



国际战略合作项目-中国/爱尔兰

ISCP★China

INTERNATIONAL STRATEGIC COLLABORATION
PROGRAMME - CHINA / IRELAND

Stimuli-responsive materials as sensors and actuators in microfluidic devices

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Dublin City University



中国爱尔兰研究通道

12/05/2014





1. Introduction

- **stimuli-responsive materials**
- **optical sensors and actuators in microfluidics**

2. Polyaniline functionalised micro-fluidic channels for:

- **pH sensing**
- **study mixing**

3. Spiropyran functionalised micro-capillaries for:

- **solvent sensing**
- **metal ion sensing**

4. Photo-actuators for:

- **micro-valve applications**



Stimuli-responsive Materials

Materials whose characteristics can be changed using an external stimulus

Thermal

Mechano

Photo

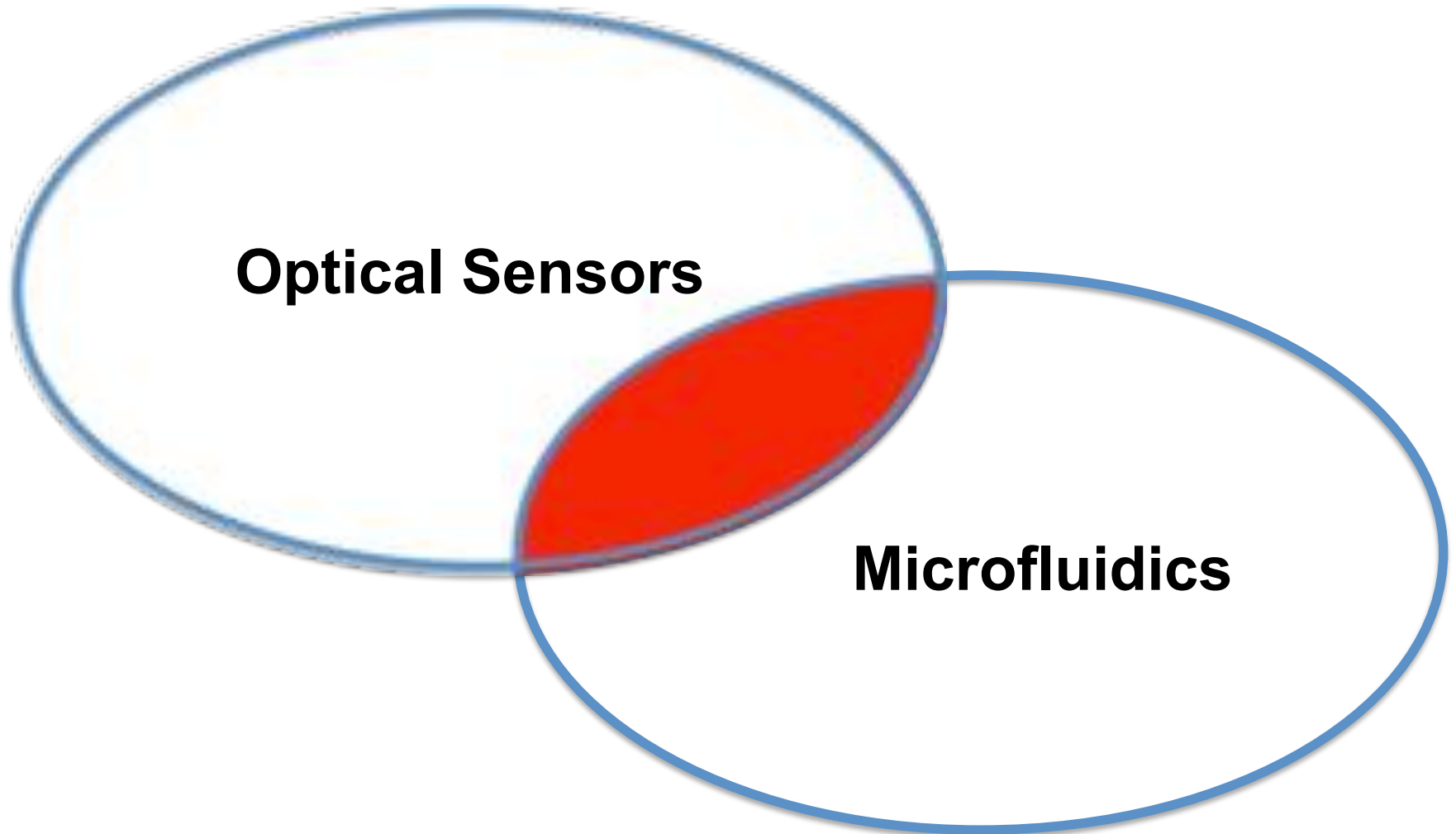
pH

Chemo





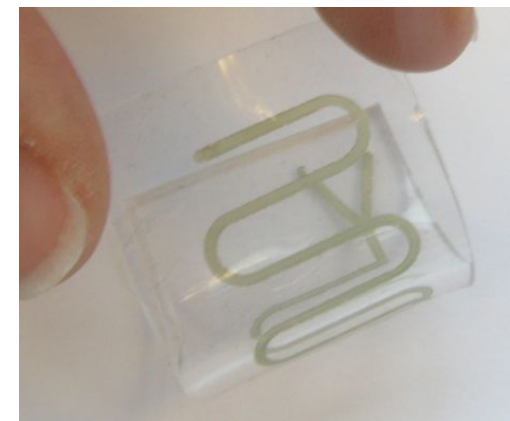
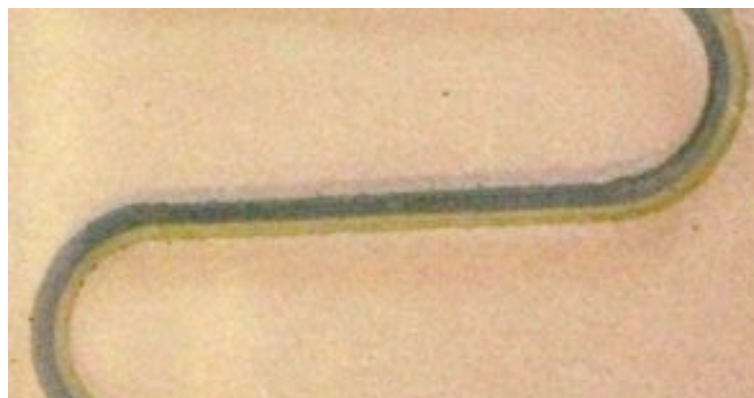
Optical Sensors in Microfluidics





2. Polyaniline functionalised micro-capillaries and micro-fluidic channels

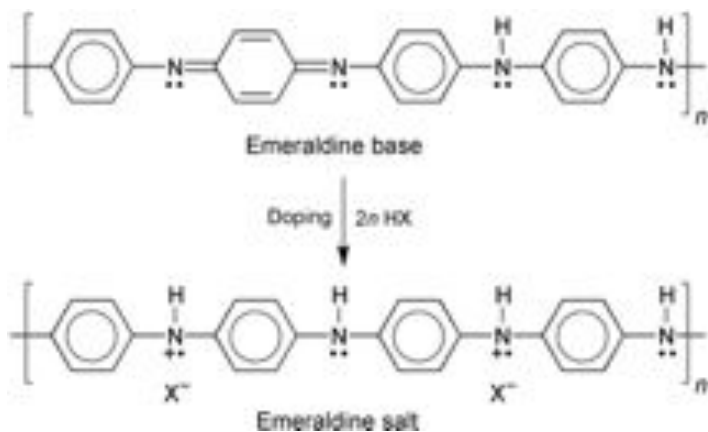
- pH sensing
- ammonia sensing
- diffusion study





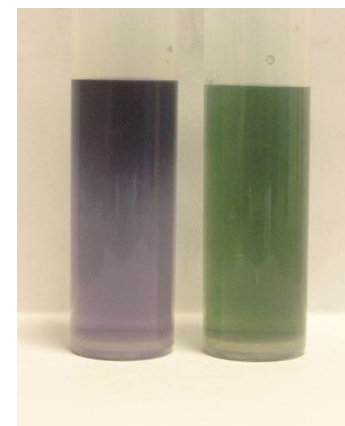
Polyaniline Nanofibres

- 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

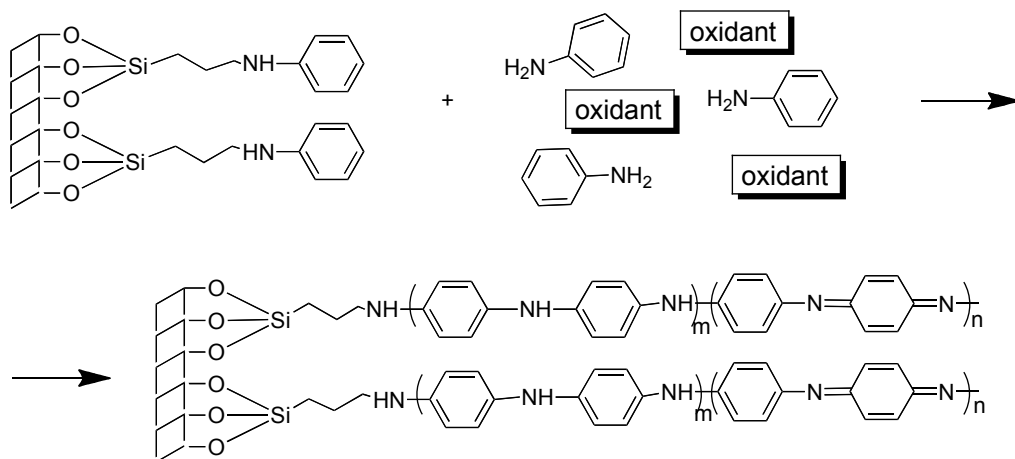
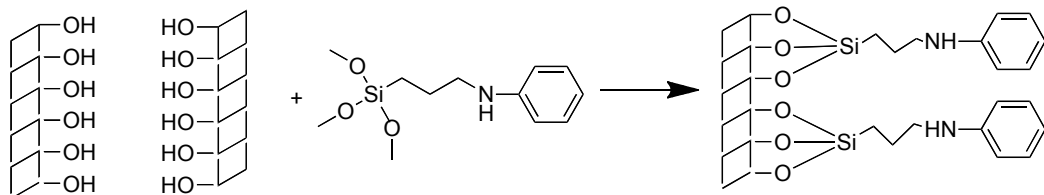




Polyaniline-coated micro-capillaries for ammonia sensing



➤ Micro-capillary functionalisation



ANALYTICA CHIMICA ACTA
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Featured Article
Polyaniline coated micro-capillaries for continuous flow analysis of aqueous solutions
Larisa Florea, Dermot Diamond and Fernando Benito-Lopez
(Published on pp. 1–7 of this issue)

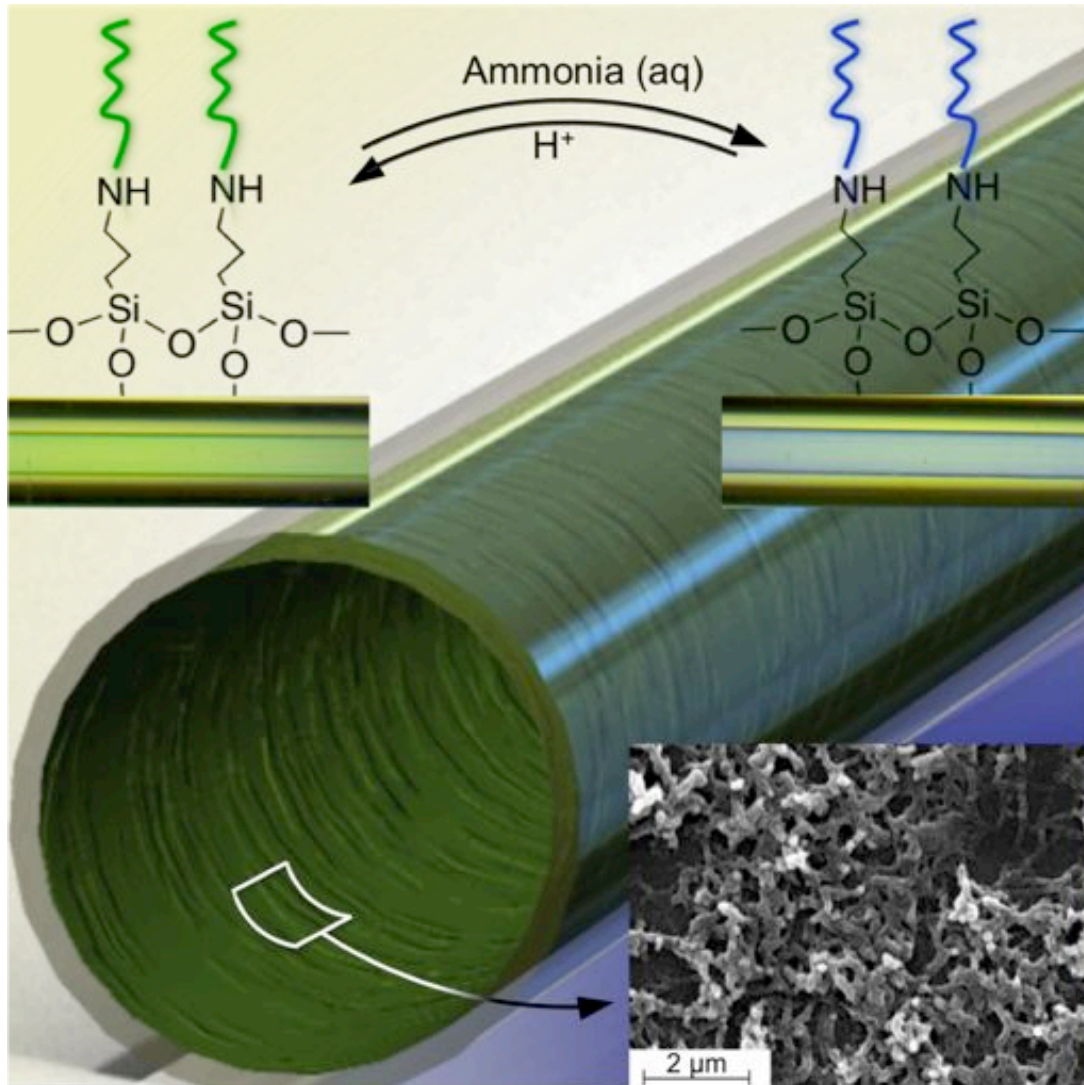
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L. Florea, D. Diamond and F. Benito-Lopez, *Anal. Chim. Acta*, 2013, 759, 1-7



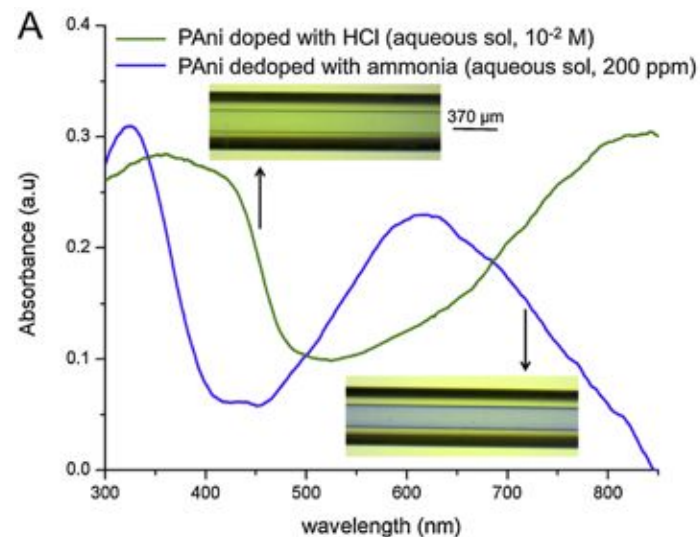
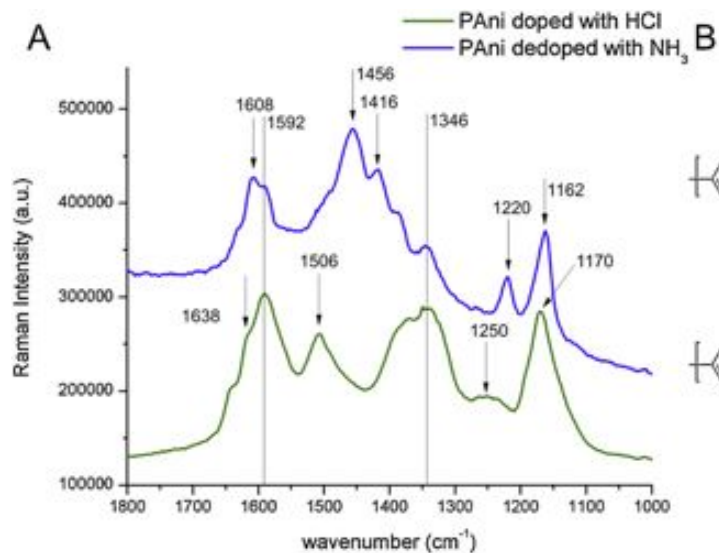
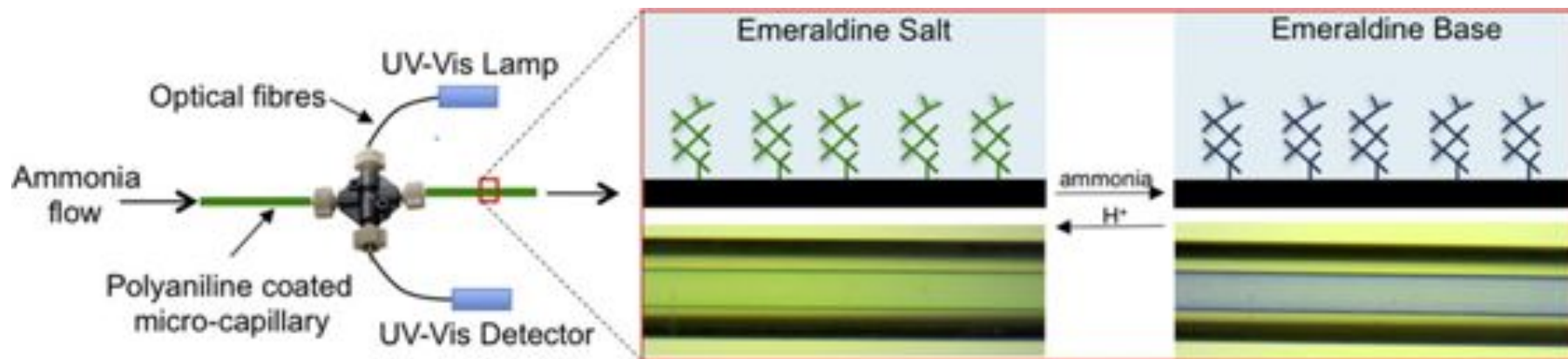


