Adaptive Coatings in Micro-Capillaries and Micro-Channels as New Means to Develop Integrated Micro-Fluidic Optical Sensors

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October 2011

Outline

I. Introduction

- optical sensors in microfluidics
- stimuli-responsive materials

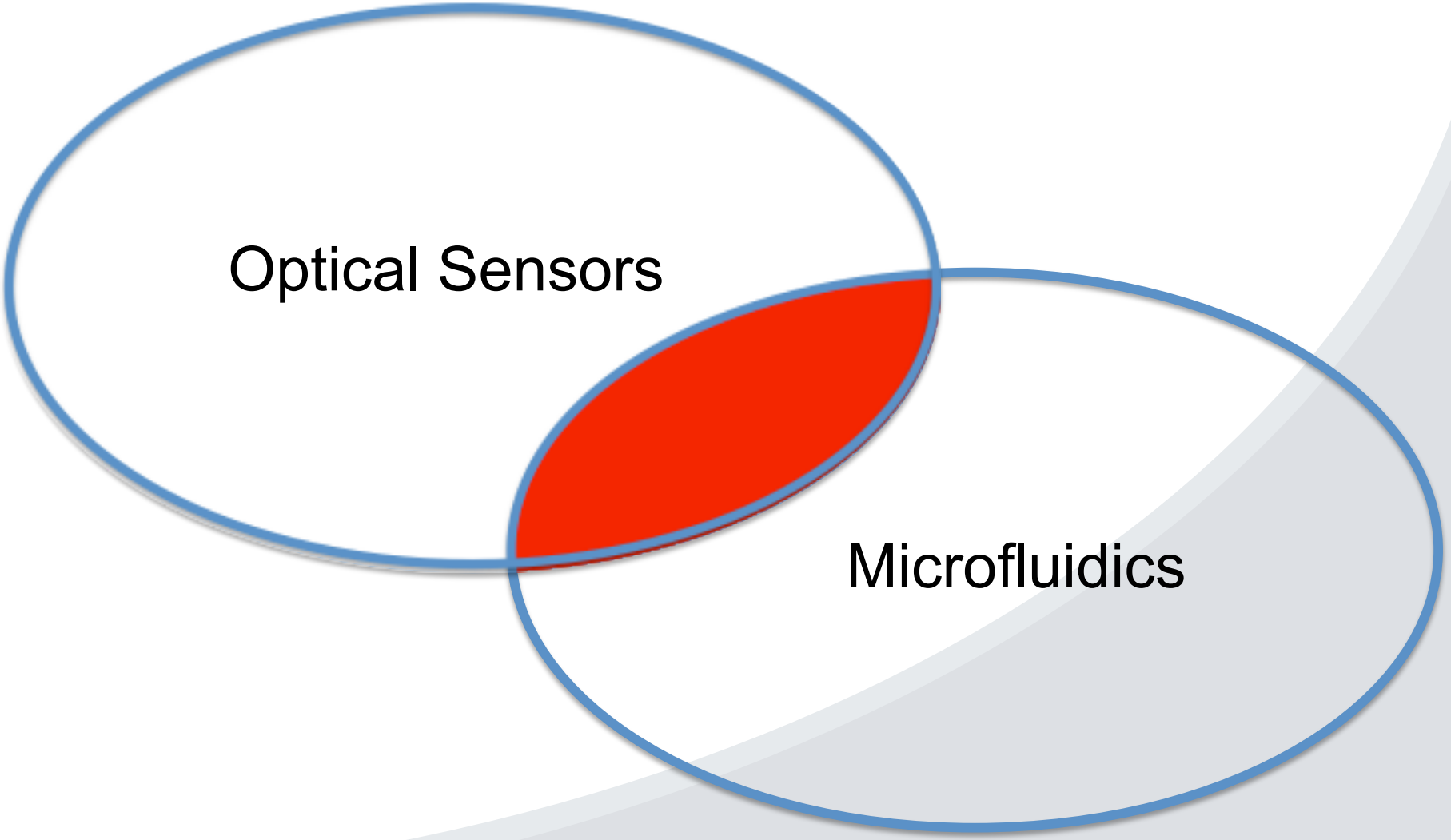
II. Polyaniline functionalised micro-fluidic channels for:

- pH sensing
- study mixing

III. Spiropyran functionalised micro-capillaries for:

- solvent sensing

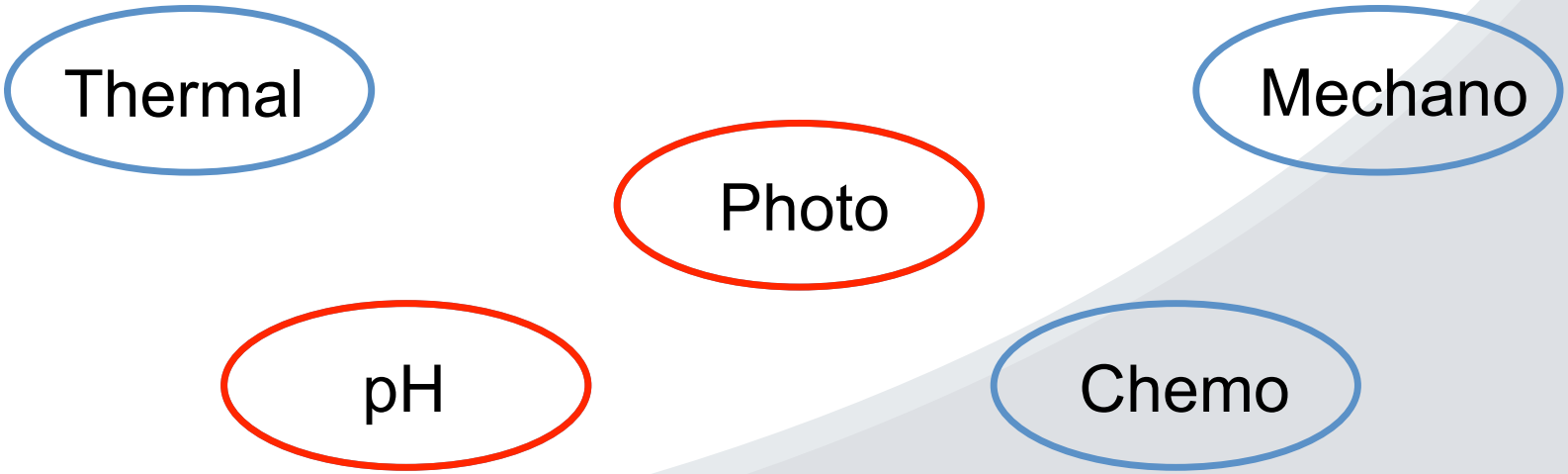
Optical Sensors in Microfluidics



I. Optical Chemical Sensors | Stimuli responsive materials

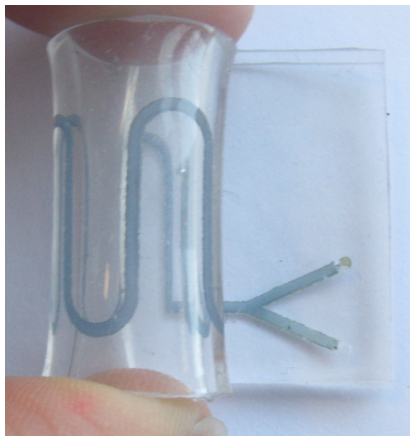
Stimuli-responsive Materials

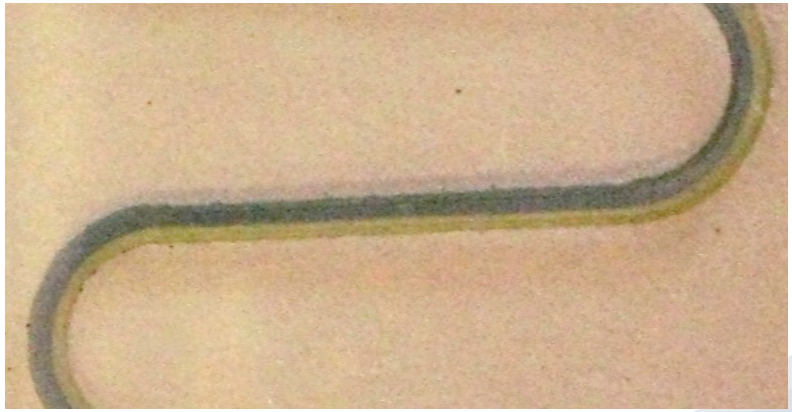
Materials whose characteristics can be changed using an external stimulus

