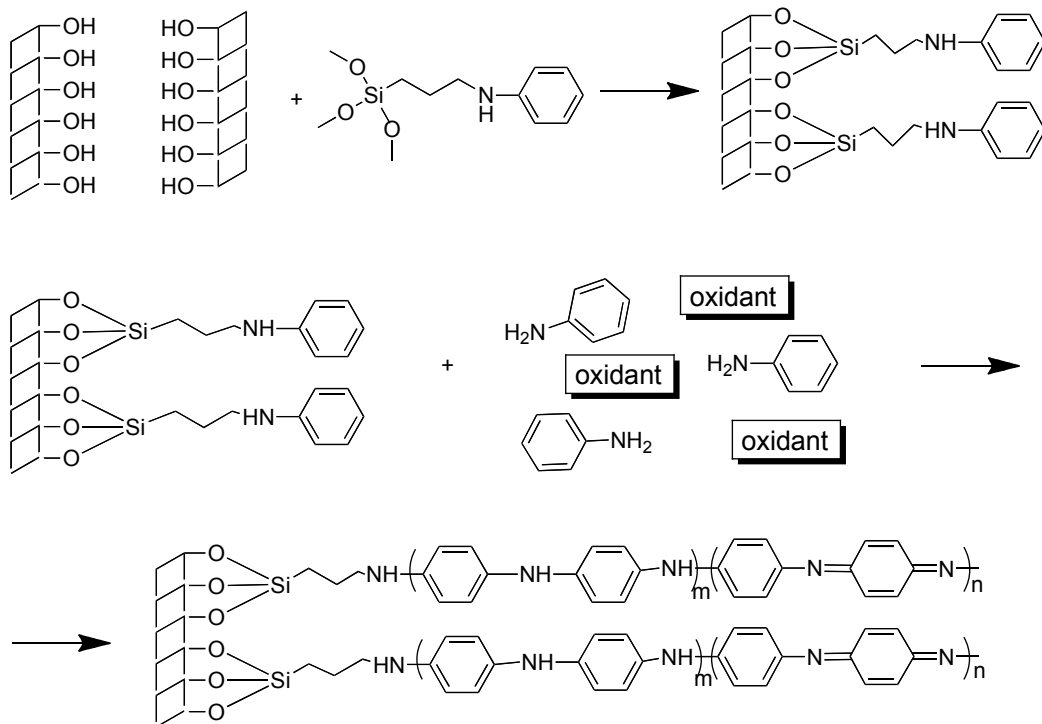


J.X. Huang, S. Viril, B.H. Weller, R.B. Kaner / J.Am.Chem.Soc. 125 (2003), 314-315



# Polyaniline-coated micro-capillaries for ammonia sensing

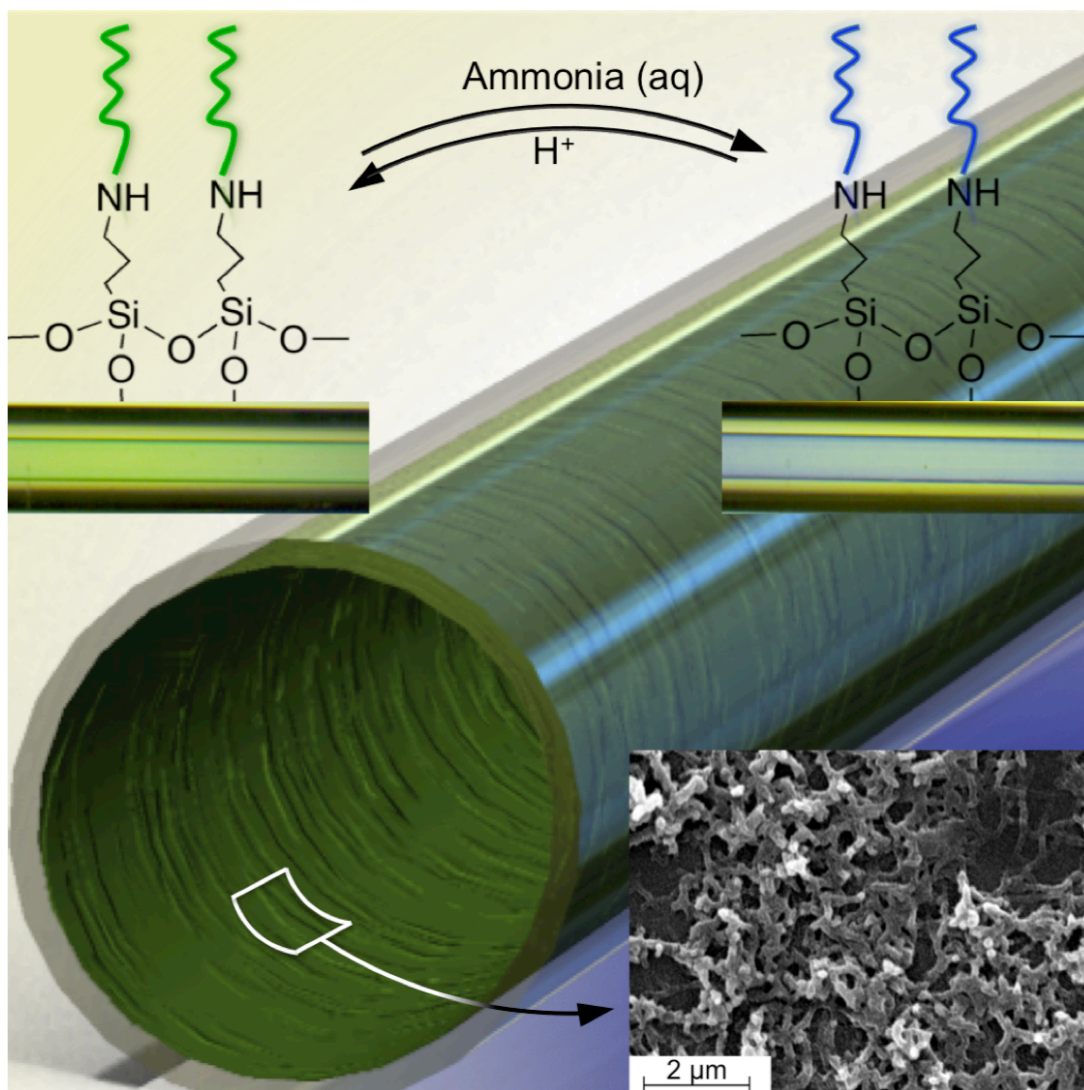
## ➤ Micro-capillary functionalisation



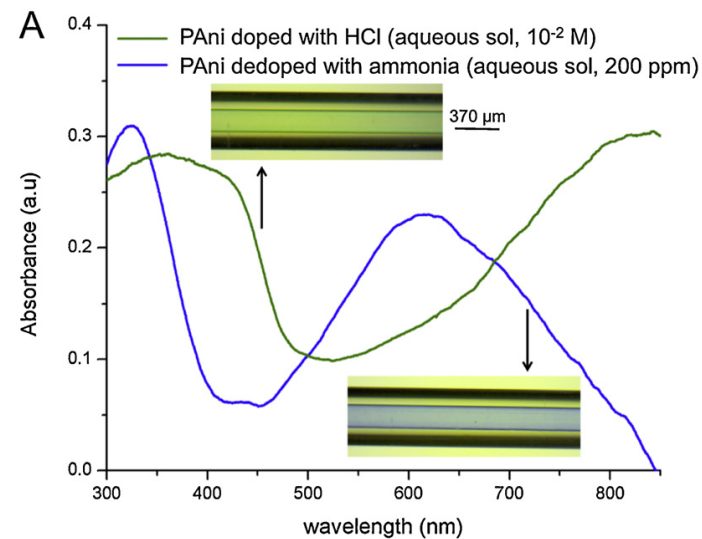
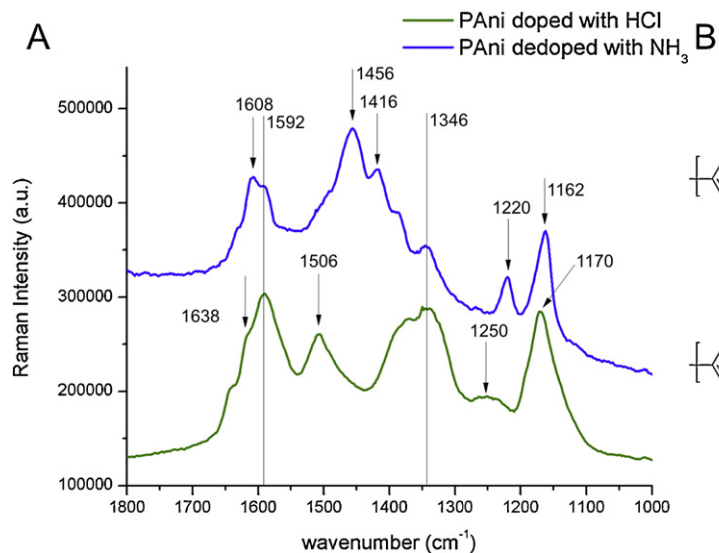
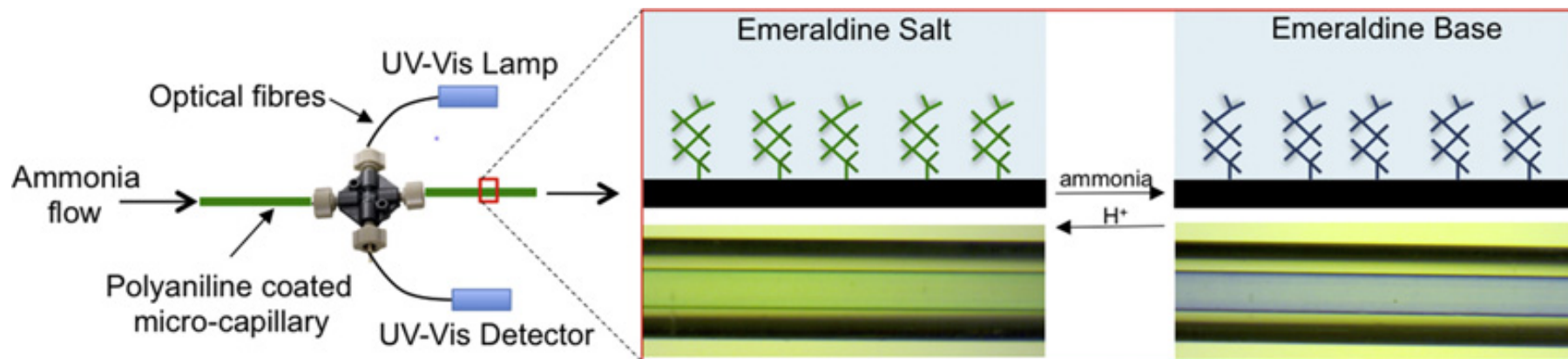
L. Florea, D. Diamond and F. Benito-Lopez, *Anal. Chim. Acta*, 2013, 759, 1-7



# Polyaniline-coated micro-capillaries for ammonia sensing



# Doping dedoping properties

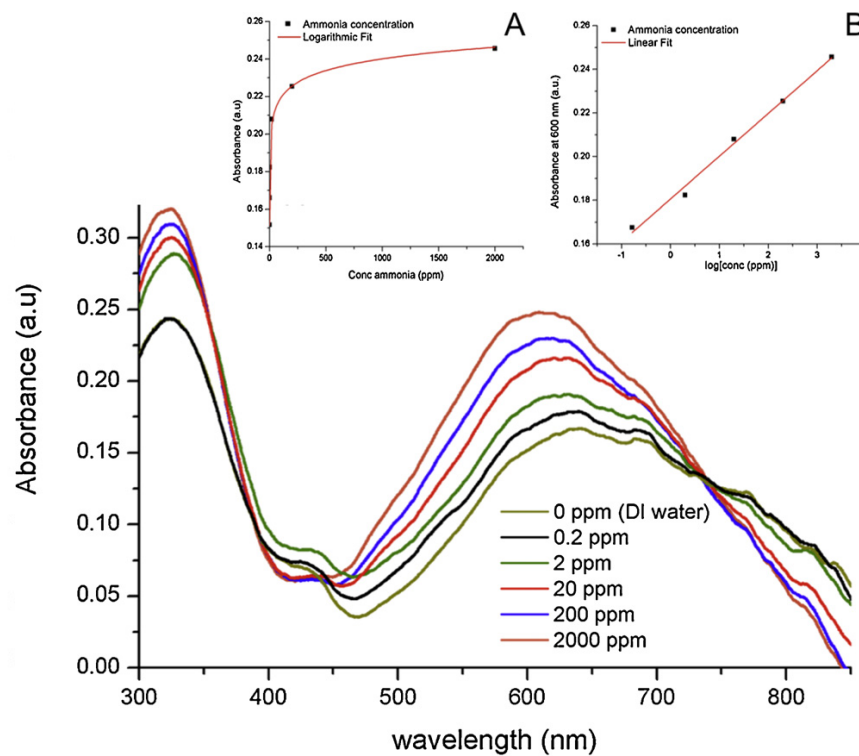
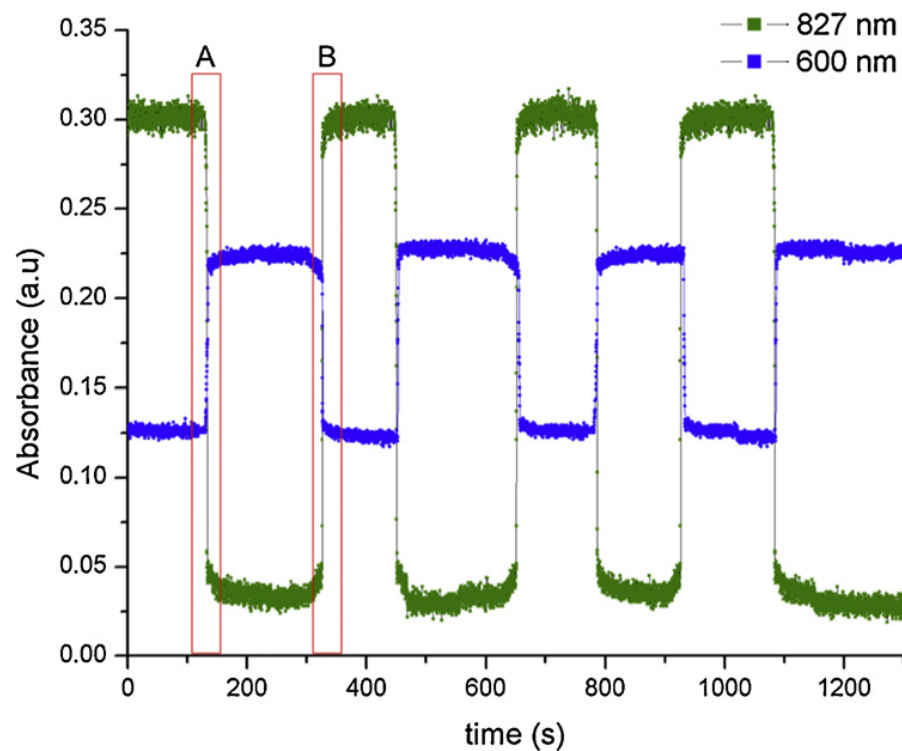


