PHOTOACTUATED IONOGEL MICROVALVES FOR WATER QUALITY ON-CHIP ANALYSIS

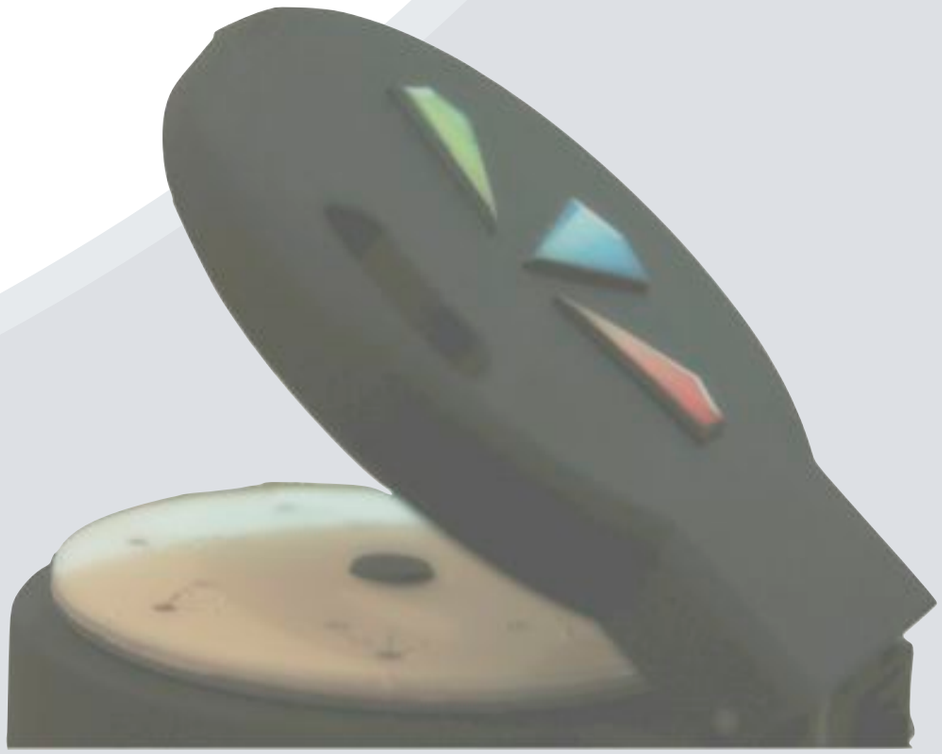
Monika Czugala

Prof. Dermot Diamond, Dr. Fernando Benito-Lopez

ATWARM MEETING NOV' 2012

Presentation outline

- **Introduction**
- **Photoswitchable materials**
- **Our challenge**



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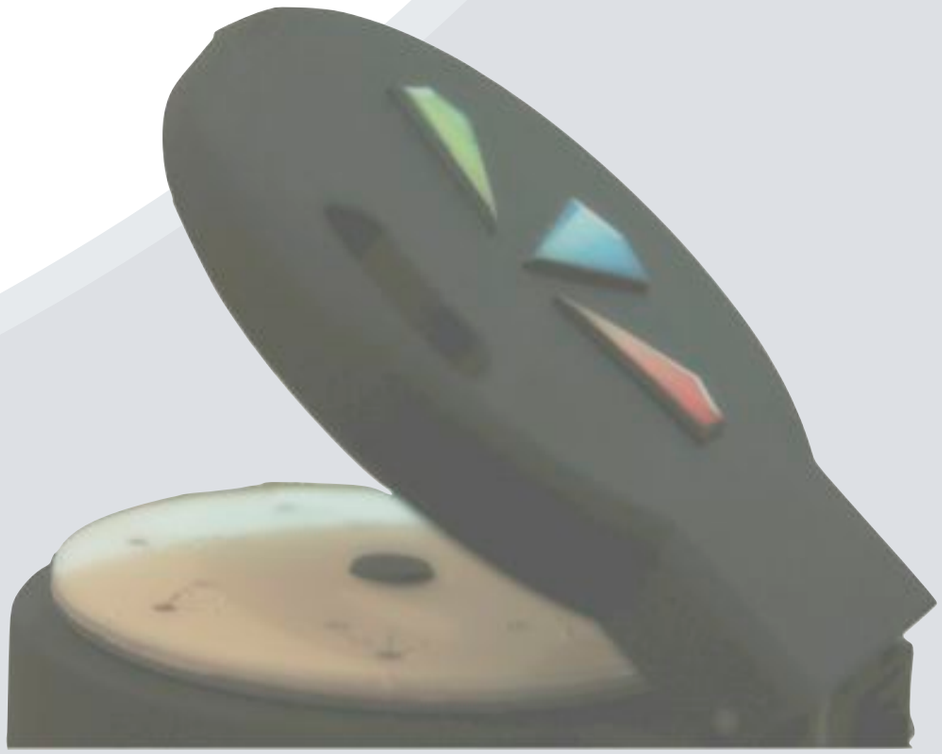

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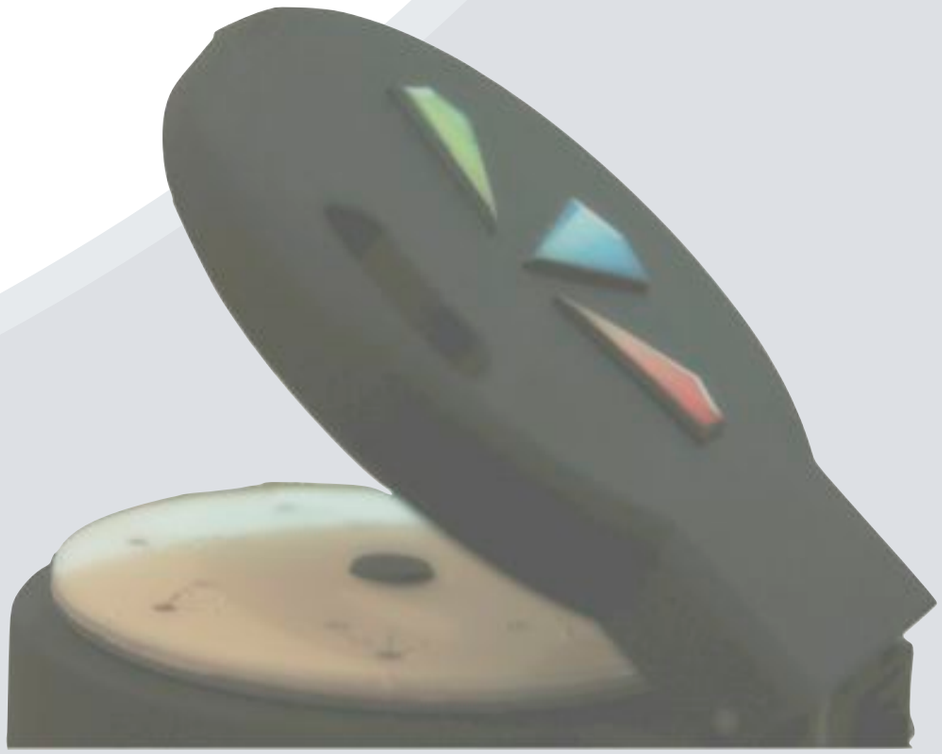
- **Performance of the valve**
- **Conclusions**