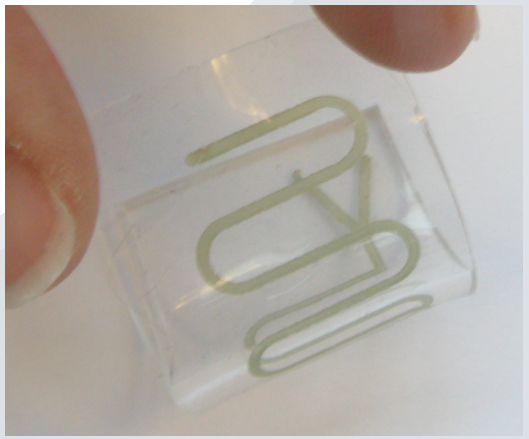


II. Polyaniline functionalised micro-fluidic channels

- pH sensing
- study mixing

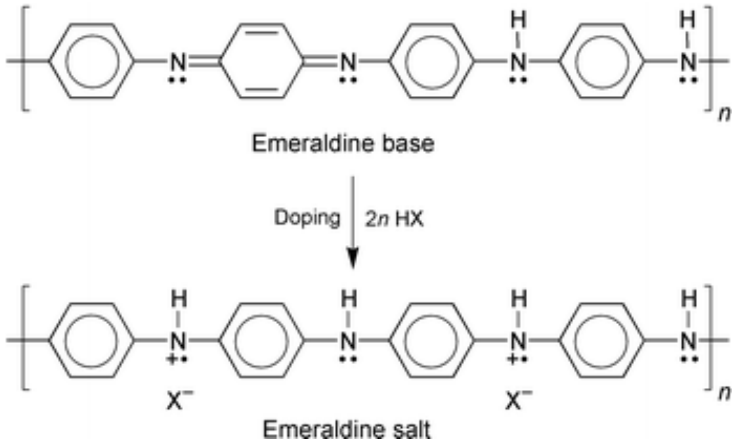






Polyaniline Nanofibres

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



Insulating State

Blue/Violet Colour

Conducting State

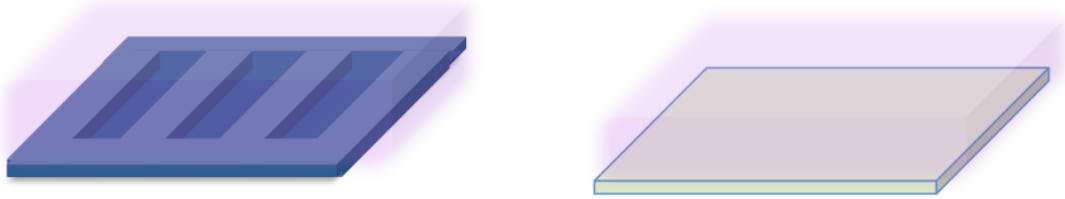
Green

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

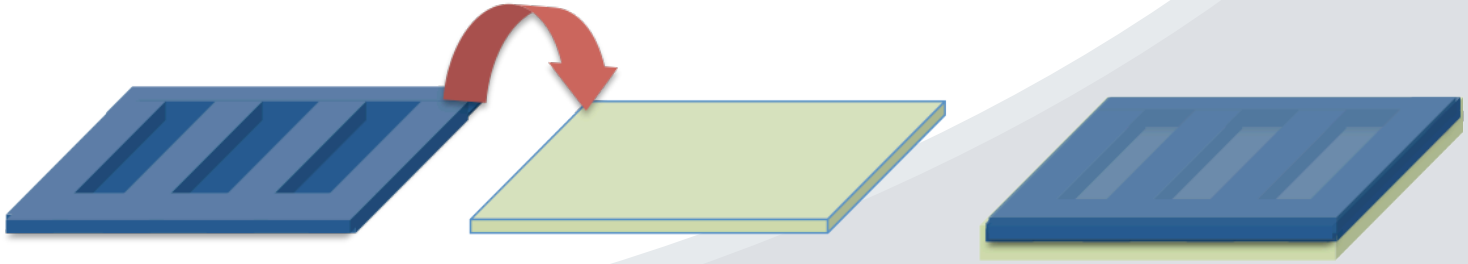
Micro-chip fabrication

✓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.

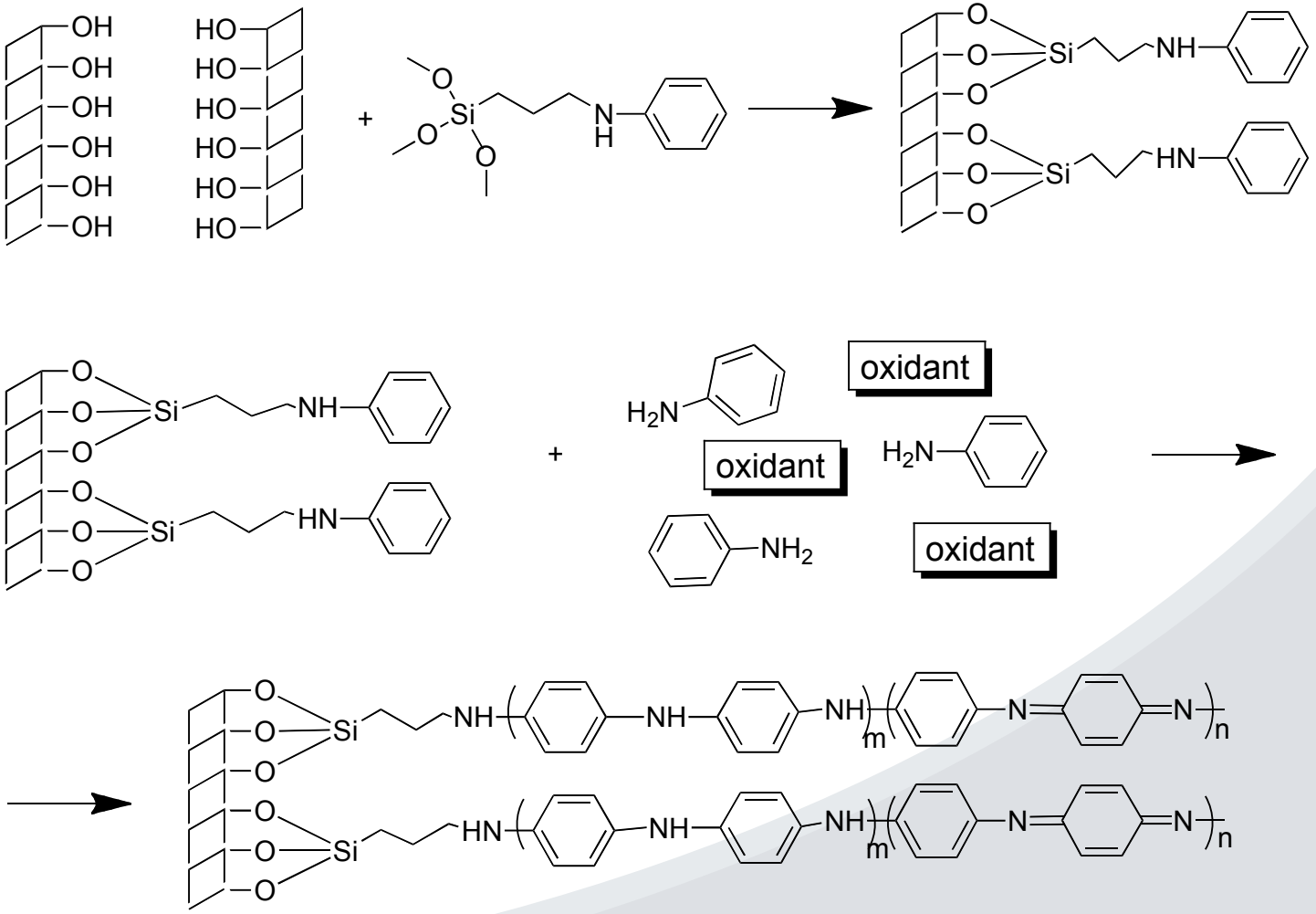


✓PDMS and glass slide are brought together.



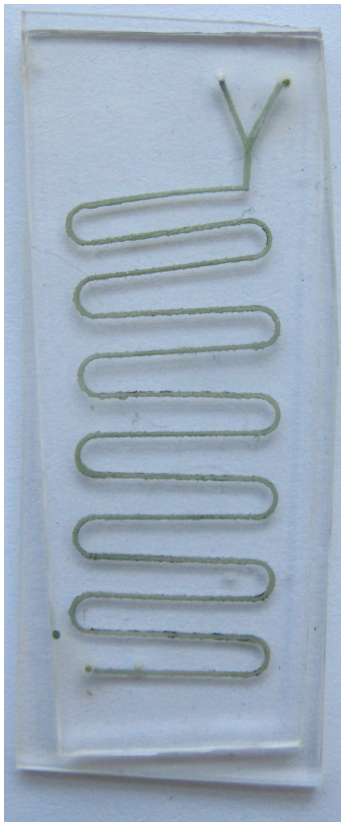
L. Yu, C.M. Li, Y. Liu *et al.* / Lab Chip, 9 (2009), 1243–1247.