Polyaniline-coated micro-capillaries for ammonia sensing





Doping dedoping properties

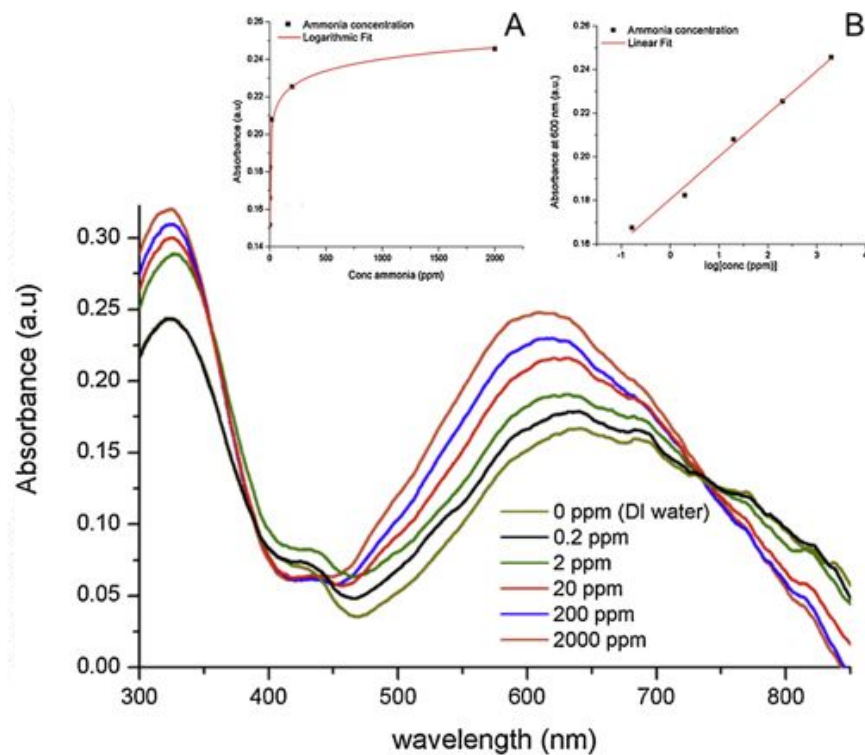
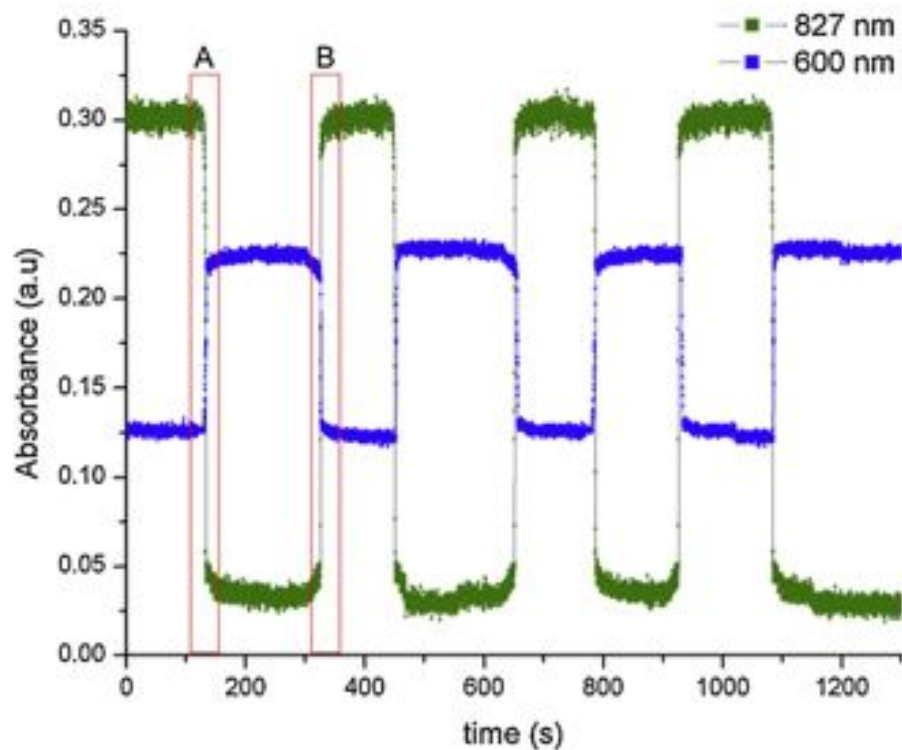


L. Florea, D. Diamond and F. Benito-Lopez, *Anal. Chim. Acta*, 2013, 759, 1-7





Ammonia sensing



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



Micro-chip fabrication

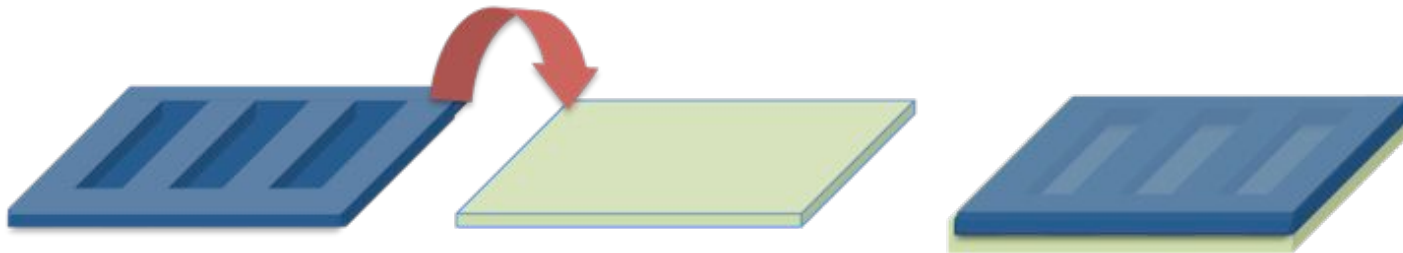
✓ PDMS is poured onto master mold, cured at 80°C for 1 h and removed from mold.



✓ PDMS and glass slide are treated with oxygen plasma.



✓ PDMS and glass slide are brought together.

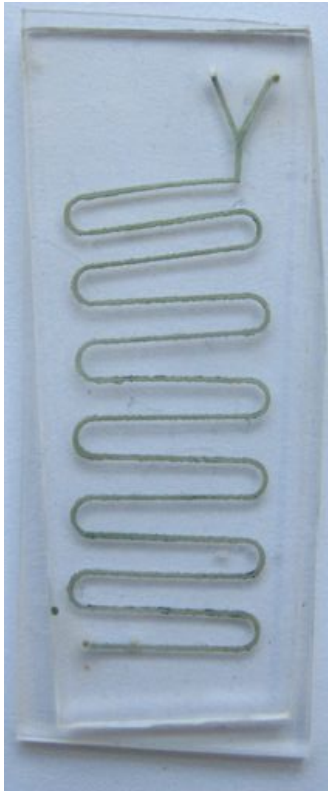


L. Yu, C.M. Li, Y. Liu *et al.* / Lab Chip, 9 (2009), 1243–1247.

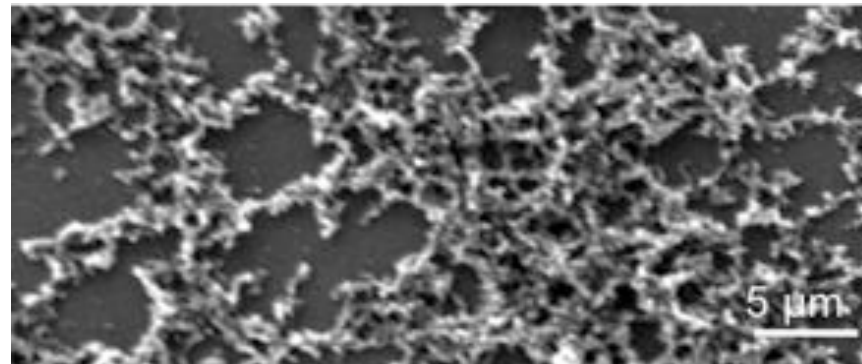
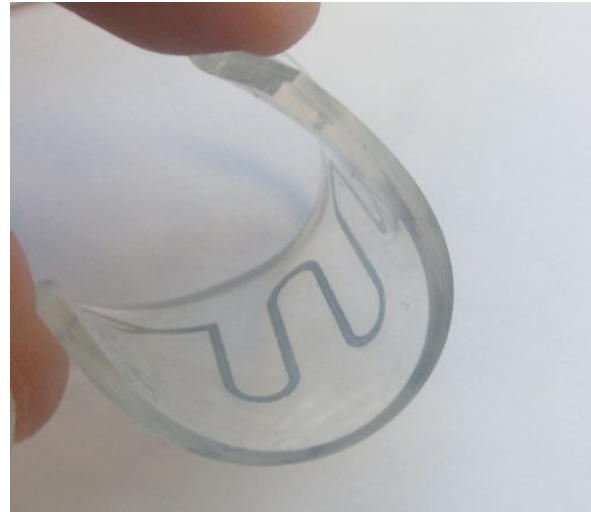


Micro-channels

500 μm x 1000 μm



1000 μm x 100 μm

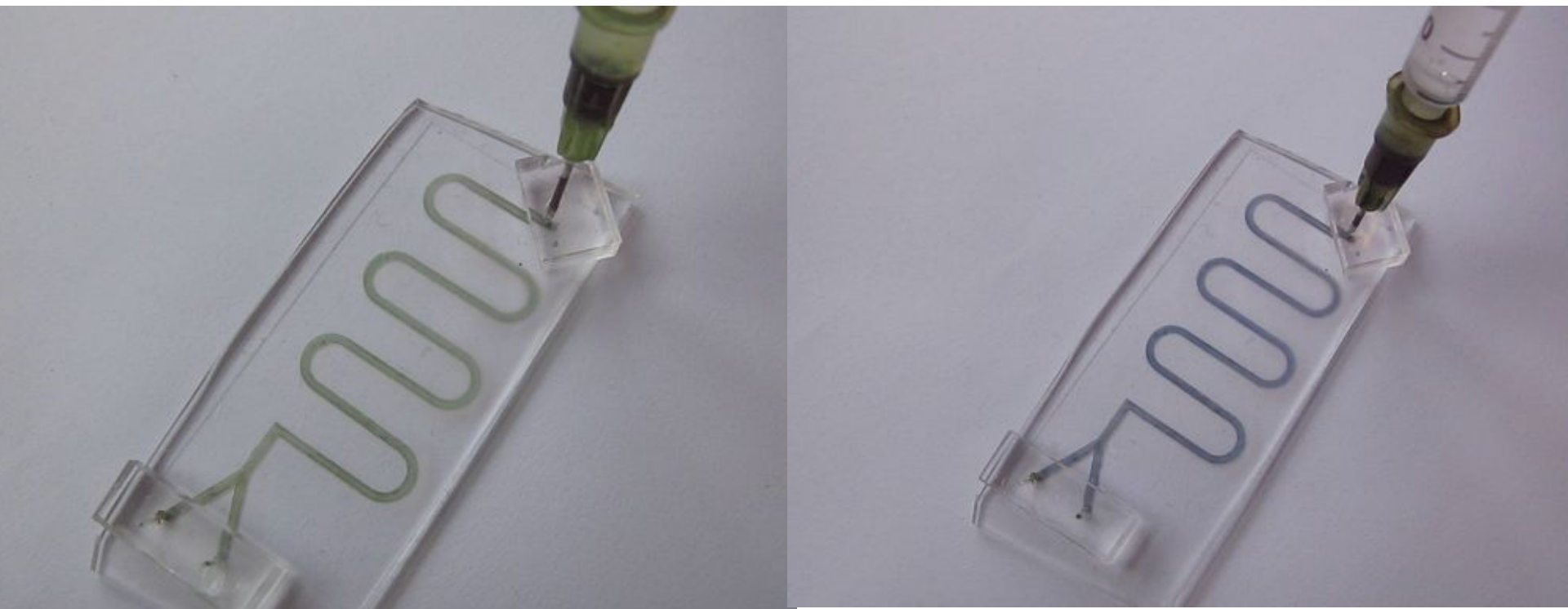


45 μm x 50 μm





Fast Response

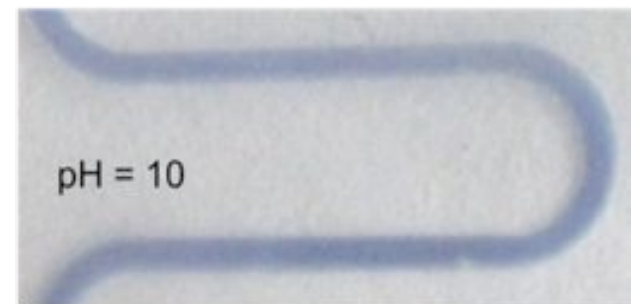
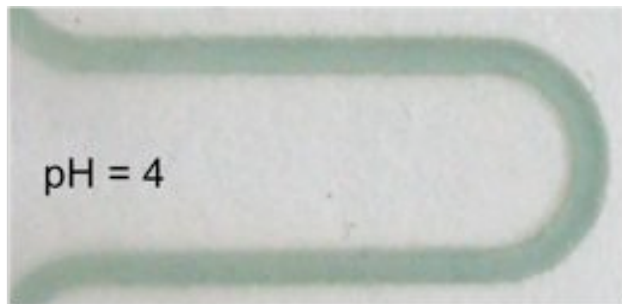
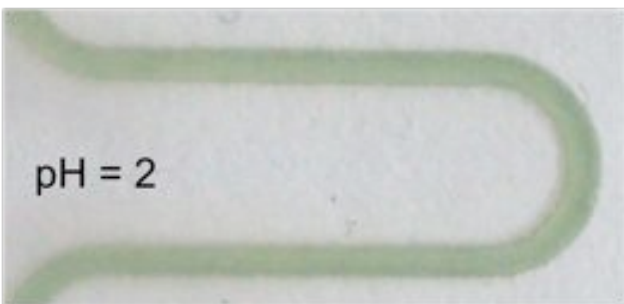


L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.

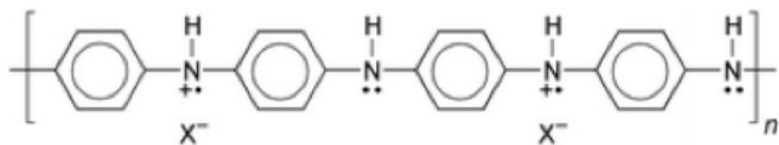




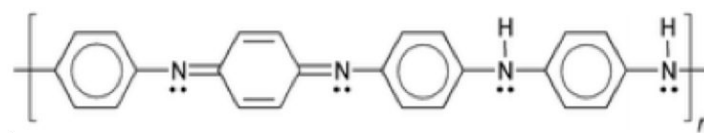
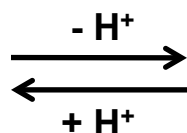
pH sensing in continuous flow



—————→
Dedoping process



Emeraldine Salt (ES)



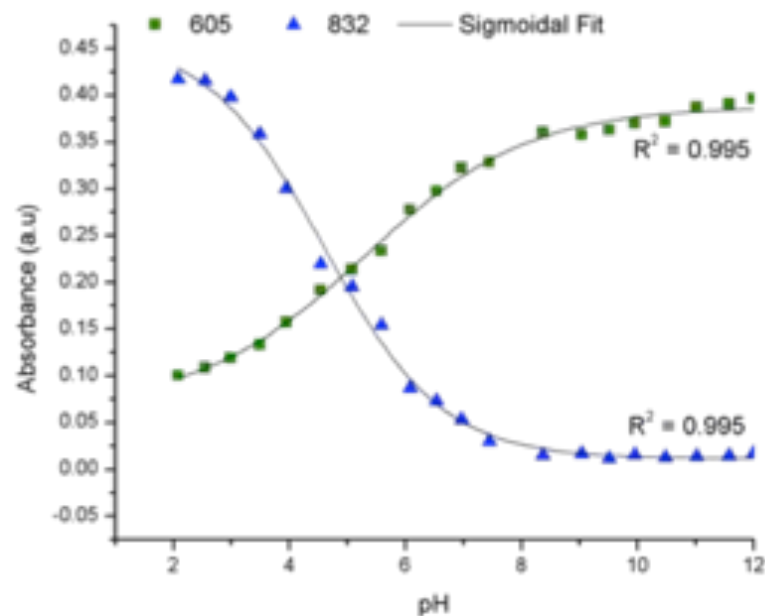
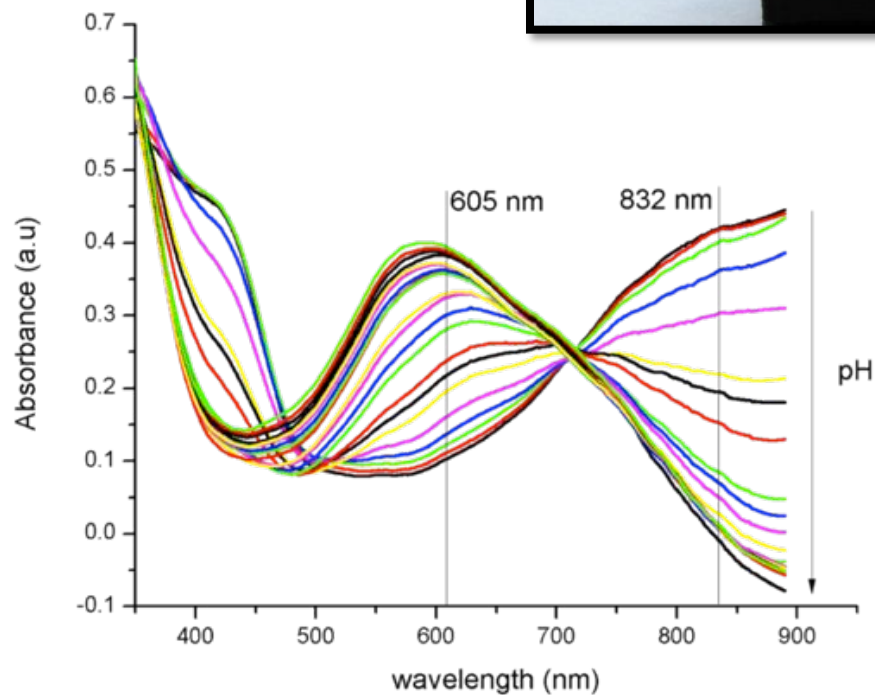
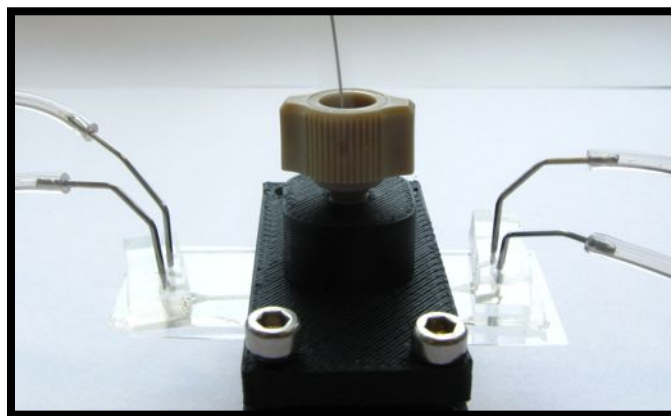
Emeraldine Base (EB)

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

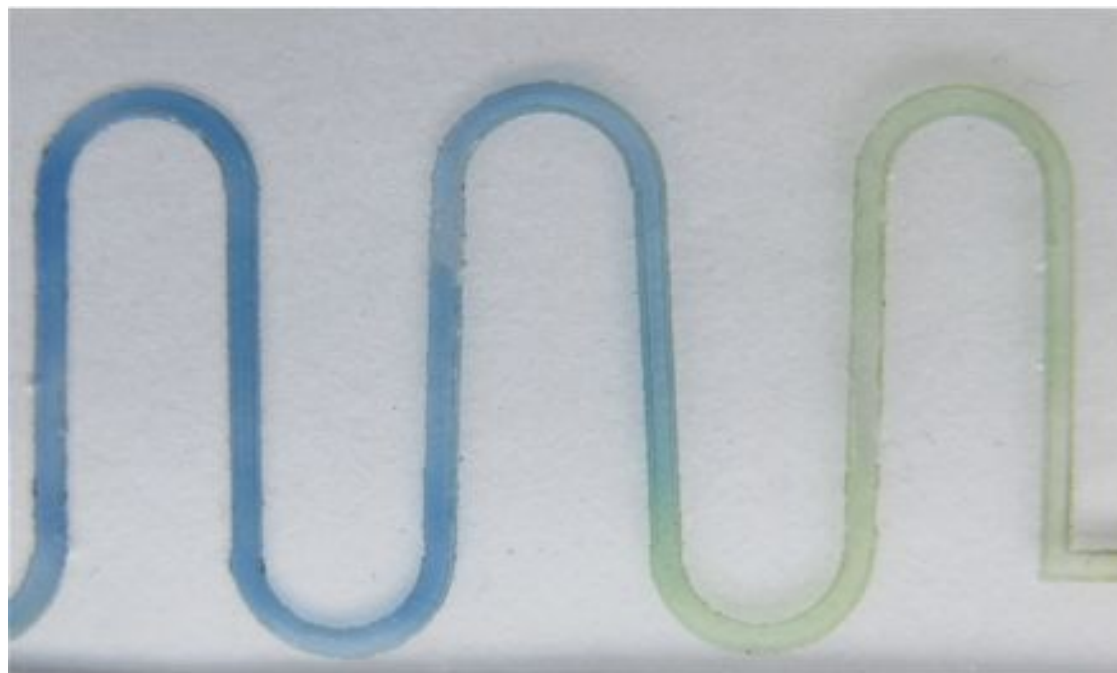


L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.