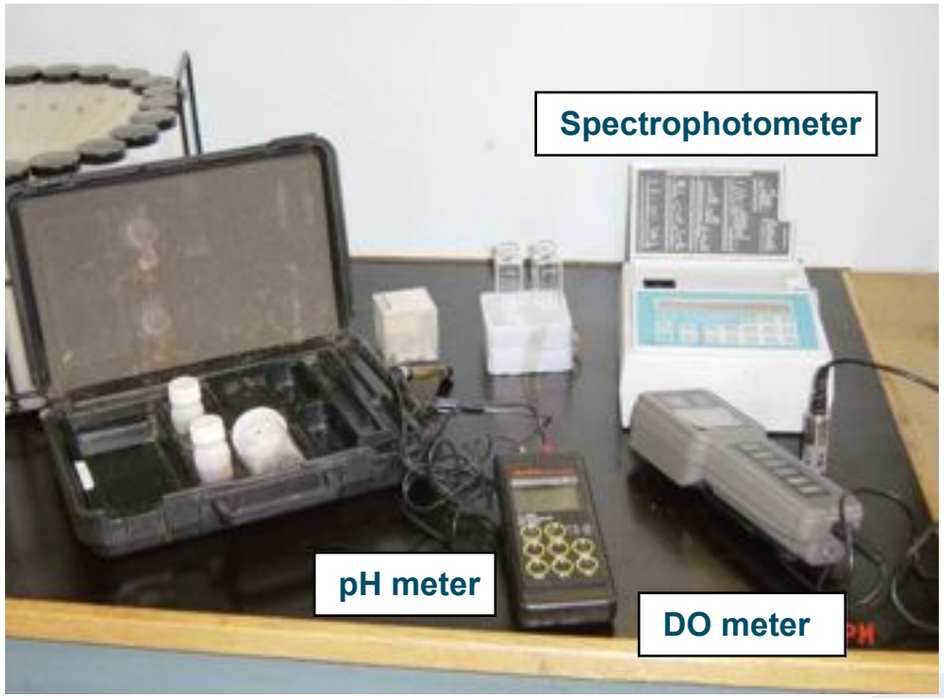


Water quality analysis techniques

Traditionally

- Current norm: manual grab samples 3 or 4 times a year.
- **Disadvantages:**
  - ✗ Low stability of natural water samples during long-term storage.[1]
  - ✗ Expensive, time consuming and requires highly trained staff.

In situ measurements



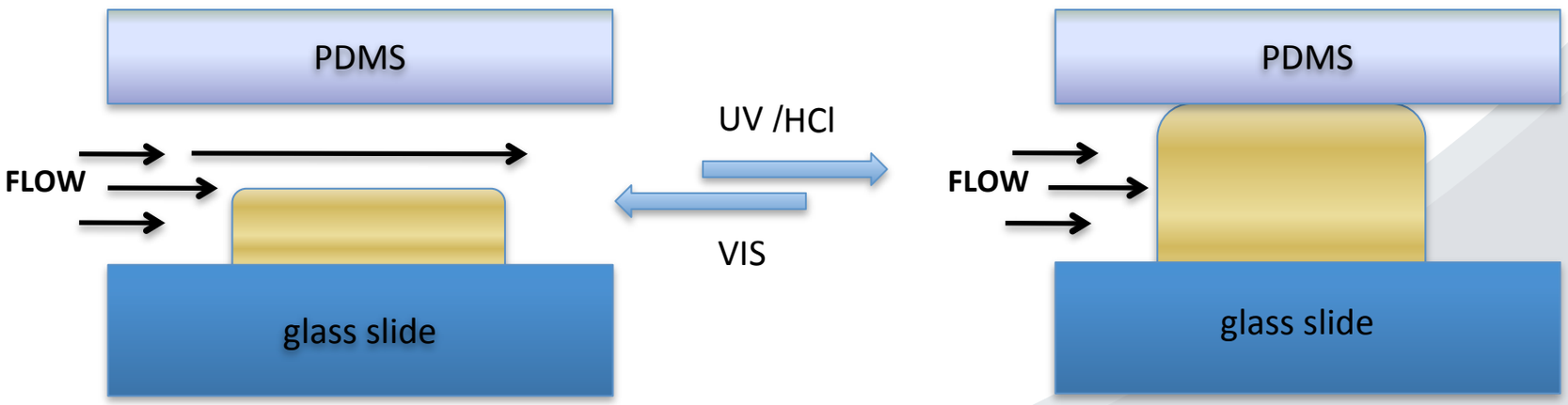
✓ portable
✓ inexpencive
✗ single probe
✗ no data saving

✓ multiprobe (temperature, pH, redox, DO, turbidity (TSS), NO_3, Na, F, etc.)
✗ €7000
✓ hand-held device

[1] G. Hanraham, J. Environ. Monit. 6, 2004, 657.