Micro-channel functionalisation process

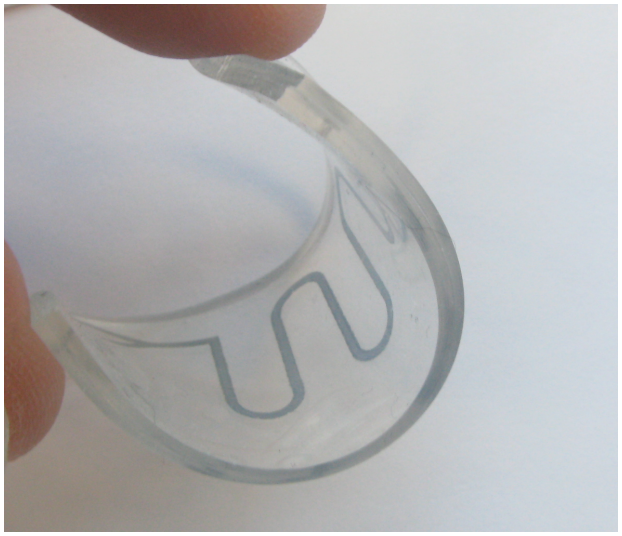


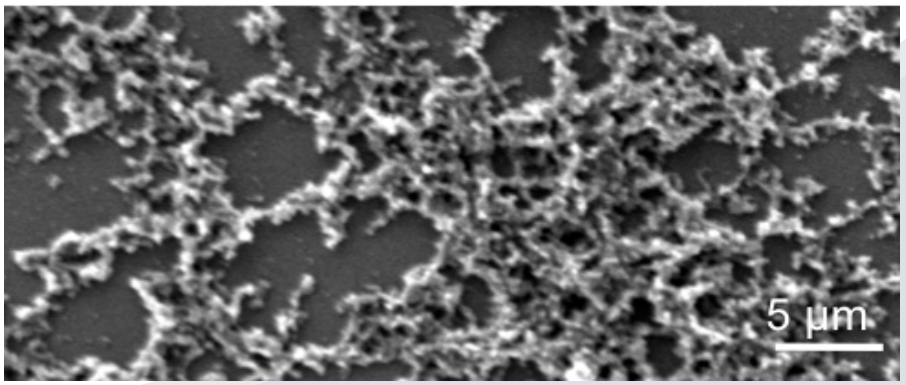
Micro-channels

500μm x 1000μm

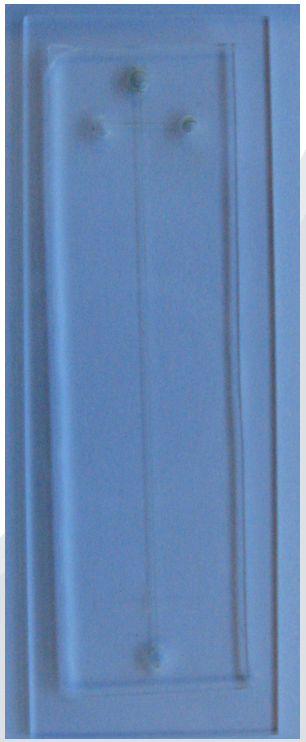


1000μm x 100μm

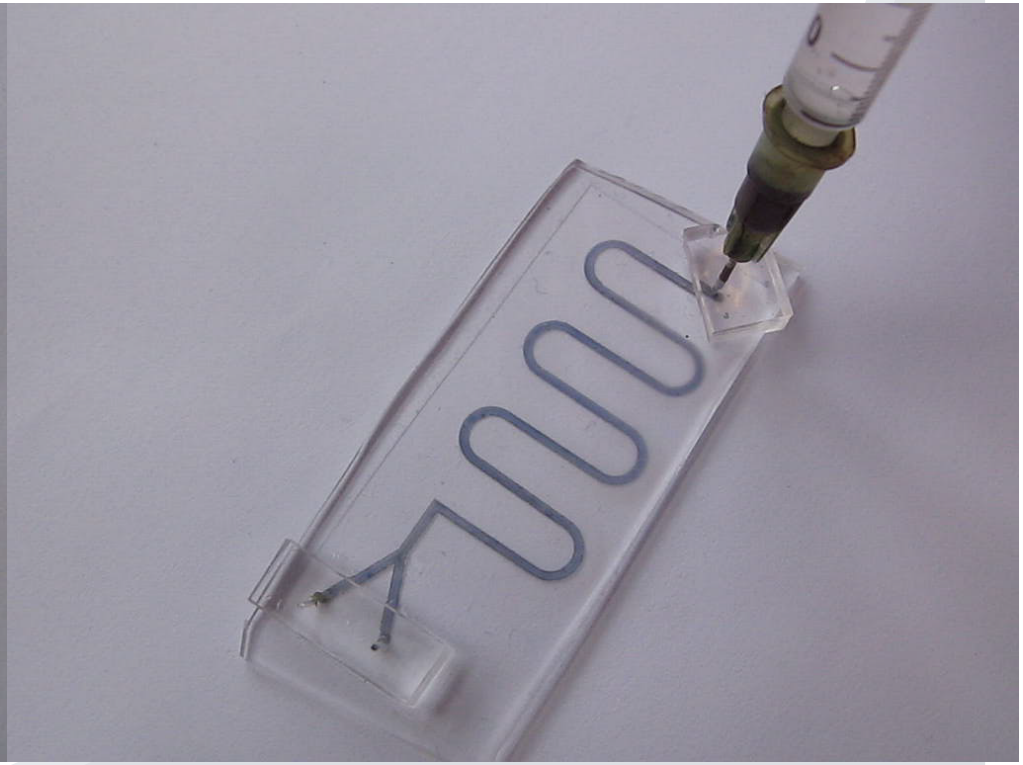




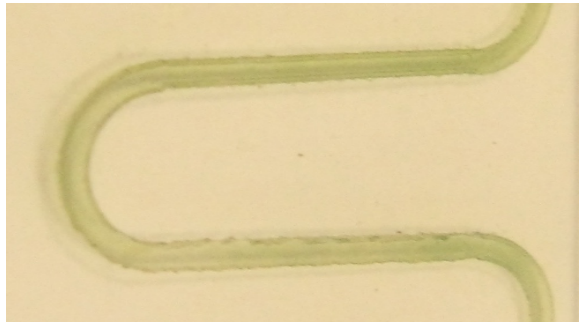
45μm x 50μm



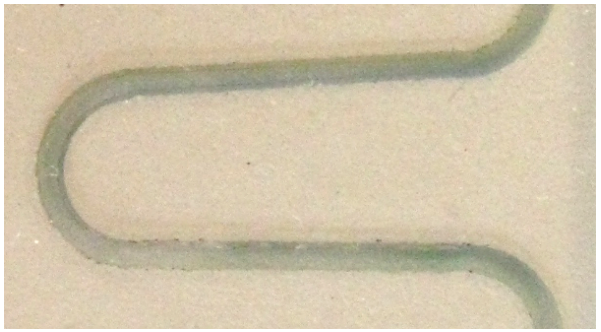
Fast Response



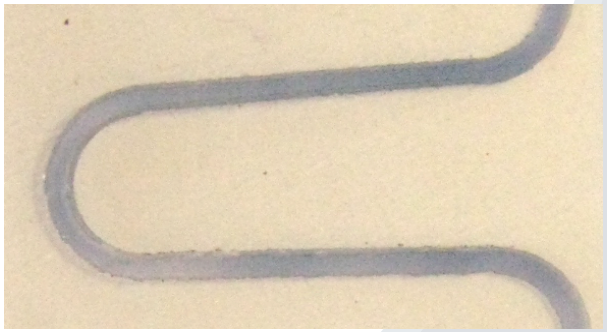
pH sensing in continous flow



pH 2

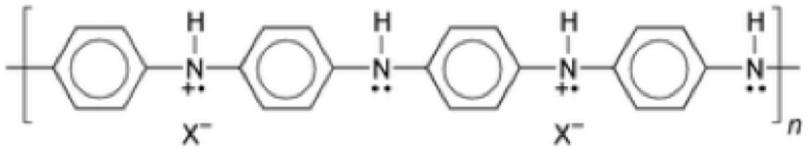


pH 4

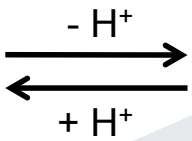


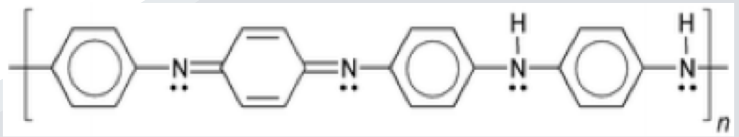
pH 12

Dedoping process



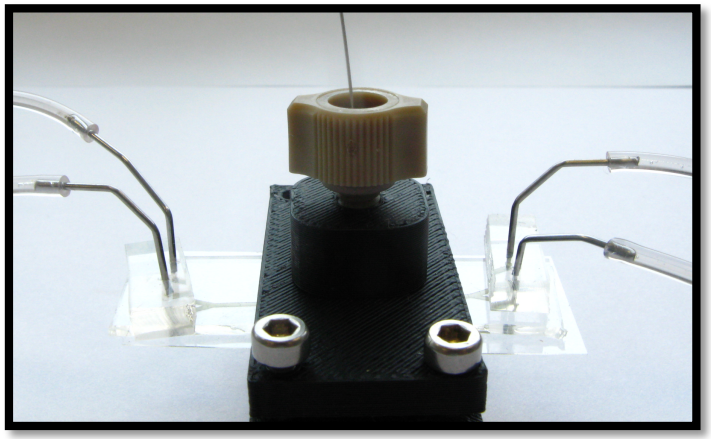
Emeraldine Salt (ES)

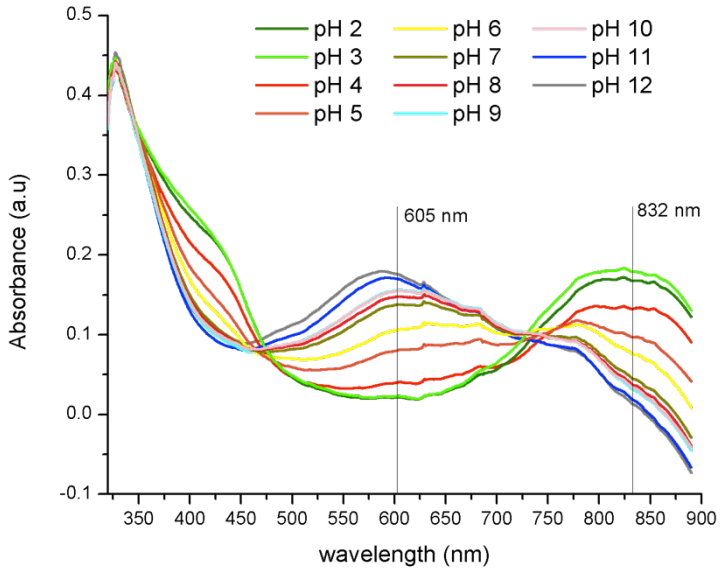


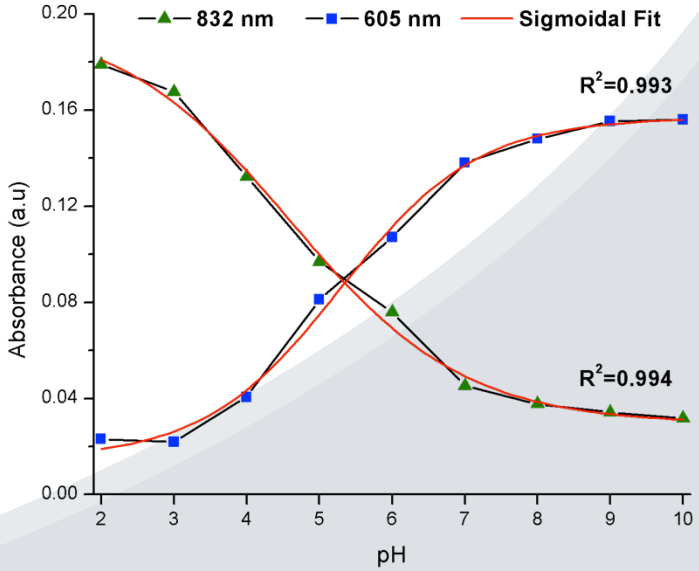


Emeraldine Base (EB)