Dynamic pH sensing



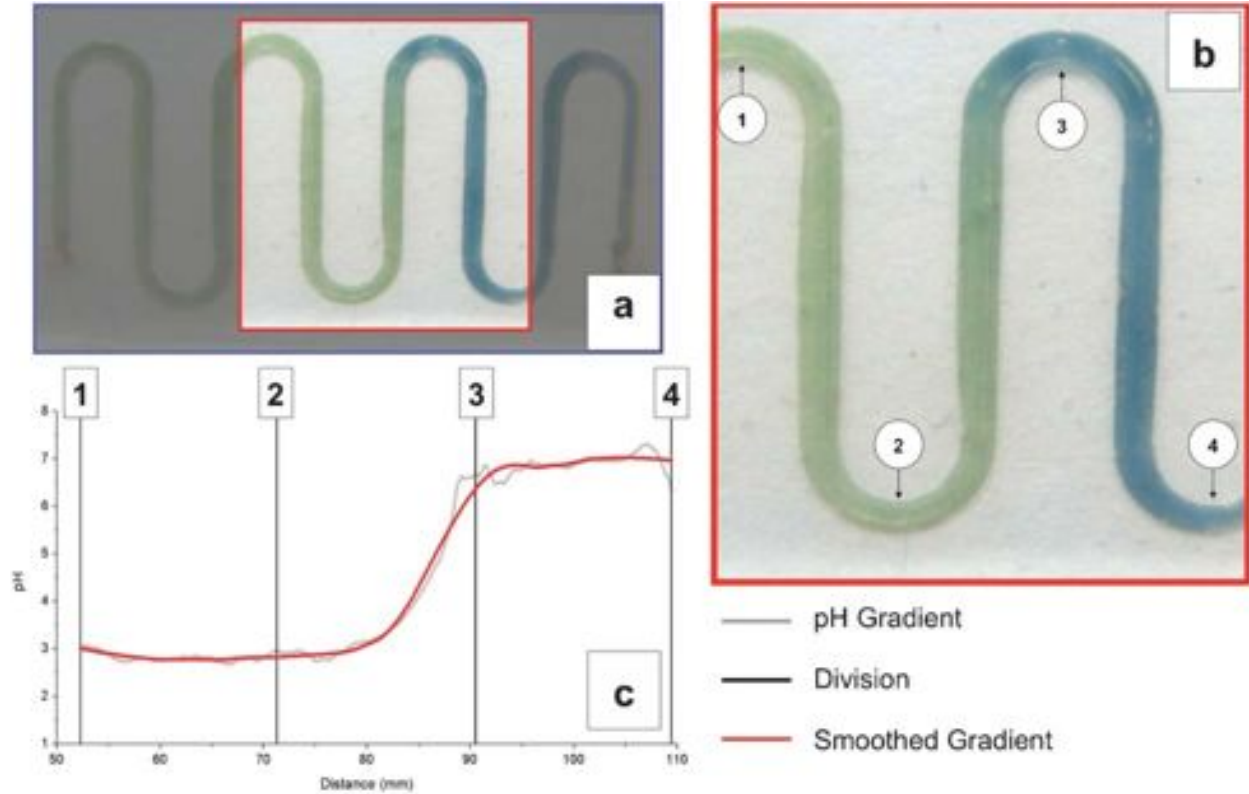
NaOH 10^{-2} M

HCl 10^{-2} M





pH gradient sensing

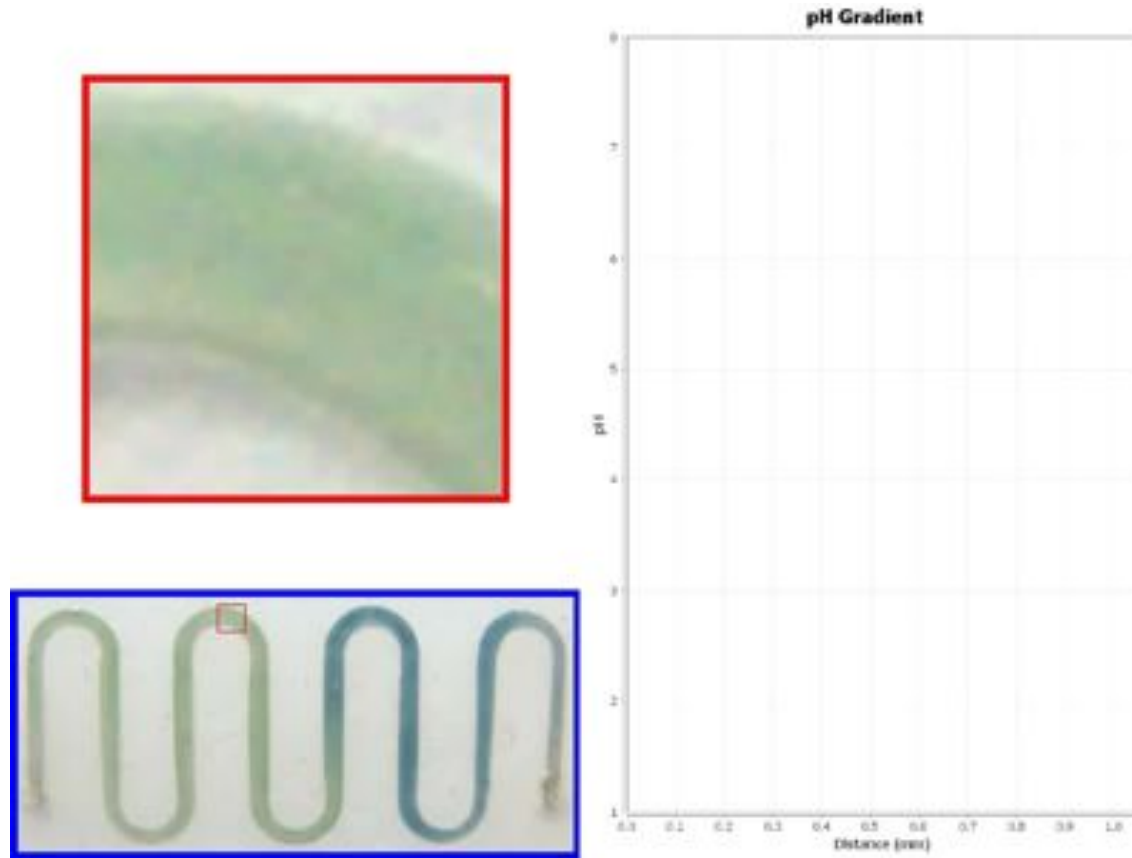


L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.





pH gradient sensing

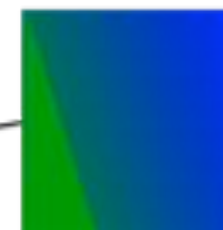
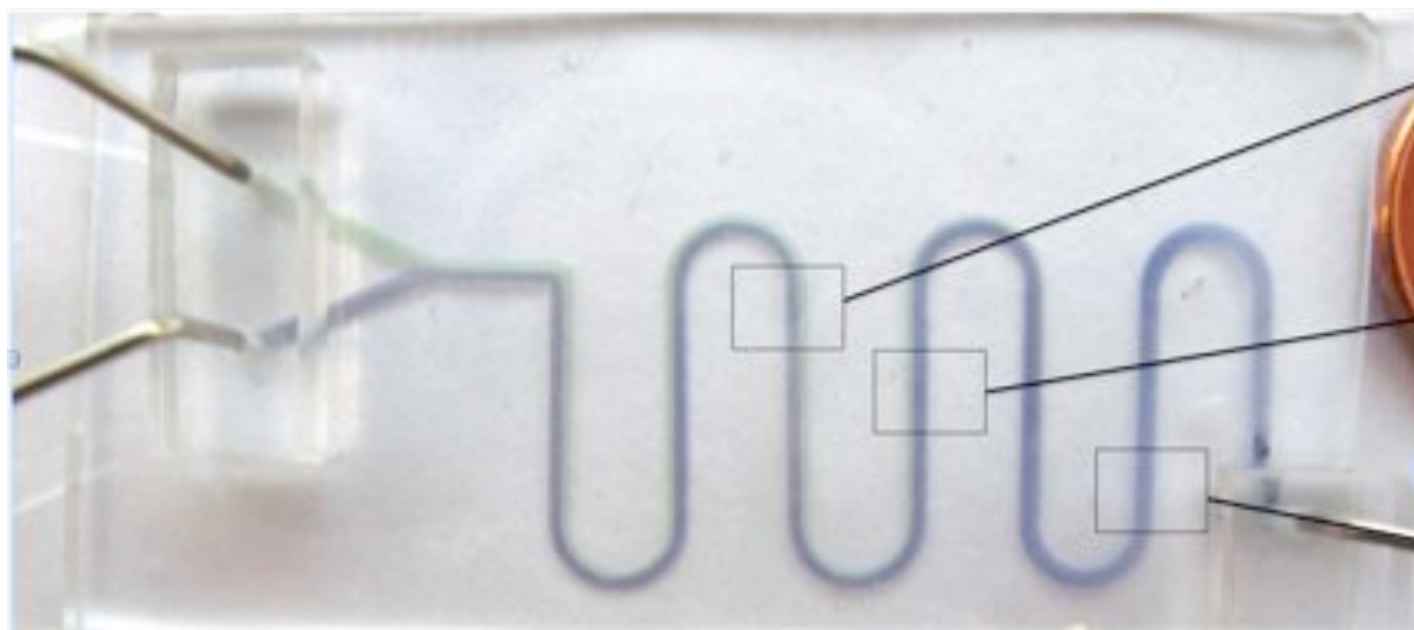


L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond and F. Benito-Lopez, *Lab Chip*, 2013, 13, 1079-1085.



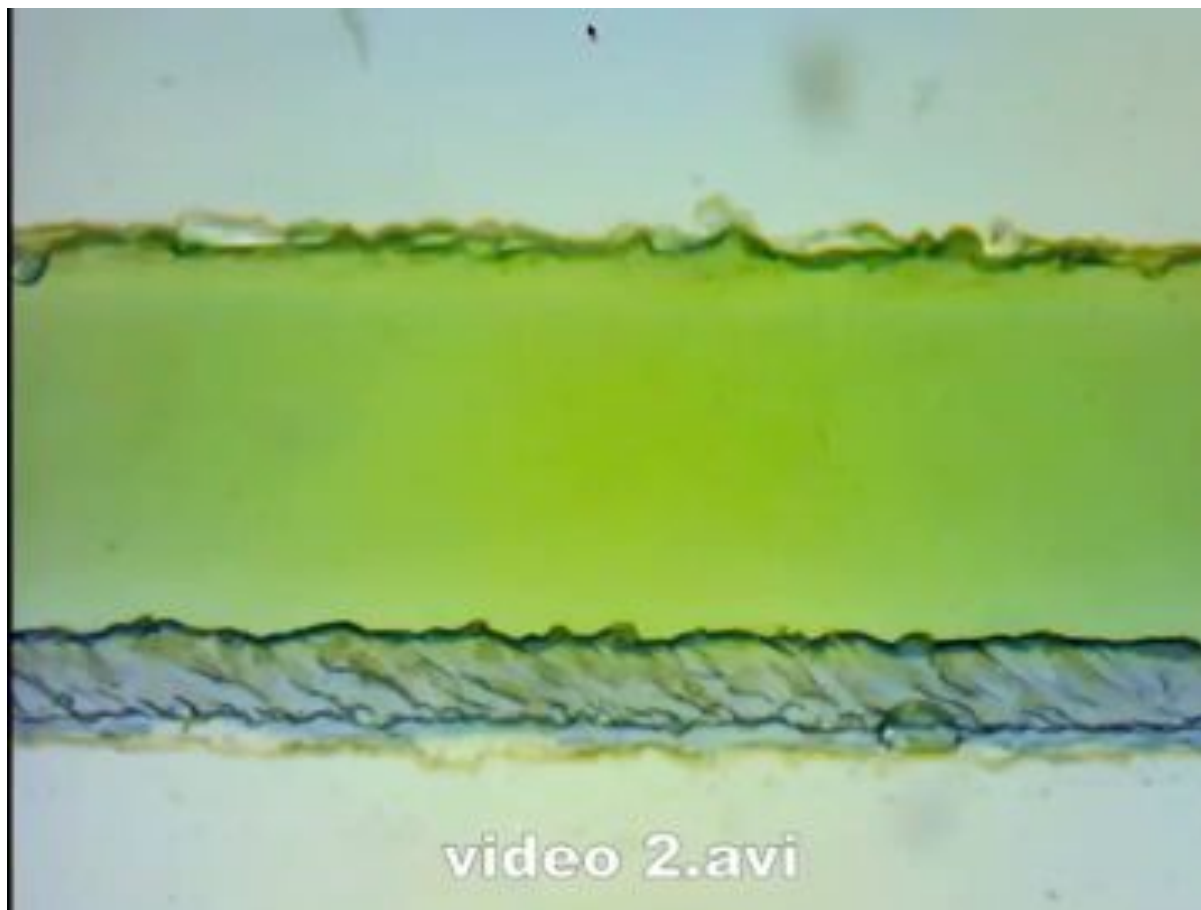


Study of diffusion process



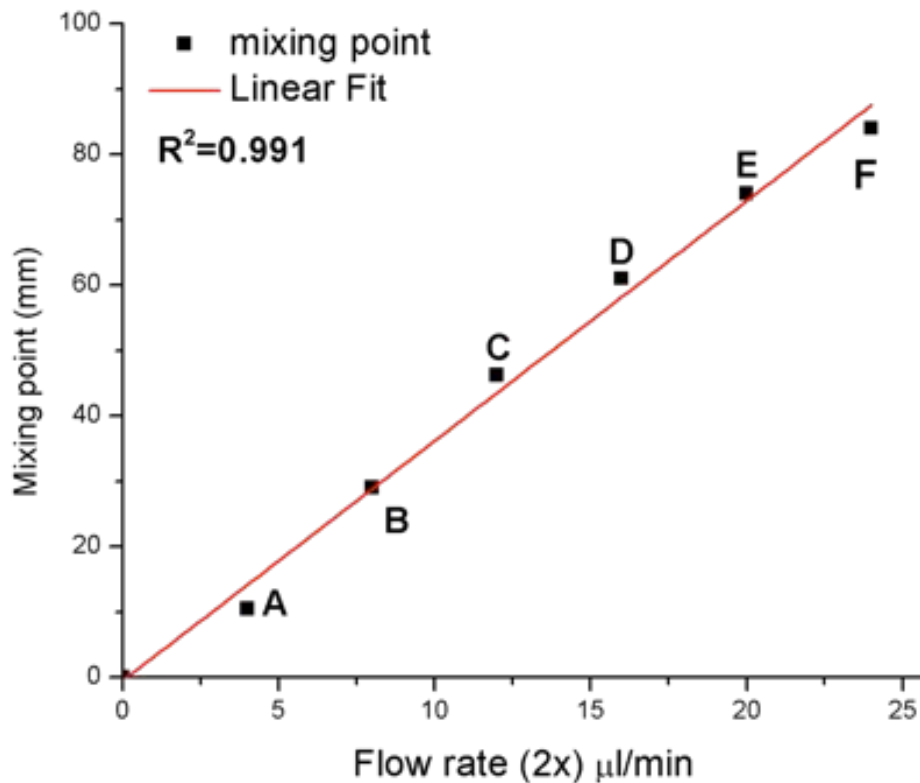
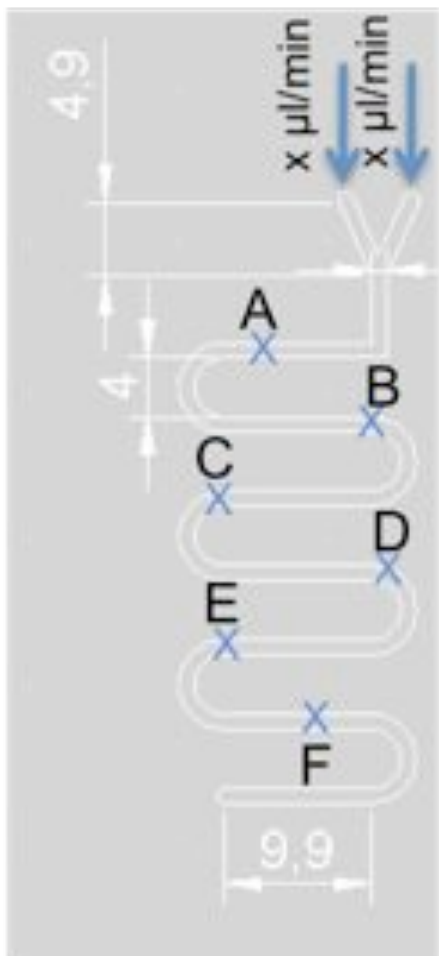


Study of diffusion process





Study of diffusion process





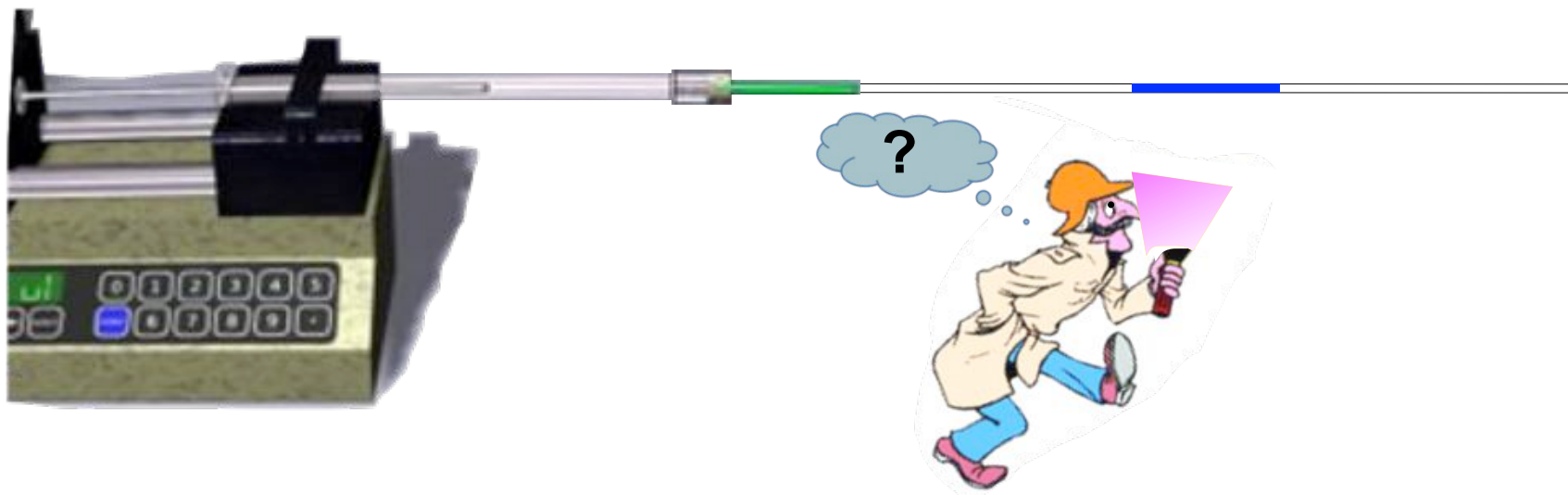
- **Self-diagnostic for continuous flow device**
- **Simple and fast photometric method to measure pH**
- **Replace the glass layer with glass-ITO -> electro-chemical sensing of redox active species**





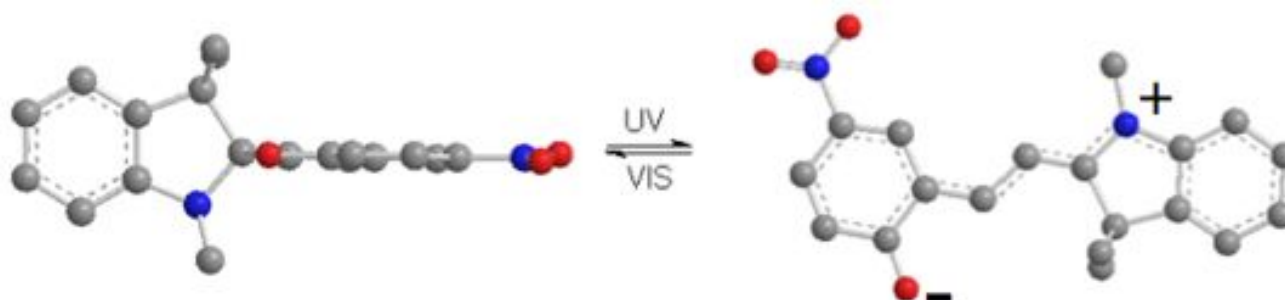
2. Spiropyran polymeric brushes functionalised micro-capillaries