L. Florea, D. Diamond and F. Benito-Lopez, *Anal. Chim. Acta*, 2013, 759, 1-7





# Ammonia sensing

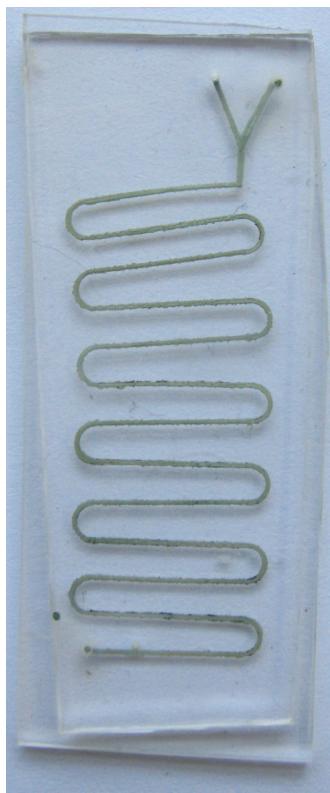


L. Florea, D. Diamond and F. Benito-Lopez, *Anal. Chim. Acta*, 2013, 759, 1-7

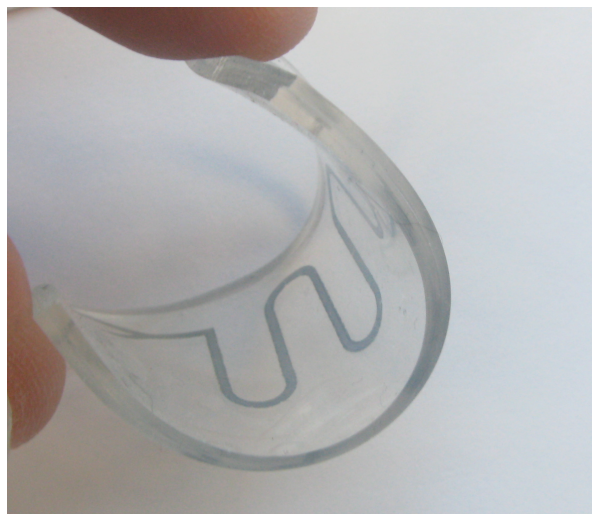


# Micro-channels

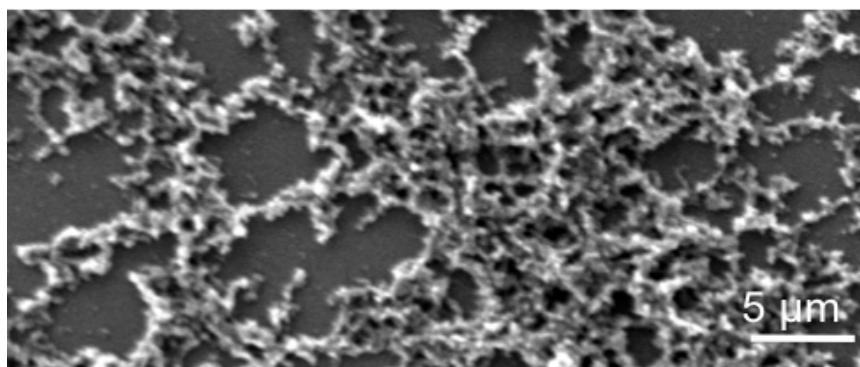
**500 $\mu$ m x 1000 $\mu$ m**



**1000 $\mu$ m x 100 $\mu$ m**

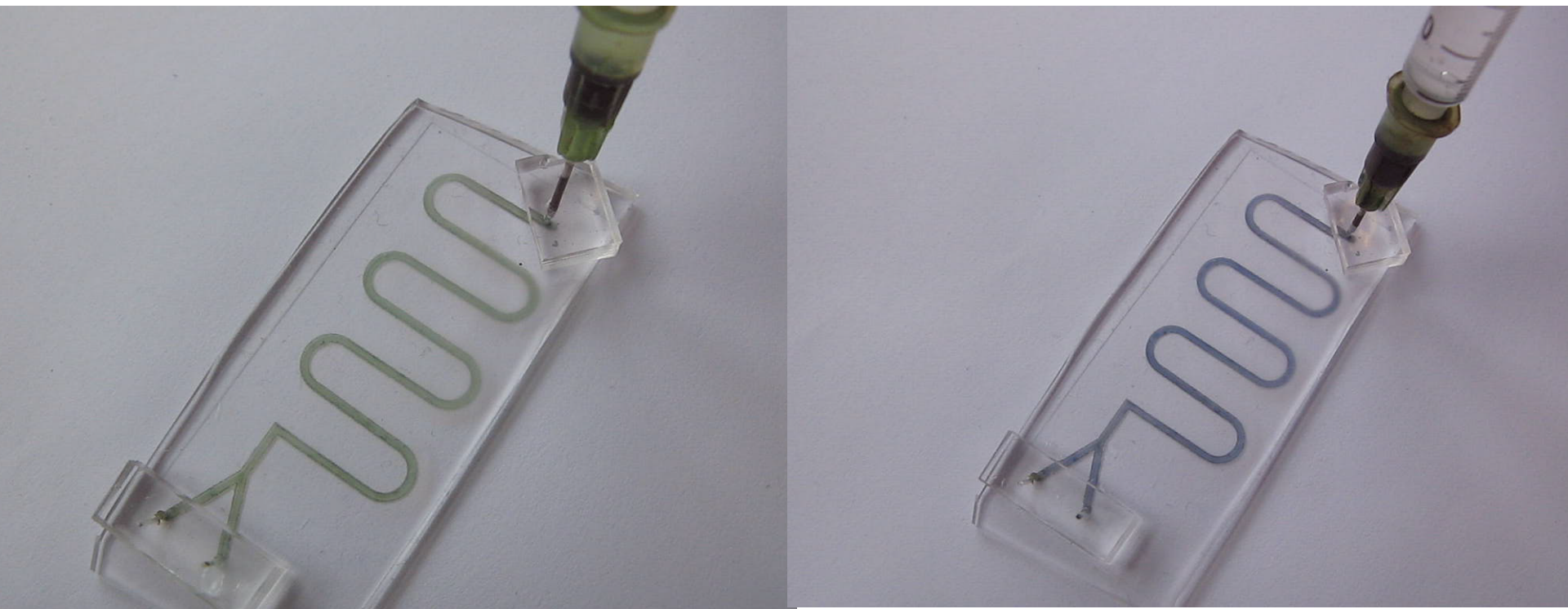


**45 $\mu$ m x 50 $\mu$ m**





# 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.

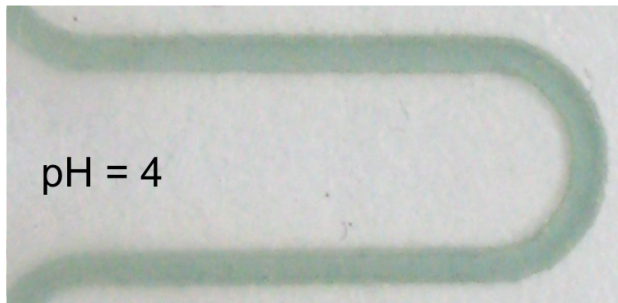




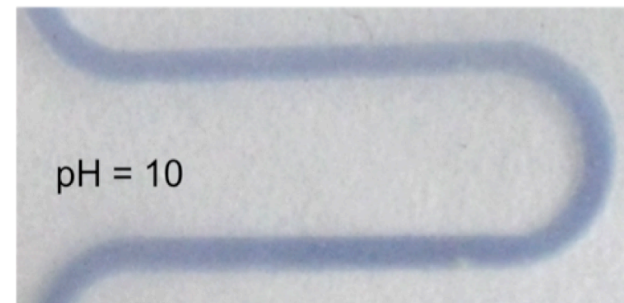
# pH sensing in continuous flow



pH = 2

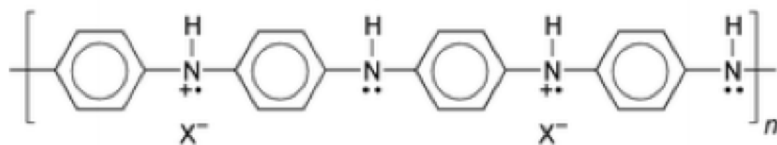


pH = 4

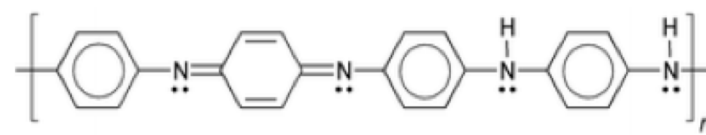
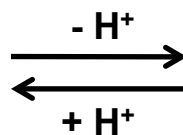


pH = 10

**Dedoping process**



**Emeraldine Salt (ES)**



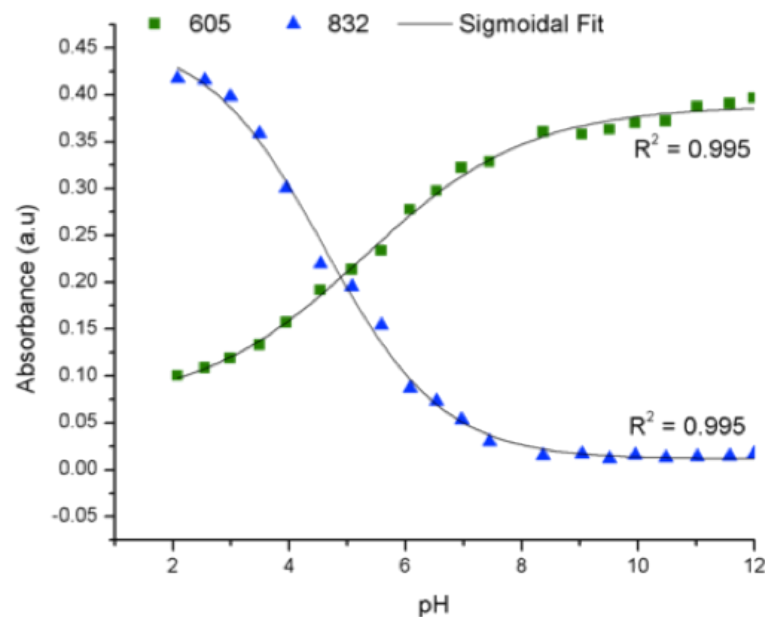
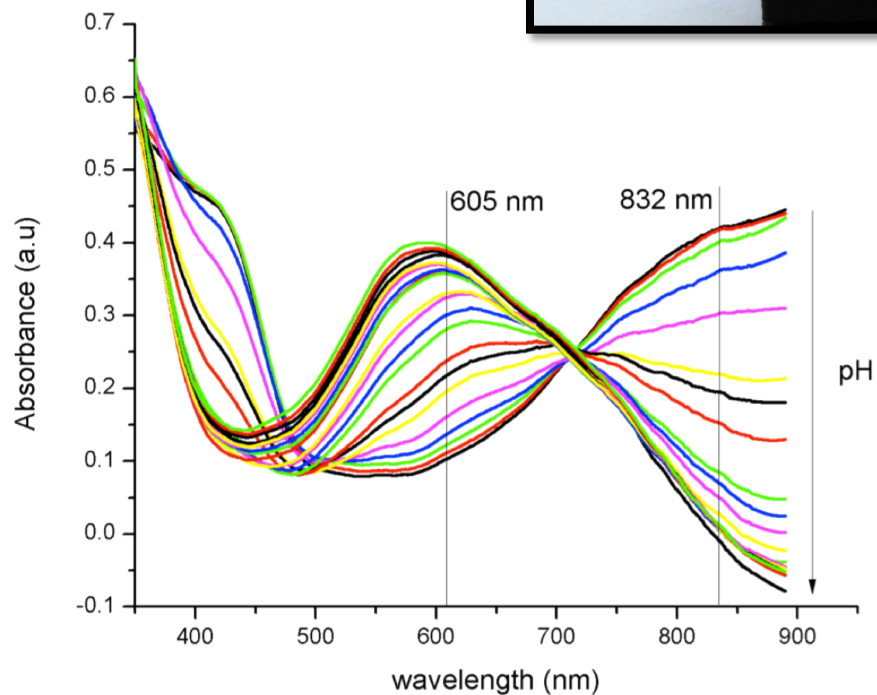
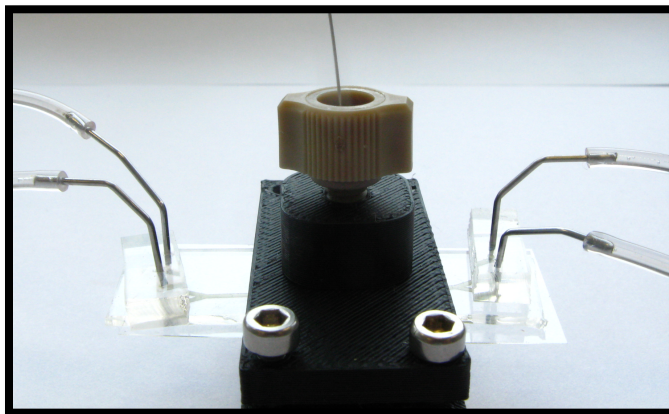
**Emeraldine Base (EB)**

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 continuous flow

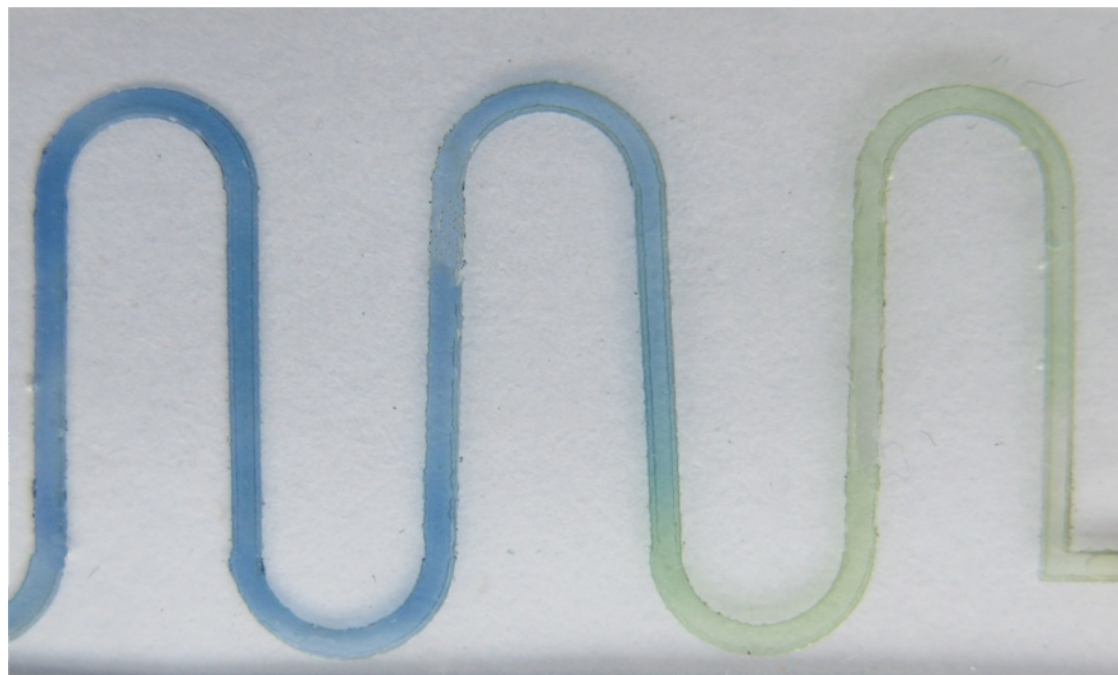


L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.





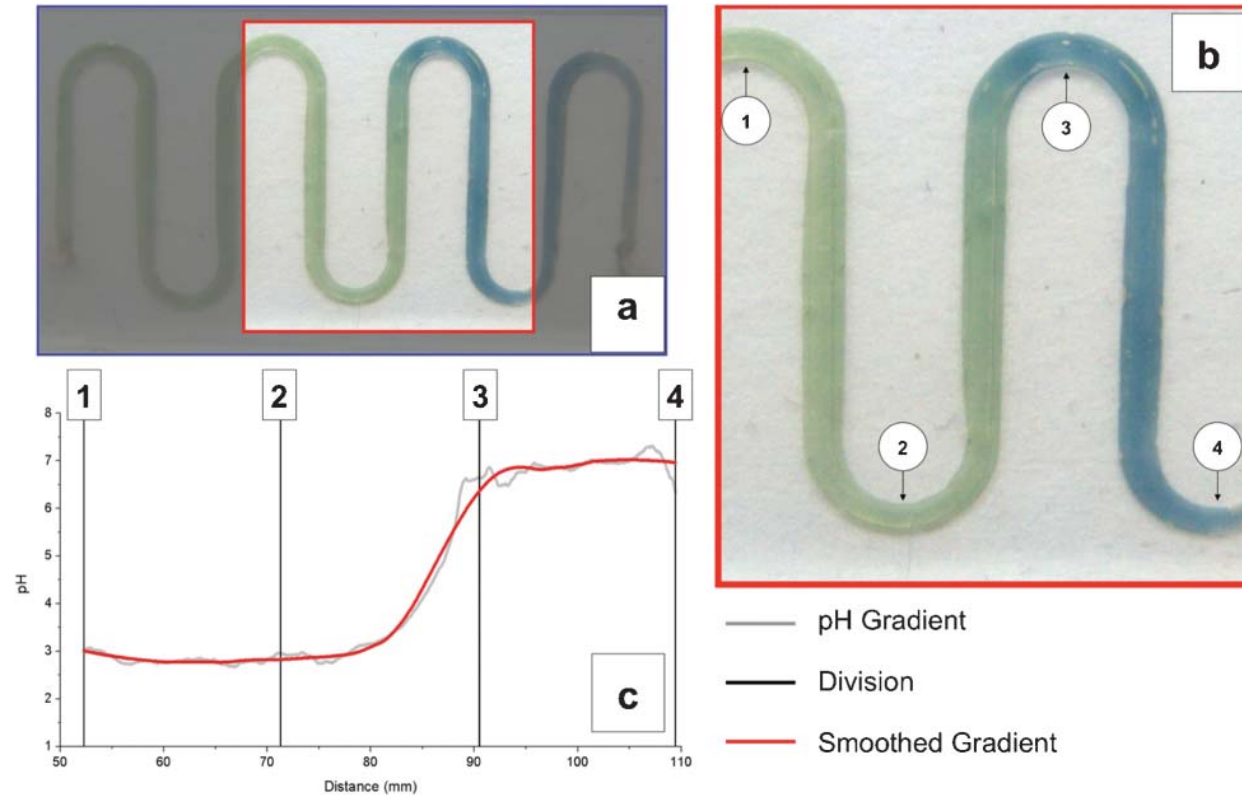
# Dynamic pH sensing



**NaOH  $10^{-2}$  M**

**HCl  $10^{-2}$  M**

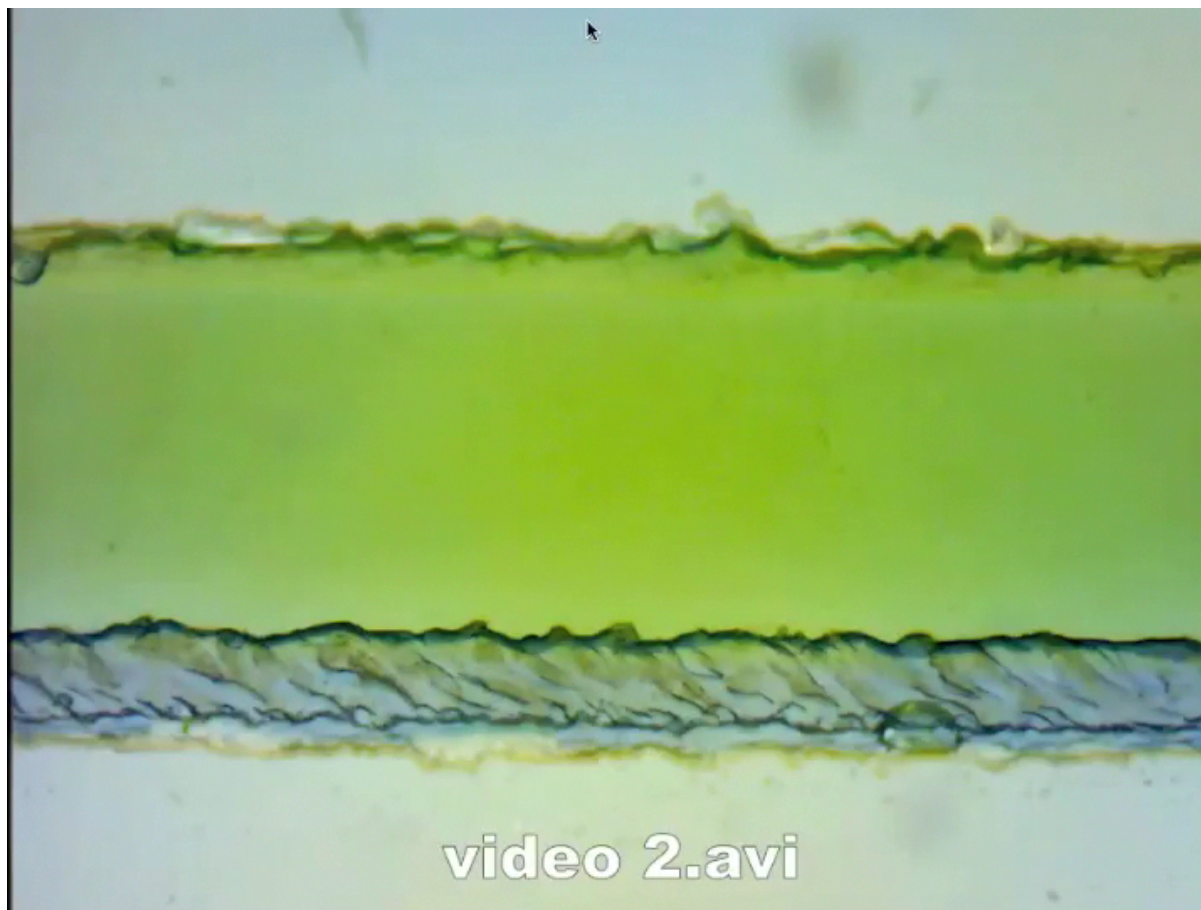




L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.