pH sensing in continous flow





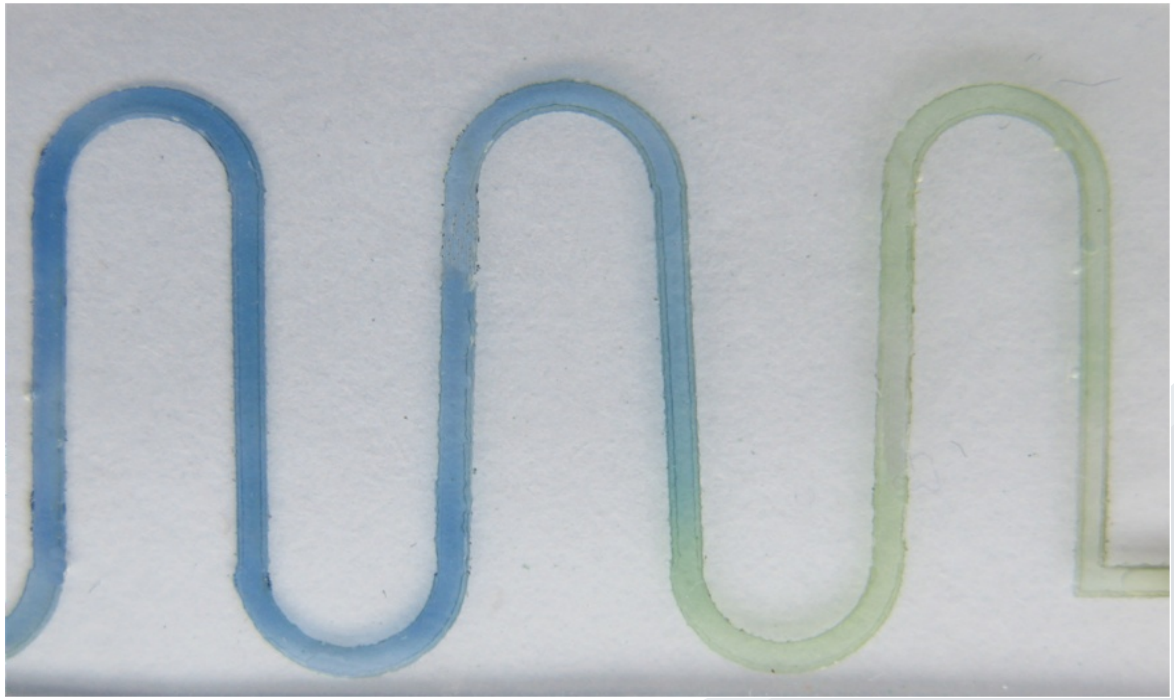


L. Florea, E. Lahiff, D. Diamond, F. Benito-Lopez / MicroTas 2011, shortlisted for best poster.

L. Florea, E. Lahiff, D. Diamond, F. Benito-Lopez / Lab Chip, to be submitted.

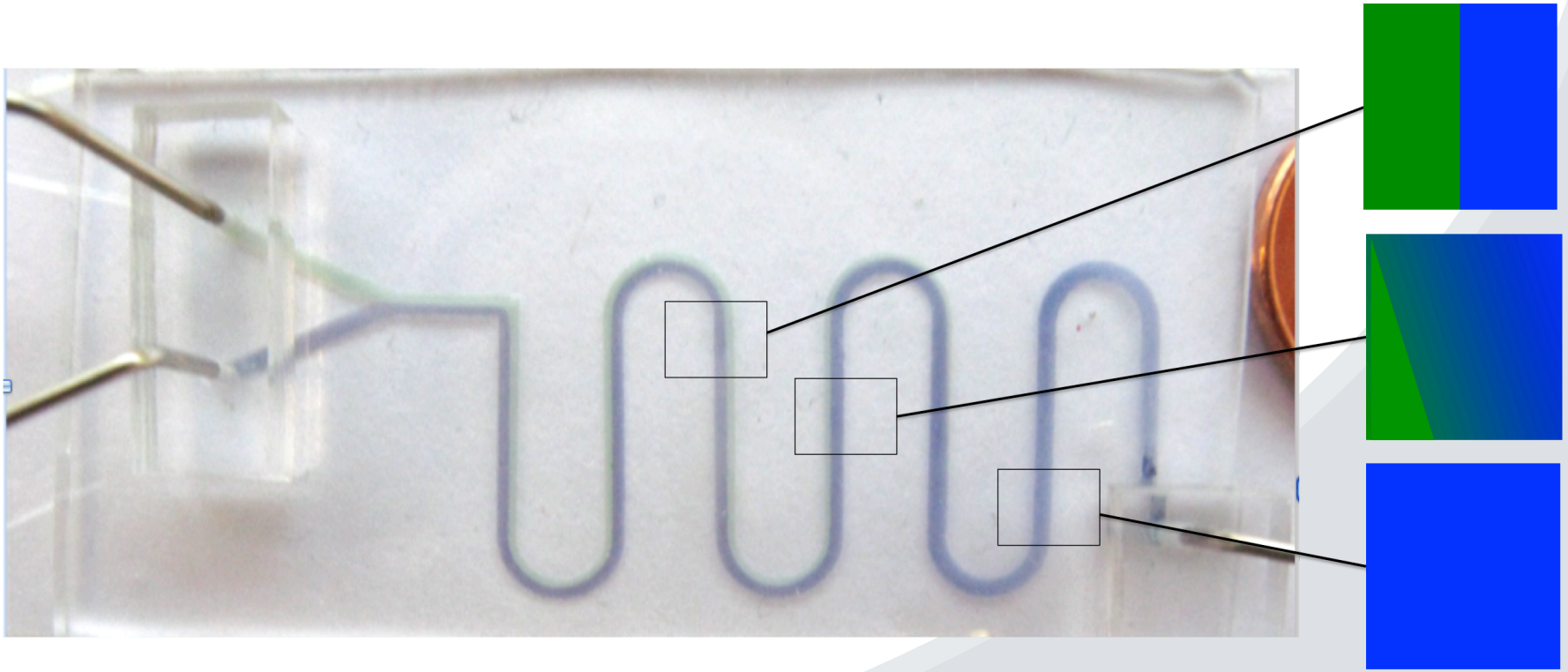
Dynamic pH sensing

NaOH 10^{-2} M



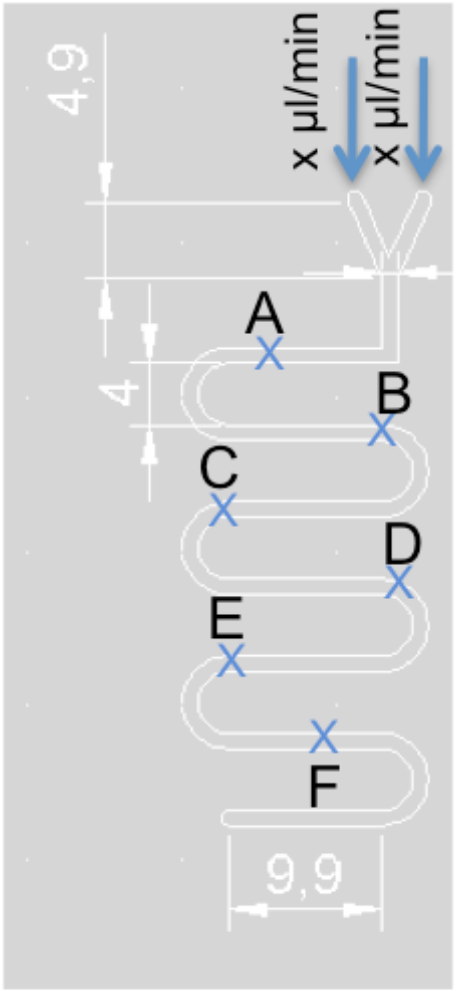
HCl 10^{-2} M

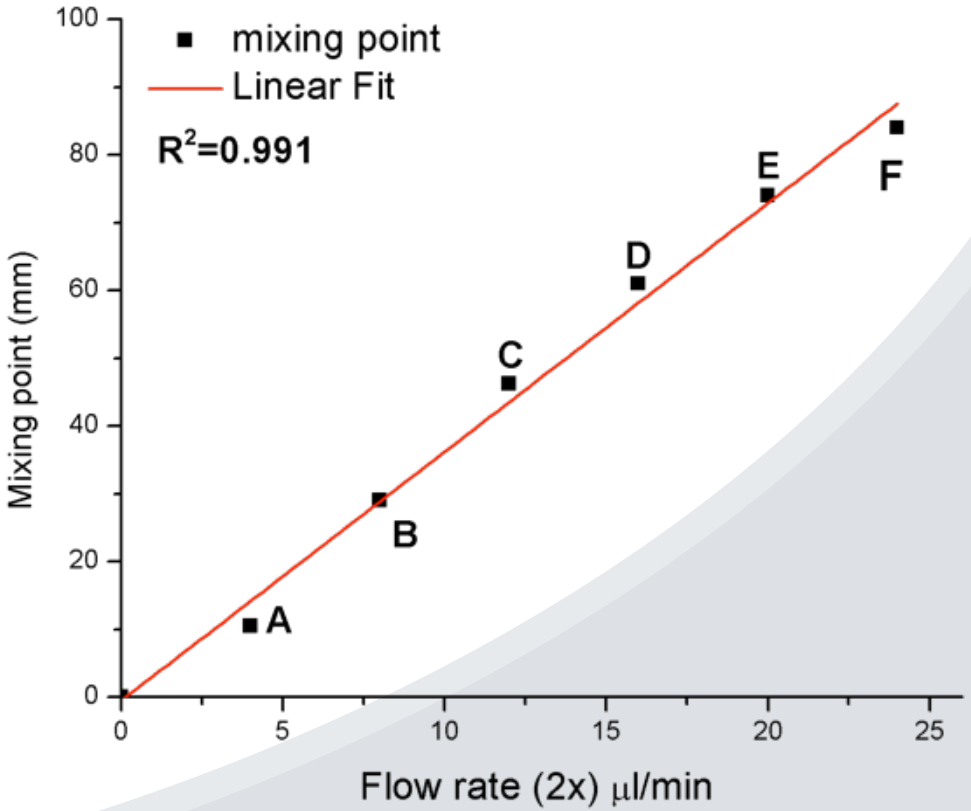
Mixing process



L. Florea, E. Lahiff, D. Diamond, F. Benito-Lopez / MicroTas 2011, shortlisted for best poster.

Mixing process

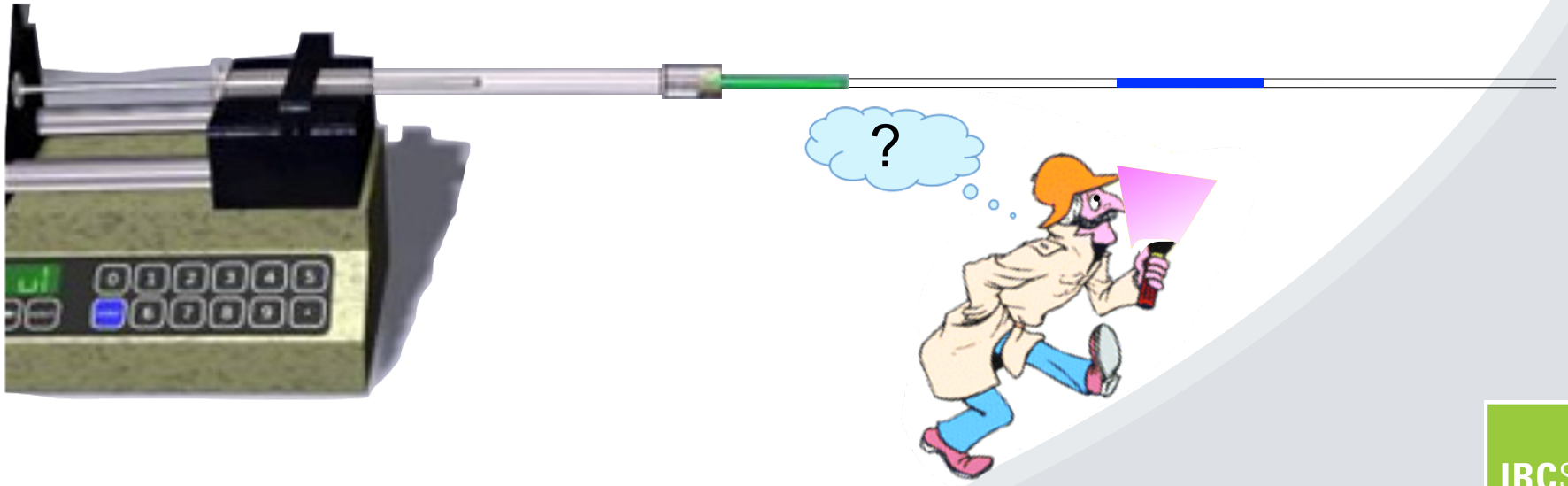




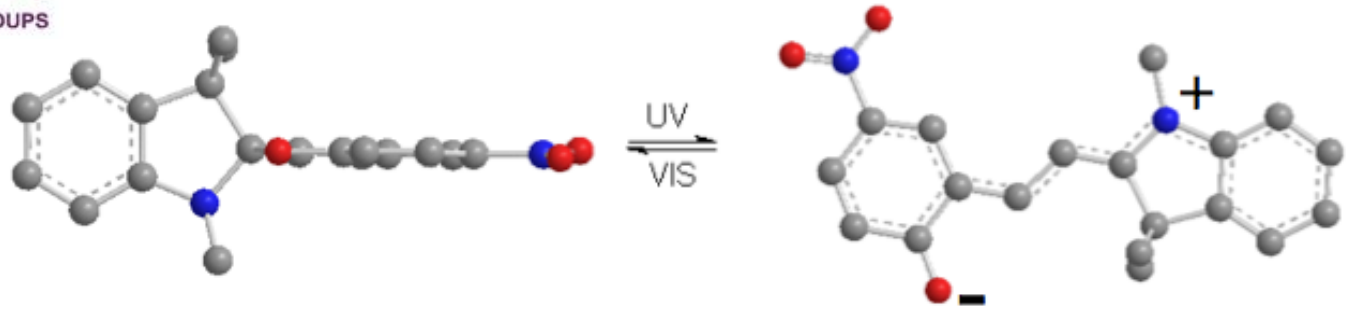
Conclusions

- First example of polyaniline coated micro-channels
- Self-diagnostic for continuous flow device