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



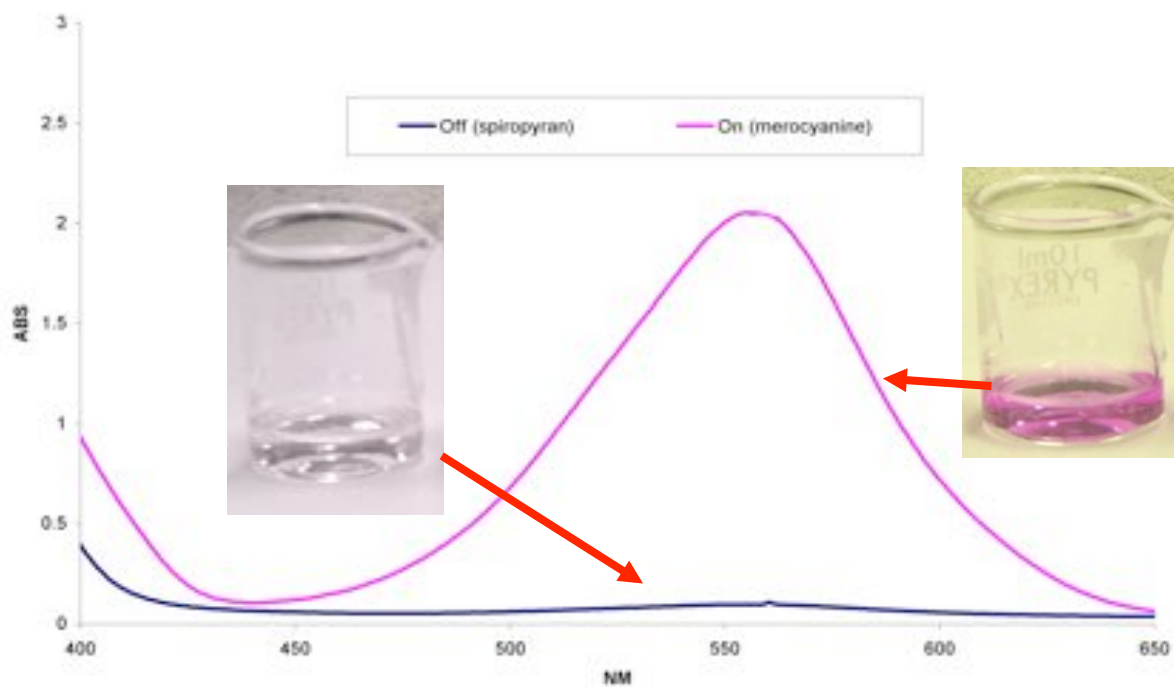


Spiropyran



A : Spiropyran SP (closed, colorless)

B : Merocyanine MC (open, colored)

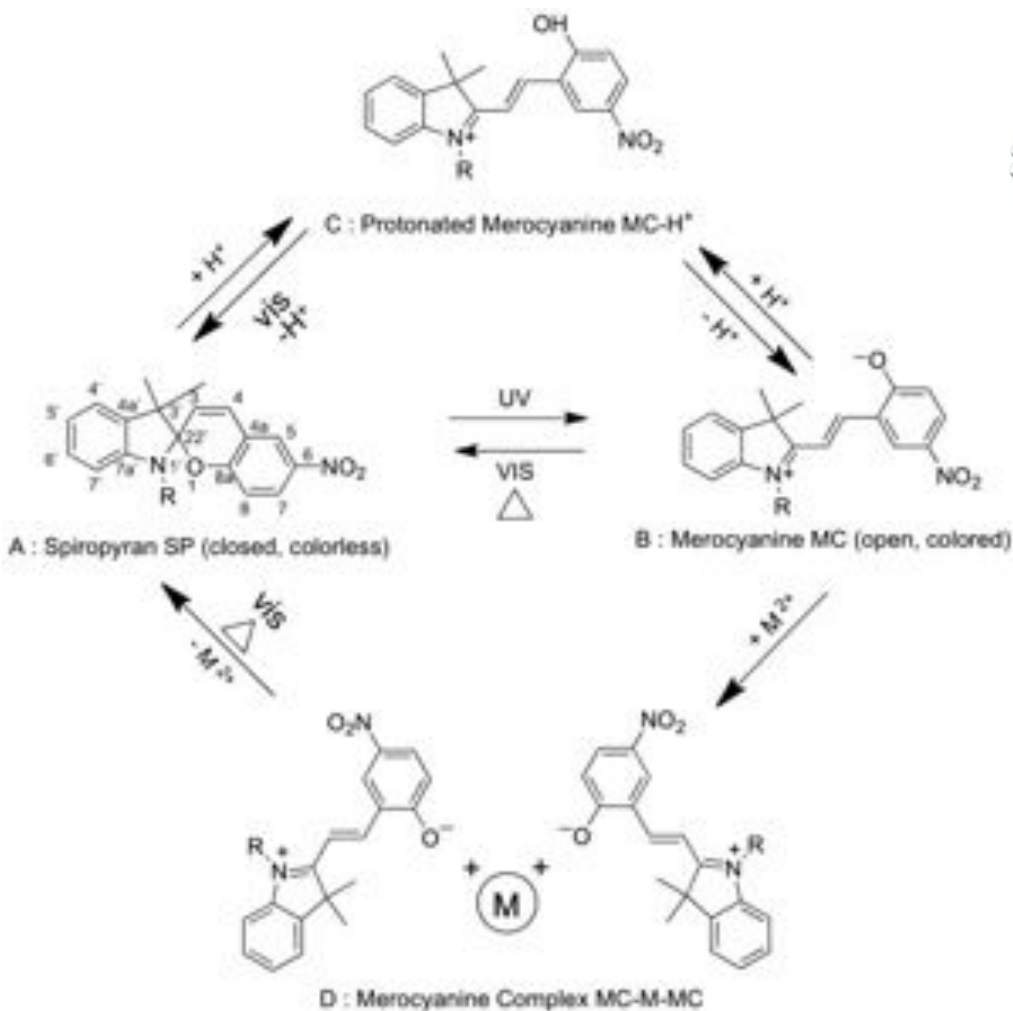




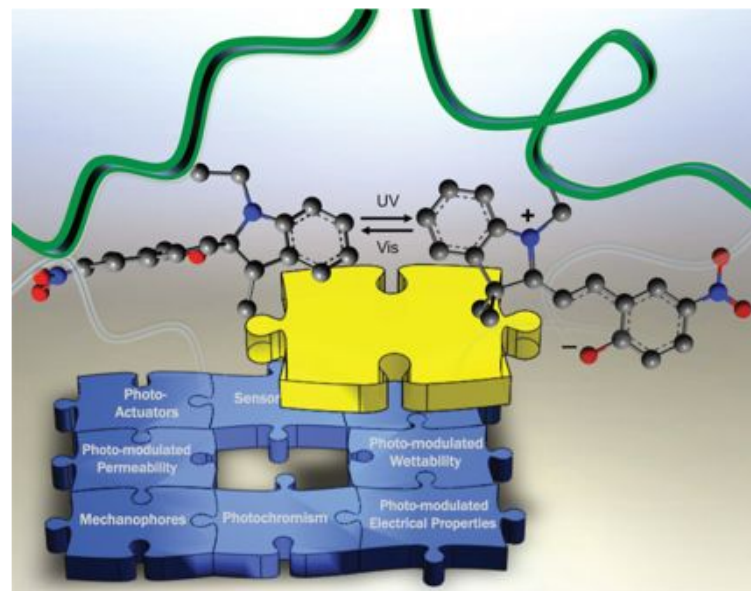
Spiropyran

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

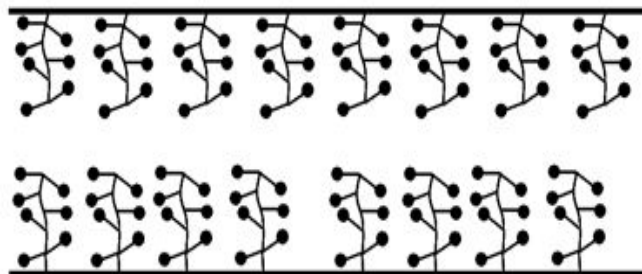
WILEY-VCH

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





Our Approach



↑ - spiropyran molecule

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

Micro-capillary : Convenient platform for rapid analysis and detection

Advantages

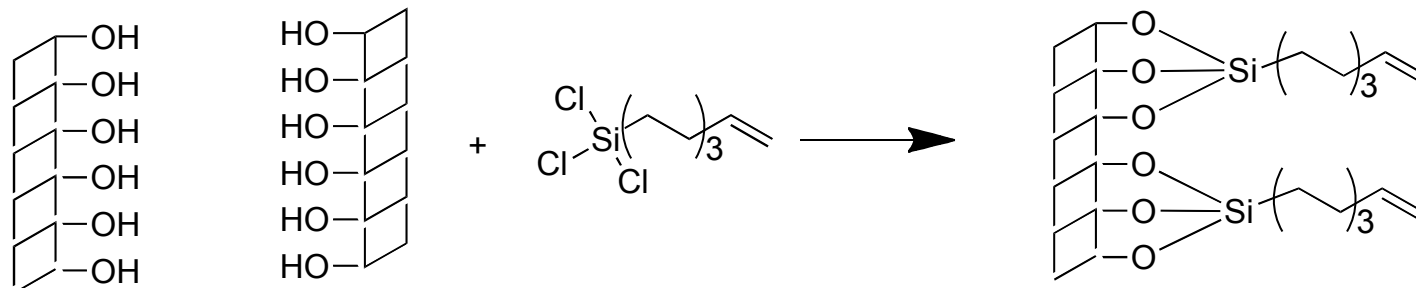
- act as a mechanical support for the optically sensitive layer
- represents an optical waveguide structure
- suitable for real-time continuous flow analysis
- requires very small volume of analyte



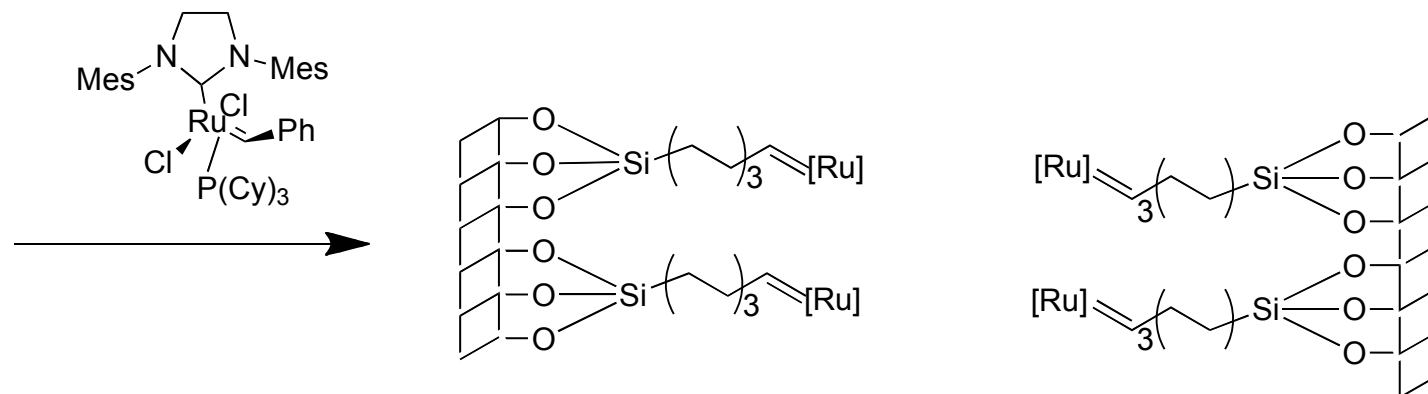


Spiropyran polymeric brushes in micro-capillaries

Silanisation

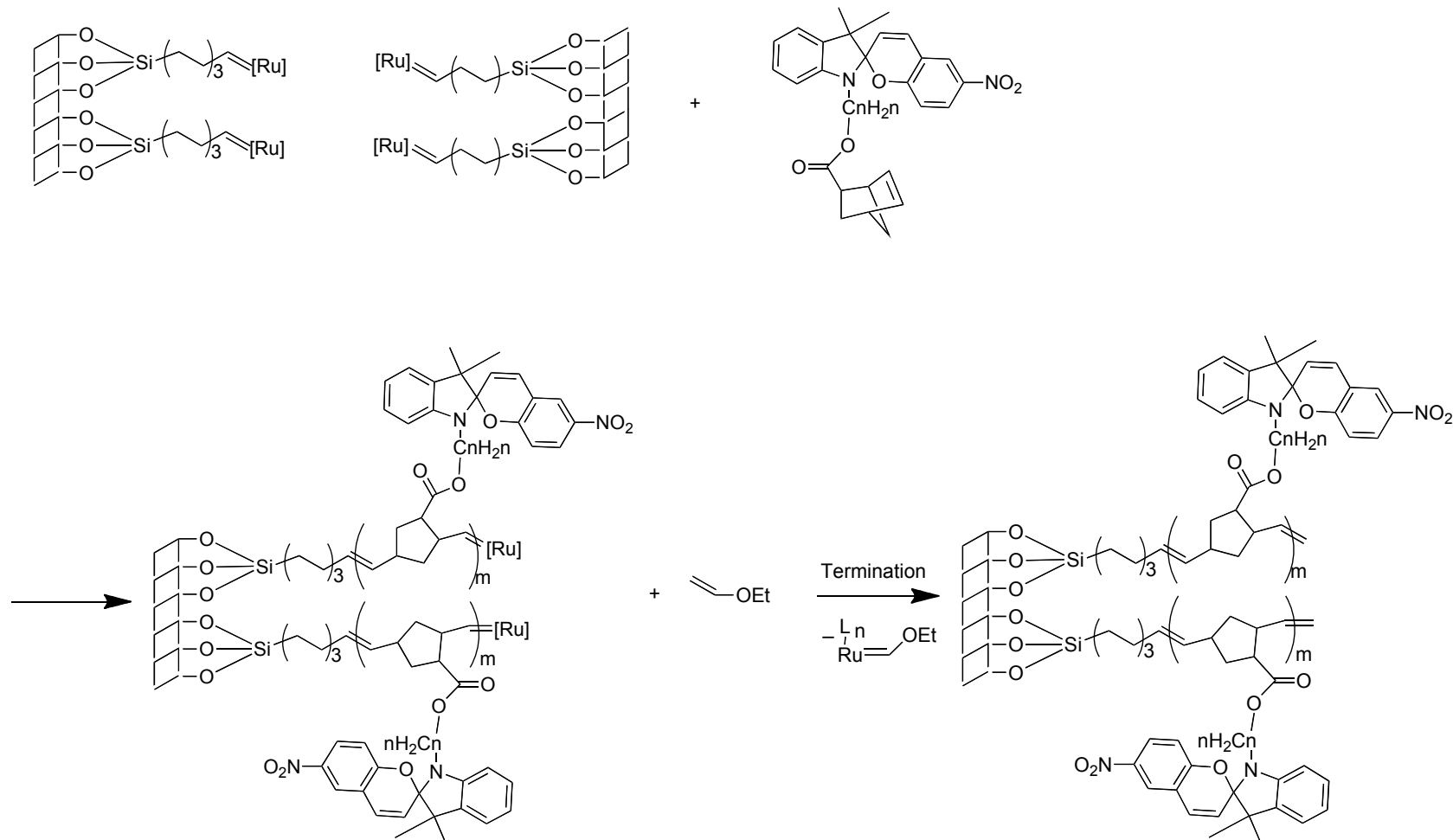


Attachment of the catalyst



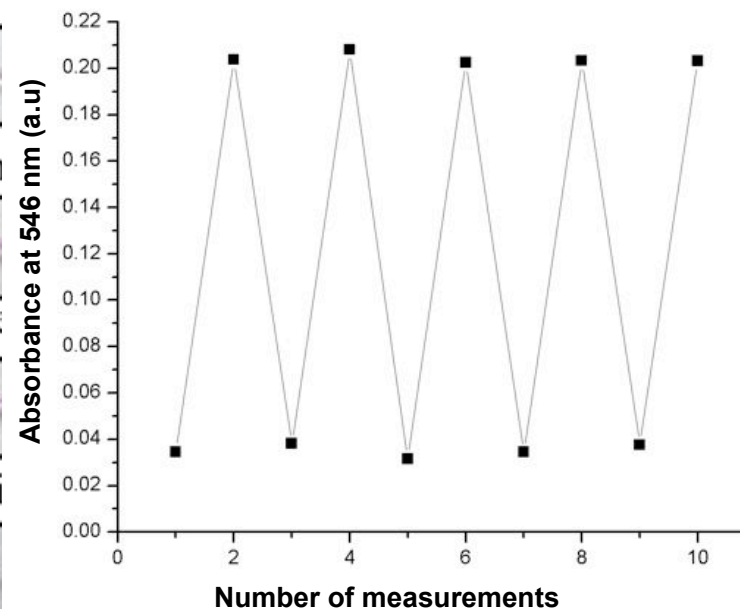
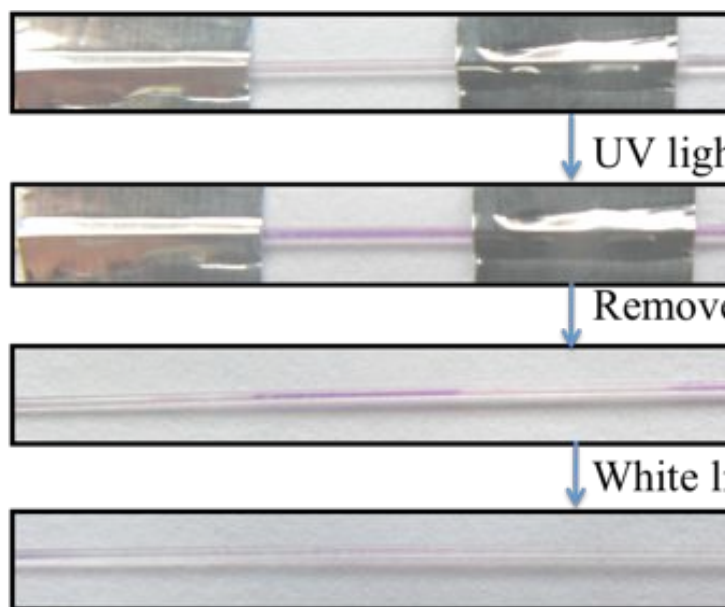
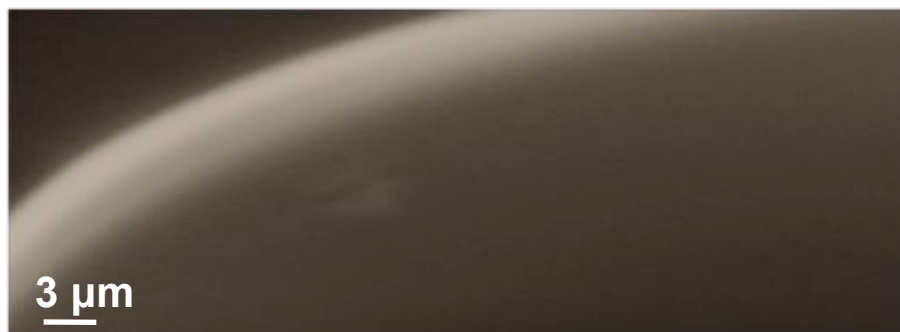


Spiropyran polymeric brushes in micro-capillaries





Characterisation



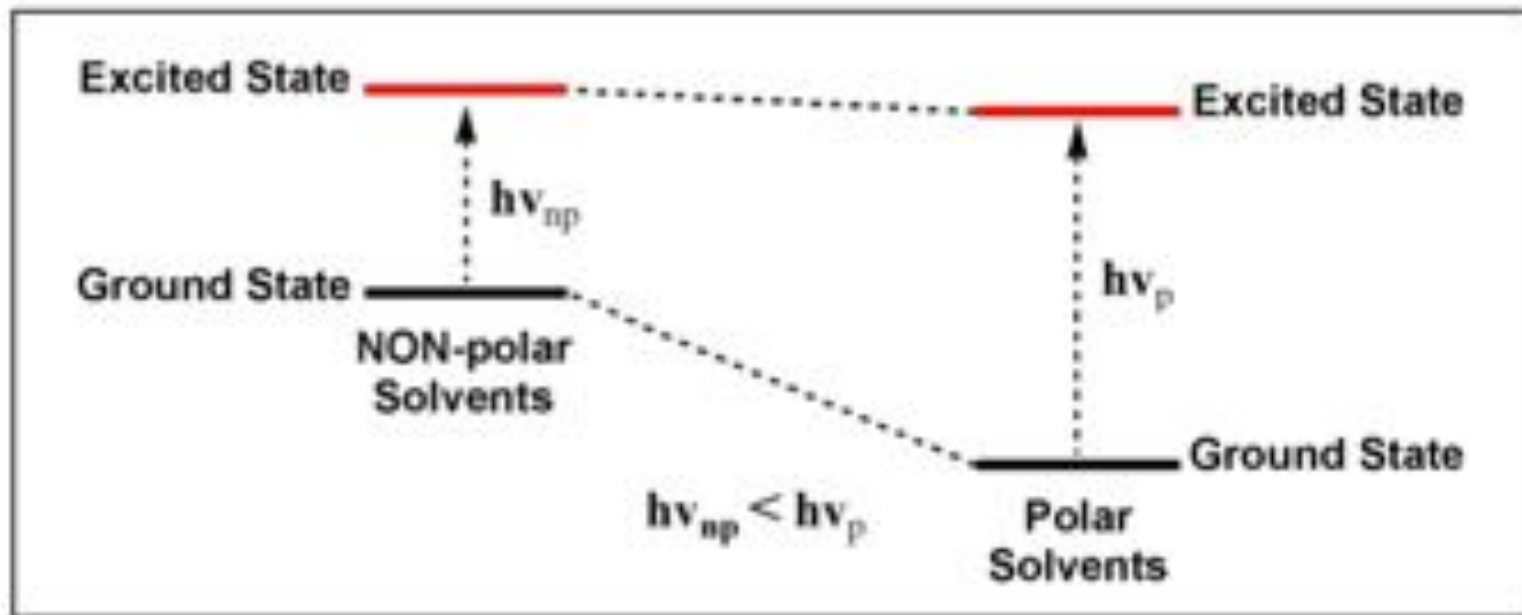
L. Florea, A. Hennart, D. Diamond and F. Benito-Lopez, *Sens. Actuators B: Chem.*, 2012, 175, 92-99.