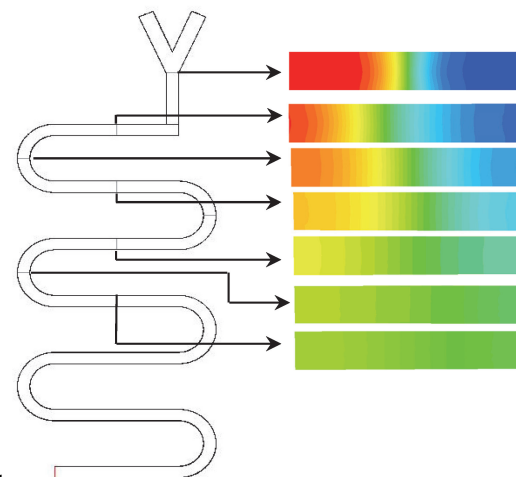
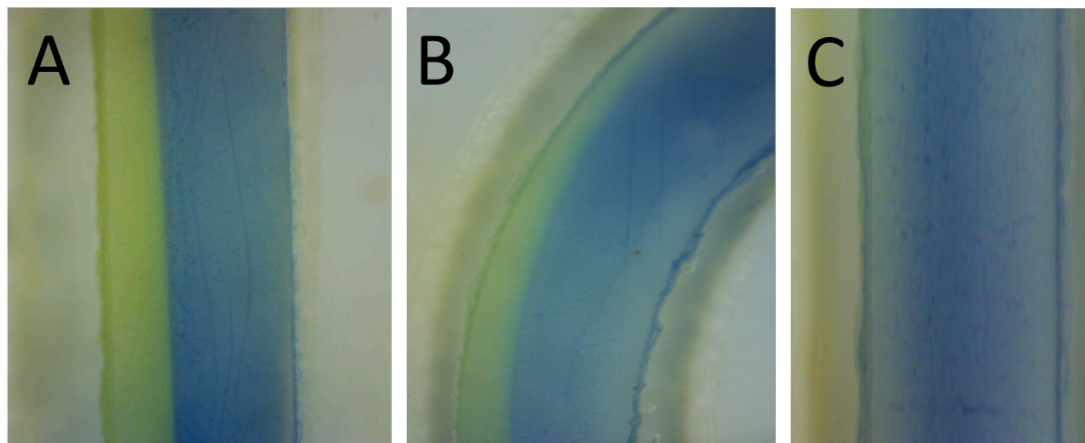
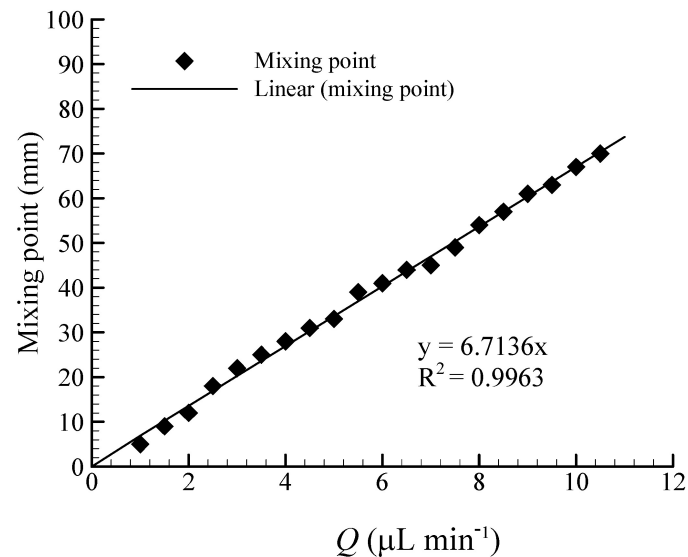
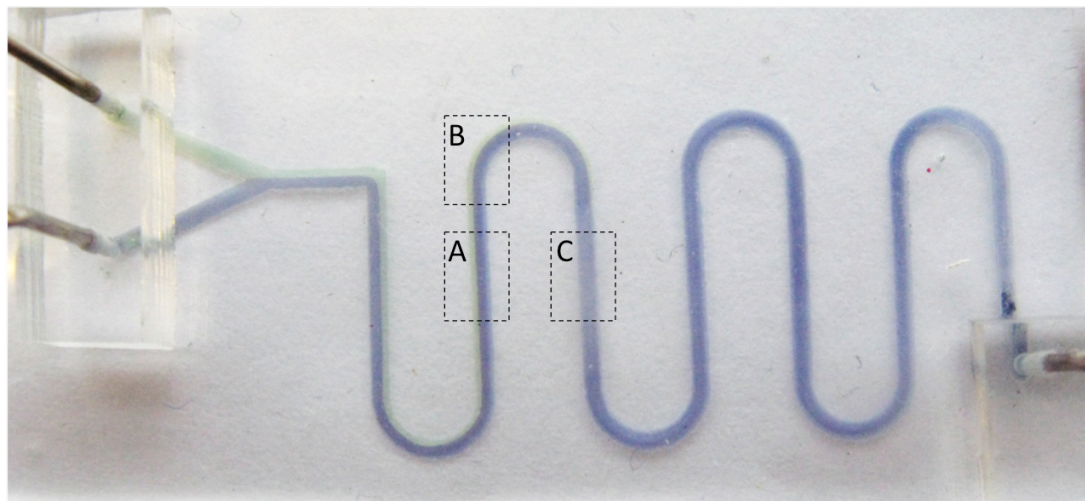


# Study of diffusion process





# Study of diffusion process



Florea, L., Martin-Mayor, A., Bou-Ali, M.M., Meagher, K., Diamond, D., Tutar, M. and Benito-Lopez, F., Sens. Act. B: Chemical 231 (2016): 744-751.

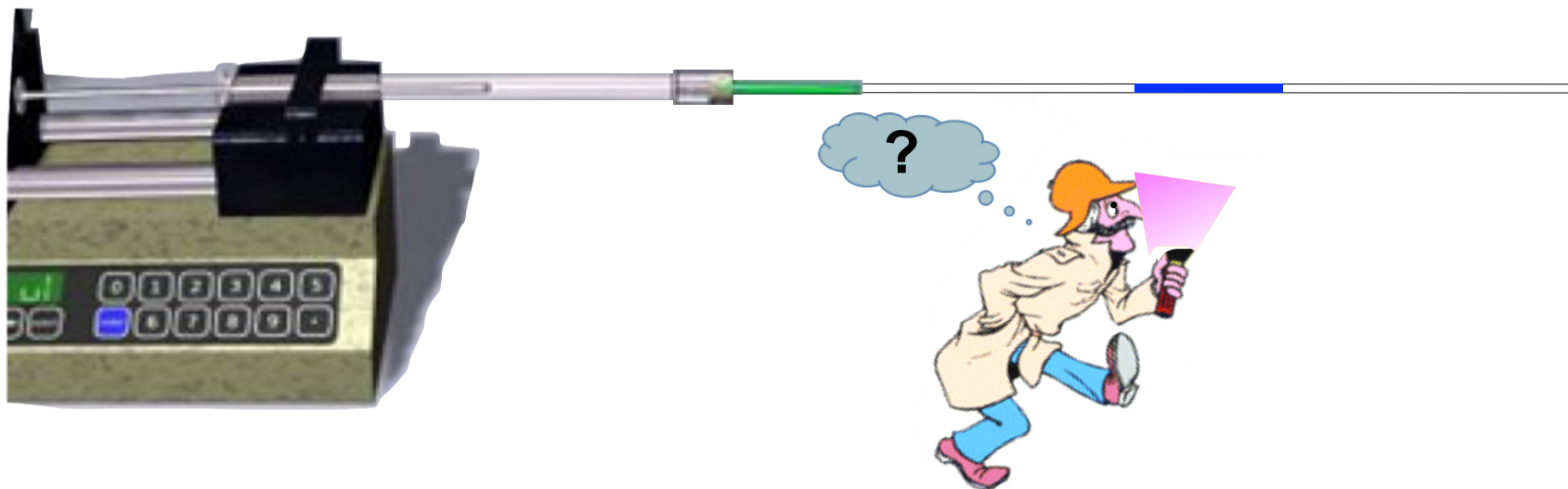






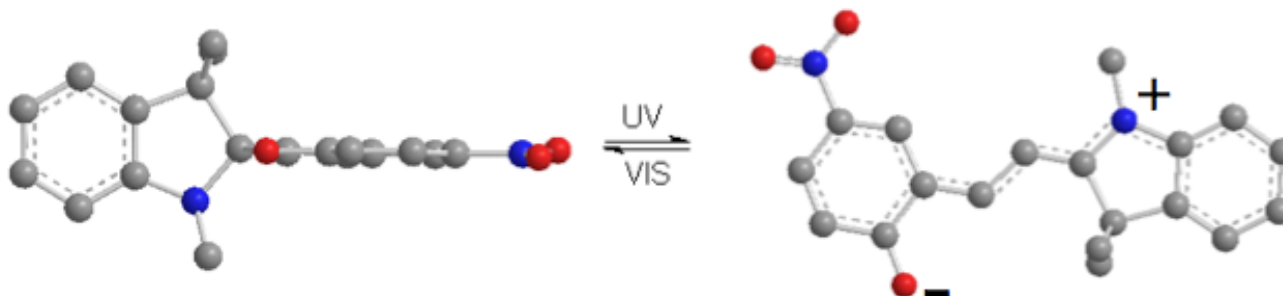
## 2. Spiropyran polymeric brushes functionalised micro-capillaries

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



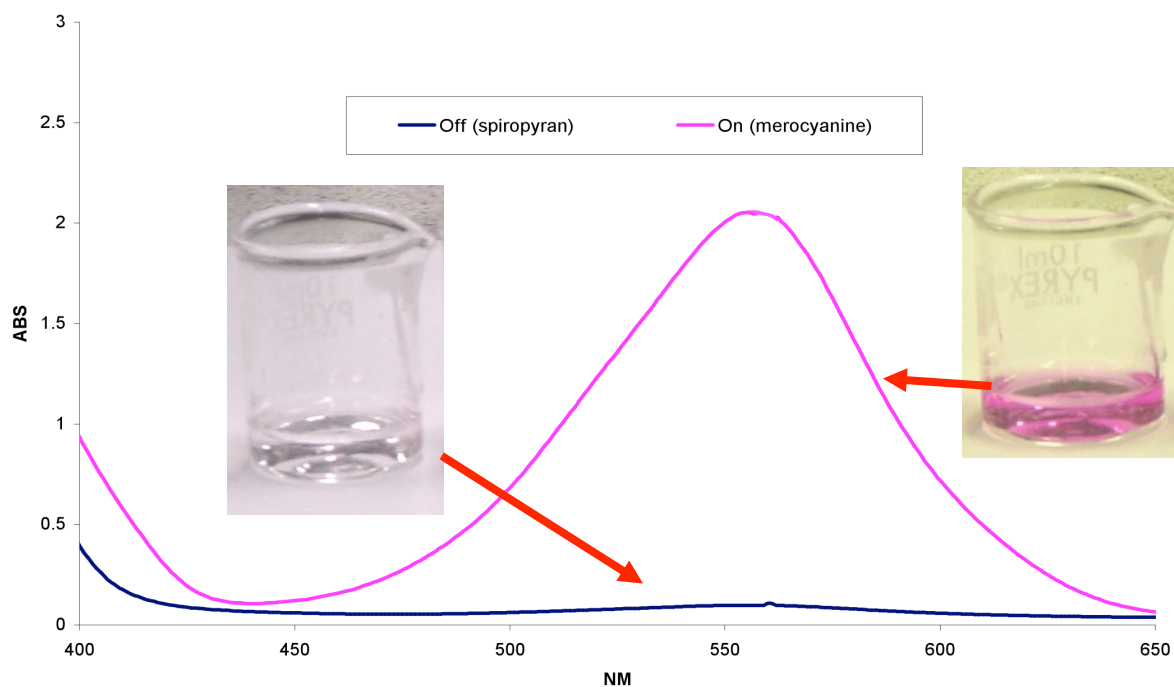


# Spiropyran



**A : Spiropyran SP (closed, colorless)**

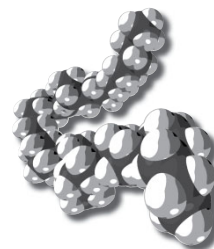
**B : Merocyanine MC (open, colored)**



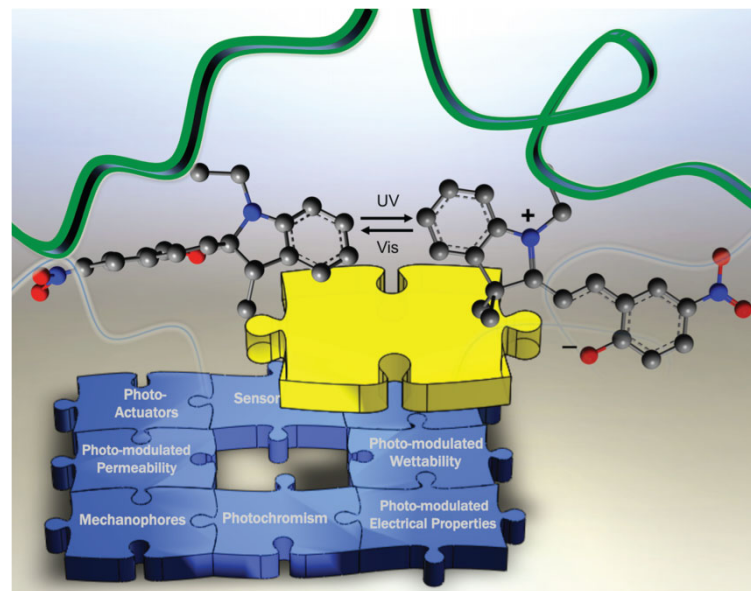
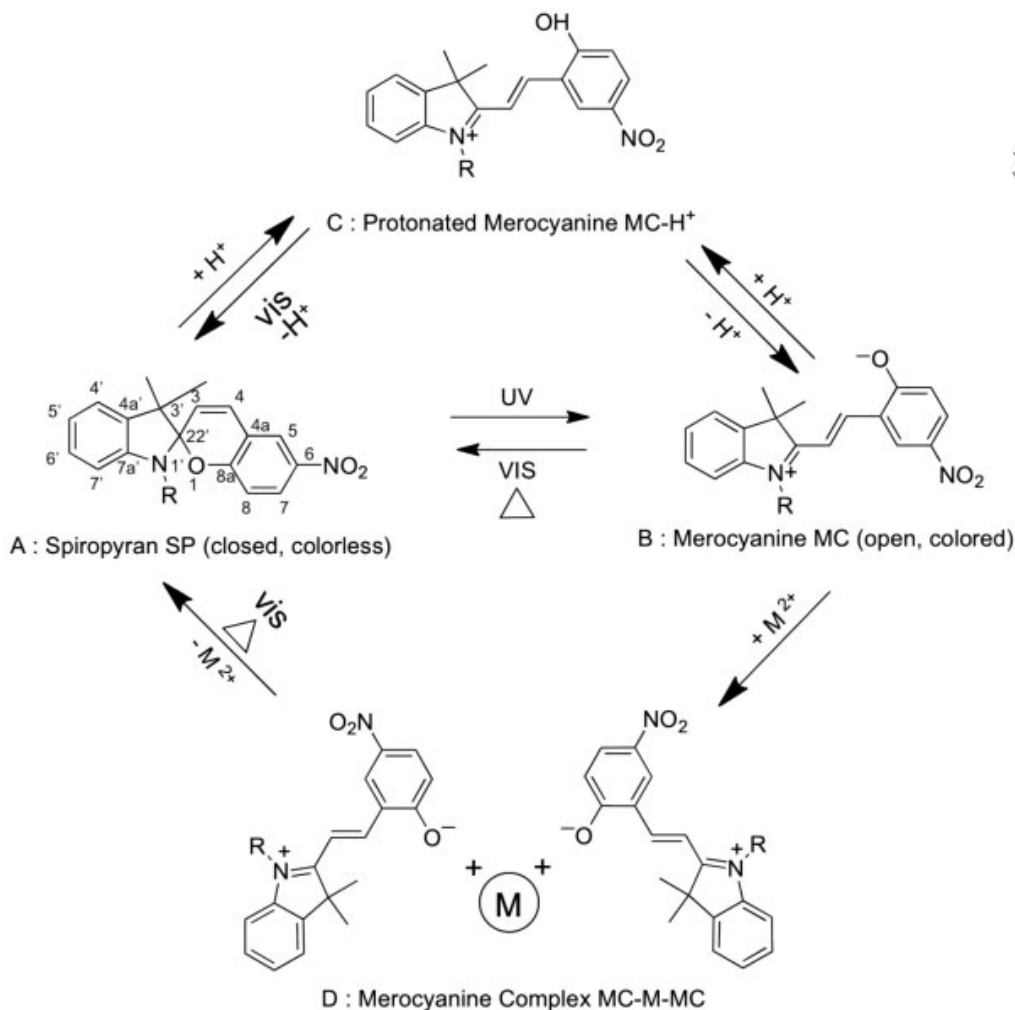
# Spiropyran