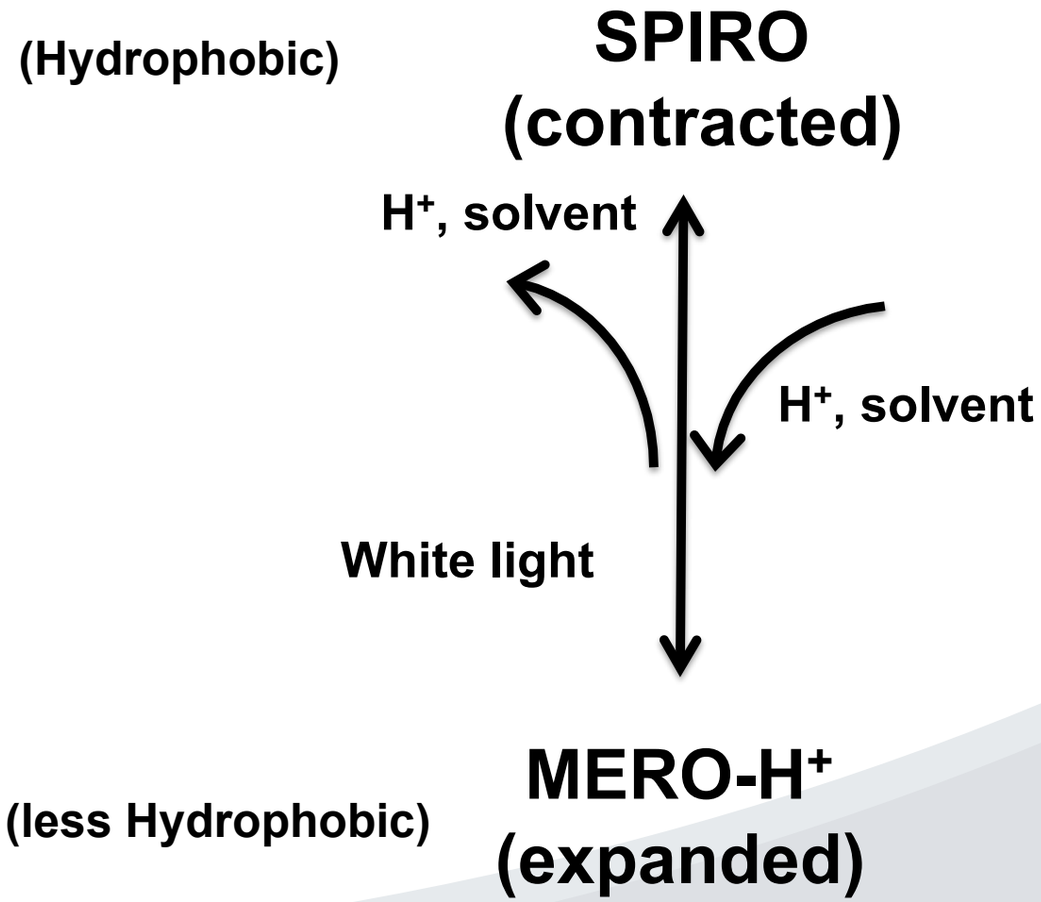
Photoswitchable materials

- Photoswitchable materials - the use of non-contact, non invasive stimuli.
- Ionogels containing spiropyran moieties with photochromism properties.
- Protonated spiropyran ionogels exhibit a drastic swelling effect.
- Shrinking process of the ionogels happen upon white light irradiation.



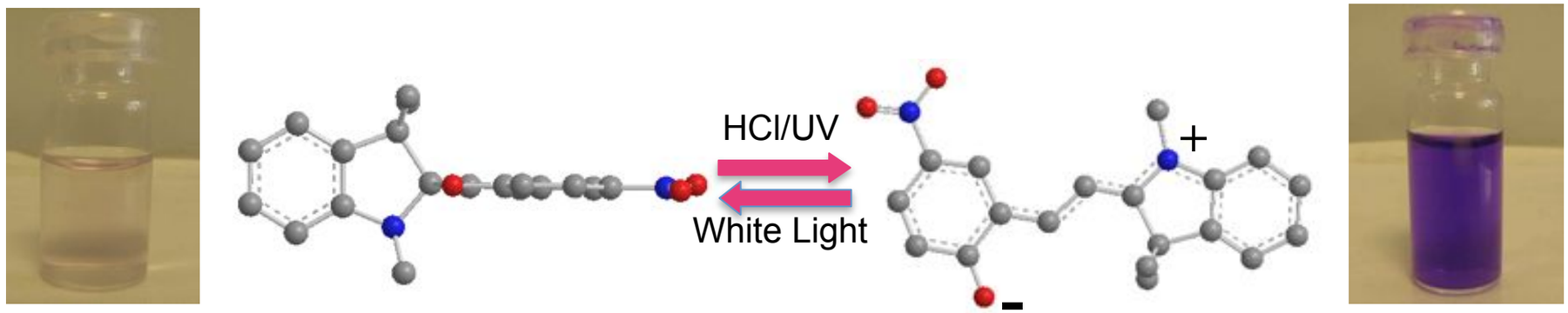
[1] G. Hanraham, J. Environ. Monit. 6, 2004, 657.

Actuation mechanism

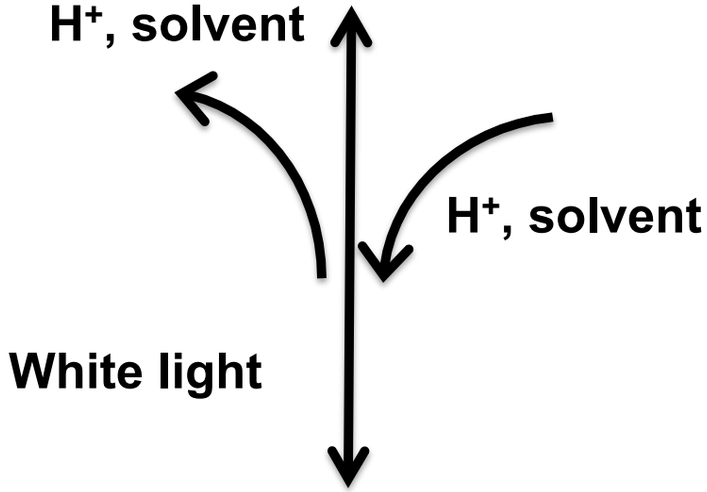


- **OPTICALLY ACTUATE BETWEEN TWO DISTINCT ISOMERS**
- **CONTROL PHYSICO-CHEMICAL PROPERTIES OF SYSTEM**
- **NON-CONTACT SPATIAL CONTROL OF ACTUATION**