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.

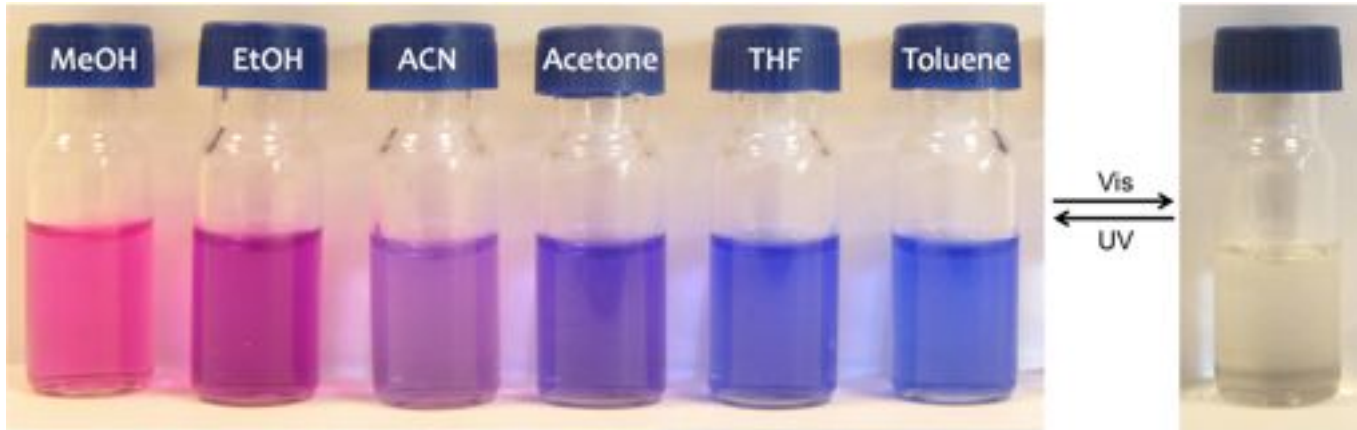




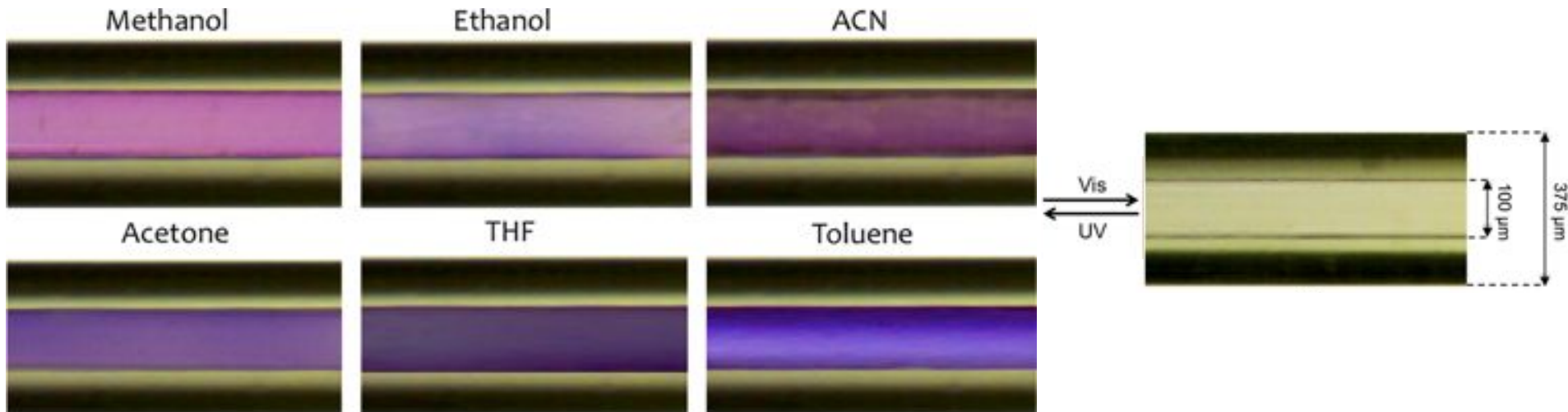
Solvatochromic Properties



➤ In solution

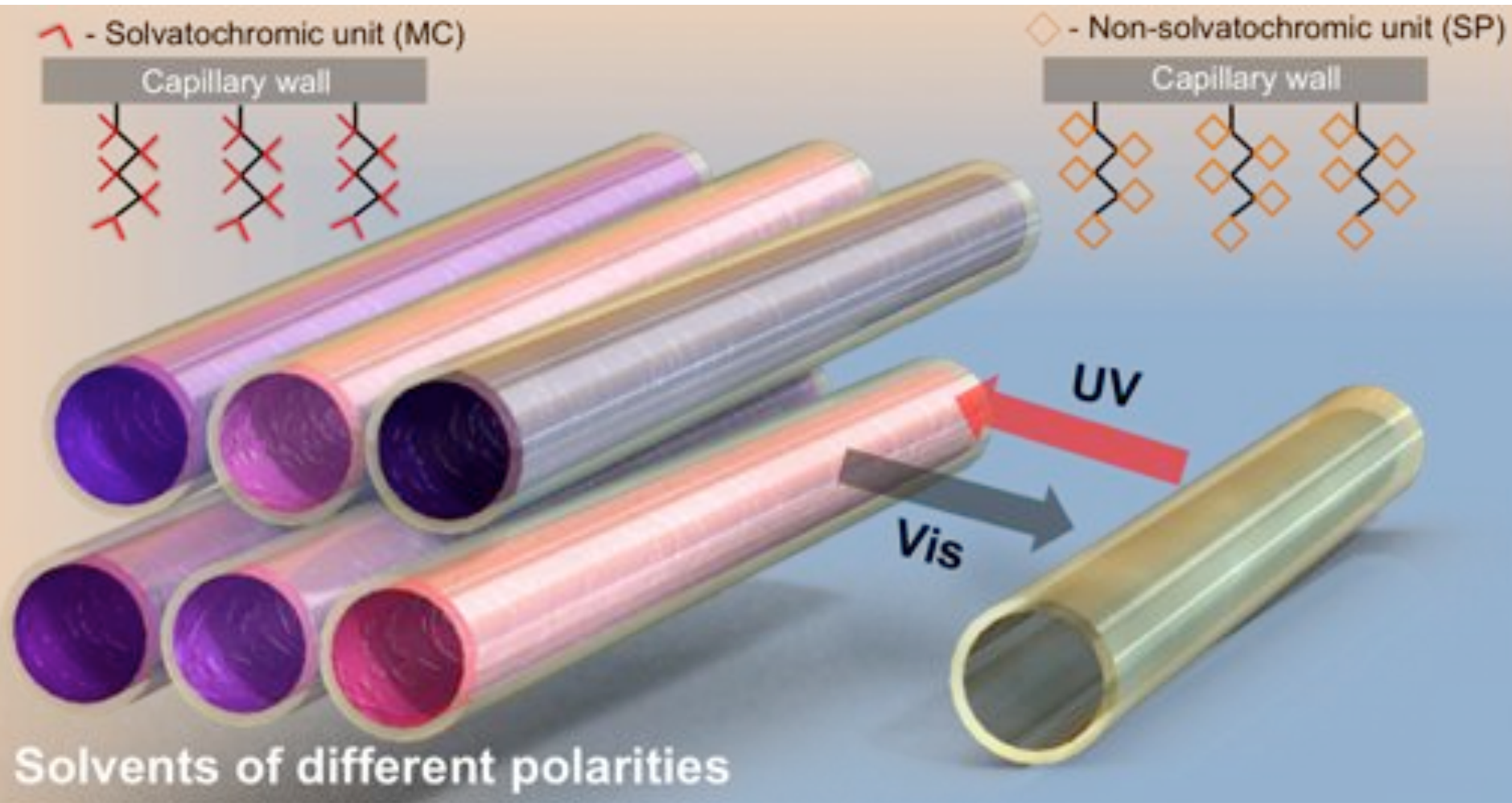


➤ Polymeric brushes





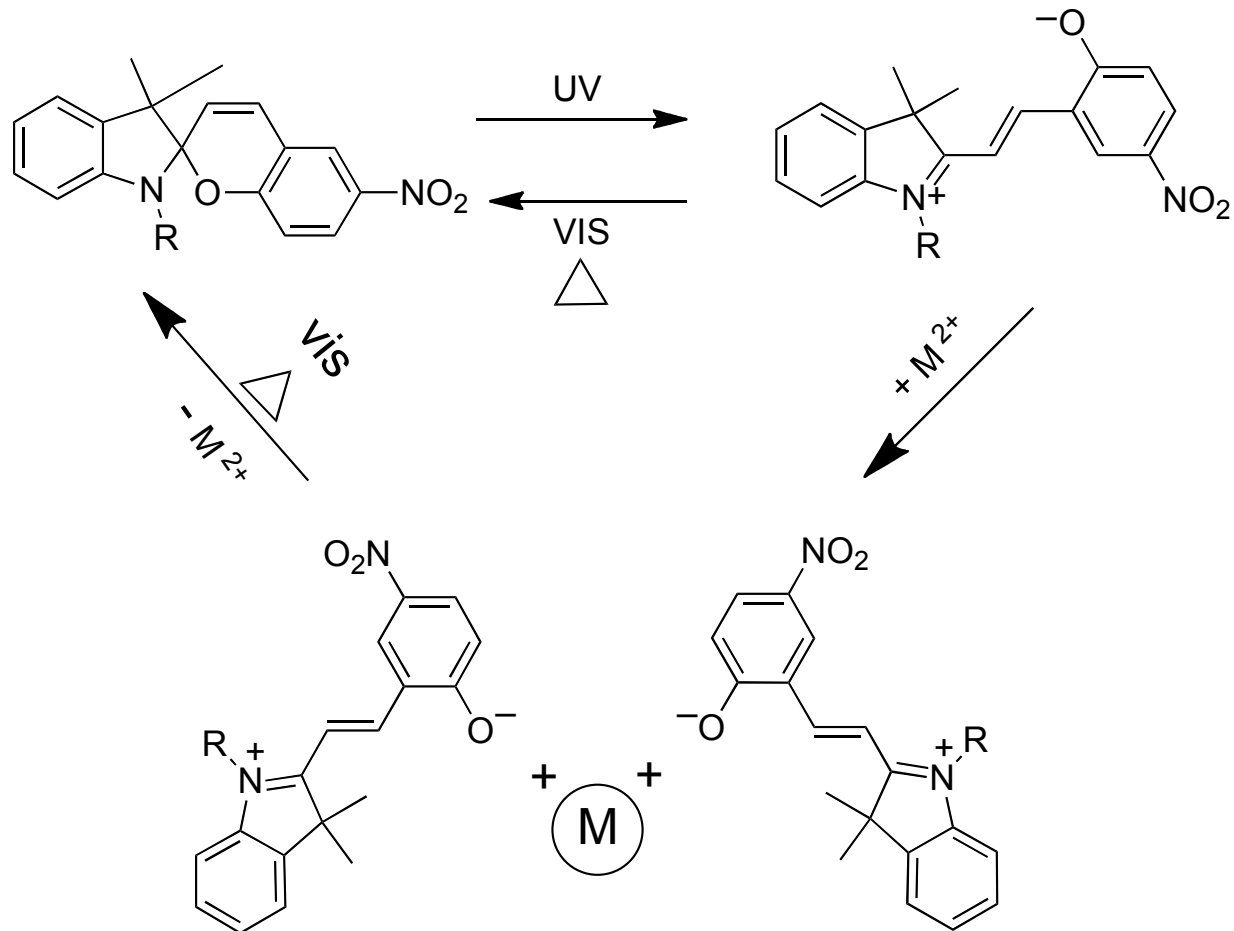
Solvatochromic Properties



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

+ Ni²⁺

+ Cd²⁺

+ Co²⁺

+ Cu²⁺

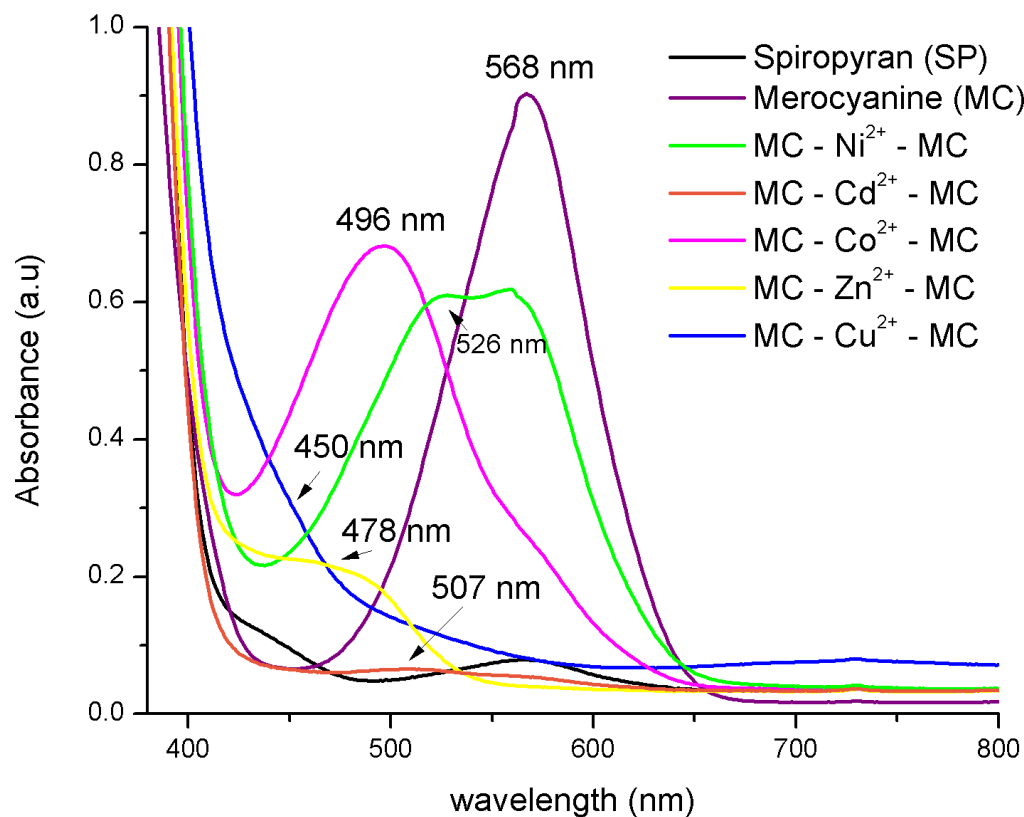
+ Zn²⁺





Metal ions sensing binding and releasing

I. Solution studies



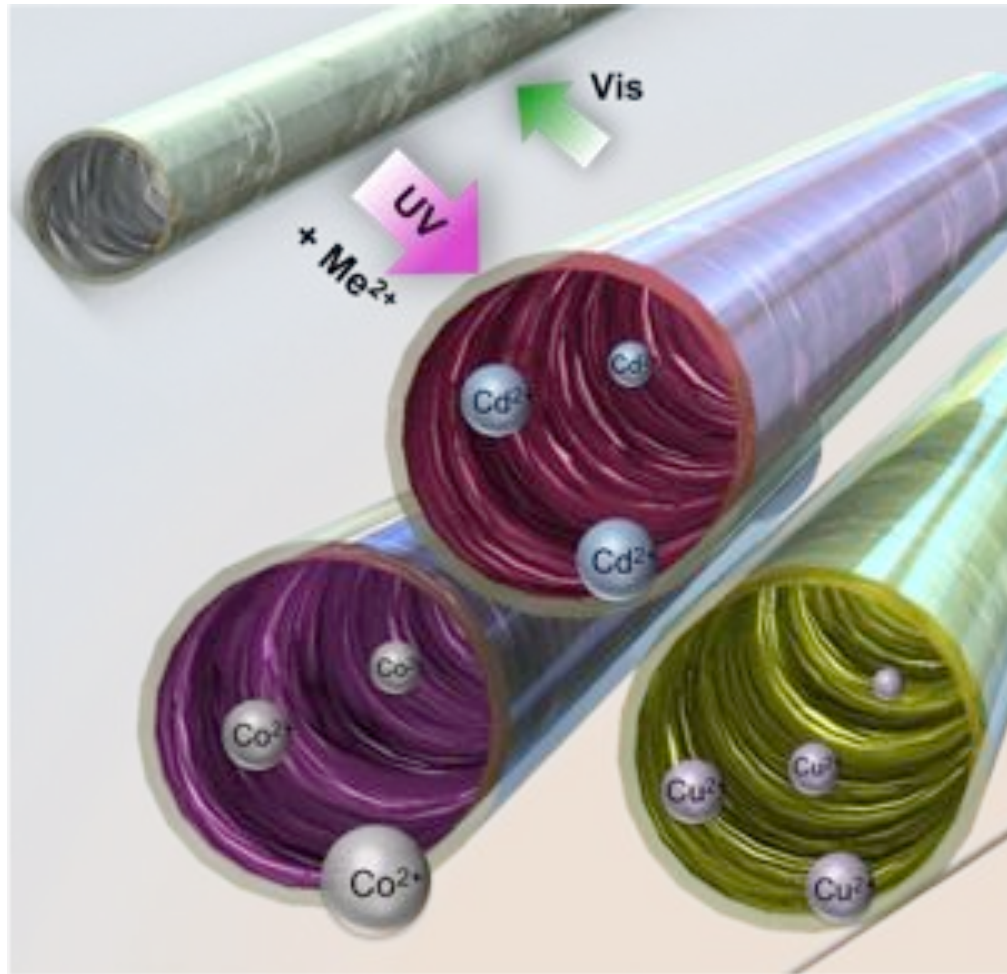
	Wavelength (nm)
MC	568
MC-Ni ²⁺	526
MC-Cd ²⁺	507
MC-Co ²⁺	496
MC-Zn ²⁺	478
MC-Cu ²⁺	450