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

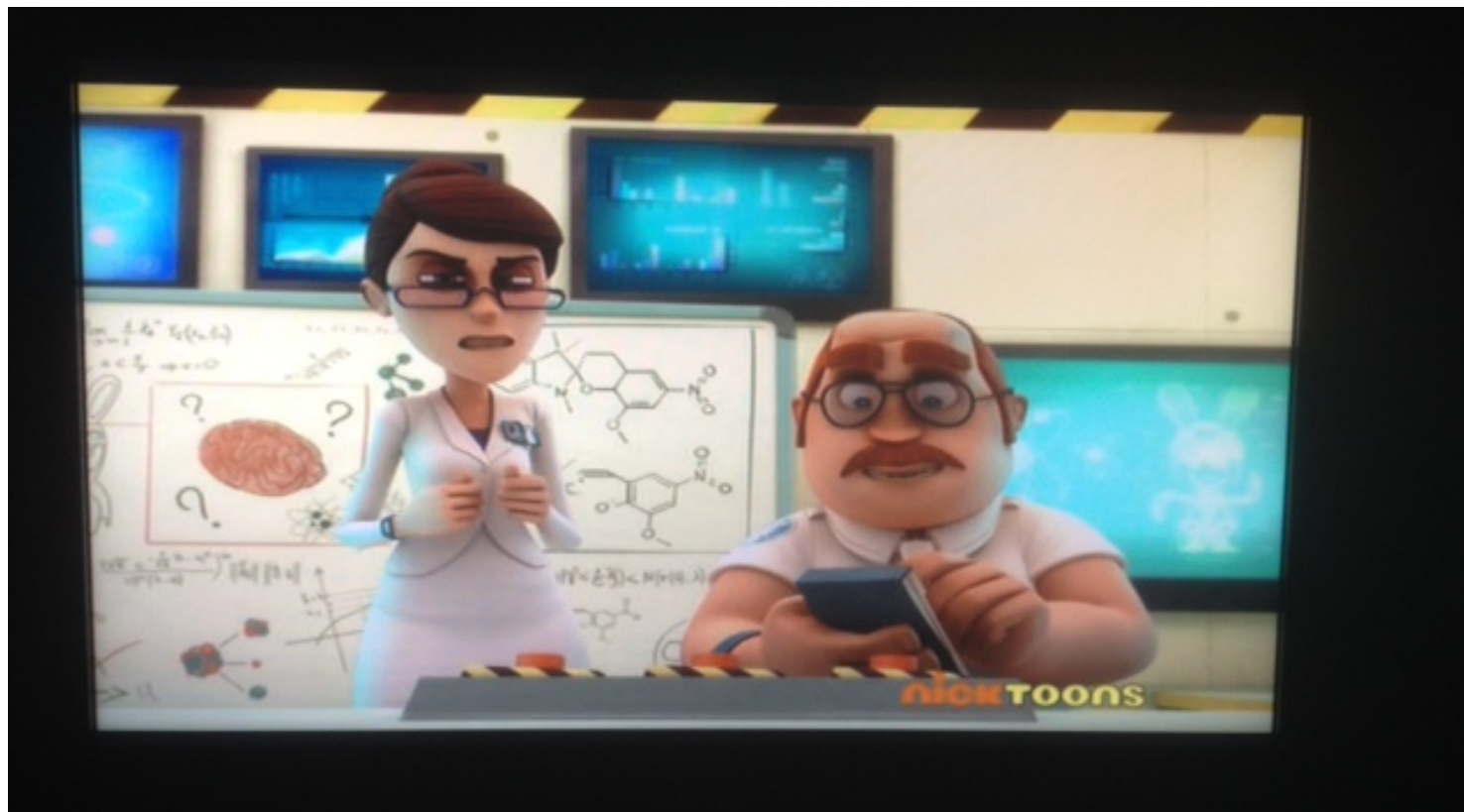
12/2012

WILEY-VCH

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



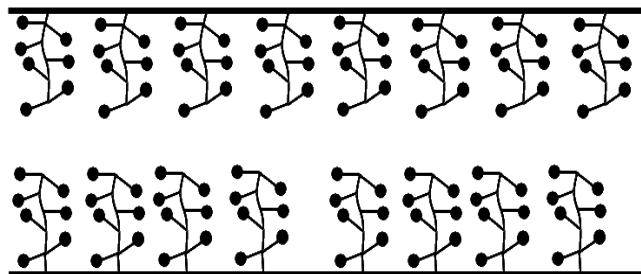
# Famous Molecule....



**Spotted on Nickelodeon Cartoons February 2015**



# Our Approach



↑ - spiropyran molecule

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

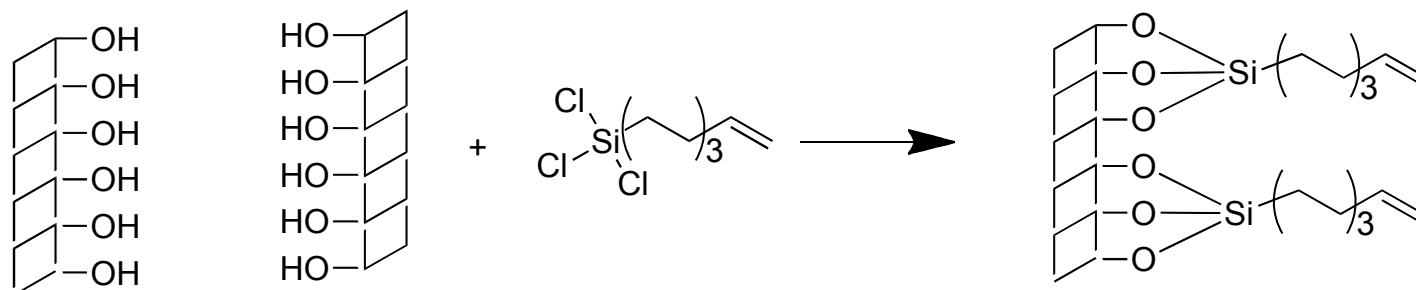
**Micro-capillary : Convenient platform for rapid analysis and detection**

## Advantages

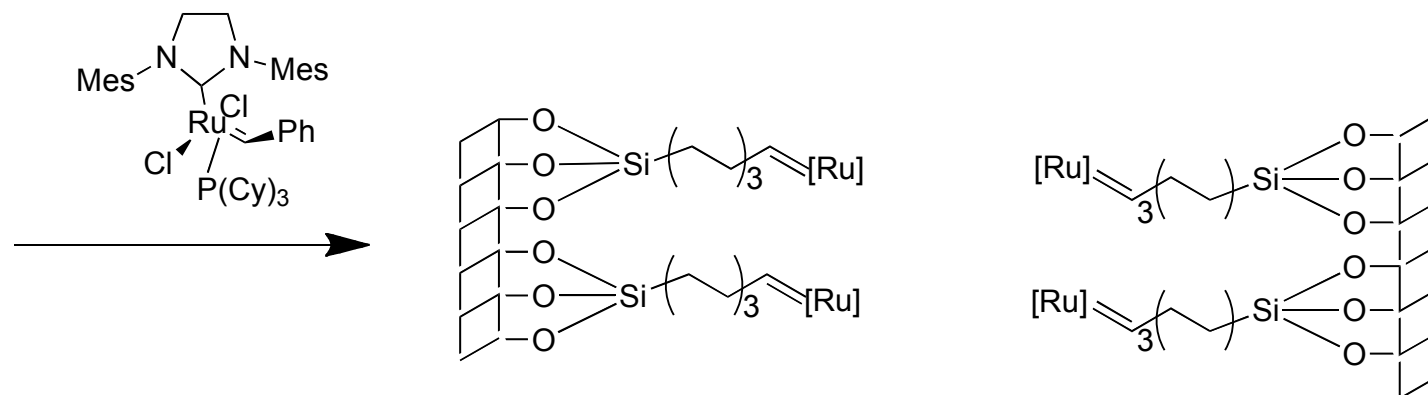
- act as a mechanical support for the optically sensitive layer
- represents an optical waveguide structure
- suitable for real-time continuous flow analysis
- requires very small volume of analyte

# Spiropyran polymeric brushes in micro-capillaries

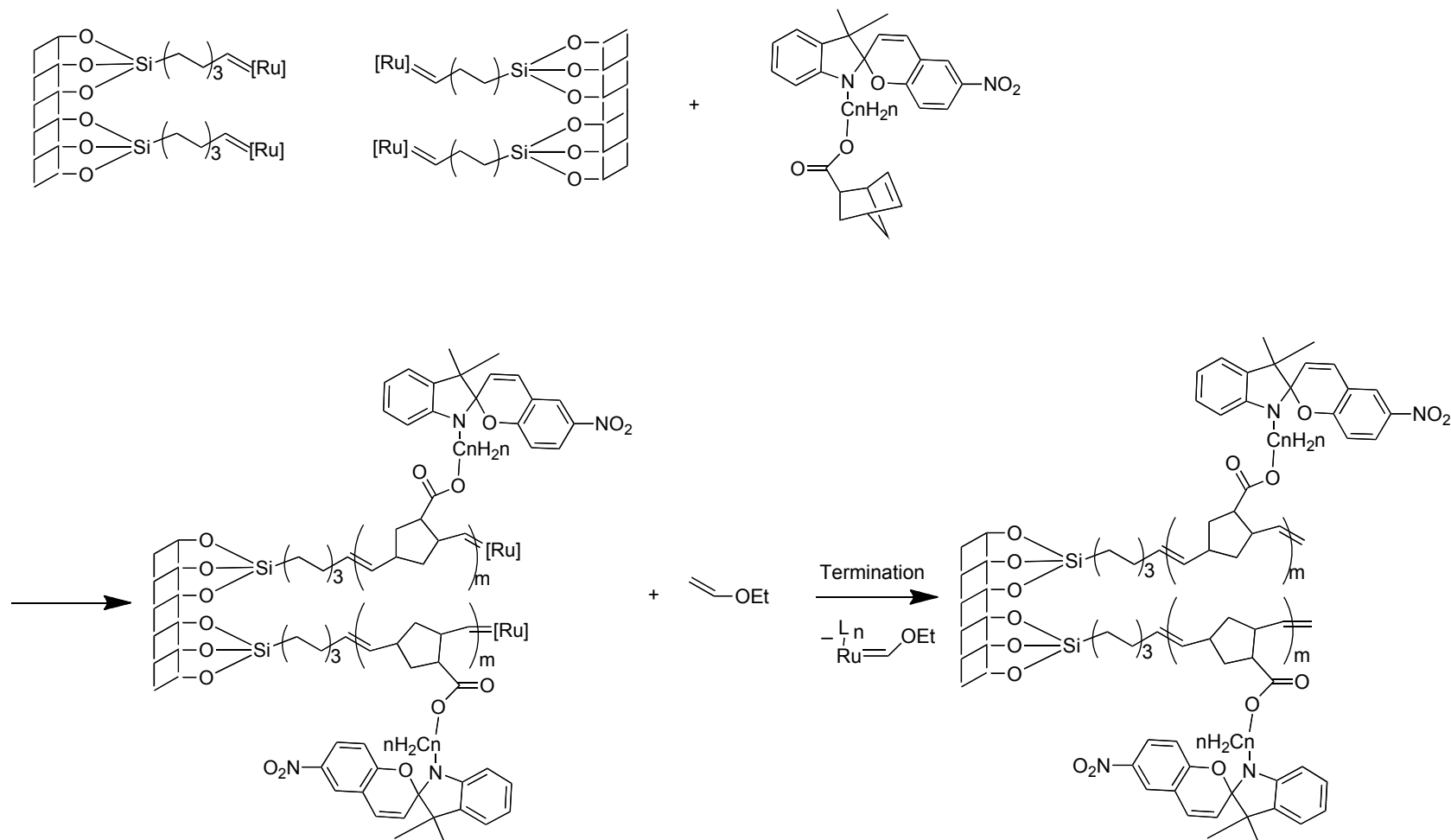
## Silanisation



## Attachment of the catalyst

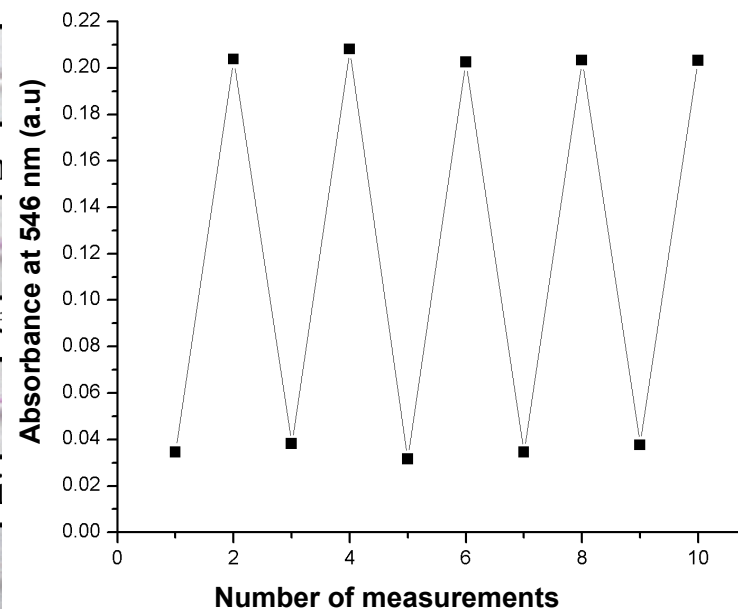
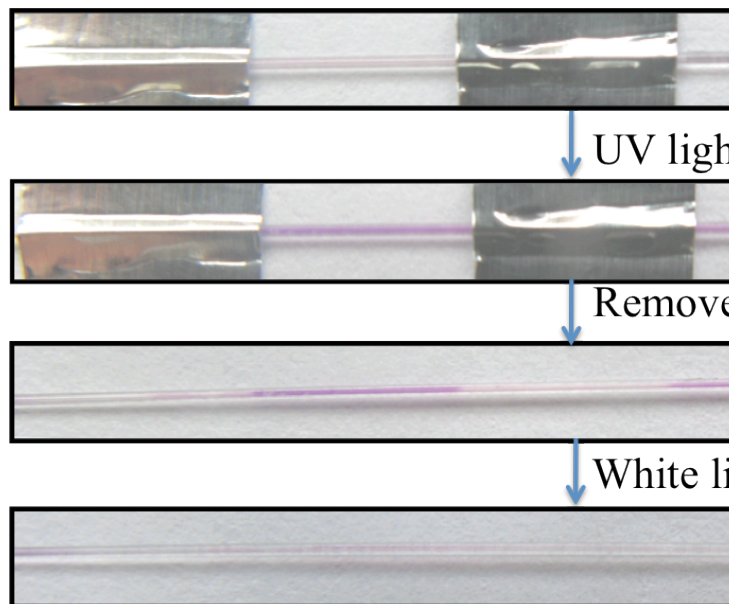
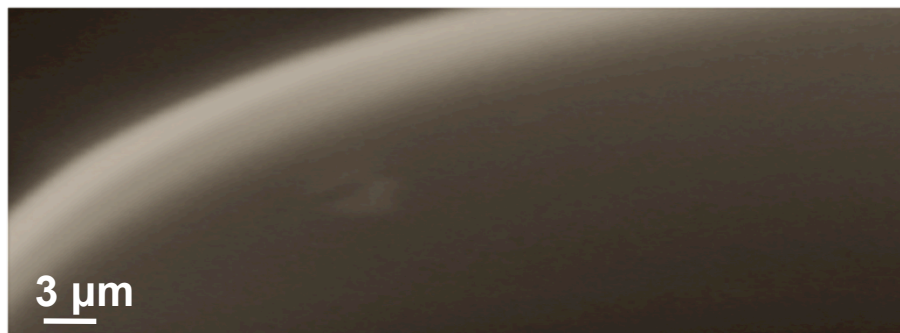