- Simple and fast photometric method to measure pH
- Replace the glass layer with glass-ITO -> electro-chemical sensing of redox active species

III. Spiropyran functionalised micro-capillaries for solvent sensing

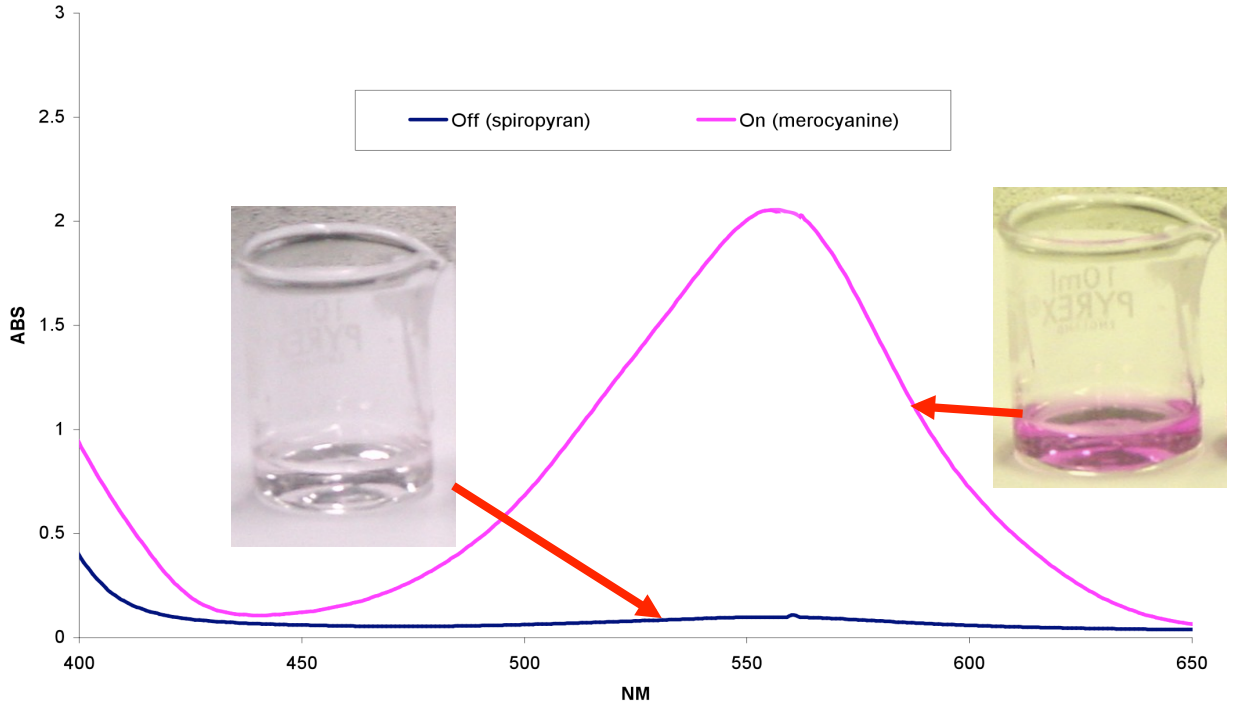


Spiropyran



A : Spiropyran SP (closed, colorless)

B : Merocyanine MC (open, colored)



Common Approach - Monolayer

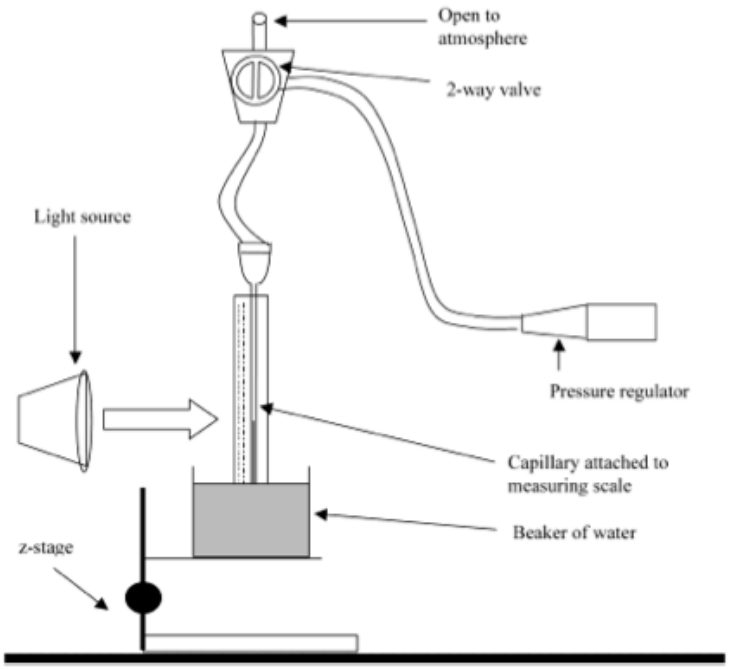


Fig 1. Experimental setup for measurement of capillary rise in a spiropyran monolayer functionalised capillary [1].

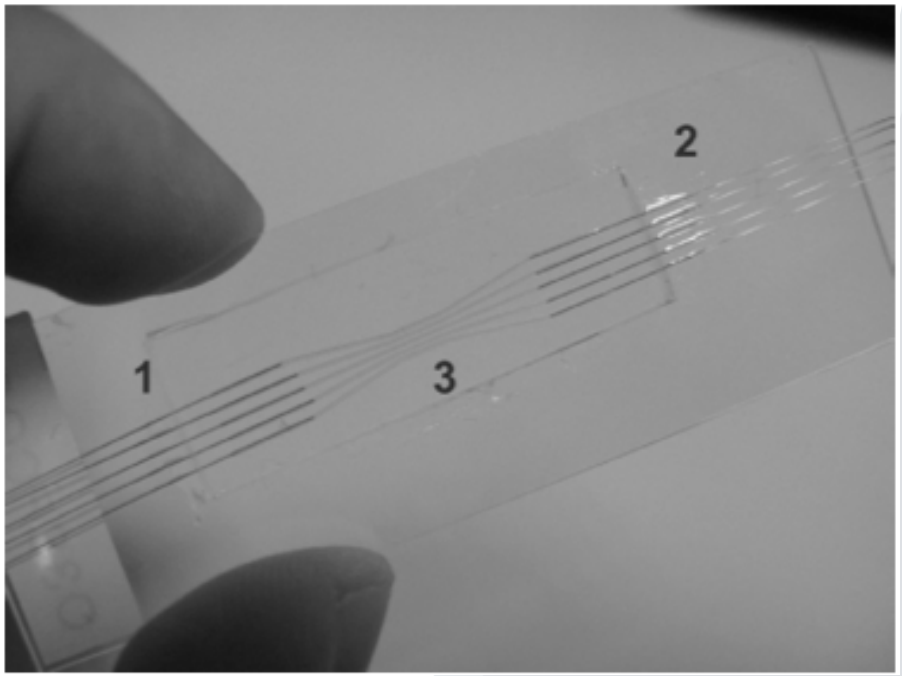


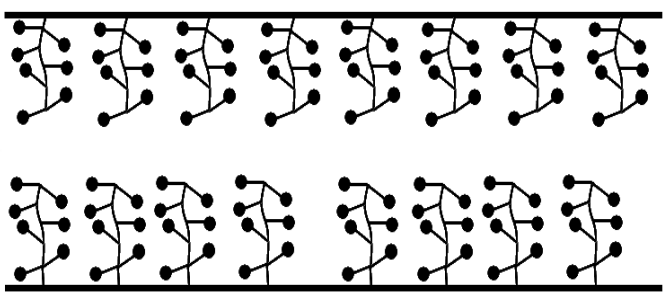
Fig 2. PDMS/glass hybrid micro-fluidic device functionalised with a monolayer of spiropyran molecules [2].