Cu²⁺ Zn²⁺ Co²⁺ Cd²⁺ Ni²⁺ MC





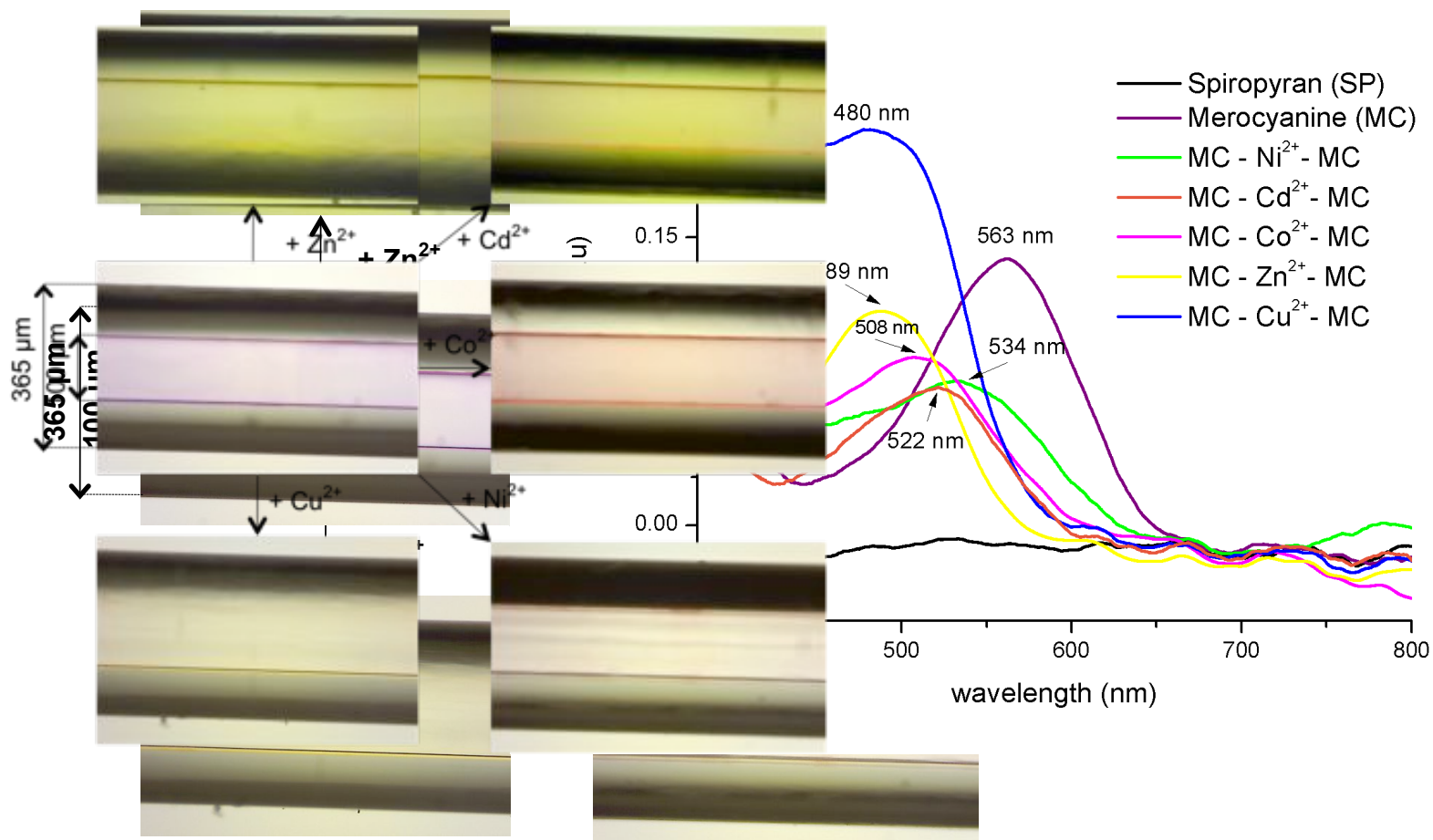
Metal ions sensing, binding and releasing





Metal ions sensing binding and releasing

II. Capillary coatings

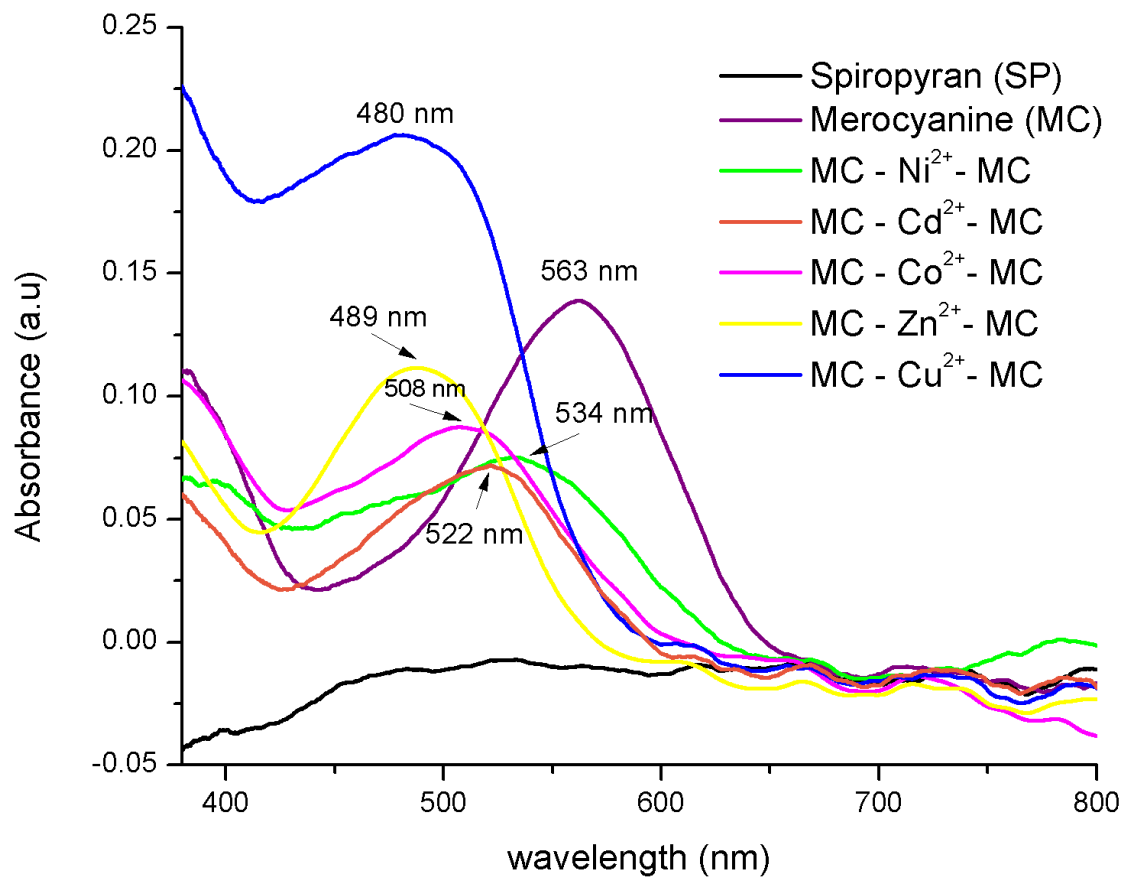




Metal ions sensing binding and releasing



II. Capillary coatings



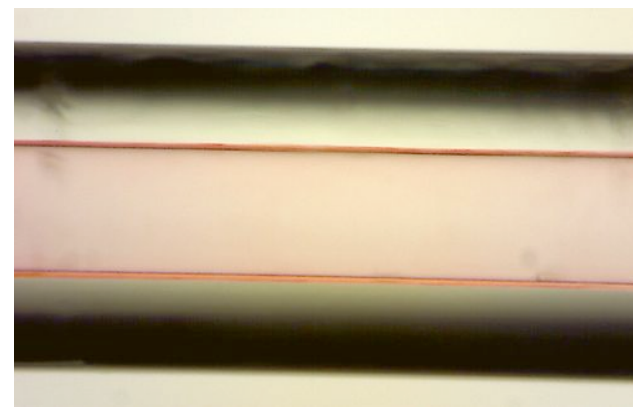
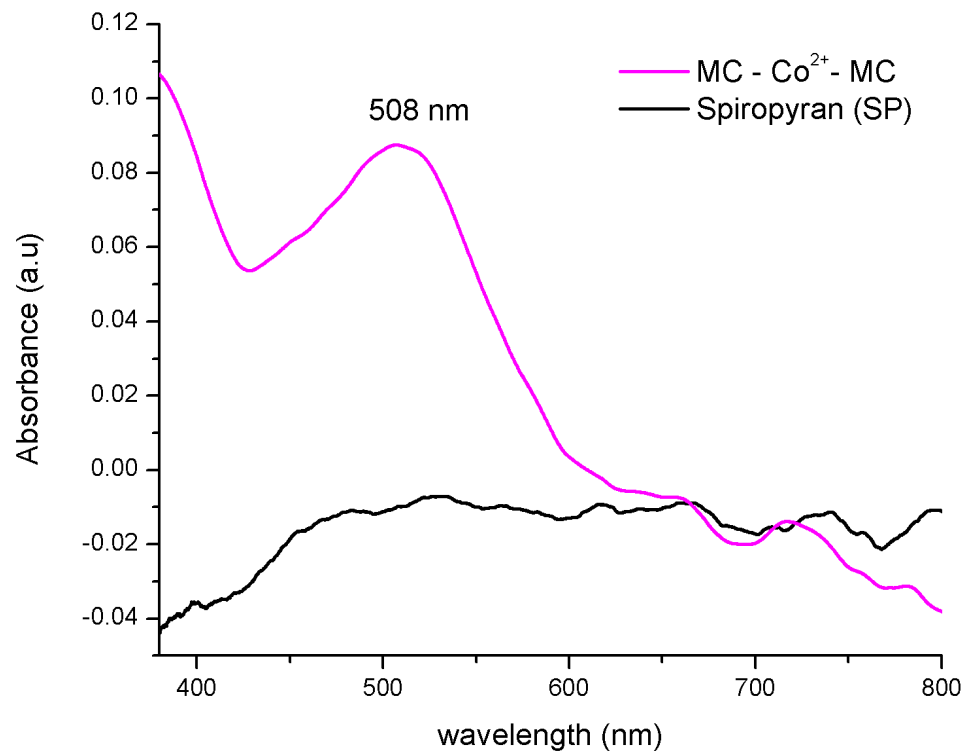
	Wavelength (nm)
MC	563
MC-Ni ²⁺	534
MC-Cd ²⁺	522
MC-Co ²⁺	508
MC-Zn ²⁺	489
MC-Cu ²⁺	480

Cu²⁺ Zn²⁺ Co²⁺ Cd²⁺ Ni²⁺ MC





Metal ions binding and releasing

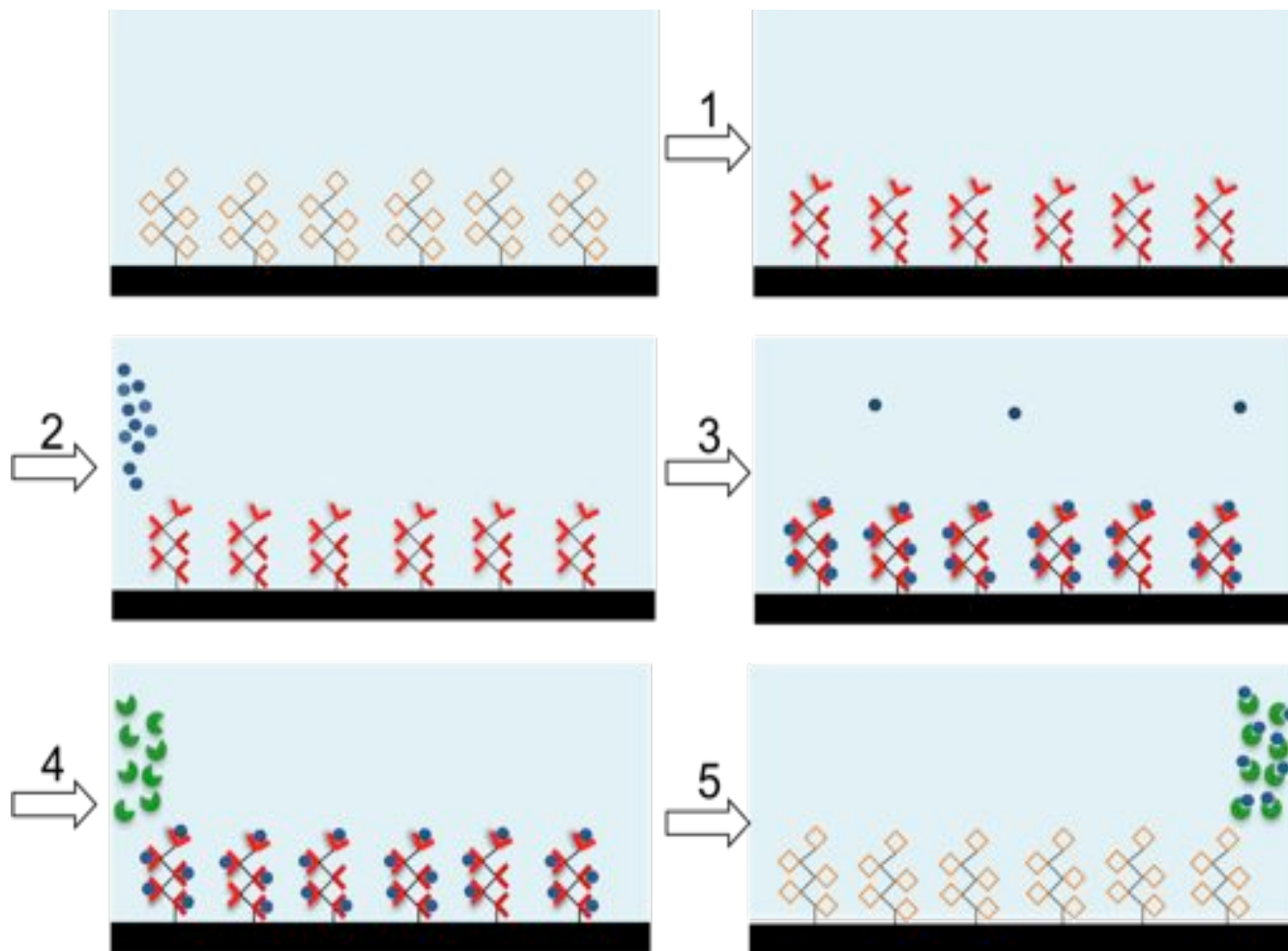






white light \downarrow \uparrow + Co²⁺ + UV light





Quantitative binding



-  Non binding form
-  Binding form
-  Cu^{2+}
-  PADAP

Binding capacity:
 $\sim 7 \times 10^{-8} \text{ Cu}^{2+} \text{ mole/}$
 $\text{mm}^3 \text{ coating.}$



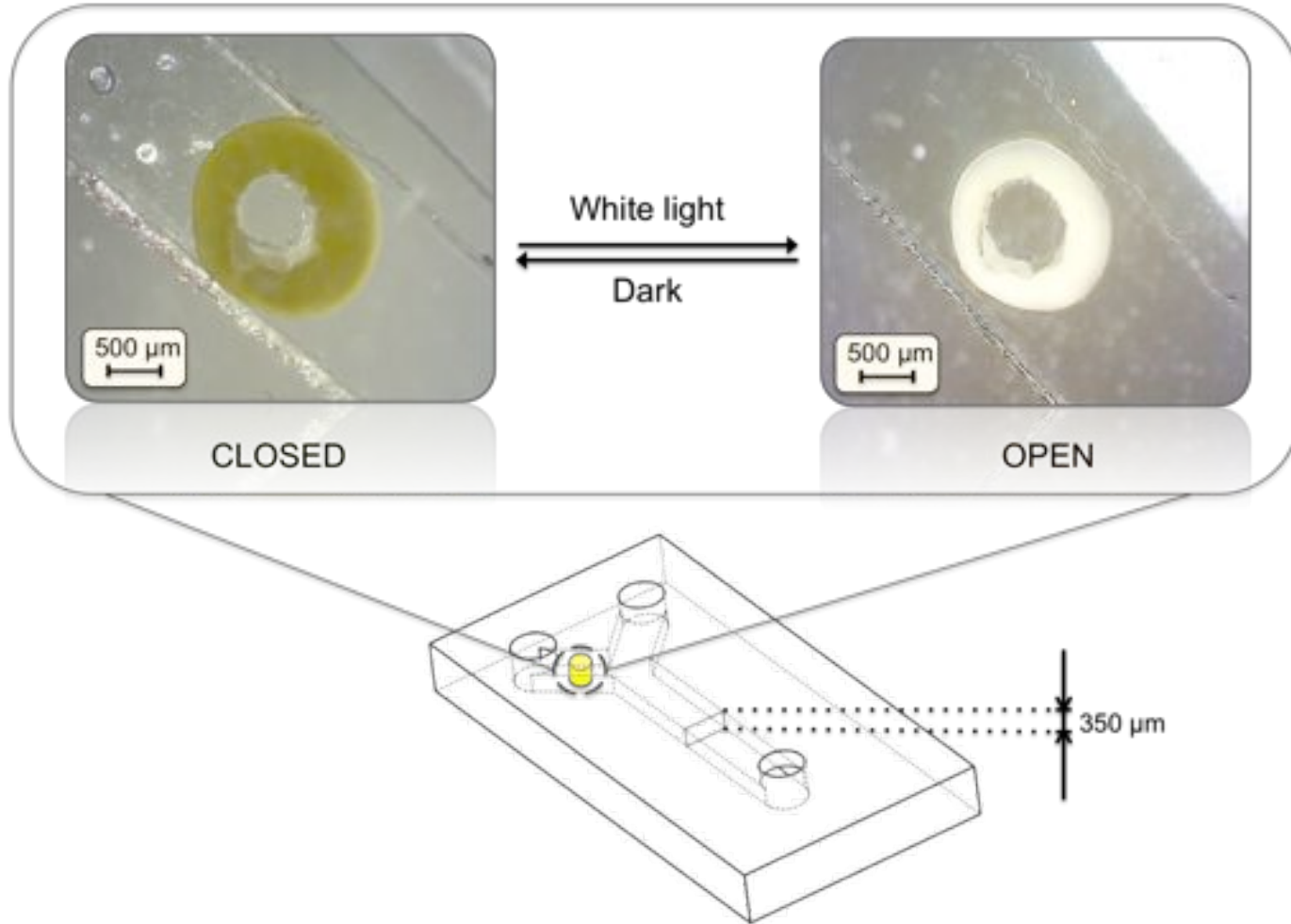


- **Self-diagnostic for continuous flow device**
- **Solvent detection and divalent metal ion detection in micro-capillaries**
- **Sensing behaviour can be switched on/off remotely using light**