# Characterisation



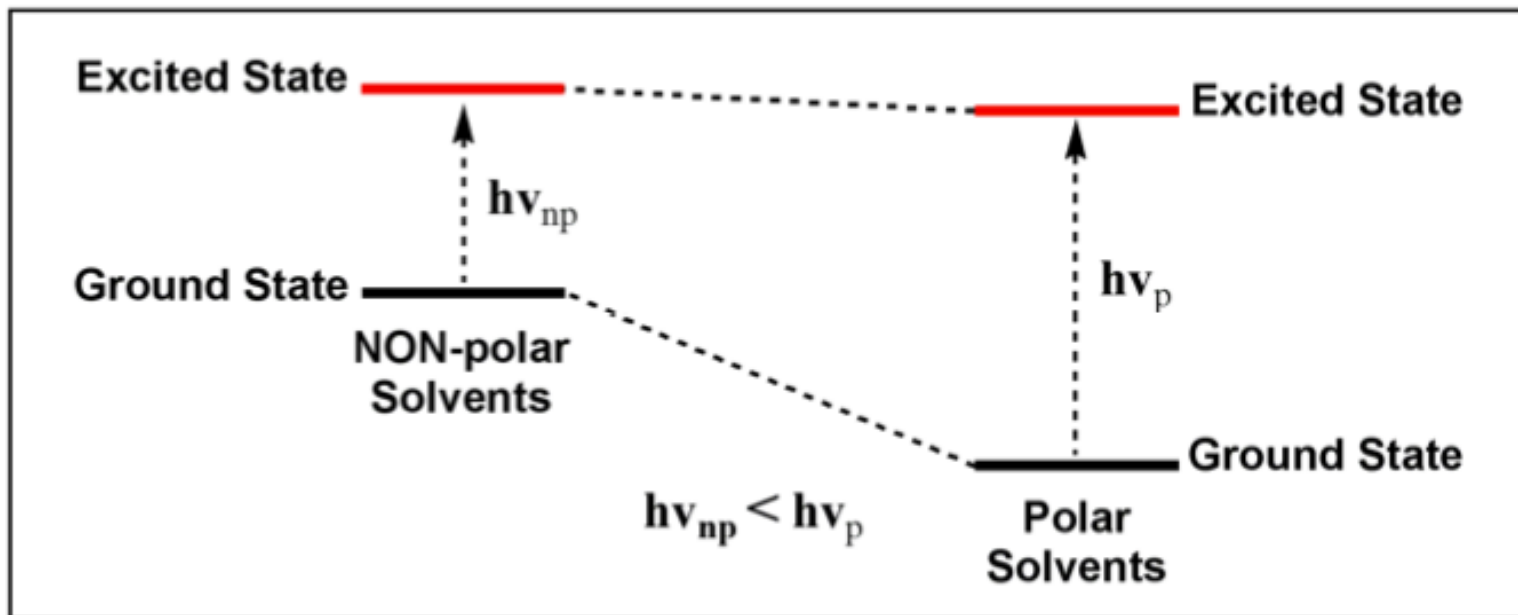
L. Florea, A. Hennart, D. Diamond and F. Benito-Lopez, *Sens. Actuators B: Chem.*, 2012, 175, 92-99.





# Solvatochromic Properties

The colour of the MC form depends on the difference in polarity between the photo-excited MC form and the conjugated zwitterionic ground state



- The absorption band of MC form undergoes a hypsochromic (blue) shift in solvents of increasing polarity (negatively solvatochromism).

U.I. Minkin / Chem. Reviews, 104 (2004) 2751-2776.

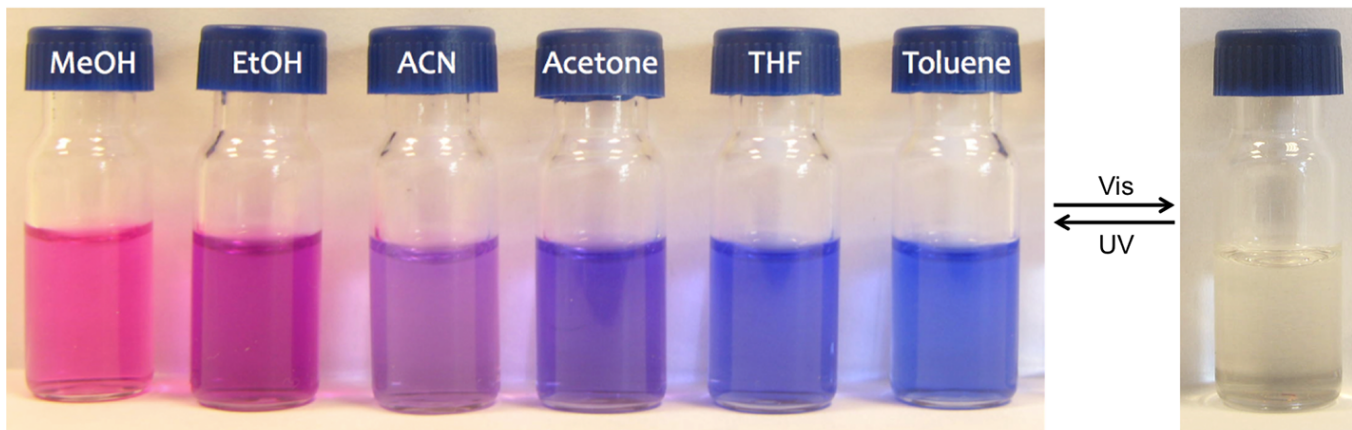




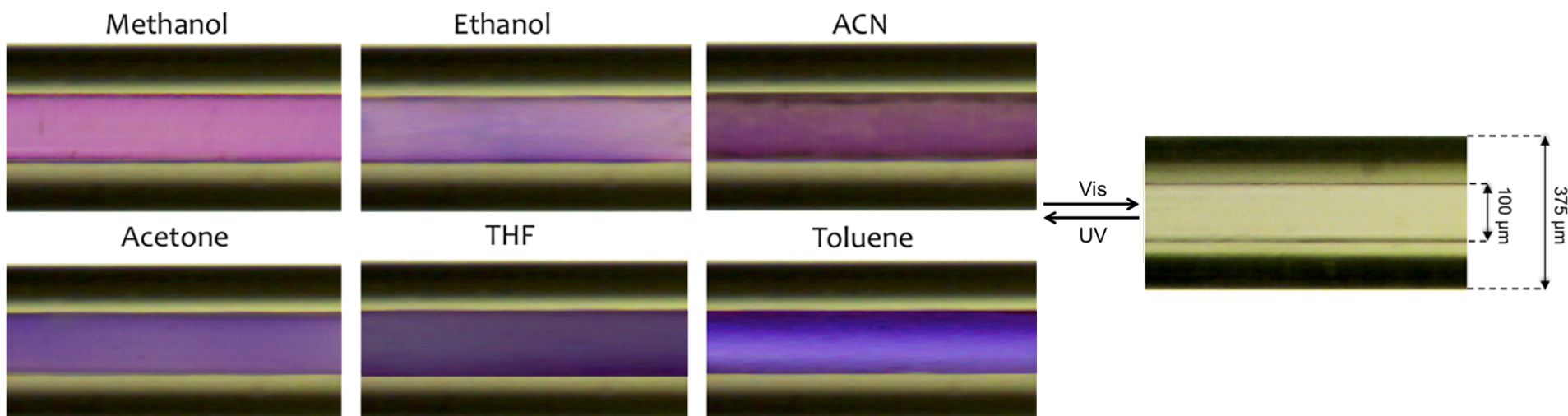
# Solvatochromic Properties



## ➤ In solution



## ➤ Polymeric brushes







# Solvatochromic Properties

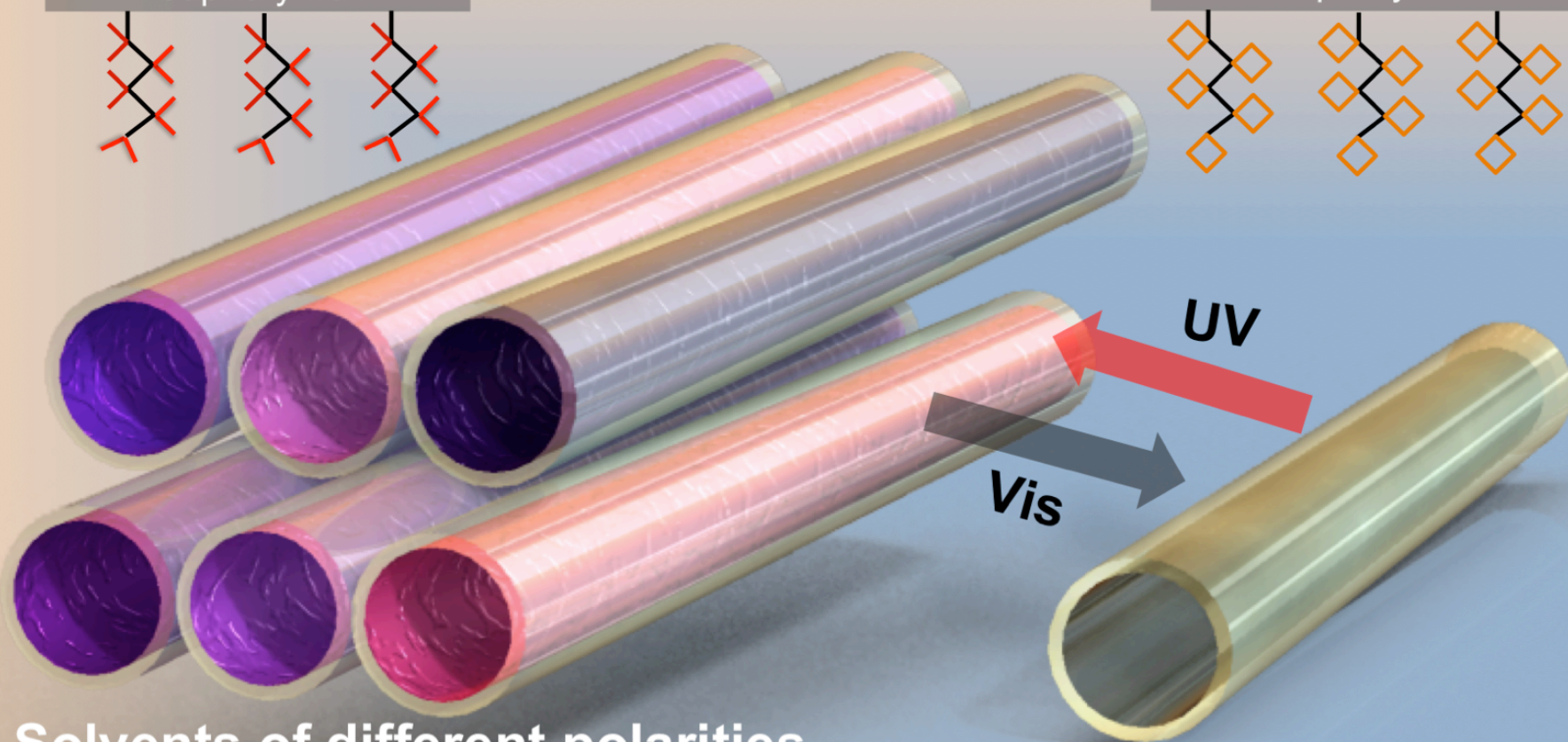


↗ - Solvatochromic unit (MC)

Capillary wall

◇ - Non-solvatochromic unit (SP)