Low loading of spiropyran molecule

[1] R. Rosario et al. / Langmuir, 18 (2002) 8062-8069

[2] F. Benito-Lopez et al. / Sensors and Actuators B 140 (2009) 295–303

Our Approach



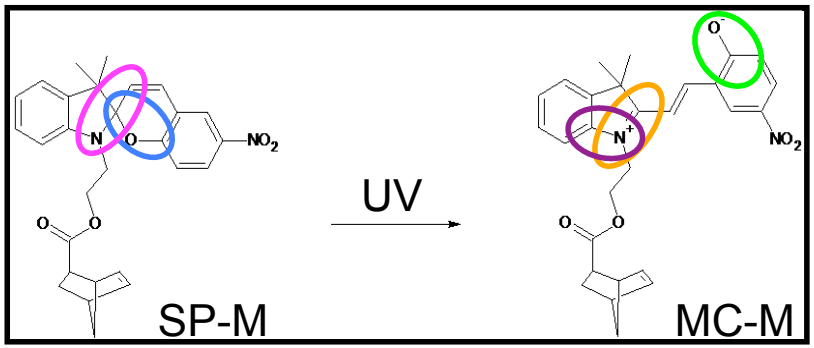
- spiropyran molecule

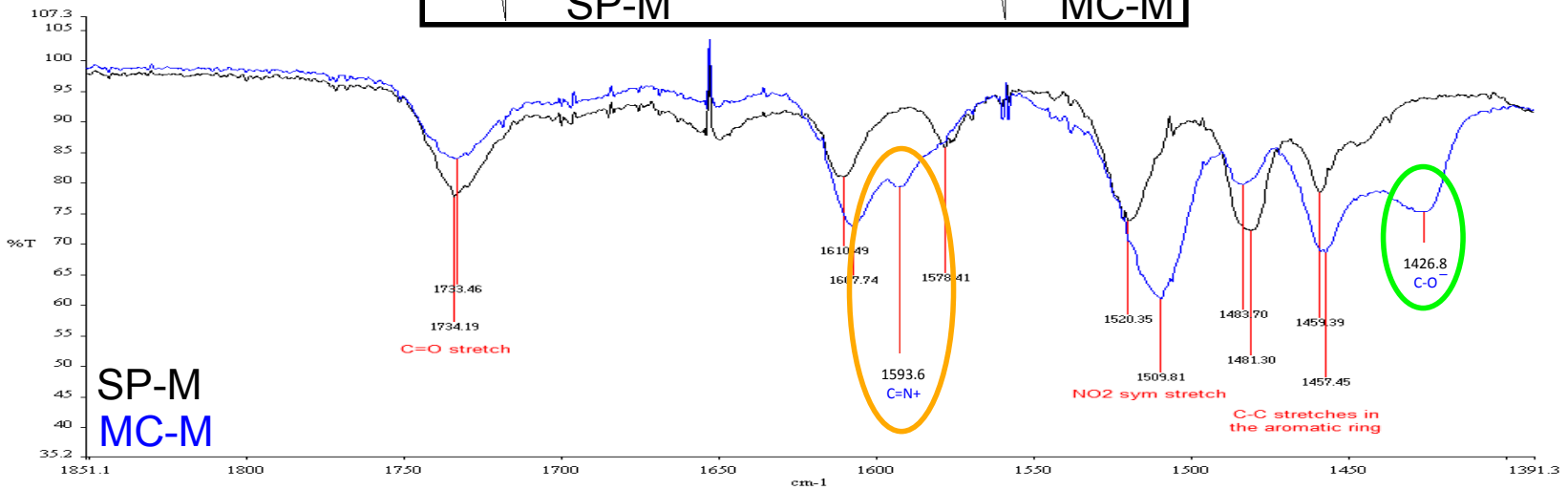
- polymer brushes
- high loading of spiropyran molecule
- 3D arrangement

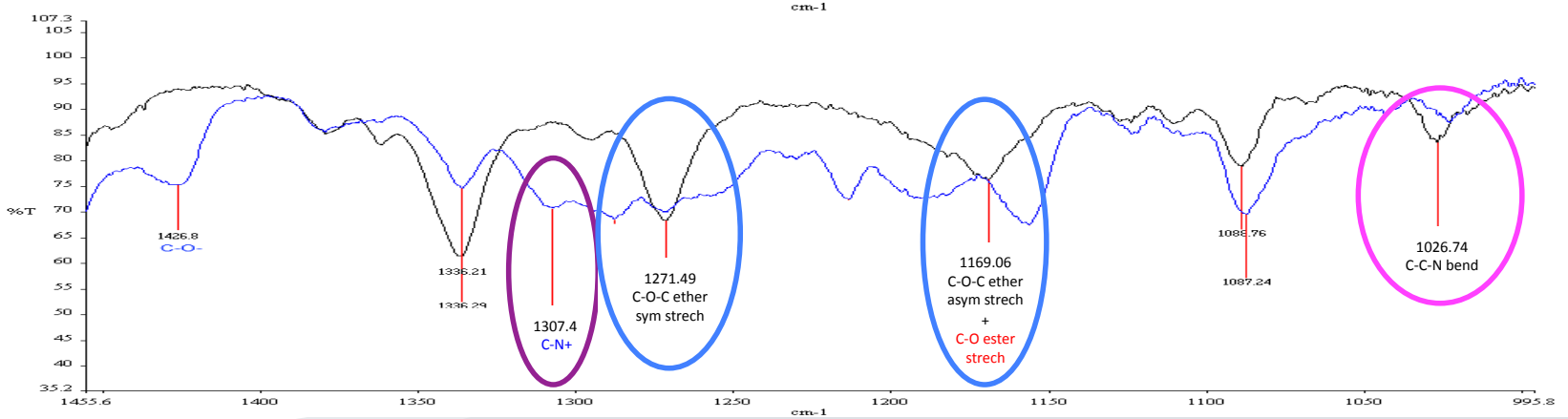
Micro-capillary : Convenient platform for rapid analysis and detection

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

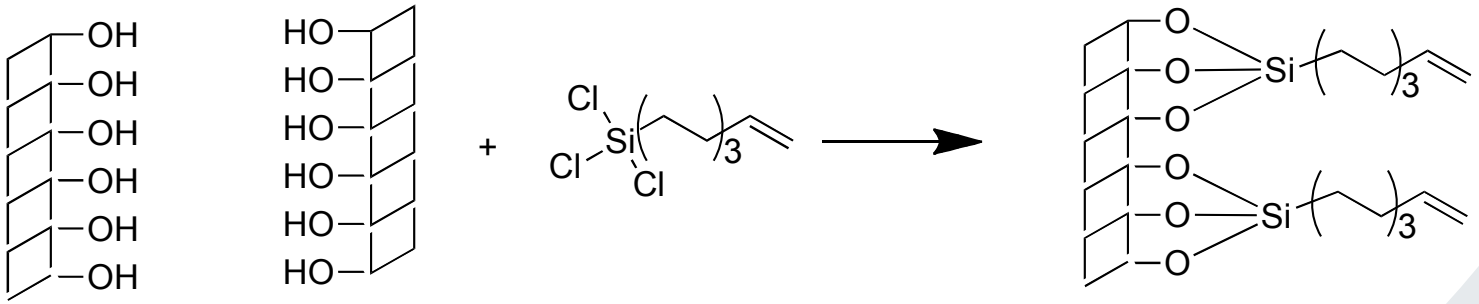

UV
SP-M
MC-M


SP-M
MC-M
%T
cm-1
1733.46
1734.19
C=O stretch
1610.49
1593.6
C=N+
1520.35
1509.81
NO2 sym stretch
1483.70
1481.30
1459.39
1457.45
C-C stretches in the aromatic ring
1426.8
C-O⁻

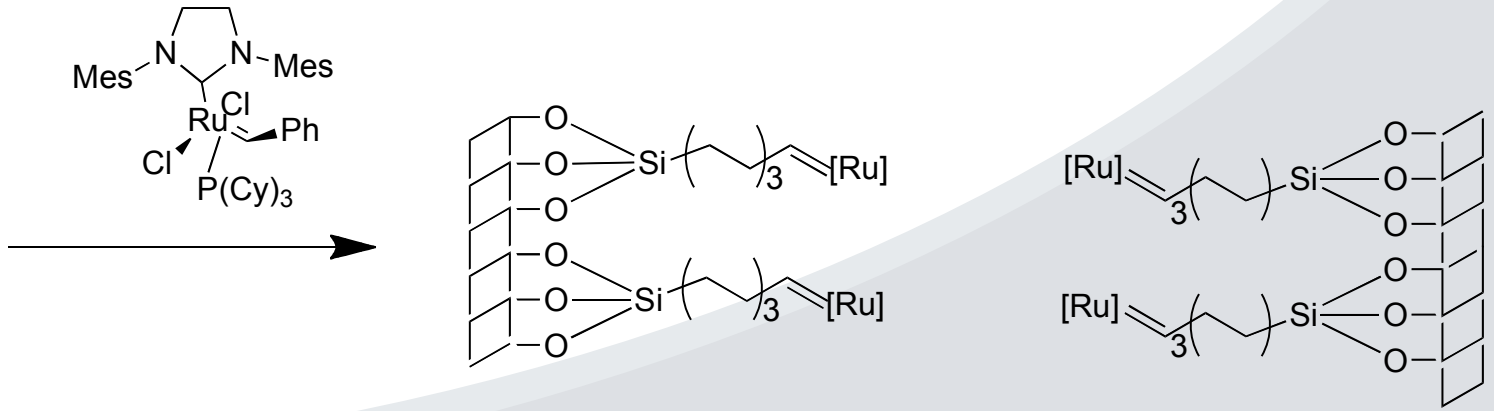

%T
cm-1
1426.8
C-O-
1336.21
1336.29
1307.4
C-N+
1271.49
C-O-C ether sym strech
1169.06
C-O-C ether asym strech
+
C-O ester strech
1088.76
1087.24
1026.74
C-C-N bend