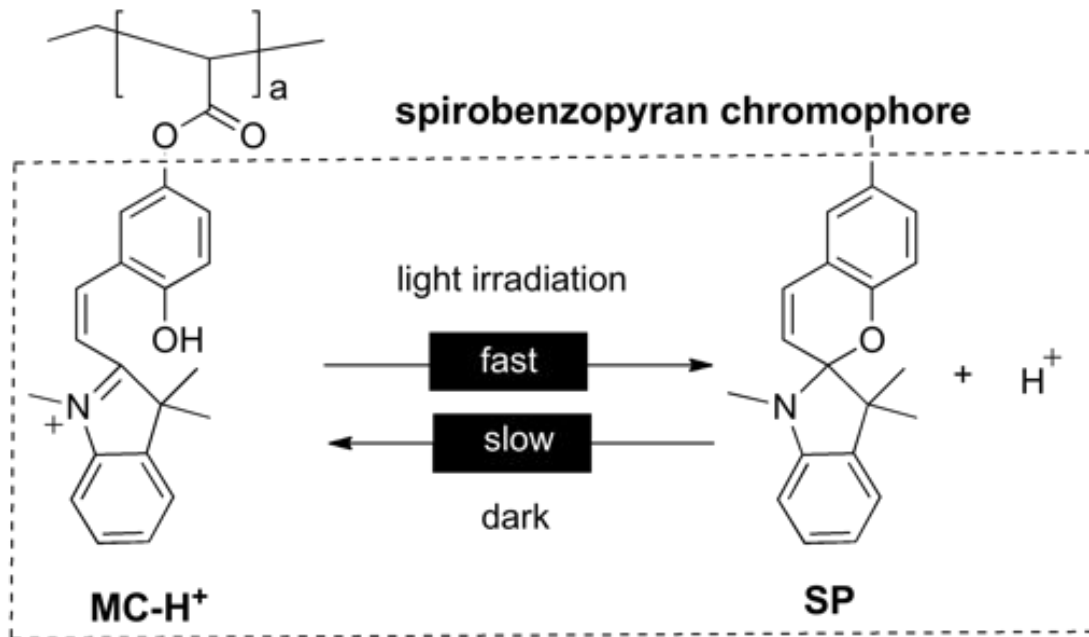
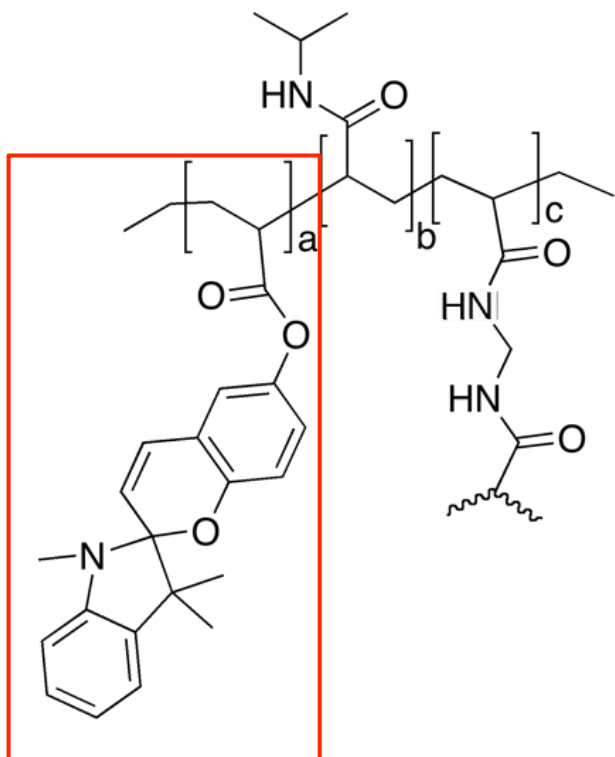


4. Photo-actuators for micro-valve applications in microfluidics





Spiropyran –pNIPAAm photo-actuators



Spiropyran

a = 1

NIPAAm

b = 100

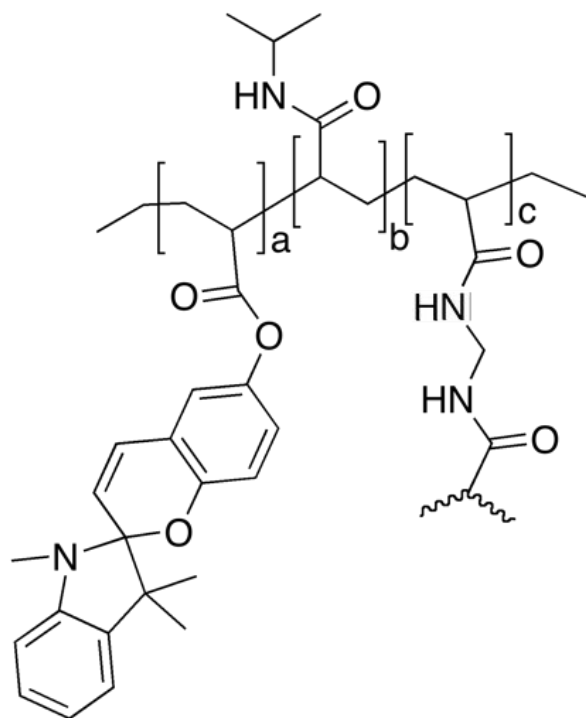
MBAA

c = 2

[1] Sugiura et al., *Sens. Act. A*, 140 (2007) 176–184



Spiropyran –pNIPAAm photo-actuators



- Size: 120-170 μm [1]
- Shrinking: to 68% of initial size after 120 s
- Maximum shrinking: to 52 % of initial size [1]
- Necessary time for reswelling: > one hour

Drawbacks

- Gels are soaked in 0.5 mM HCl overnight
- Operating only in acidic environment
- Suitable for single-use only

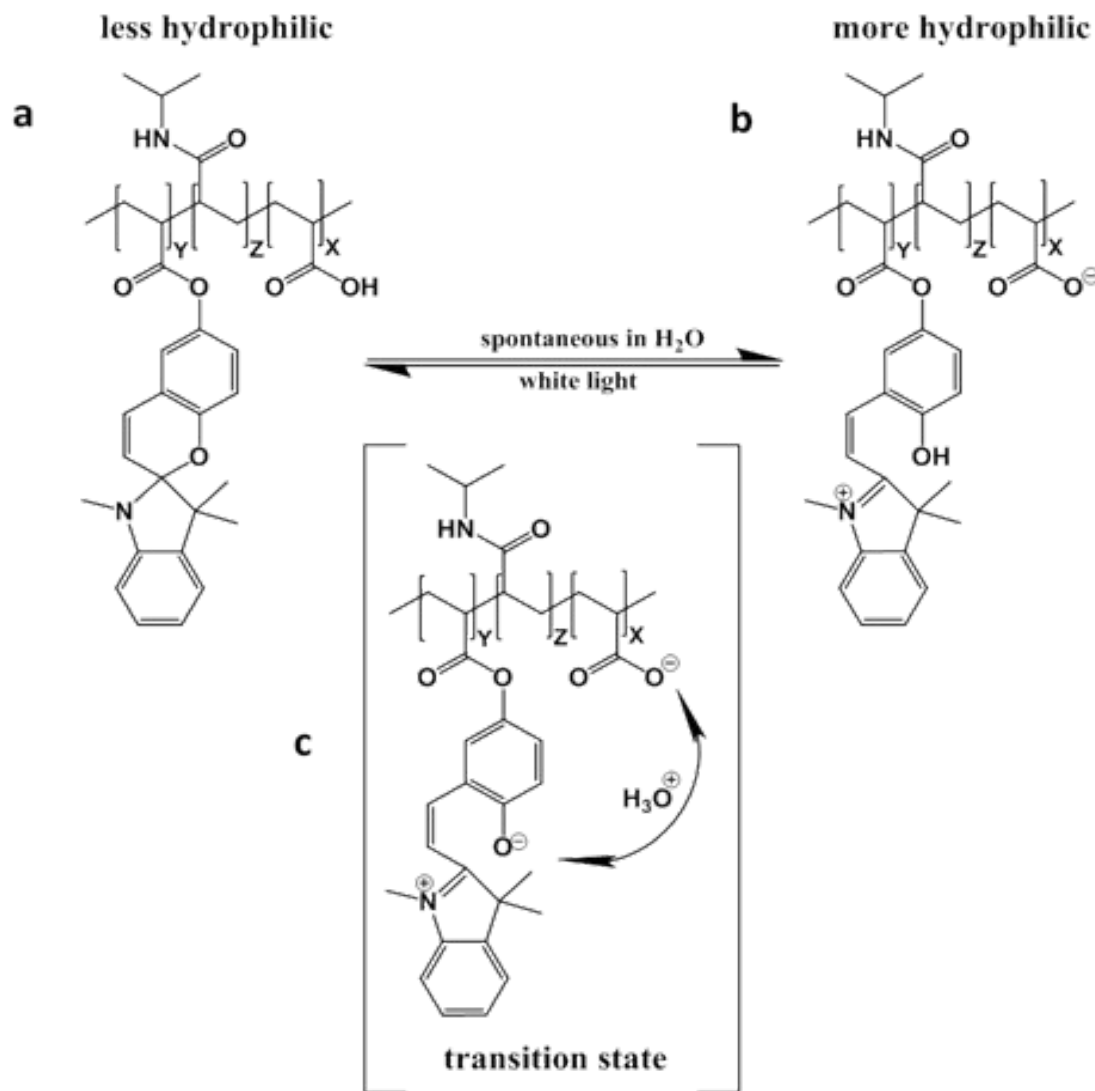
Spiropyran a = 1

NIPAAm b = 100

MBAA c = 2

[1] Sugiura et al., Sens. Act. A, 140 (2007) 176–184

Self-protonating hydrogels

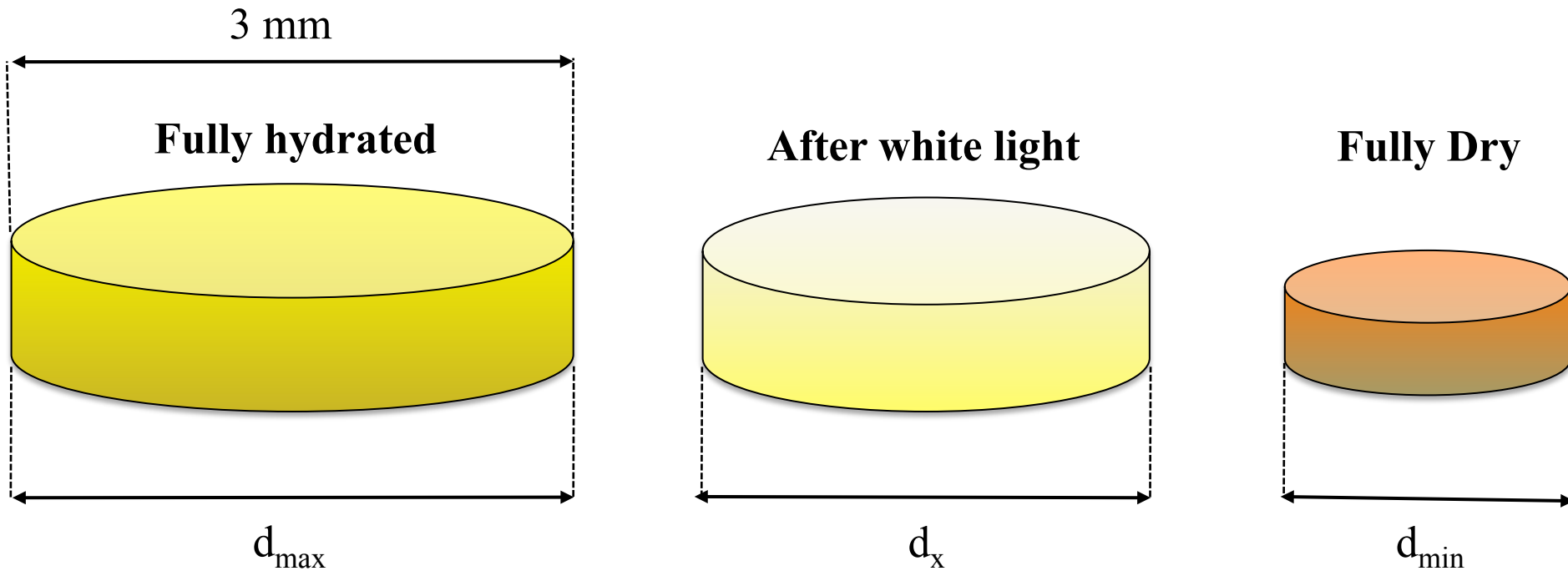


B. Ziolkowski, L. Florea, J. Theobald, F. Benito-Lopez and D. Diamond, *Soft Matter*, 2013, 9, 8754-8760.





- Photo-polymerised in circular PDMS moulds



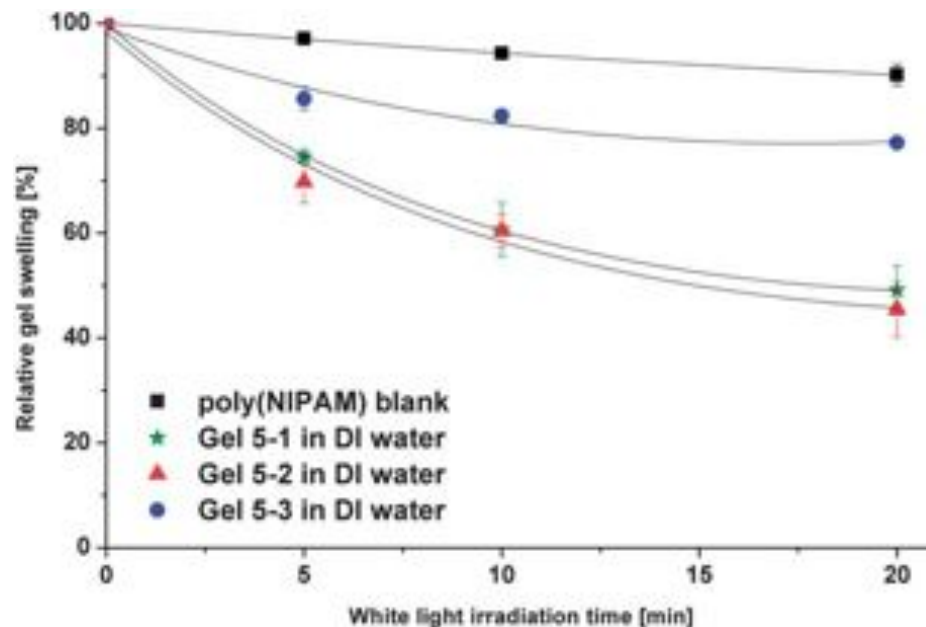
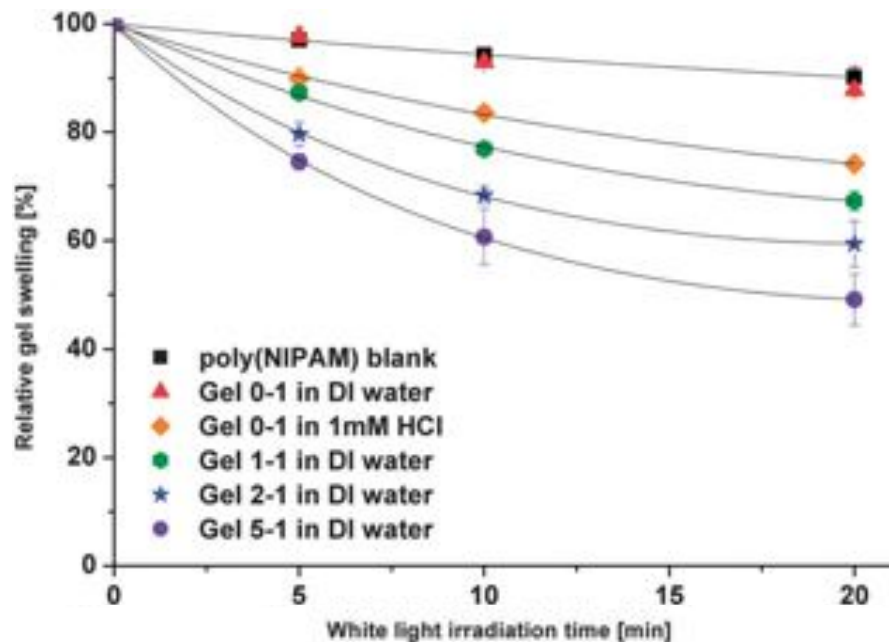
$$D\% = \left[1 - \frac{(d_{\max} - d_x)}{(d_{\max} - d_{\min})} \right] \times 100\%$$



Optimization of hydrogel composition



- Photo-induced shrinking



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



Shrinking/Reswelling Behaviour

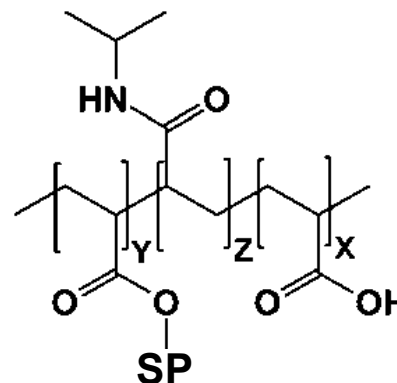
sample	20 [min] (Vis. light)	std dev	60 [min] (in darkness)	std dev
poly(NIPAM) blank	87.85 %	1.18	97.44 %	1.60
1 % AA, 1 % BSP-A	67.33 %	1.85	100.45 %	0.64
2 % AA, 1 % BSP-A	59.37 %	4.26	96.48 %	1.34
5 % AA, 1 % BSP-A	49.10 %	4.73	97.35 %	1.93
2 % AA, 2 % BSP-A	61.31 %	5.20	83.69 %	1.27
5 % AA, 2% BSP-A	45.50 %	5.33	82.69 %	3.33
5 % AA, 3 % BSP-A	77.22 %	1.12	76.44 %	1.46