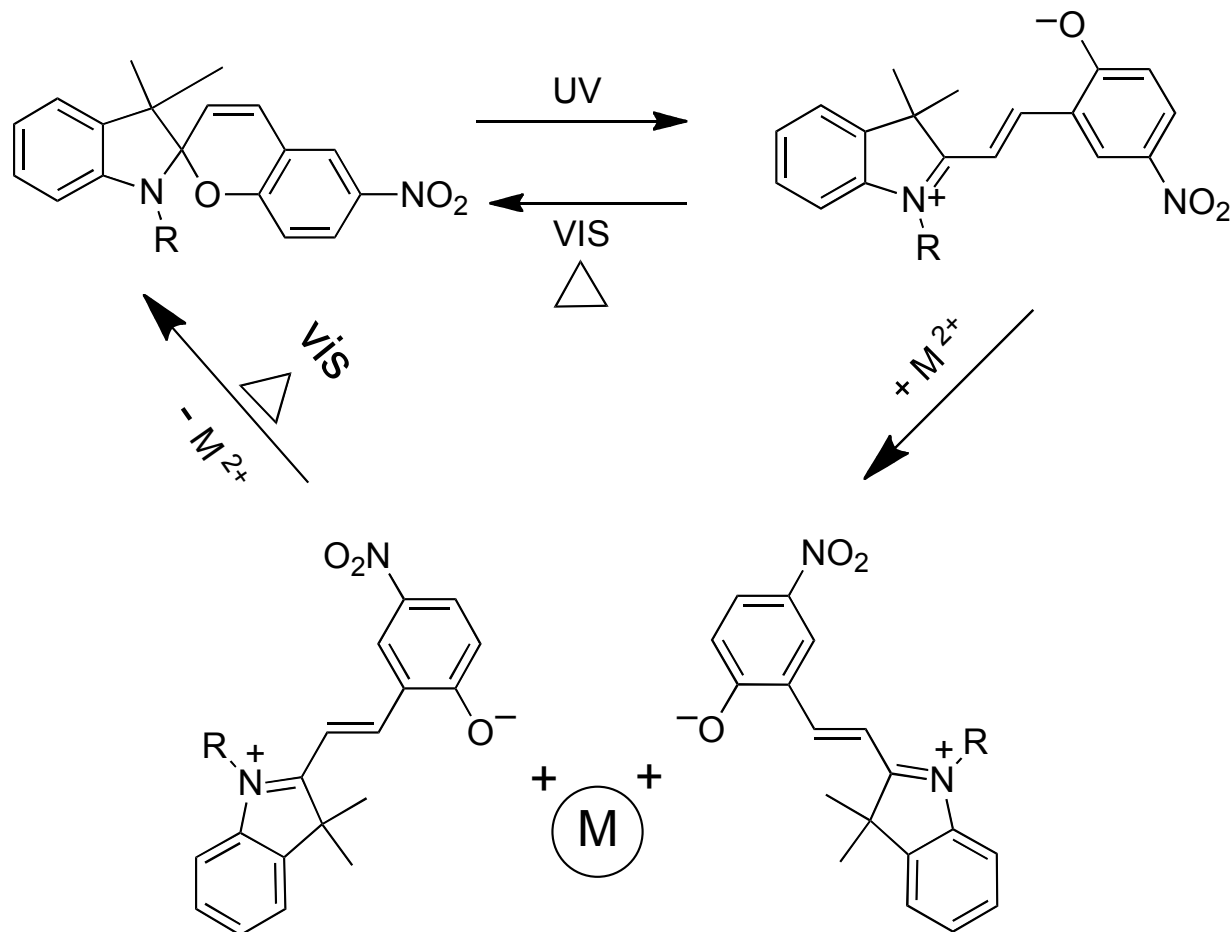
Capillary wall



Solvents of different polarities

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

**SP-M sol in ACN**

**20 s UV light**

**+ Ni<sup>2+</sup>**

**+ Cd<sup>2+</sup>**

**+ Co<sup>2+</sup>**

**+ Cu<sup>2+</sup>**

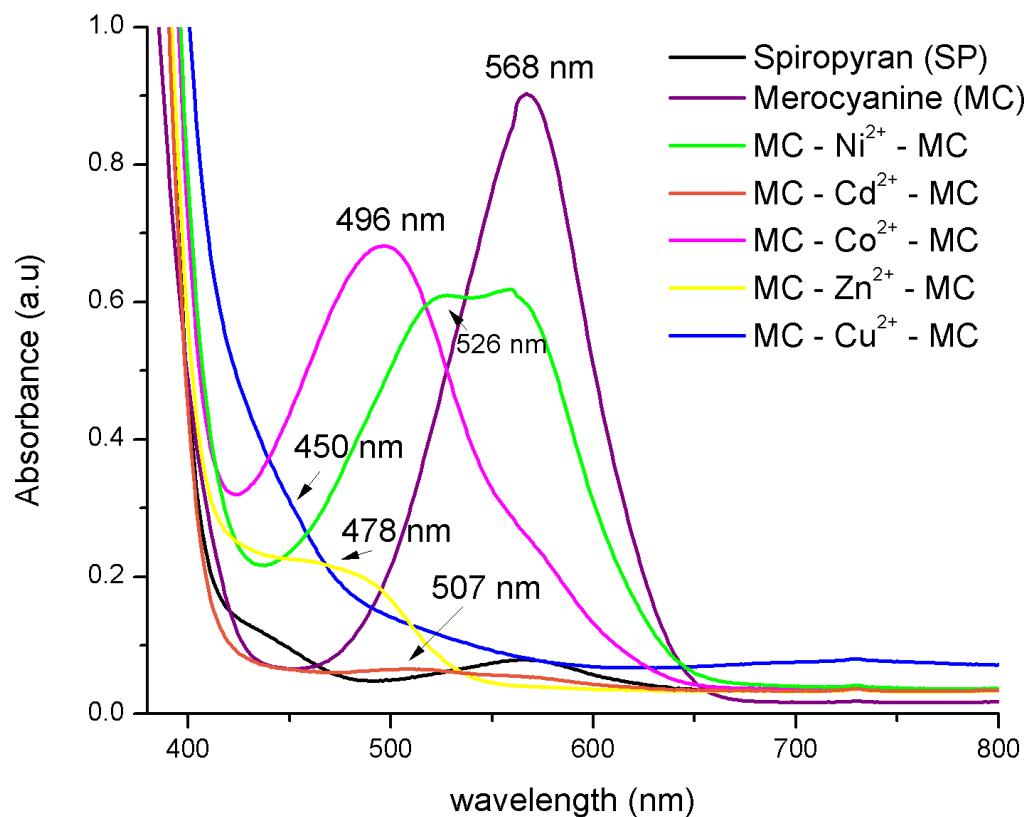
**+ Zn<sup>2+</sup>**





# Metal ions sensing binding and releasing

## I. Solution studies



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

$\text{Cu}^{2+}$

$\text{Zn}^{2+}$

$\text{Co}^{2+}$

$\text{Cd}^{2+}$

$\text{Ni}^{2+}$

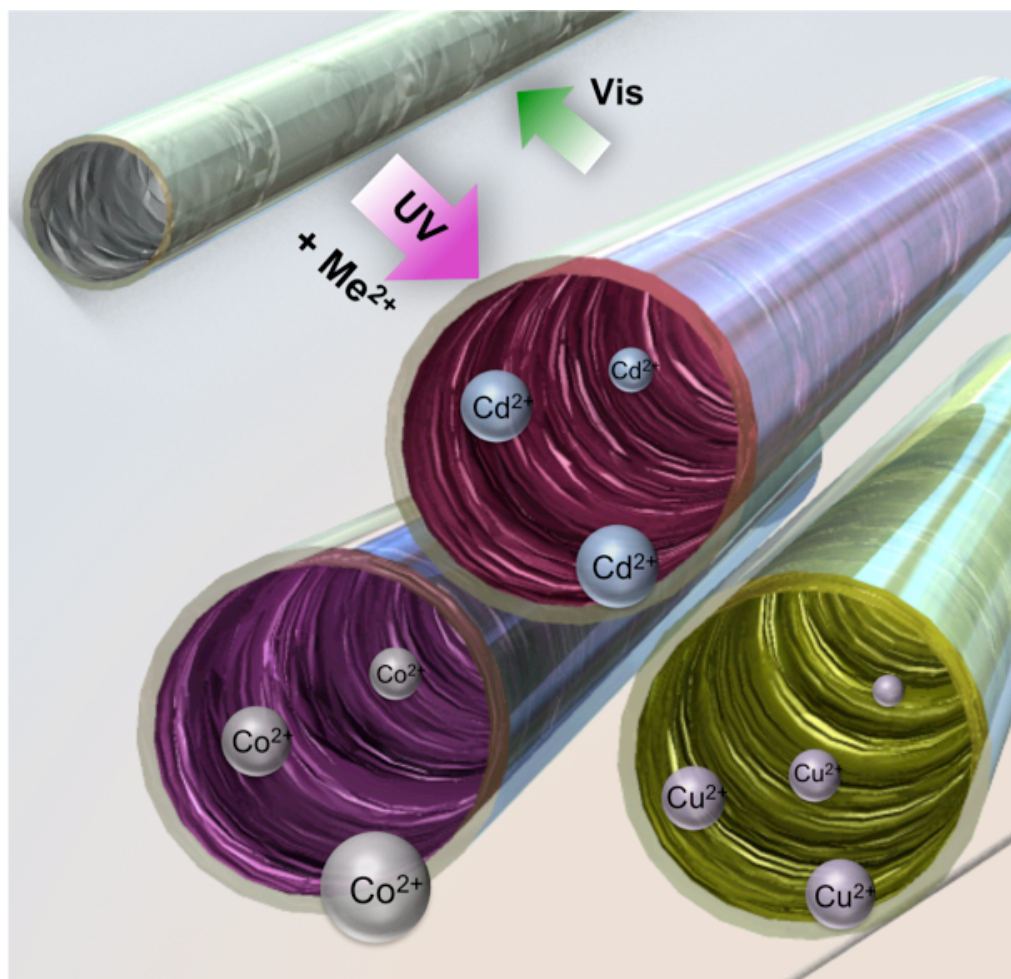
MC







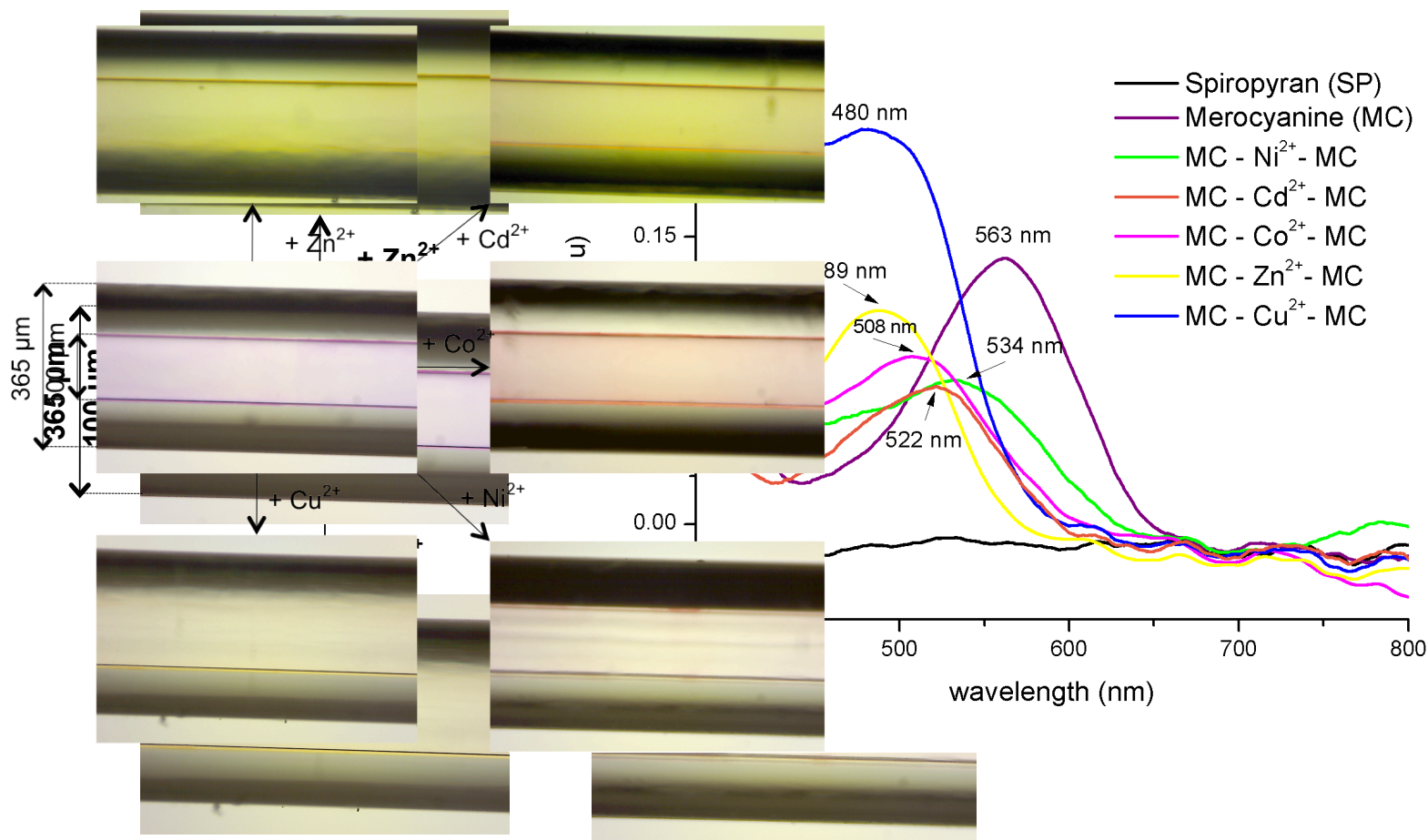
# Metal ions sensing, binding and releasing





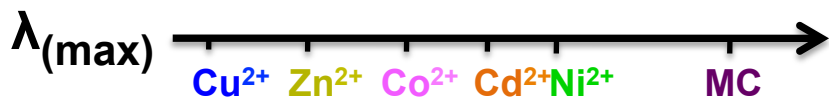
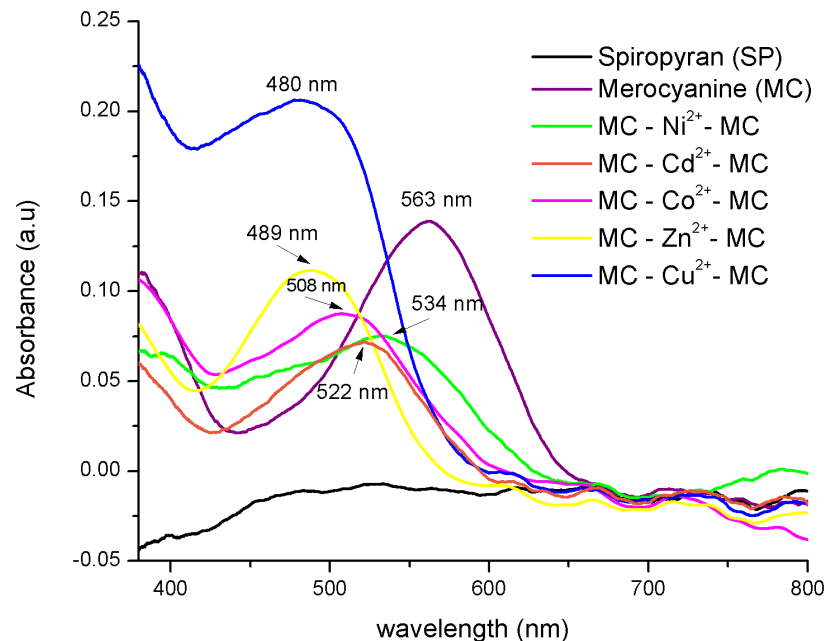
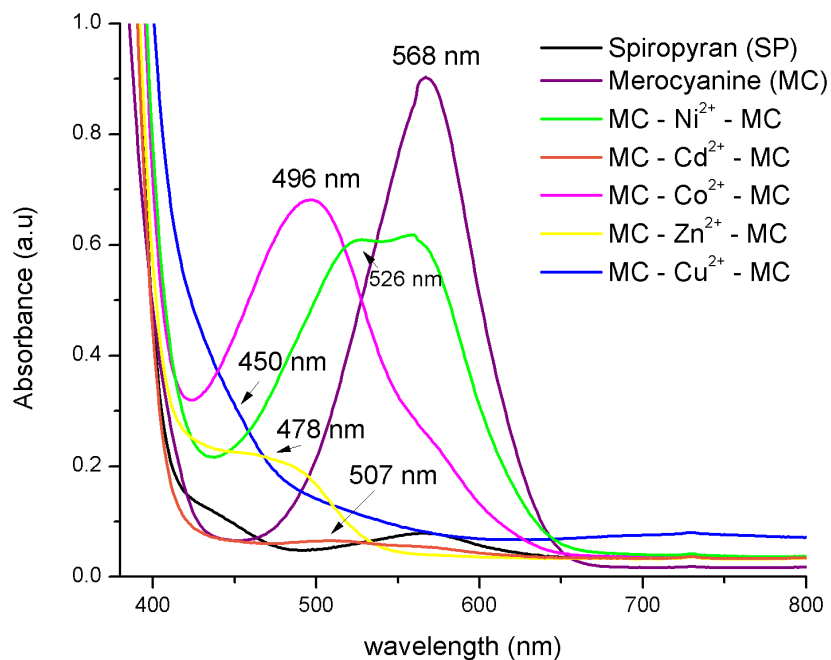
# Metal ions sensing binding and releasing

## II. Capillary coatings





# Response to Metal Ions



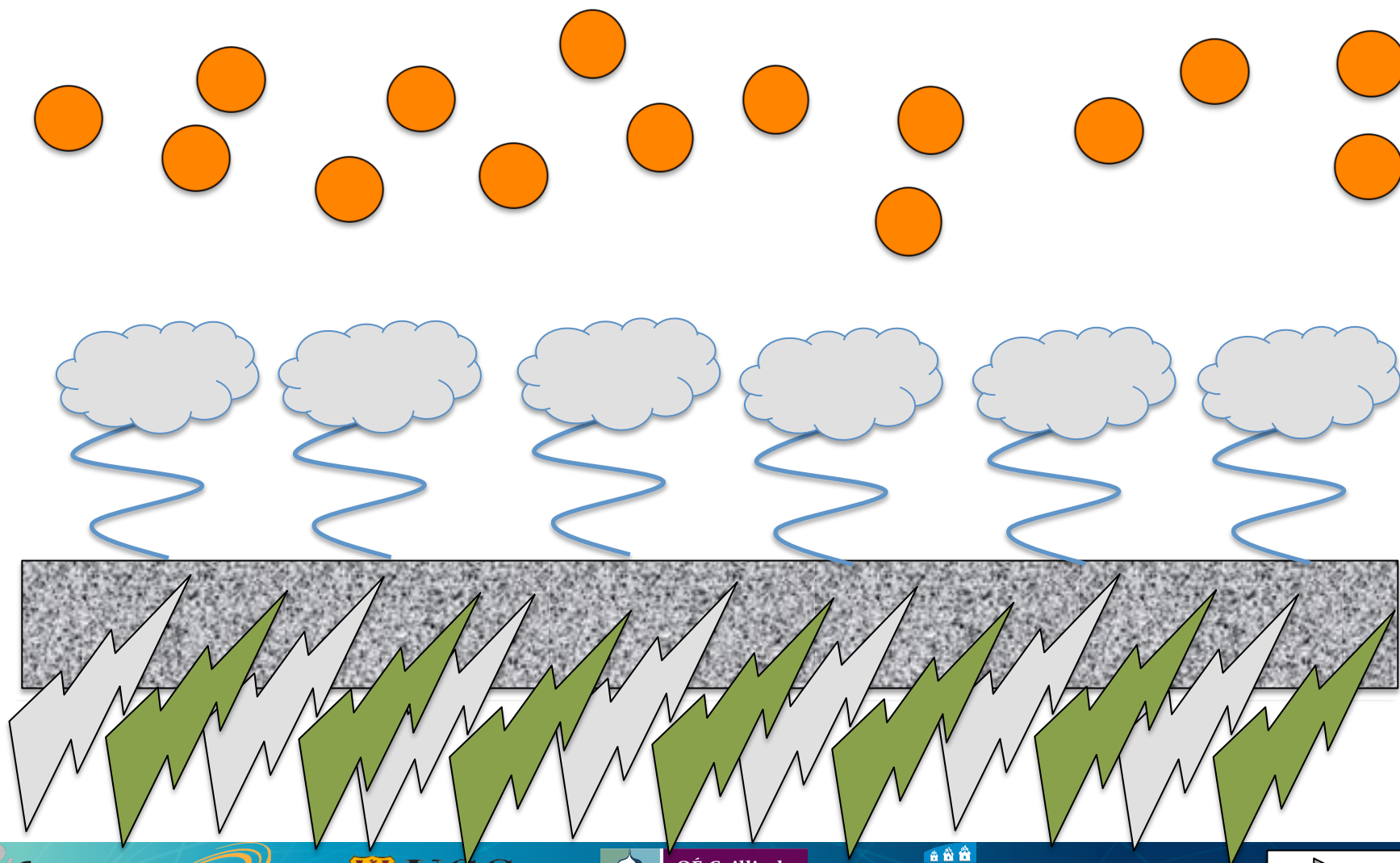
**Solution Phase**



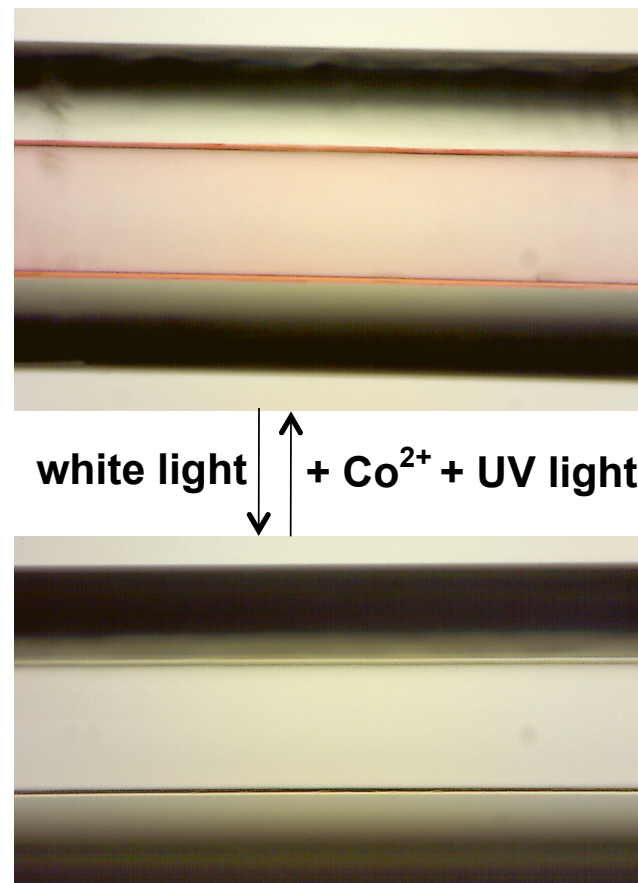
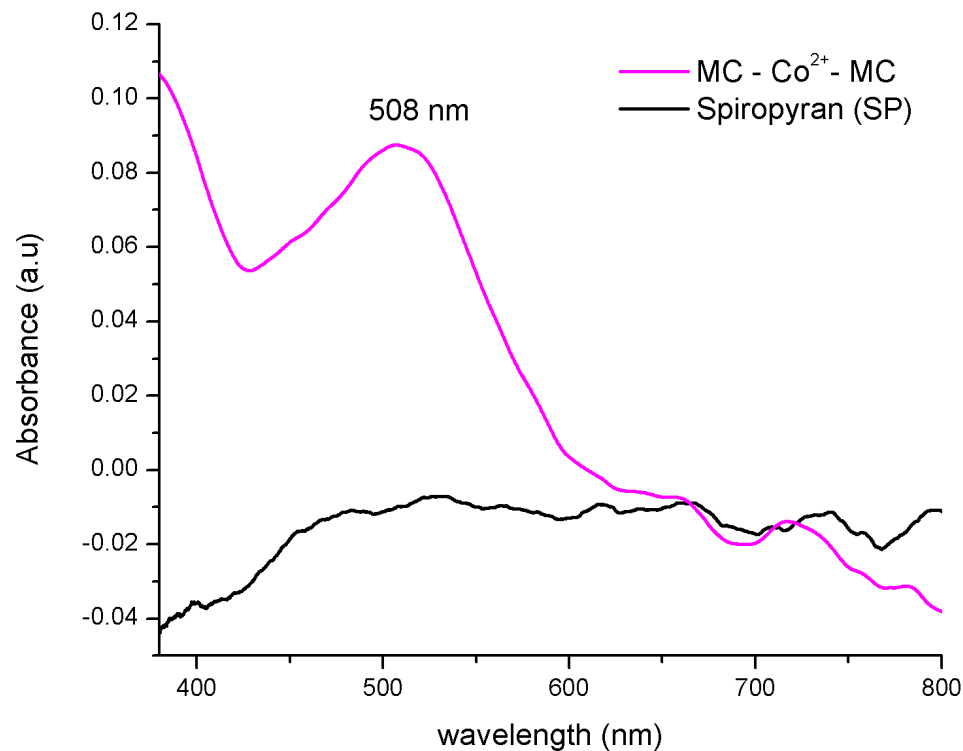
**Surface Bound**