Actuation mechanism



(Hydrophobic) **SPIRO (contracted)**



(less Hydrophobic) **MERO-H⁺ (expanded)**

- **OPTICALLY ACTUATE BETWEEN TWO DISTINCT ISOMERS**
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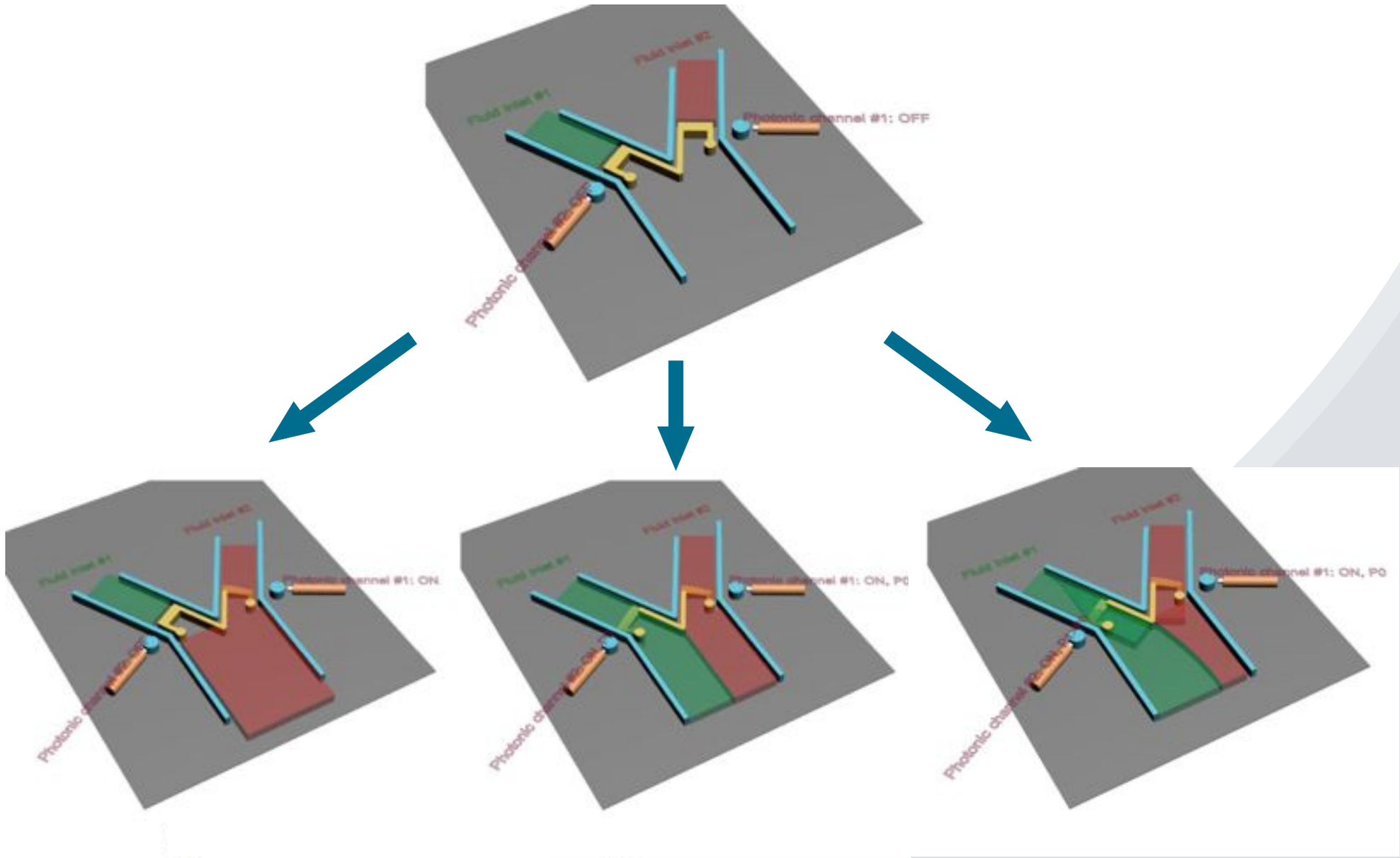
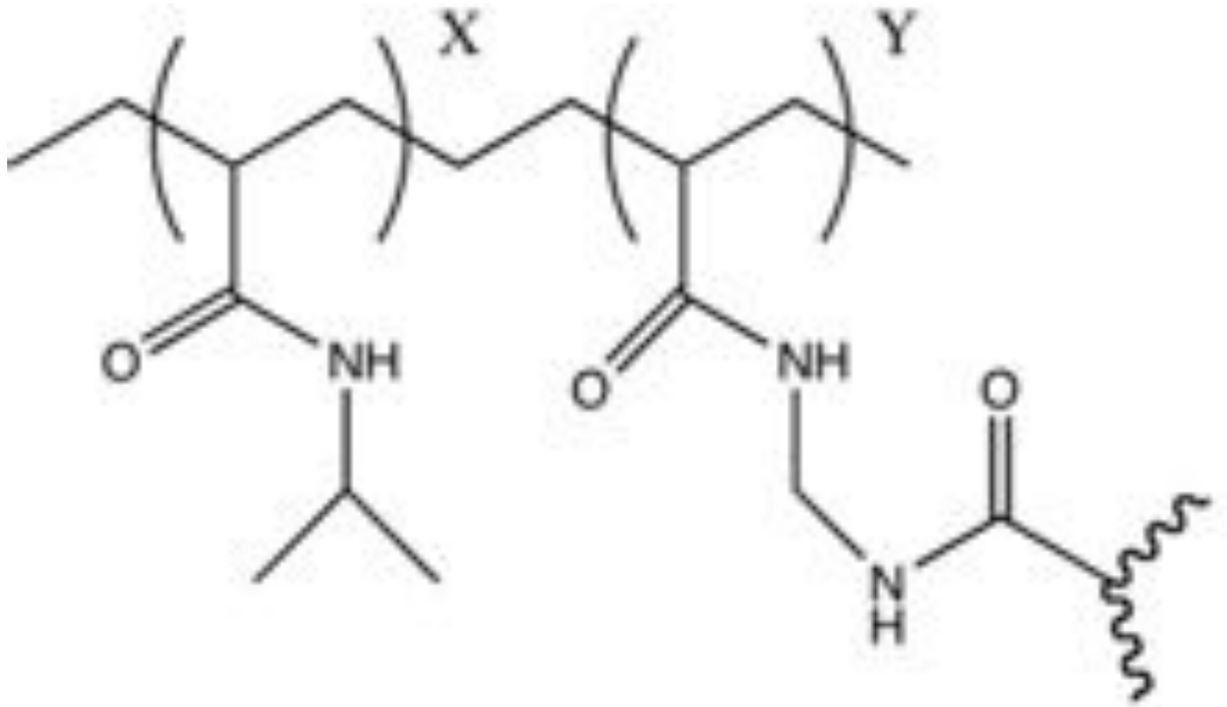
Our challenge



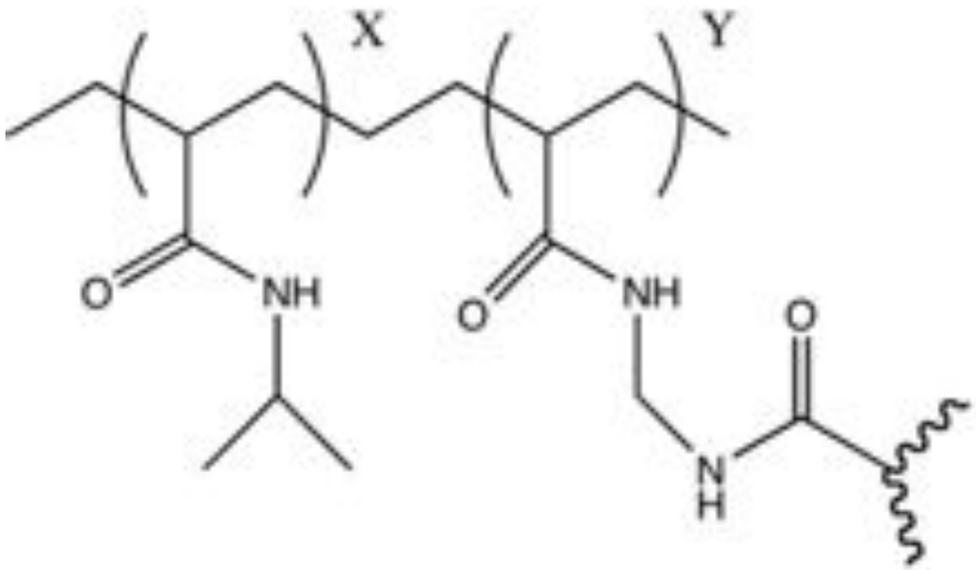
Variety of actuations on photonic channels

Materials



A Poly(*N*-isopropyl-acrylamide) and *N,N*-methylene-bis(acrylamide) cross- linked polymer 100 (x):5 (y)