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

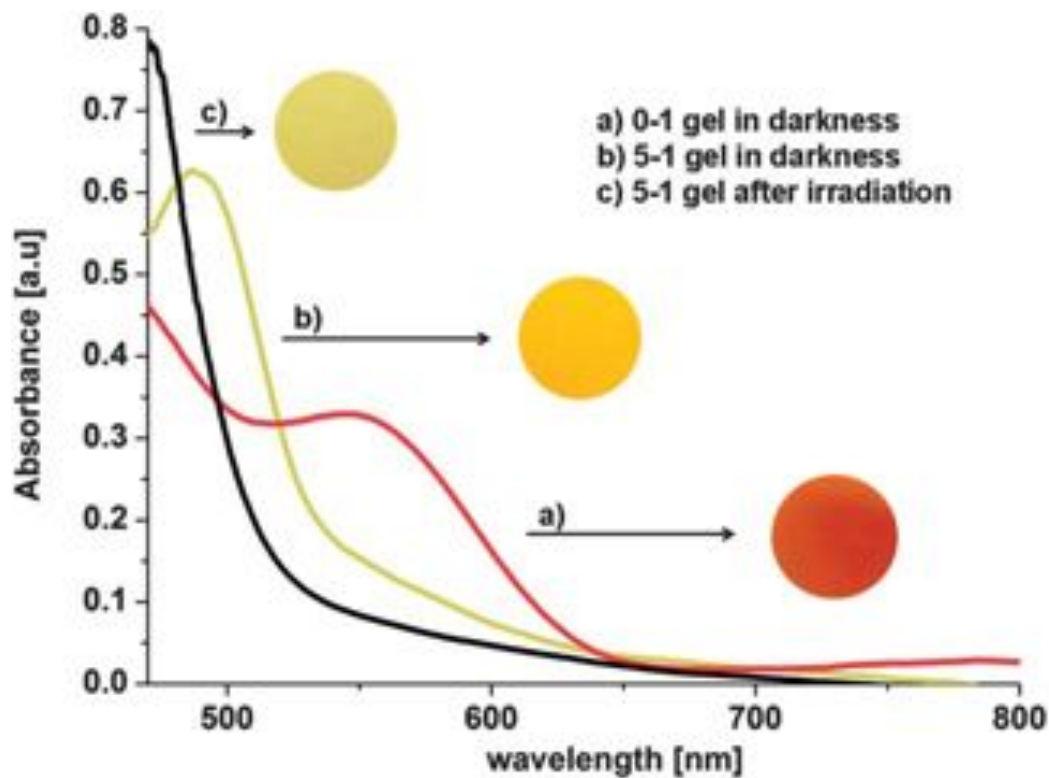




Hydrogel 5-1



x = 5
y = 1
z = 100

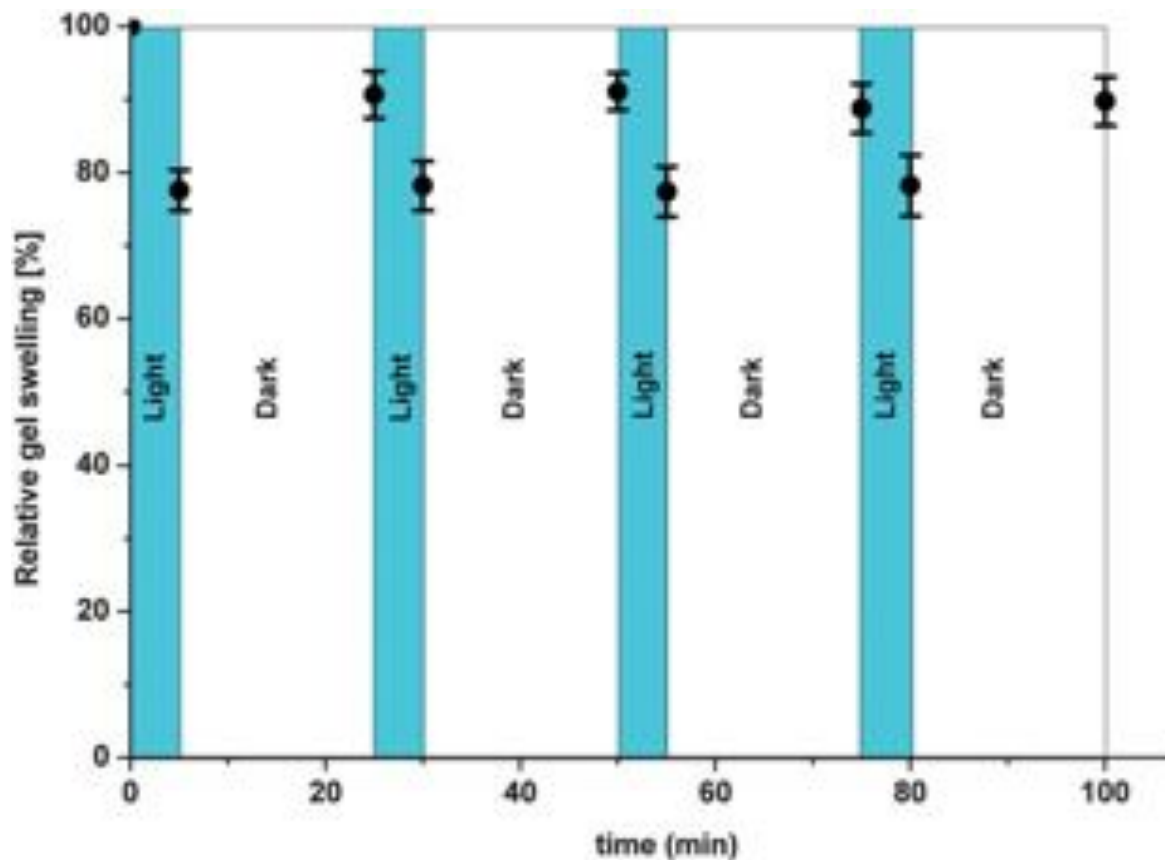




Reproducible actuation



- **DI water**
- **No external proton source**

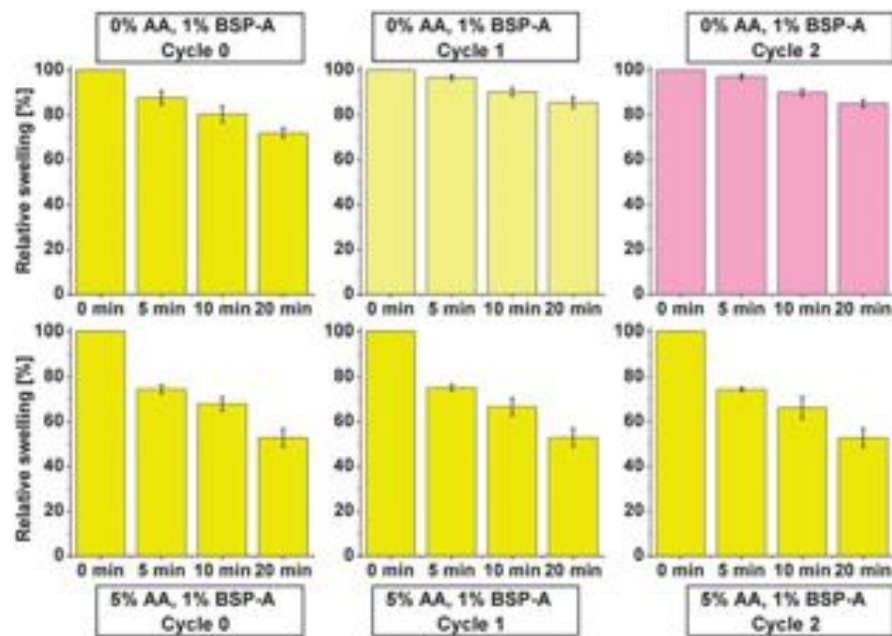
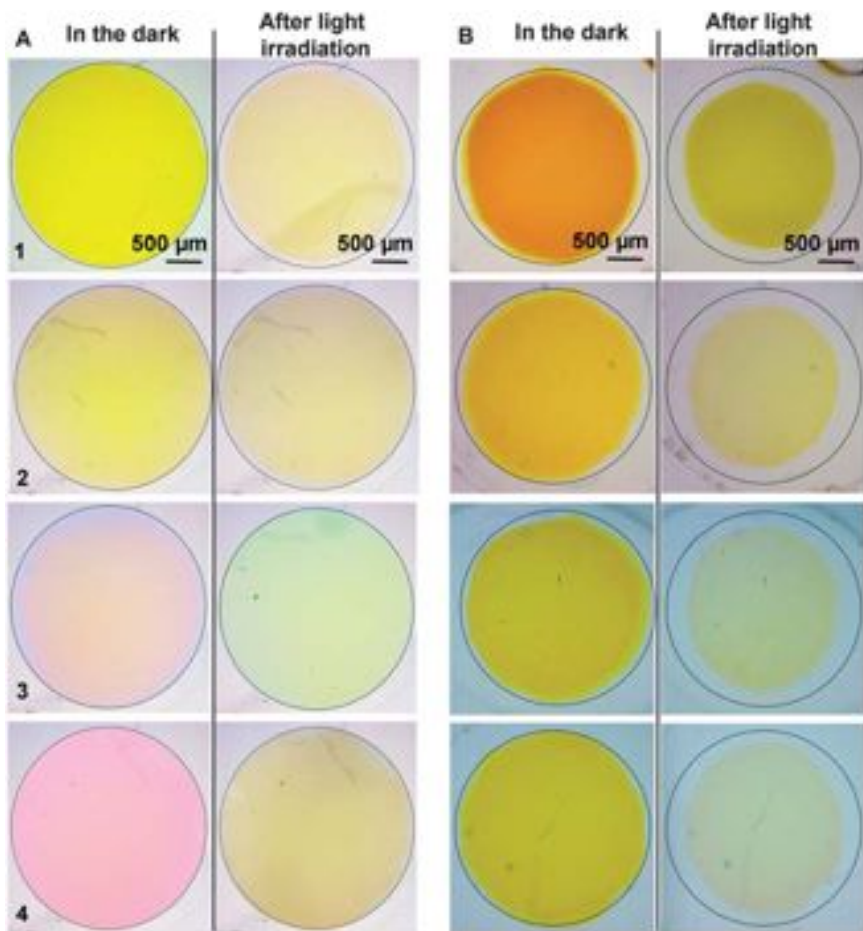




Reproducible actuation



- Comparison between with 5-1 and 0-1 hydrogels



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





Improved actuation kinetics

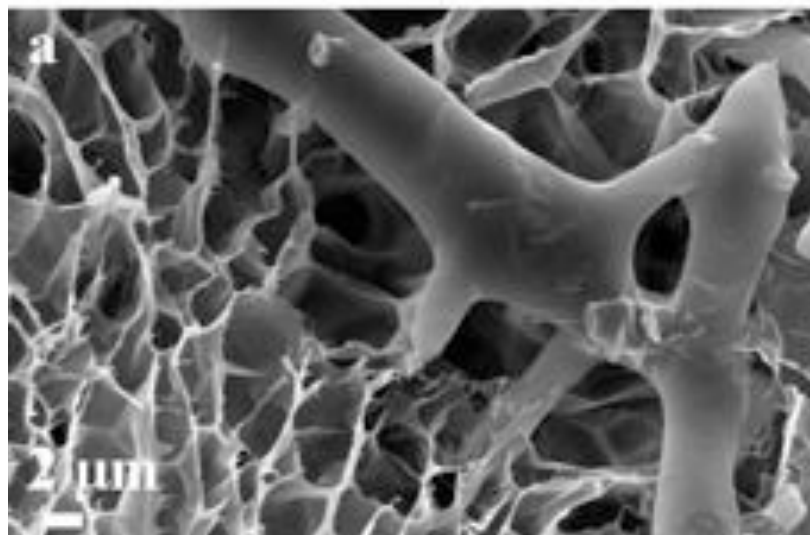
- **5-1 Hydrogel**
- **poly(ethylene glycol) $M_w = 2000$ g/mol**
 $M_w = 20000$ g/mol

		Blank gel	2k gel	20k gel
AA	[mol %]	5	5	5
BSP	[mol %]	1	1	1
MBIS	[mol %]	3	3	3
PBPO	[mol %]	1	1	1
NIPAM	[mg]	200	200	200
PEG 2k	[mg]	-	400	-
PEG 20k	[mg]	-	-	200
Solvent	[μ L]	500	500	500





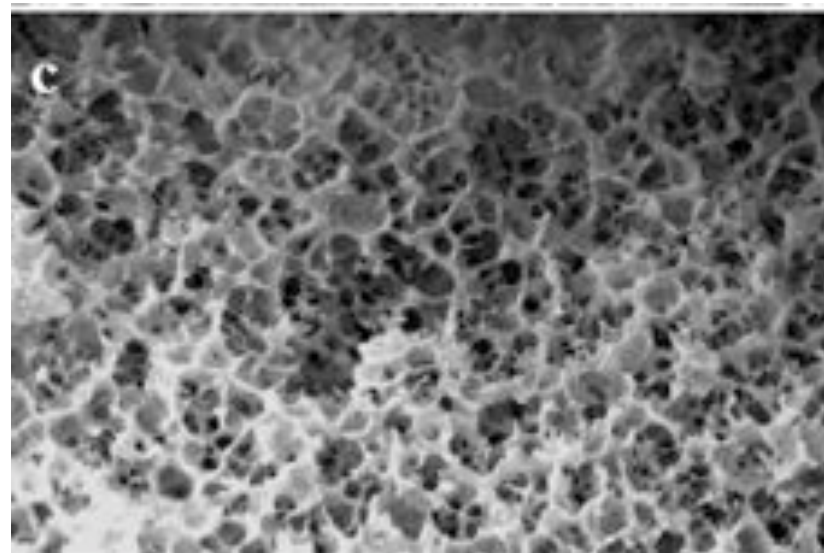
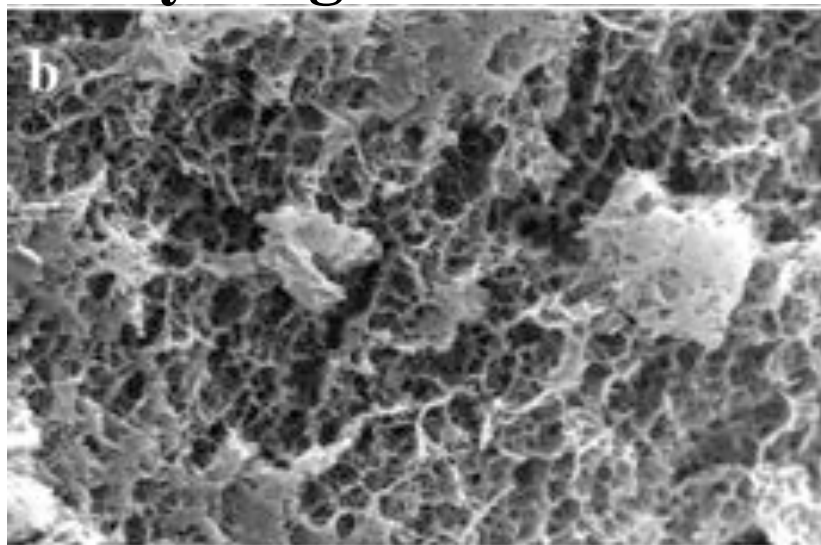
Porosity control



Blank hydrogel

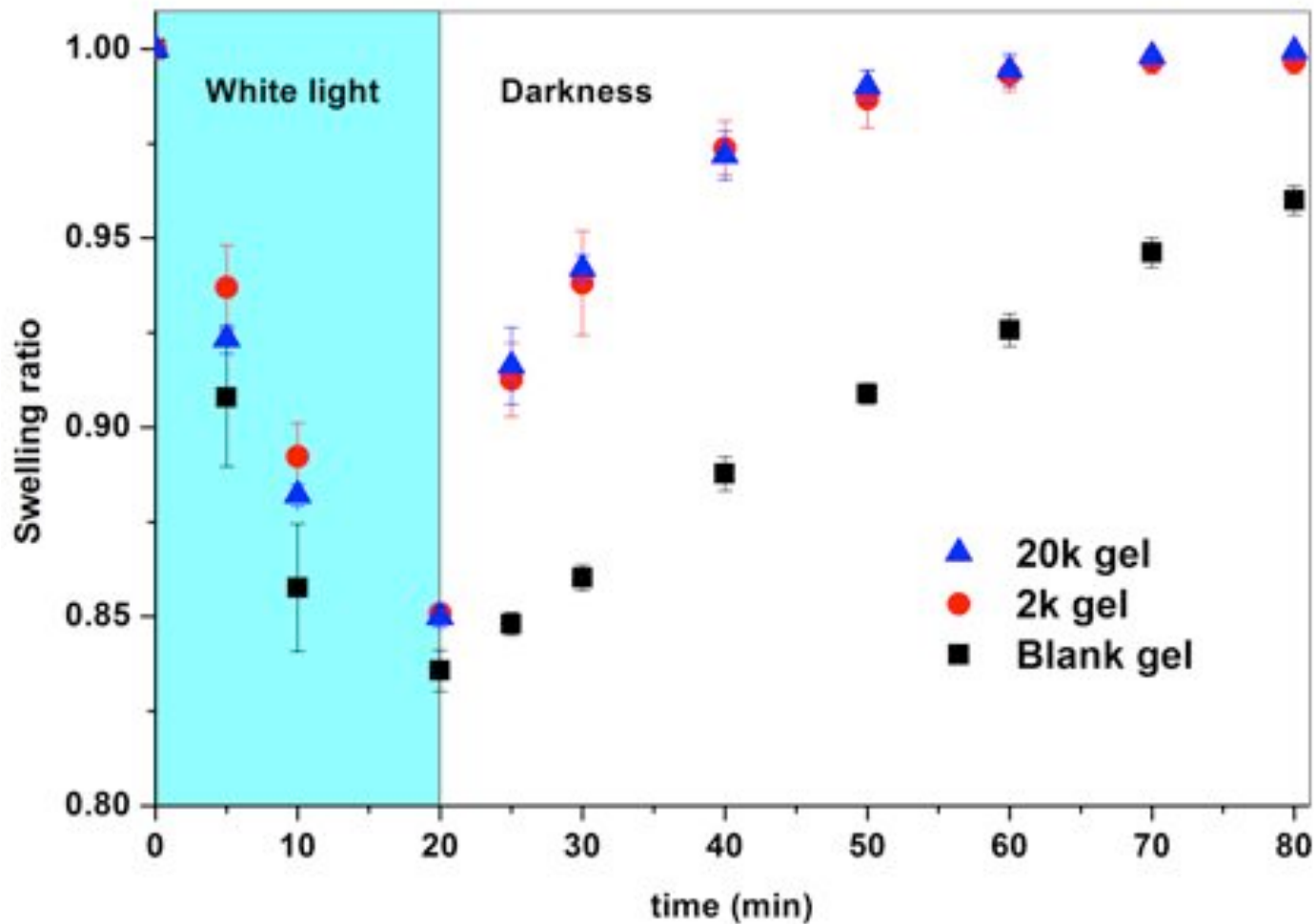
2k hydrogel

20k hydrogel



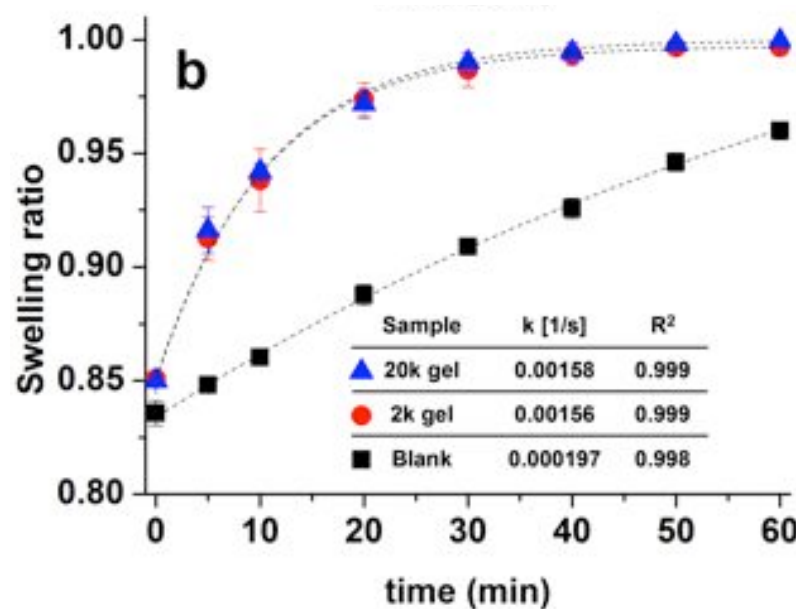
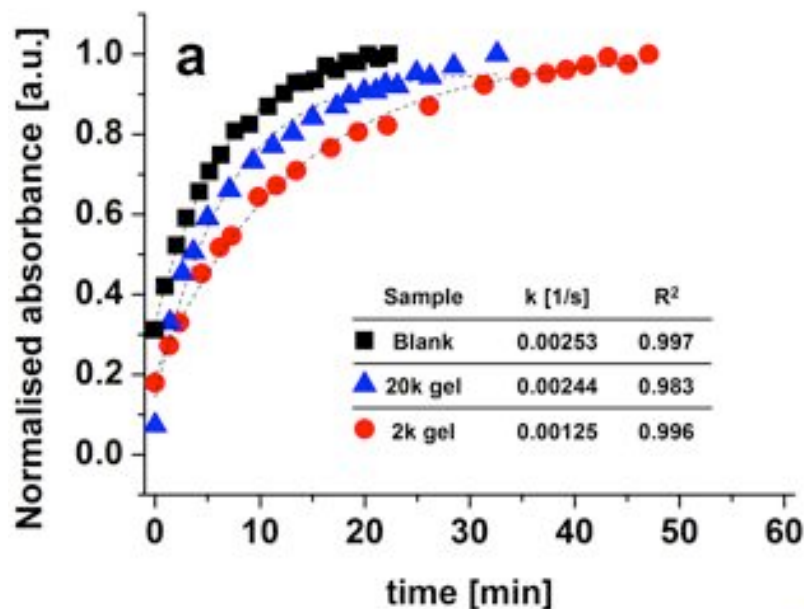


Shrinking/Reswelling Behaviour





Swelling and protonation kinetics



$k_{\text{blank}} \sim 2.53 \times 10^{-3} \text{ [s}^{-1}\text{]}$
 $k_{2k} \sim 1.25 \times 10^{-3} \text{ [s}^{-1}\text{]}$
 $k_{20k} \sim 2.44 \times 10^{-3} \text{ [s}^{-1}\text{]}$

$k_{\text{blank}} \sim 2 \times 10^{-4} \text{ [s}^{-1}\text{]}$
 $k_{2k} \sim 1.6 \times 10^{-3} \text{ [s}^{-1}\text{]}$
 $k_{20k} \sim 1.6 \times 10^{-3} \text{ [s}^{-1}\text{]}$





- **Self-protonating hydrogels**
- **Capable of performing in DI water and neutral pH solutions**
- **Reproducible photo-actuation**
- **Porous hydrogels for improved reswelling kinetics**





Conclusions



- ✓ **Novel sensors and actuators**
- ✓ **Advantages of integrating stimuli-responsive materials and fluidic functionalities at the microscale**
- ✓ **Nanostructured materials ensure short diffusion-paths and fast response times.**



Acknowledgments



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- **Prof. Dermot Diamond**
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Thank you!