# Controlling Guest Binding and Release using Light

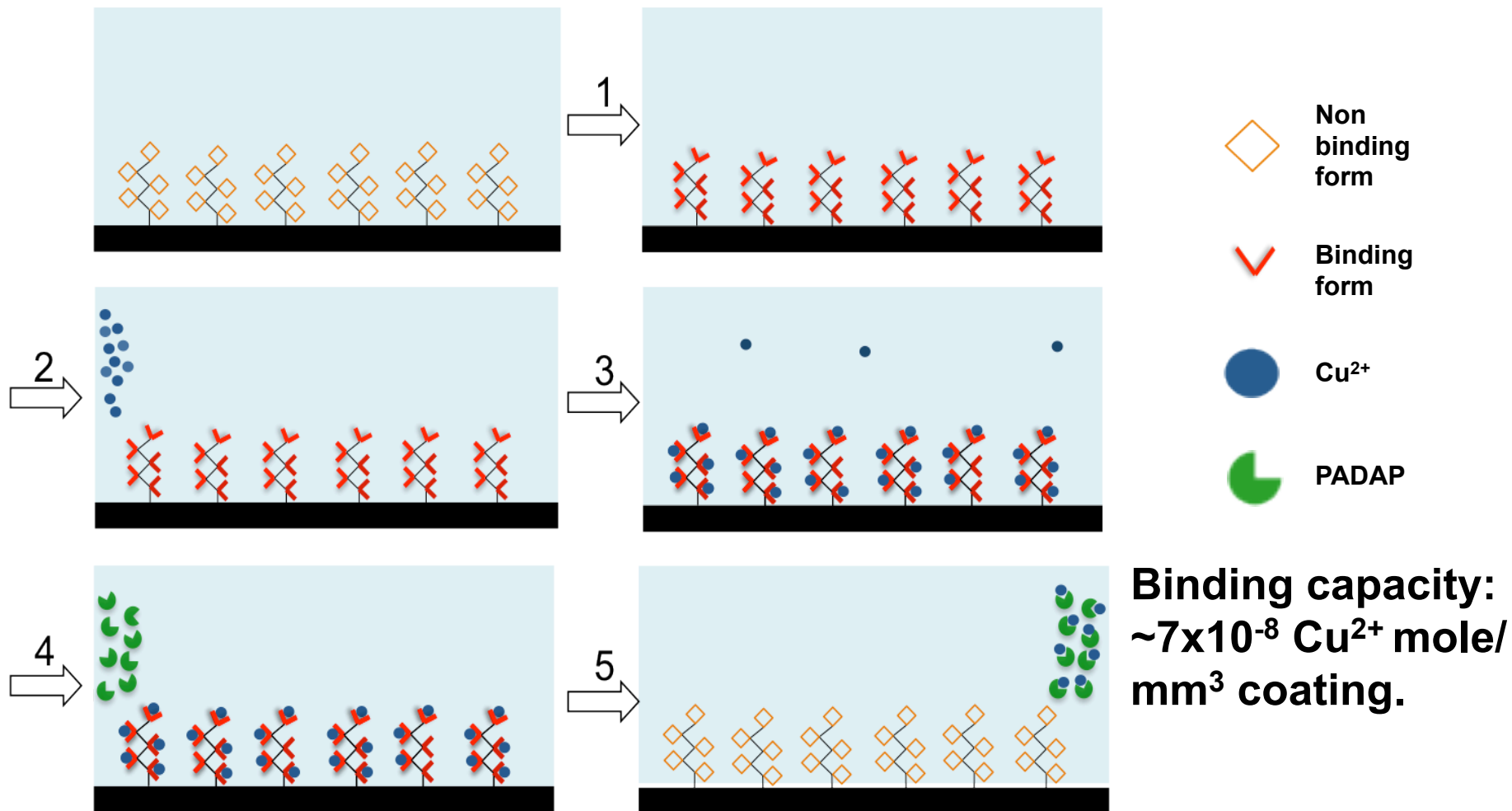


# Metal ions binding and releasing





# Quantitative binding



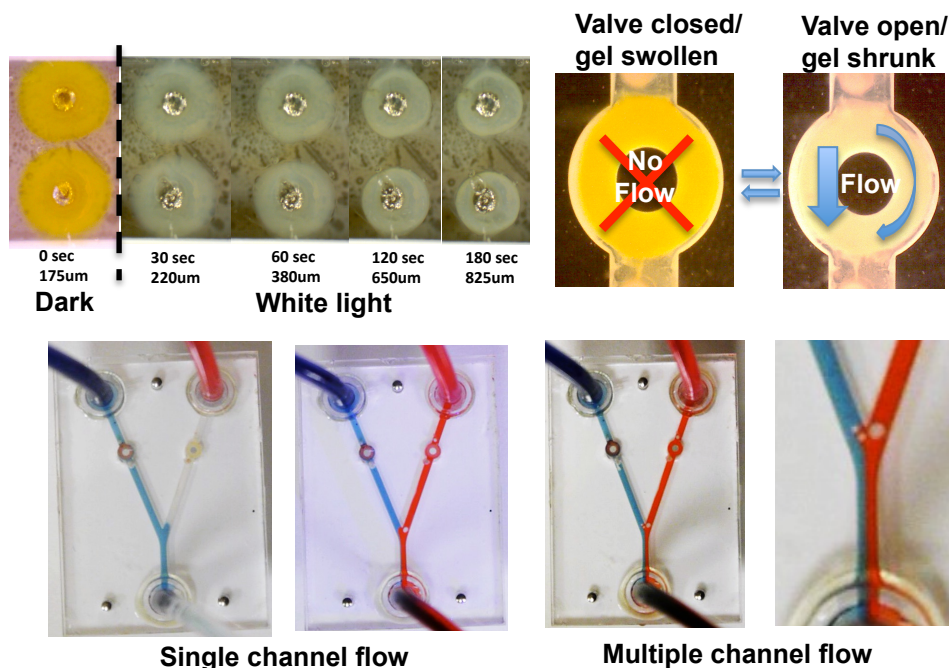


- **Self-diagnostic for continuous flow device**
- **Solvent detection and divalent metal ion detection in micro-capillaries**
- **Sensing behaviour can be switched on/off remotely using light**



### 3. Photo-switchable actuators

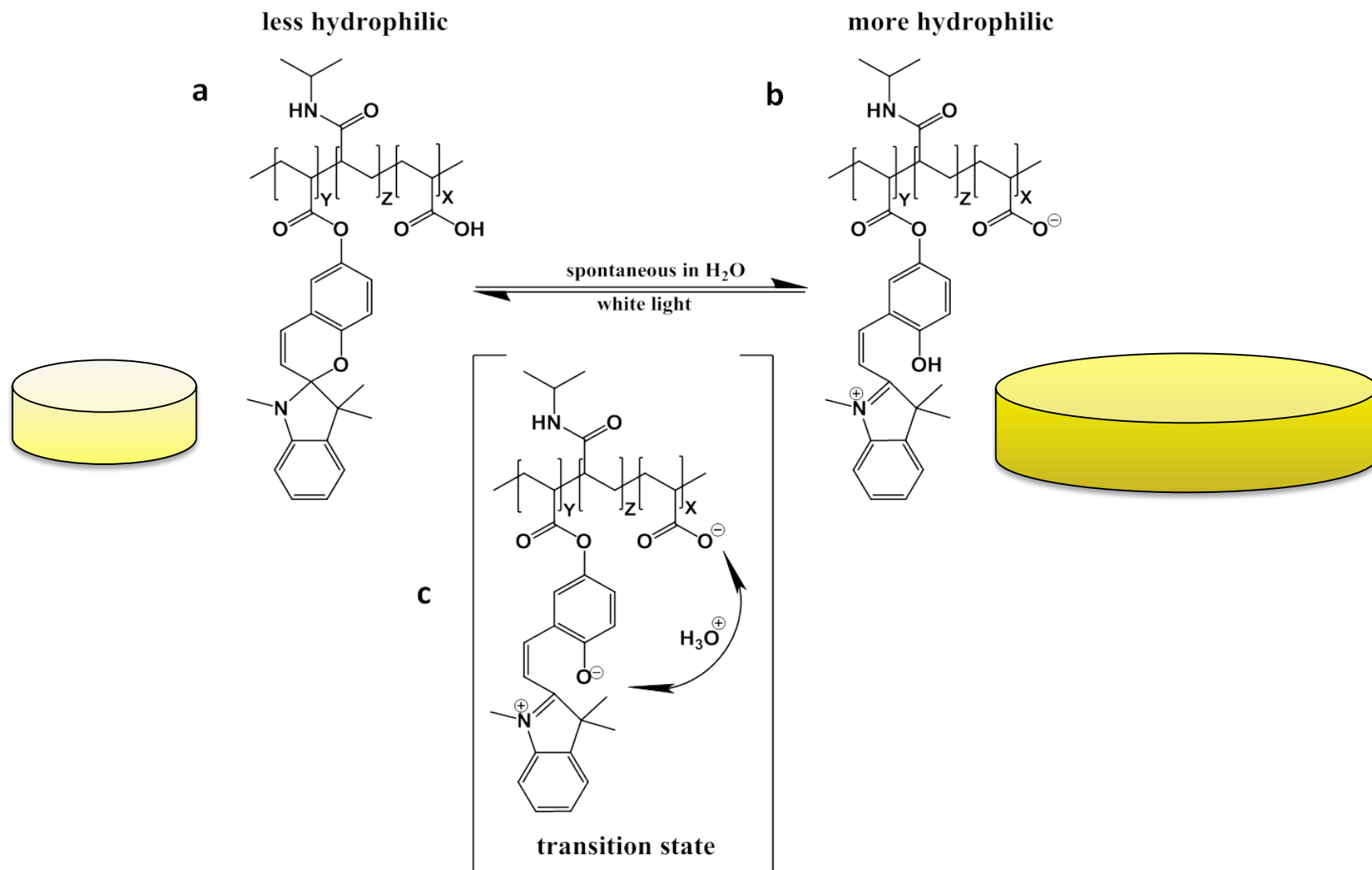
- **ON/OFF flow modulation**
- **photo-control of flow in microfluidic devices**