Materials



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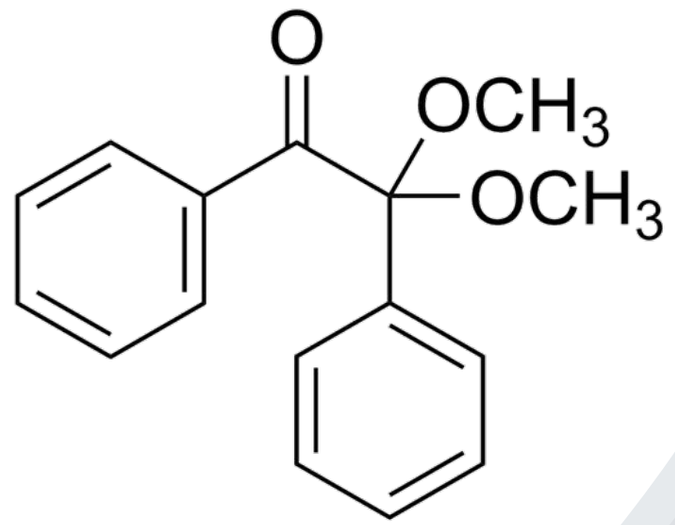
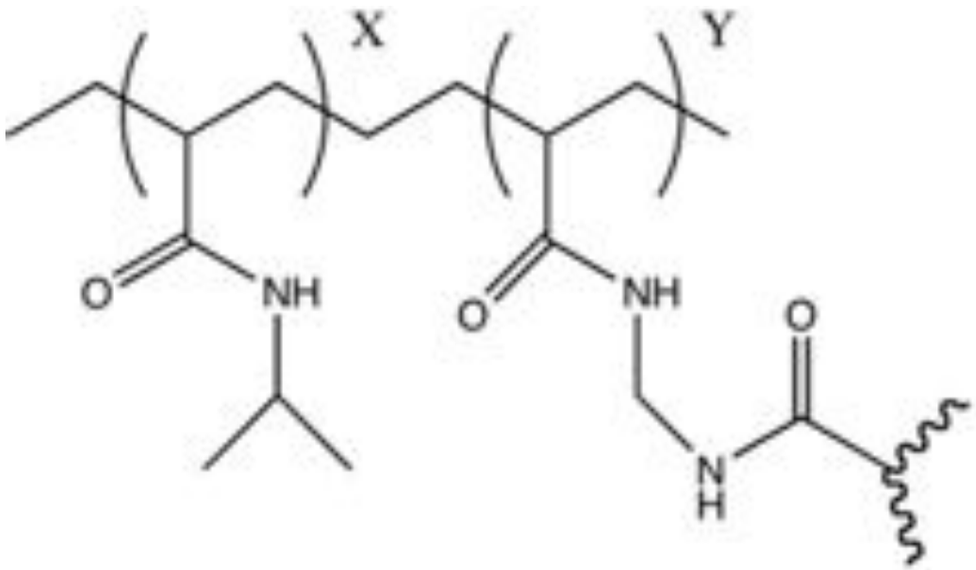


B 2,2-dimethoxy-2-phenyl acetophenone (DMPA)

Materials



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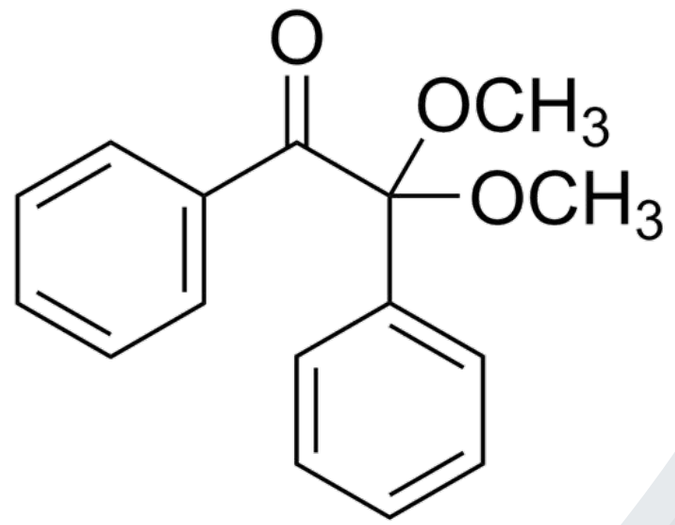

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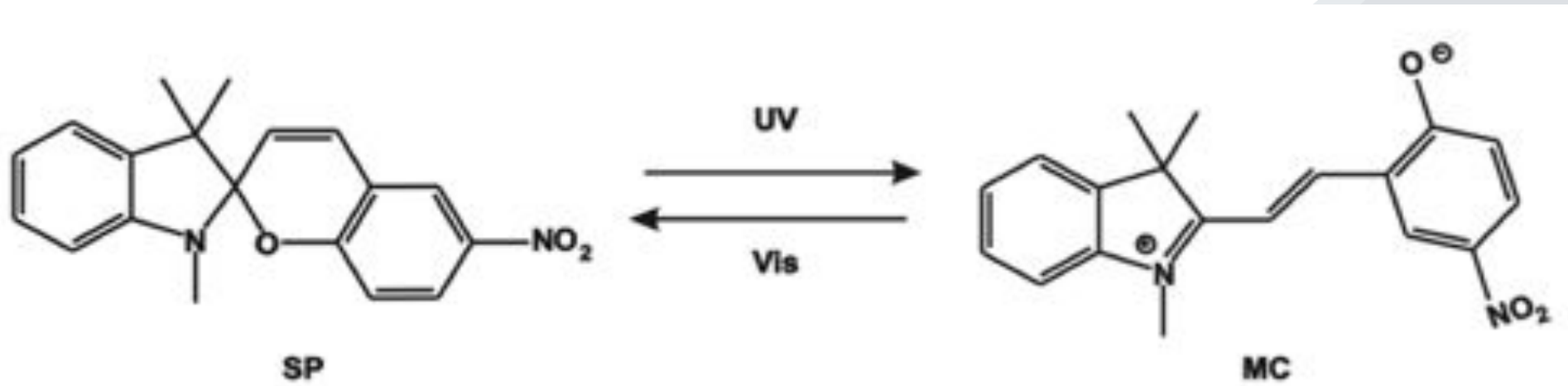
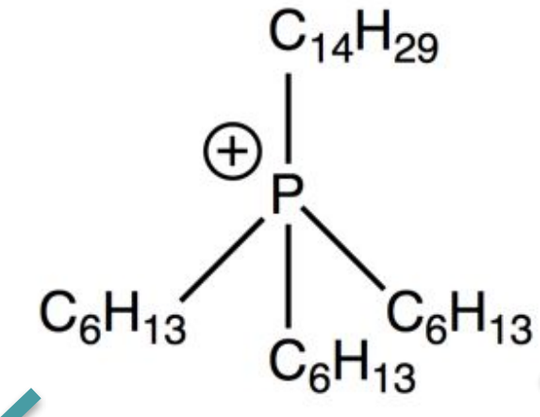


C Benzospiropyran

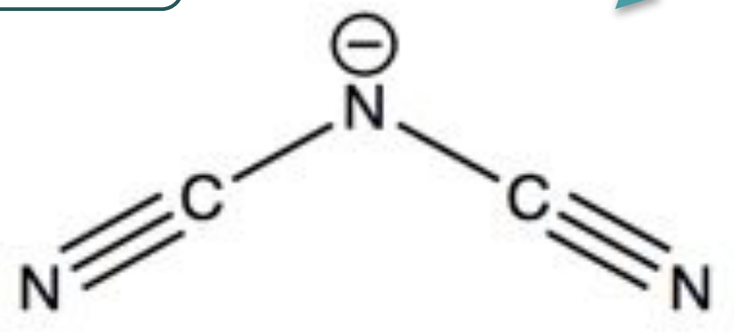
Materials

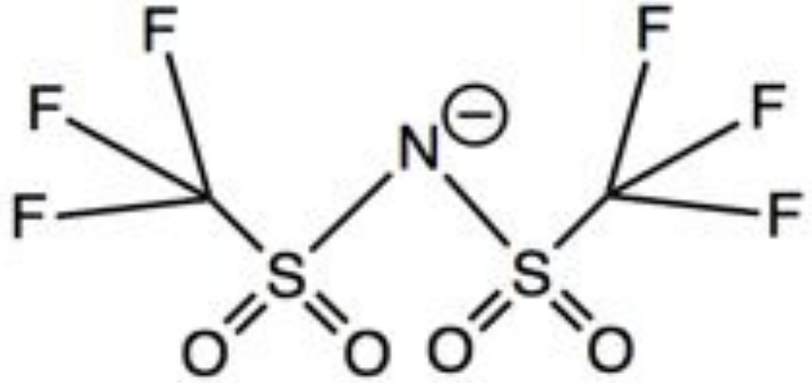
D Ionic liquid

Cation:



Anion:



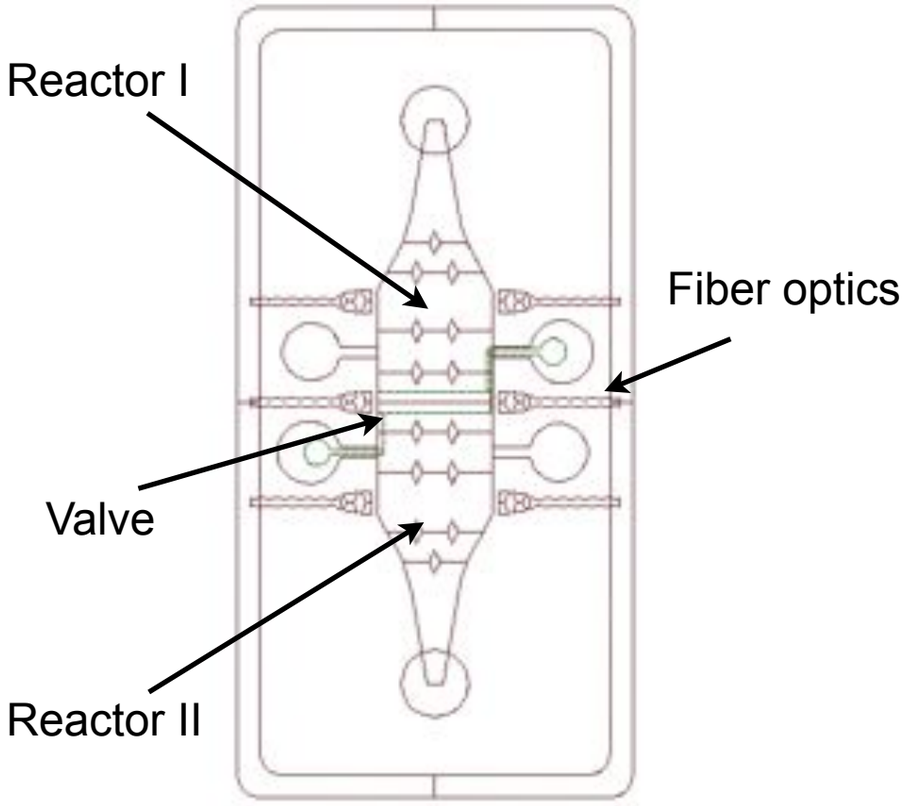


1. Trihexyl (tetradecyl) phosphonium dicyanomide ($[P_{6,6,6,14}][DCA]$)

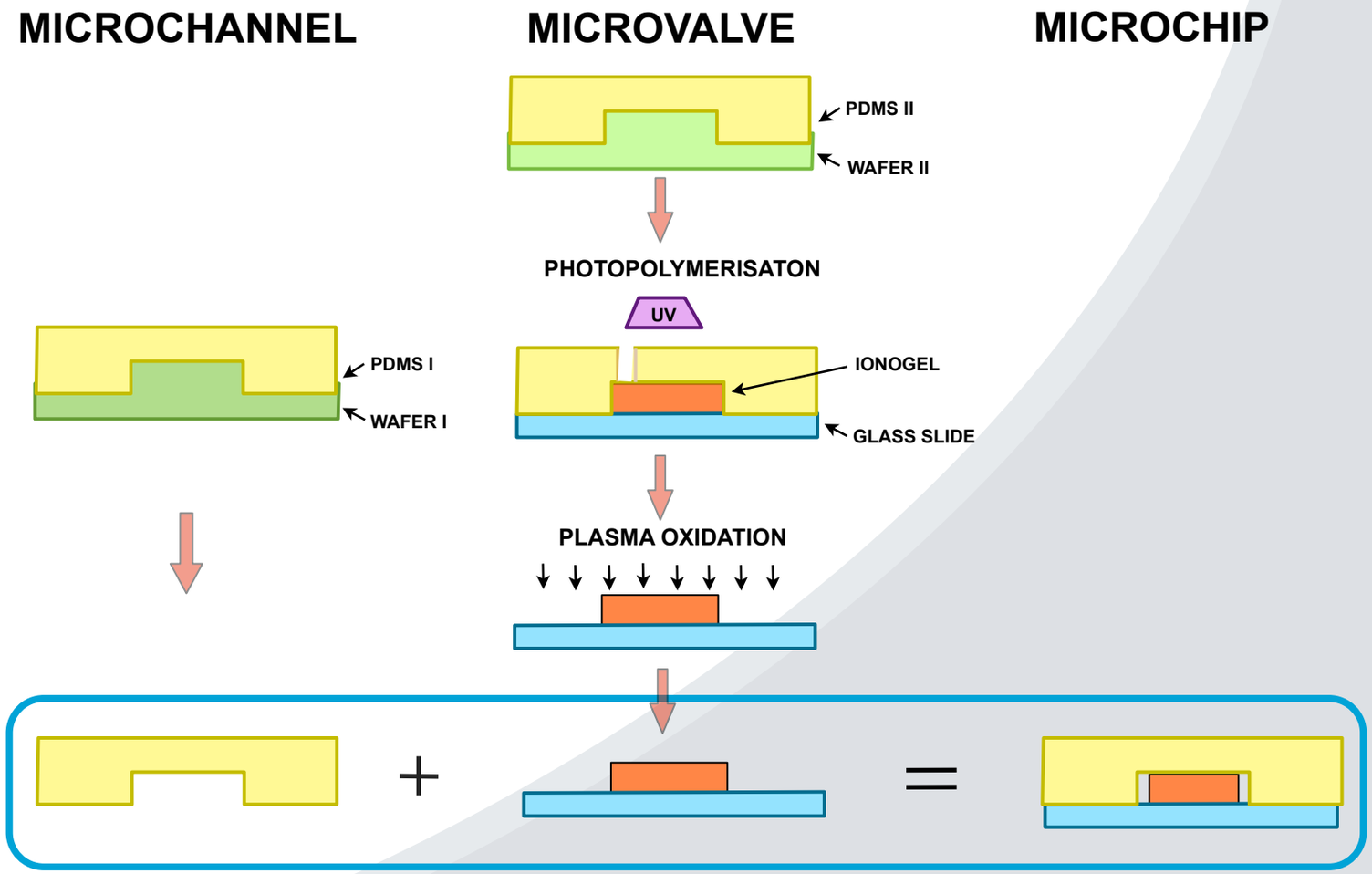
2. Trihexyl (tetradecyl) phosphonium chloride ($[P_{6,6,6,14}][Cl]$)