Spiropyran polymeric brushes in micro-capillaries

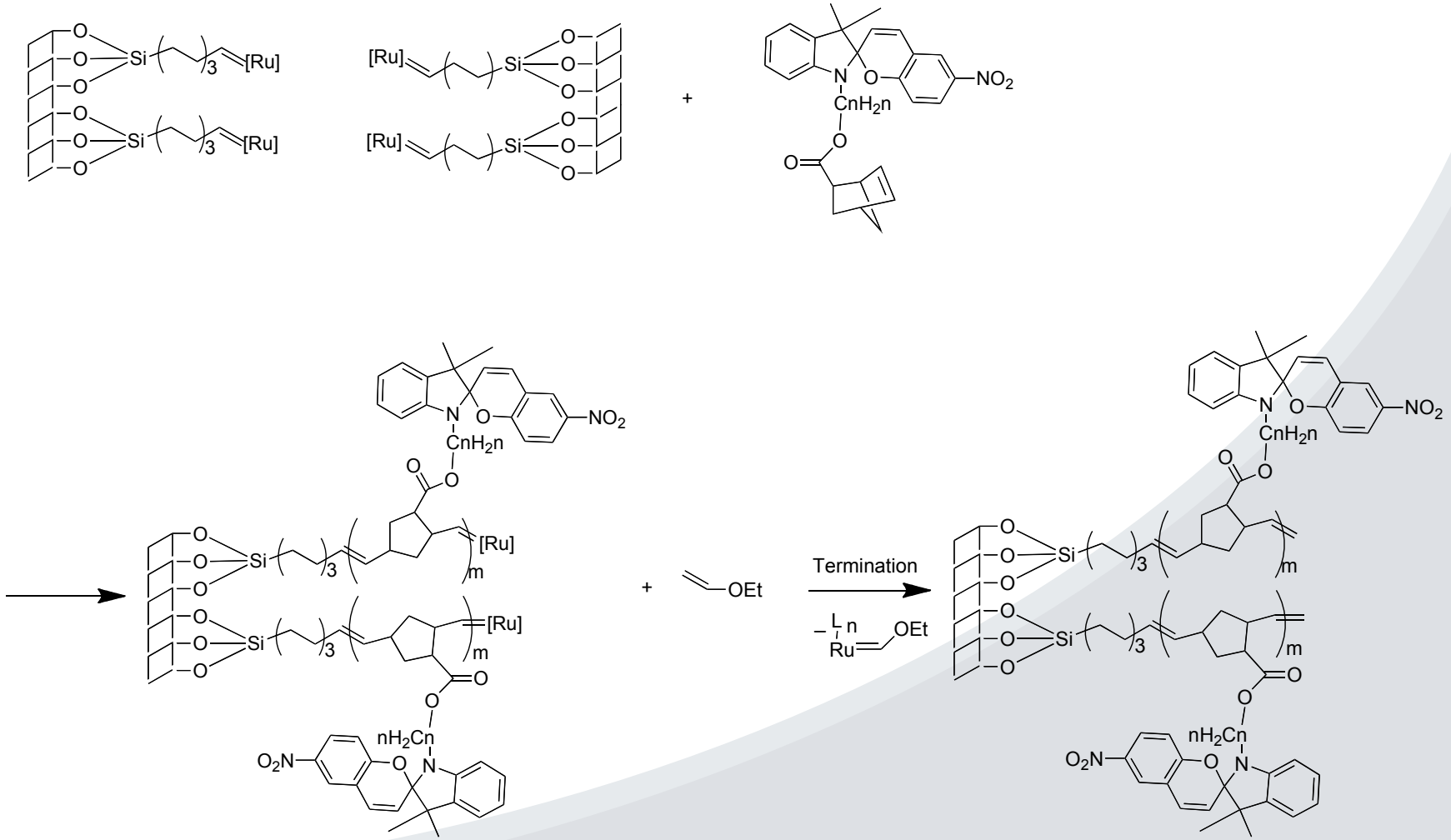
Silanisation



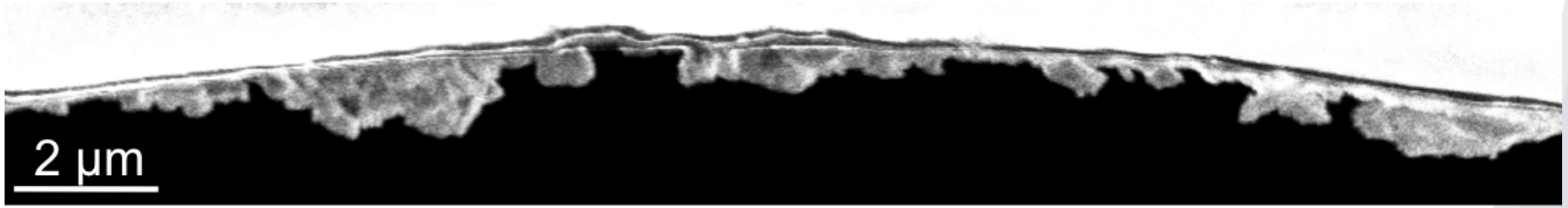
Attachment of the catalyst

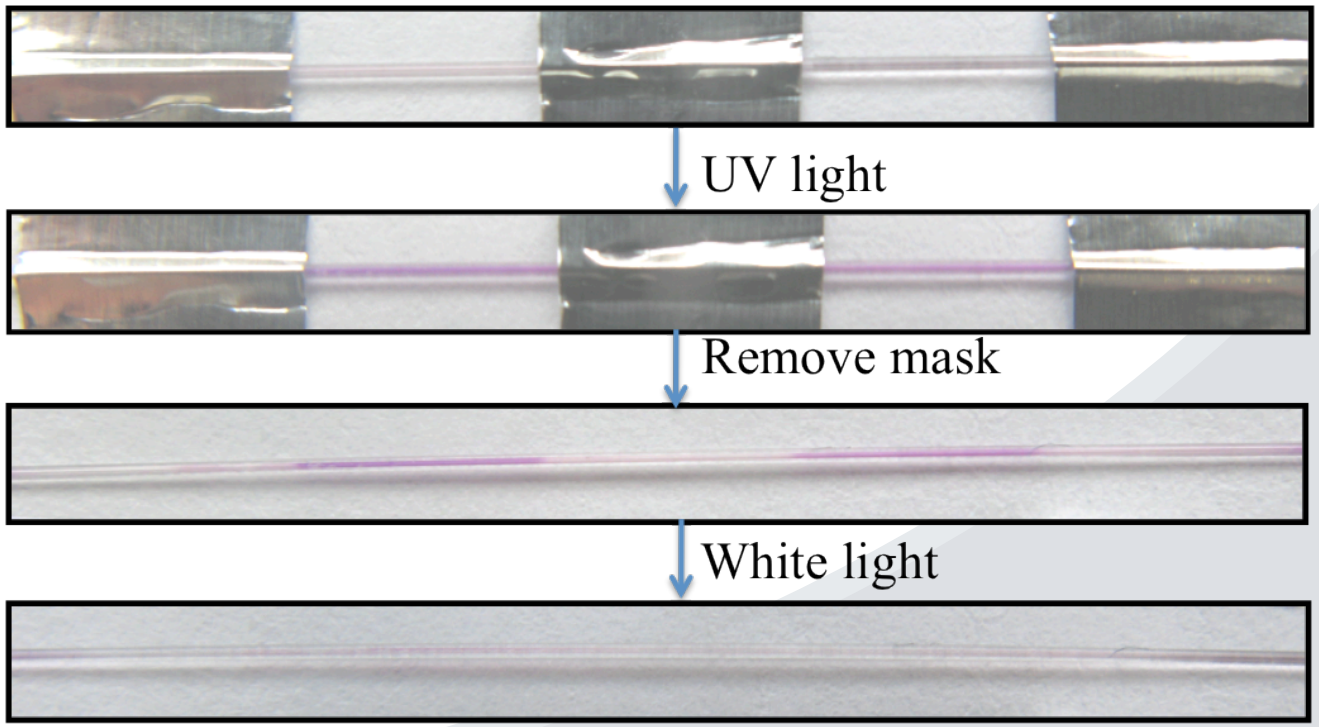


Spiropyran polymeric brushes in micro-capillaries



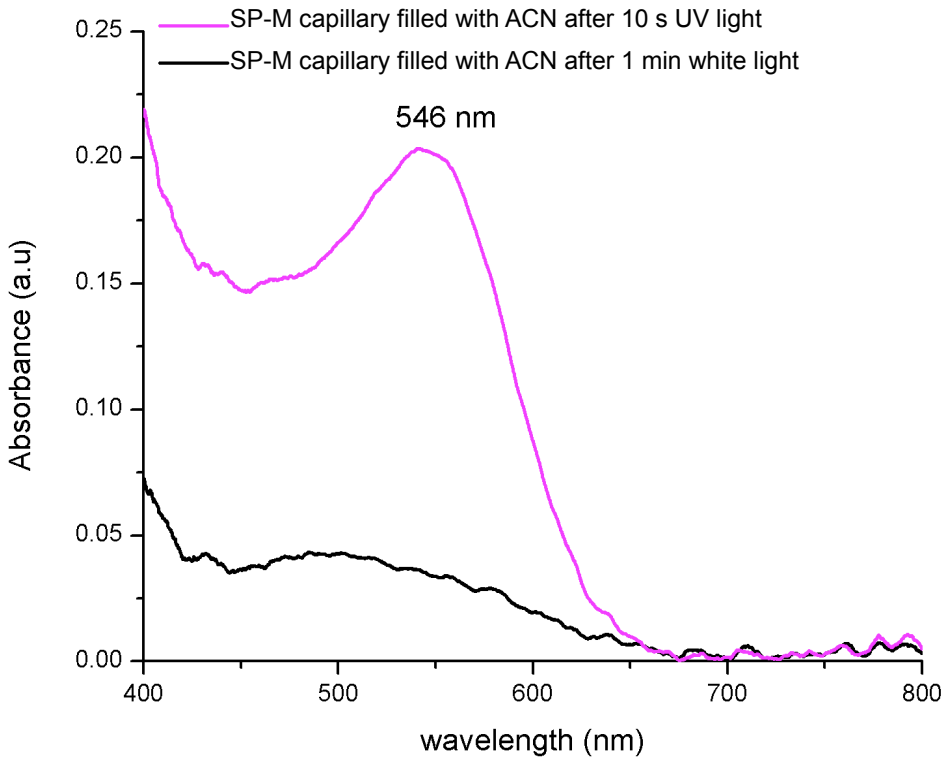
Characterisation

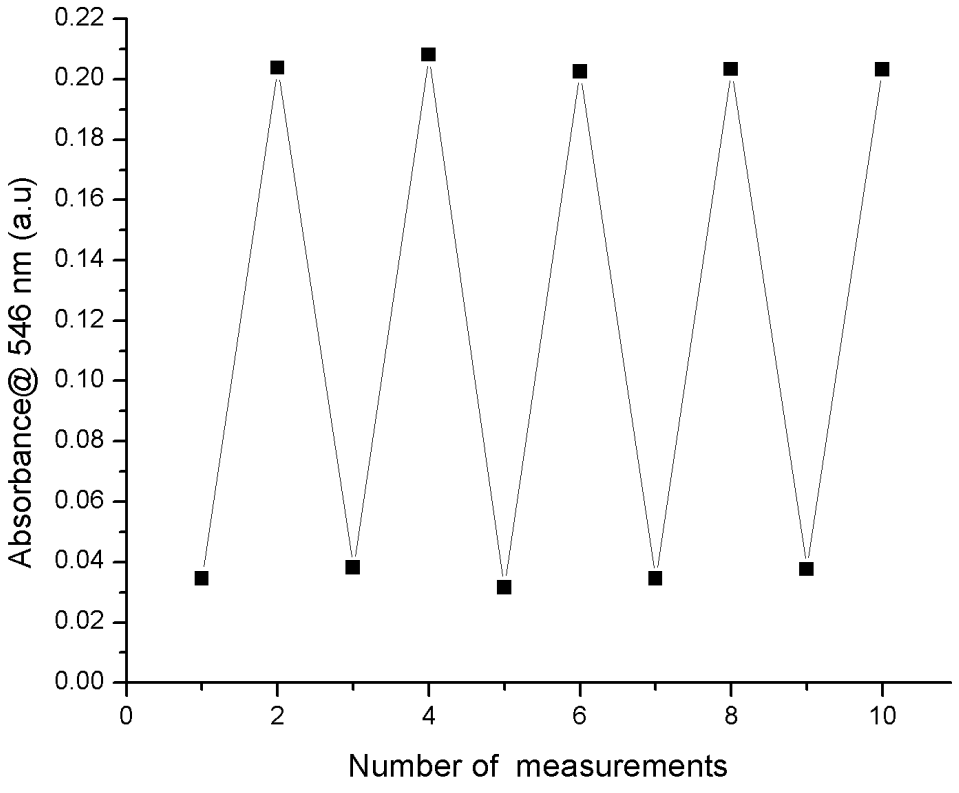




L. Florea, A. Hennart, D. Diamond, F. Benito-Lopez / Sens. Actuators B, submitted.

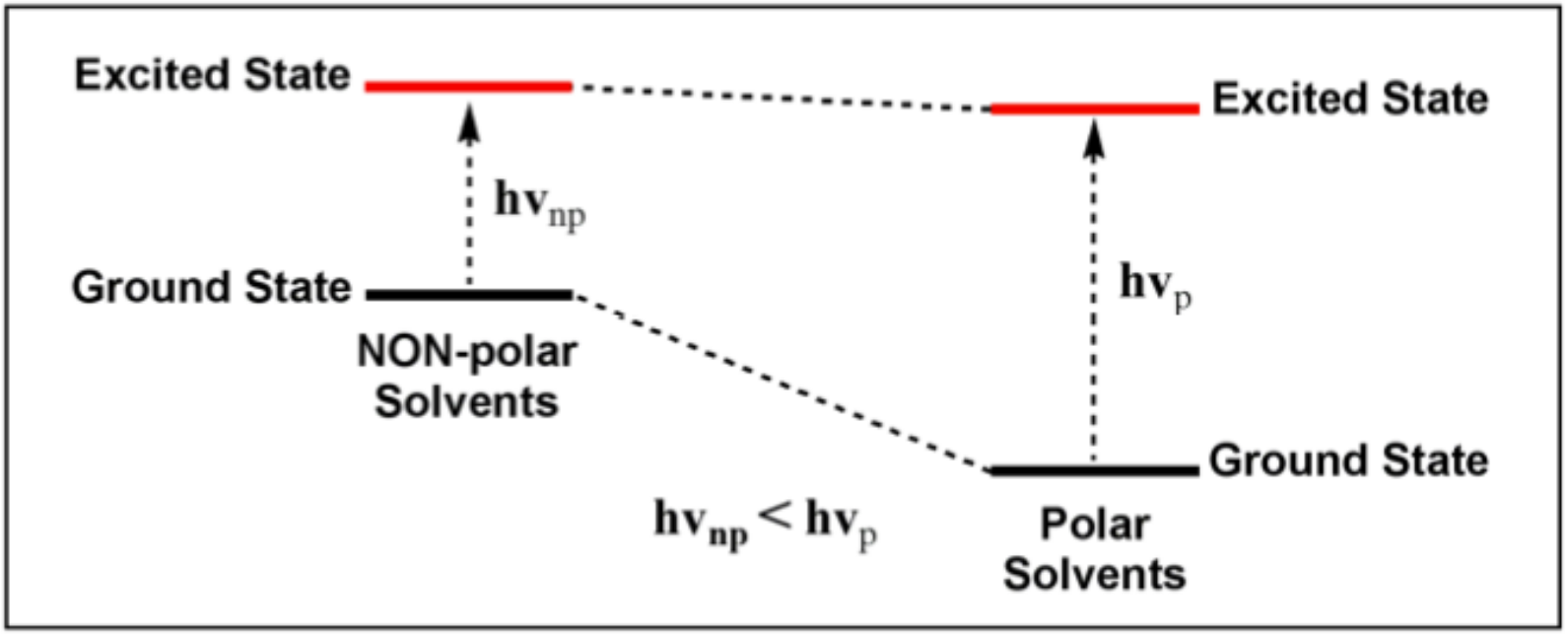
Characterisation





Solvatocromic Proprieties

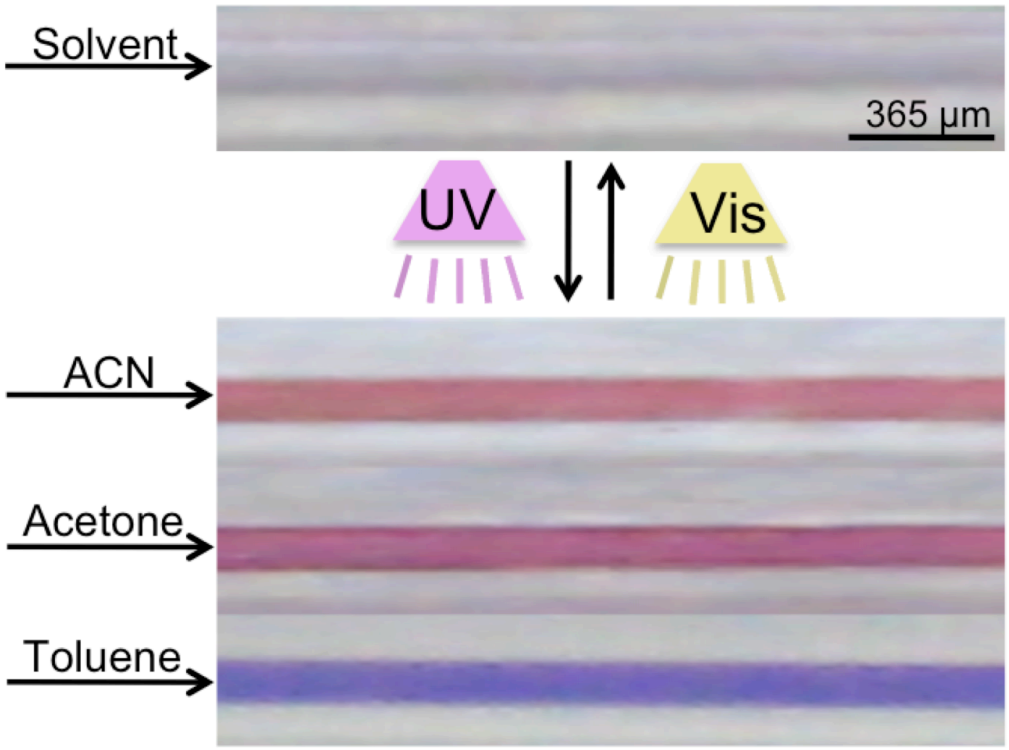
The colour of the MC form depends on the difference in polarity between the photo-excited MC form and the conjugated zwitterionic ground state

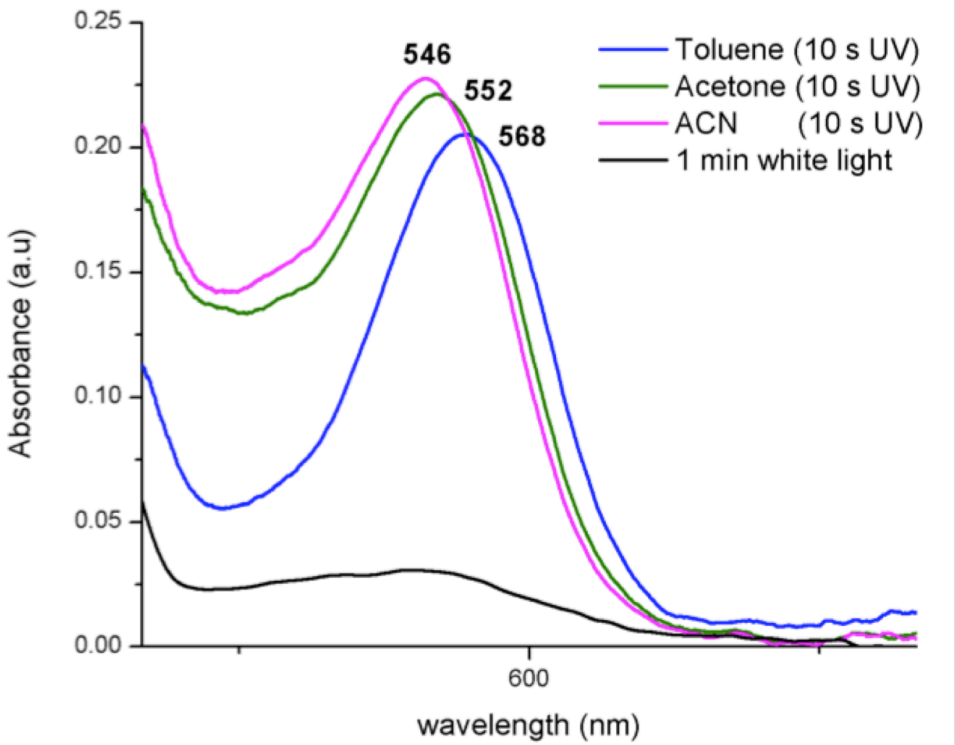


- The absorption band of MC form undergoes a hypsochromic (blue) shift in solvents of increasing polarity (negatively solvatochromism).

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

Solvent Detection





L. Florea, A. Hennart, D. Diamond, F. Benito-Lopez / Chem Comm., submitted.

Conclusions

- First example of spiropyran polymer brushes in micro-capillaries
- Self-diagnostic for continuous flow device
- Solvent detection in micro-capillaries
- Sensing behaviour can be switched on/off remotely using light

Acknowledgments

- Dr. Fernando Benito-Lopez
- Alexandre Hennart
  University of Namur, Belgium
- Dr. Kevin Fraser
- Dr. Emer Lahiff
- Prof. Dermot Diamond
- IRCSET – Embark Initiative
- CLARITY – award (07/CE/ I1147)

NCSR RESEARCH GROUPS

CLARITY clarity-centre.org

Thank you for your attention !!

IRCSET Investing in People and Ideas

Irish Research Council for Science, Engineering and Technology