**Light actuated polymer valves for fluid control**



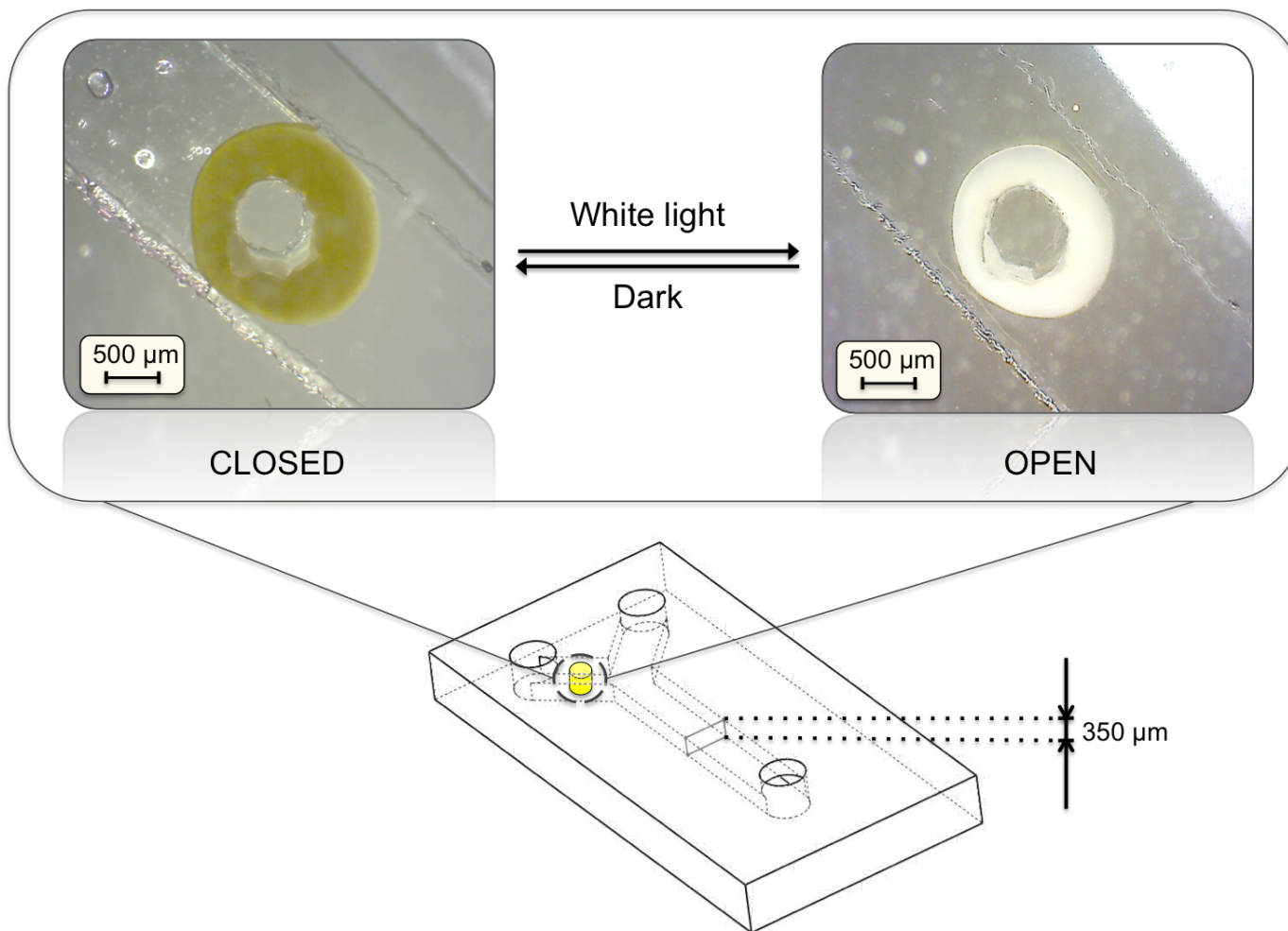
# Self-protonating hydrogels



B. Ziolkowski, L. Florea, J. Theobald, F. Benito-Lopez and D. Diamond, *Soft Matter*, 2013, 9, 8754-8760.



# Photo-actuators for micro-valve applications in microfluidics

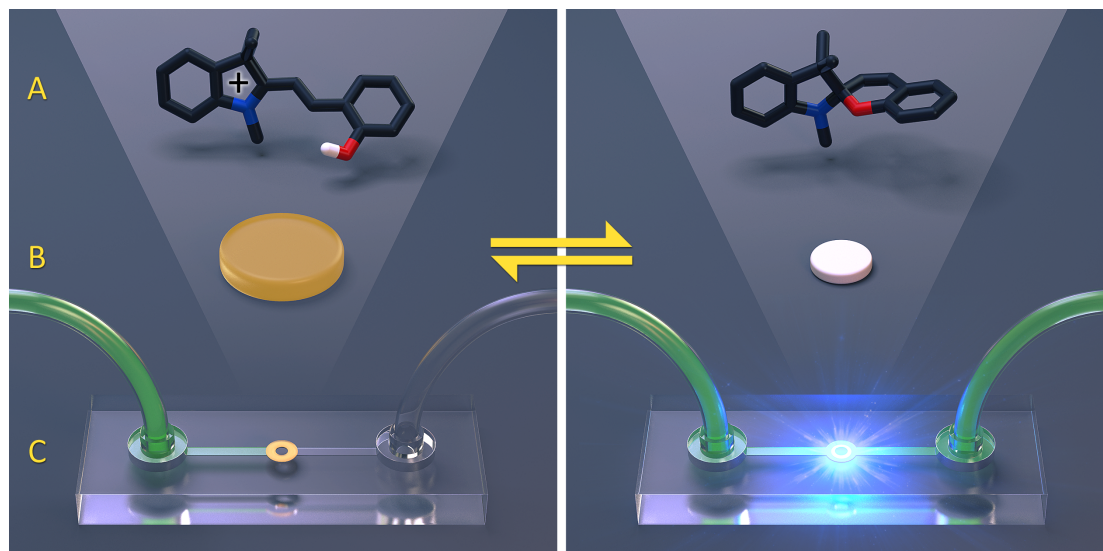




# Reversible Photo-Switching of Flow



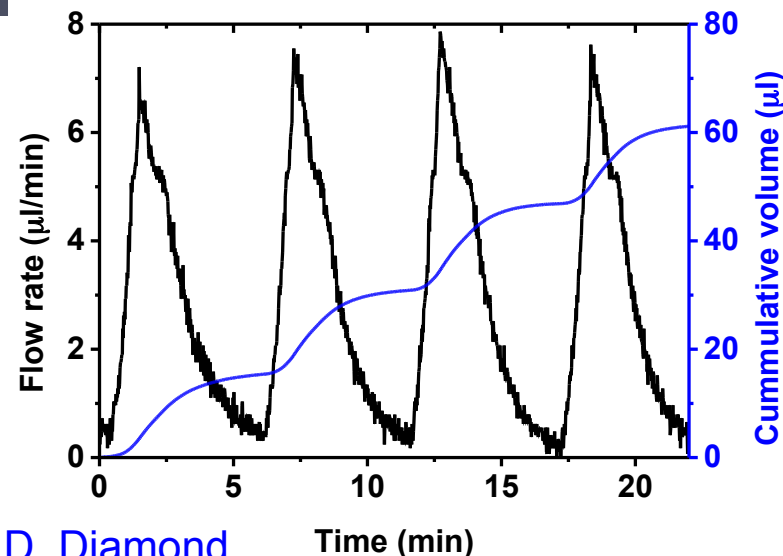
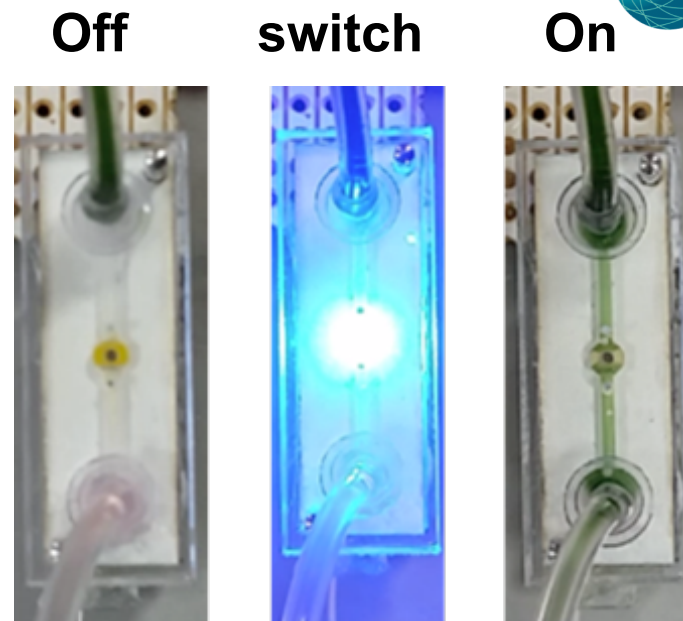
With Albert Schenning and Dirk Broer, TU Eindhoven



**Above:** scheme showing switching process protonated MC-H<sup>+</sup> photoswitched to SP triggering p(NIPAAm-co-AA-co-SP) gel contraction and opening of the channel.

**Right, Top:** Photos of the valve in operation before (flow OFF) and after (flow ON) one minute of blue light irradiation.

**Right, Bottom:** Flowrate and cumulative volume measurements showing repeated opening and closing of microvalve: 1 min blue light irradiation opens valve followed by ~5.5 min thermal relaxation to close.



J. ter Schiphorst, S. Coleman, J.E. Stumpel, A. Ben Azouz, D. Diamond and A. P. H. J. Schenning, Chem. Mater., 27 (2015) 5925–5931.



# 4. Photo-actuated surfaces



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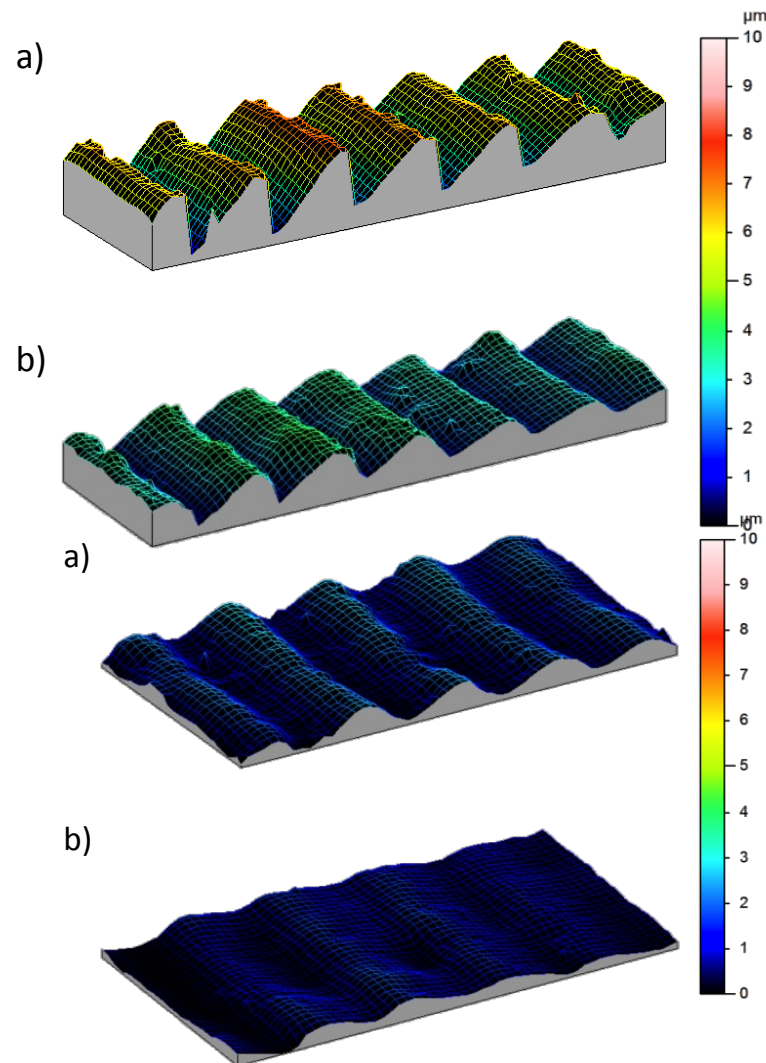
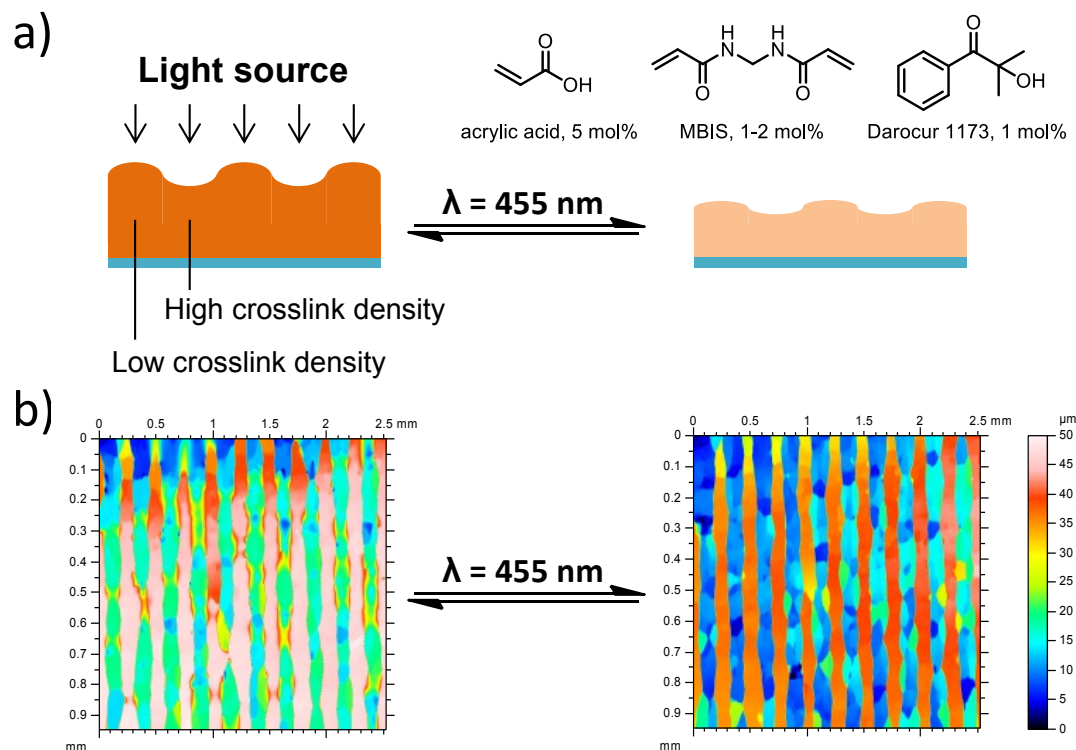
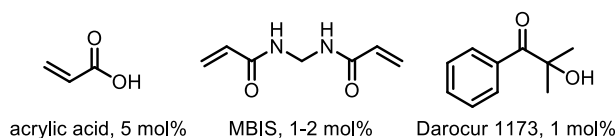
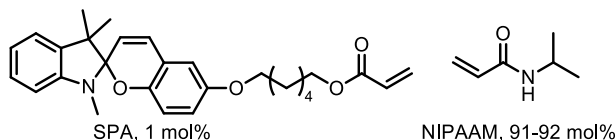
Research Article

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ACS applied materials & interfaces, 6 (2014) 7268-7274

## Photoswitchable Ratchet Surface Topographies Based on Self-Protonating Spiropyran–NIPAAm Hydrogels

Jelle E. Stumpel,<sup>†</sup> Bartosz Ziolkowski,<sup>‡</sup> Larisa Florea,<sup>‡</sup> Dermot Diamond,<sup>‡</sup> Dirk J. Broer,<sup>\*,†,§</sup>  
and Albertus P. H. J. Schenning<sup>\*,†,§</sup>







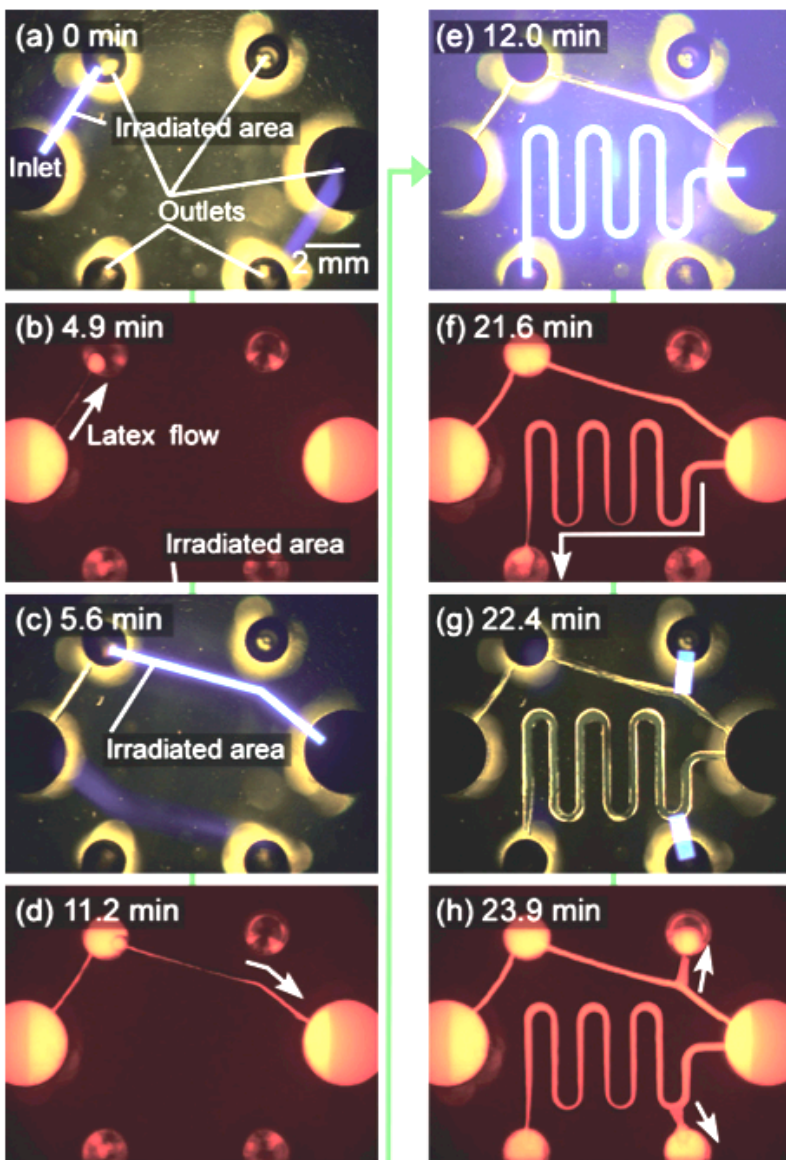
# 5. Photo-generated micro-channels



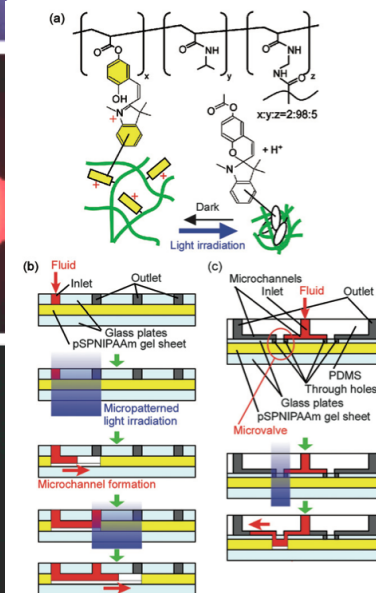
On-demand microfluidic control by micropatterned light irradiation of a photoresponsive hydrogel sheet

Shinji Sugiura, András Szilágyi, Kimio Sumaru,\* Koji Hattori, Toshiyuki Takagi, Genovéva Filipcsei, Miklos Zrínyi and Toshiyuki Kanamori

Lab Chip, 2009, 9, 196–198



**Fig. 2** On-demand formation of microchannels with arbitrary pathways in the universal microfluidic system by micropatterned light irradiation. White arrows indicate the flow direction of a fluorescently labeled latex bead suspension. (a) Microchannel formation by micropatterned light irradiation of the pSPNIPAAm hydrogel sheet. (b) Latex bead suspension flow through the microchannel after irradiation. Flow of the red colored latex bead suspension from the inlet to the upper-left-side outlet is slightly visible. (c)–(h) Three consecutive sequences of micropatterned light irradiation and microchannel formation.



**Fig. 1** Schematics of pSPNIPAAm hydrogel and of two types of microfluidic systems for on-chip fluid control by micropatterned light irradiation. (a) Chemical structure and a schematic of the photoinduced shrinkage of pSPNIPAAm hydrogel. (b) Universal microfluidic system for on-demand formation of arbitrary microchannels by micropatterned light irradiation. (c) PDMS microchannel network equipped with microvalves for independent and parallel flow control in microchannels by micropatterned light irradiation.





# Conclusions

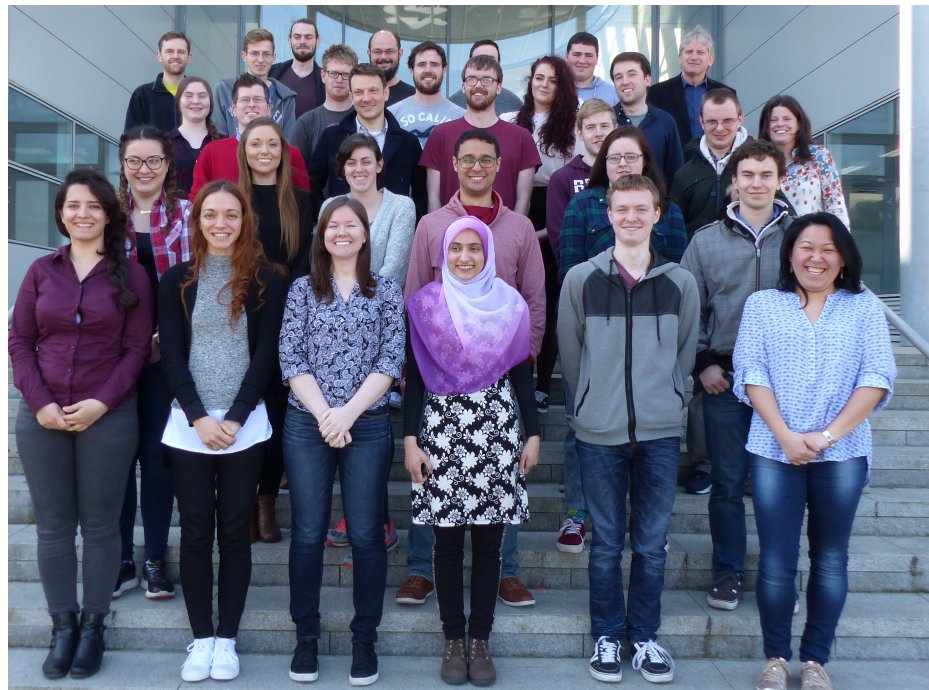


- Analytical flow systems of the future will require significantly improved reliability at a dramatically lower price point
- Advanced functional materials coupled with effective **fabrication techniques** is the key to progress



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- Prof. Dermot Diamond
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- Dr. Fernando Benito-Lopez
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