3. Trihexyl (tetradecyl) phosphonium bis(trifluoro-methanesulfonyl)-imide ($[P_{6,6,6,14}][DCA]$)

Microreactor with photoswitchable valve

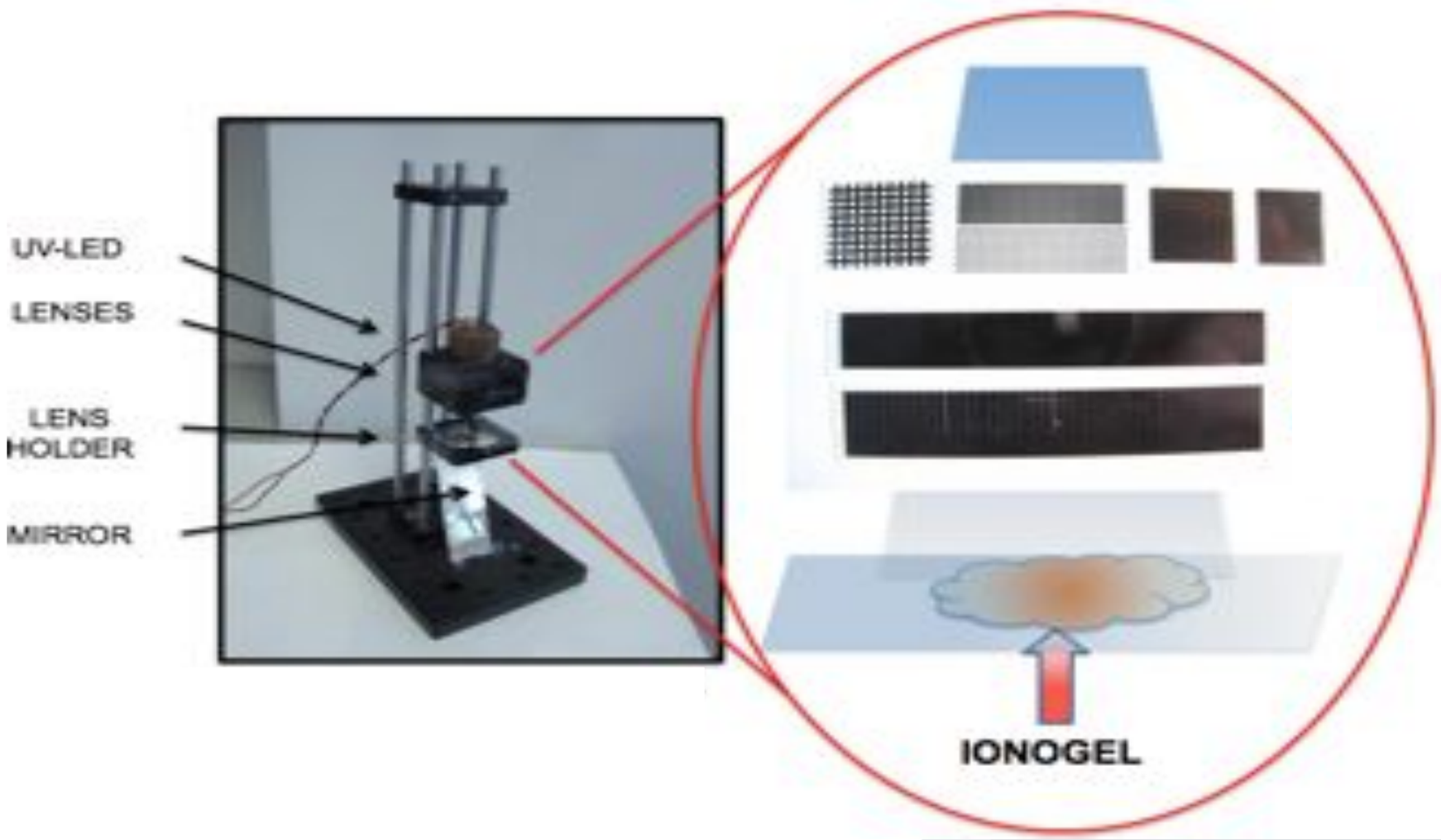


Design of the microreactor



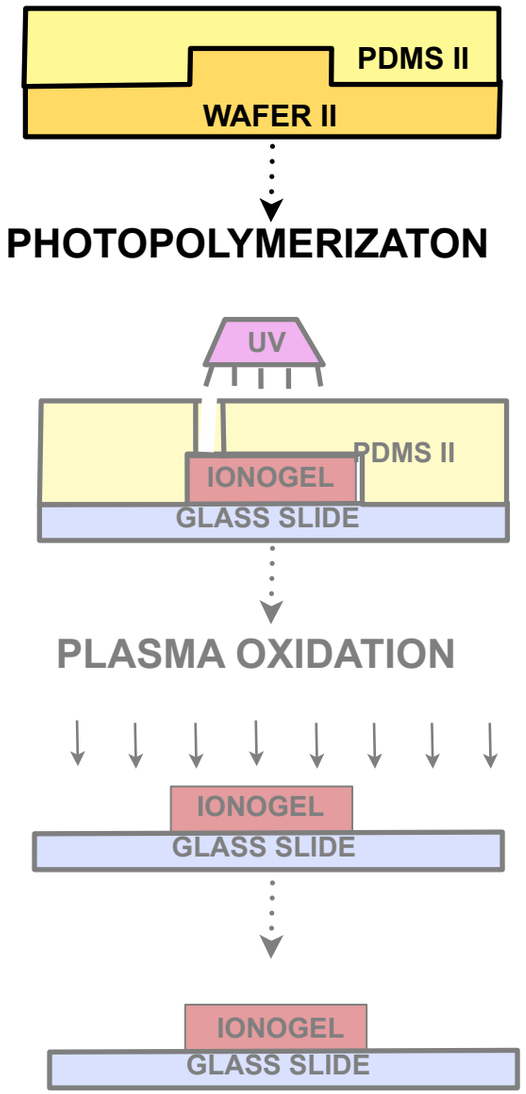
Schematic of the microreactor fabrication

Photoswitchable valve



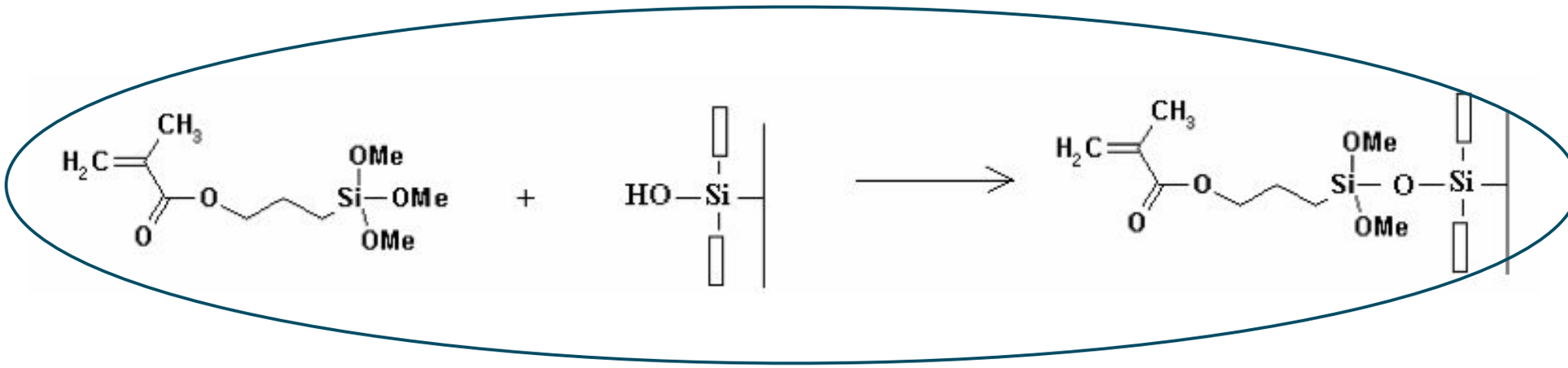
UV LED setup for photopolymerisation

Surface modification



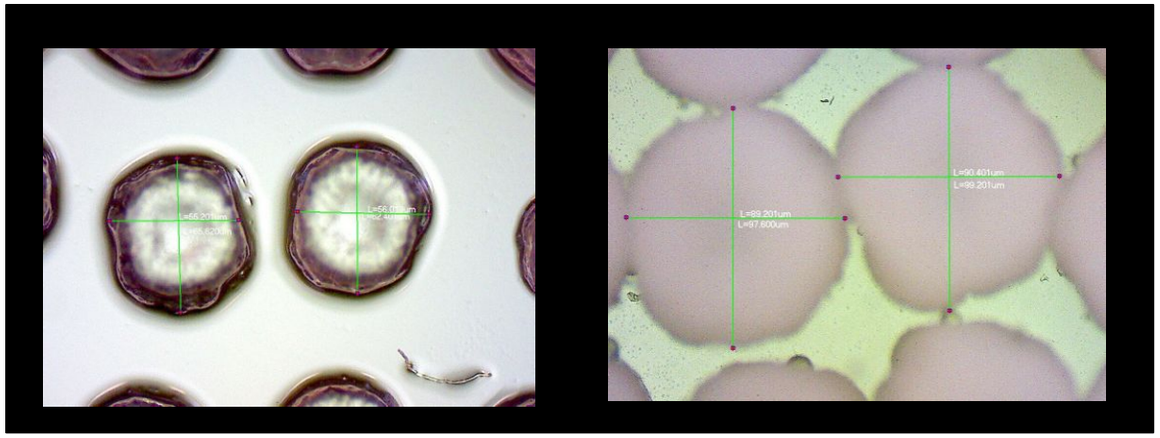
SILANISATION

- dipping in 1M NaOH solution,
- dipping in water solution of silane agent (3- (Trimethoxysilylpropylmethacrylate)



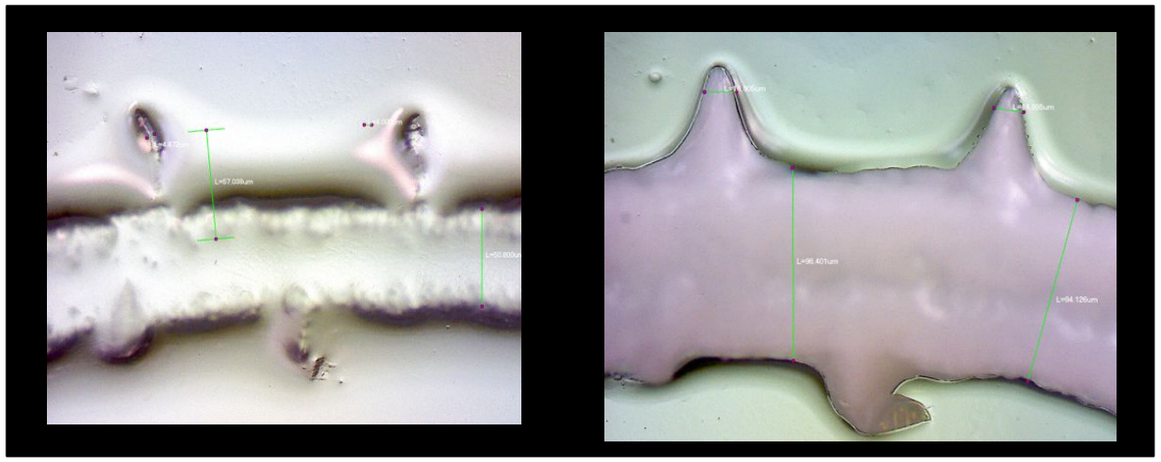
[3] B. Candice, A Two-Chromophore photolithography photopolymerization, IPM Fraunhofer, 2010

Photoswitchable microstructures

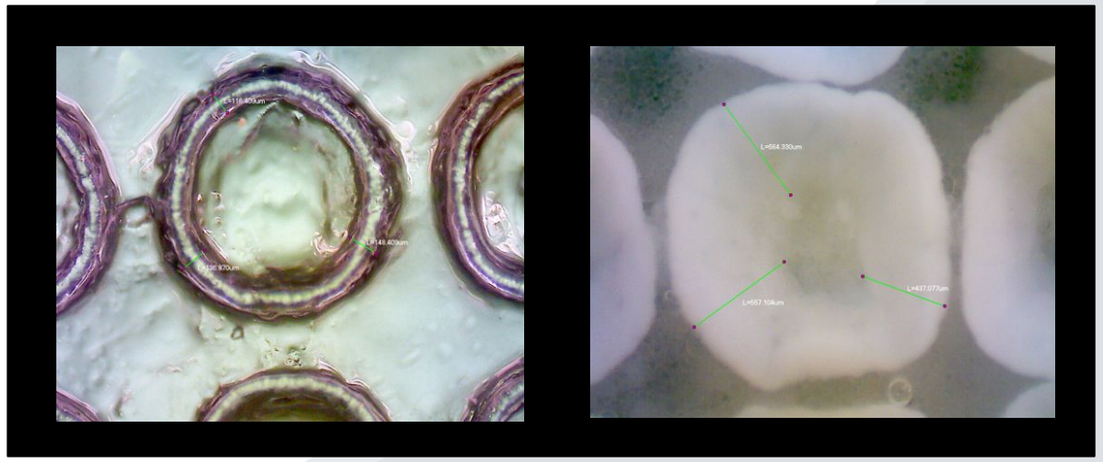


Small circles

Big circles



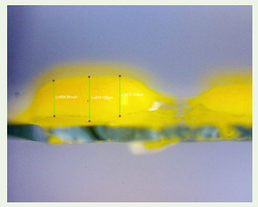
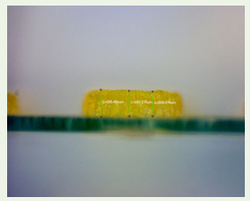
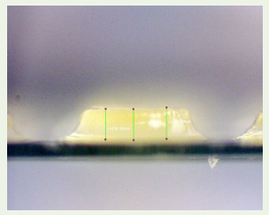
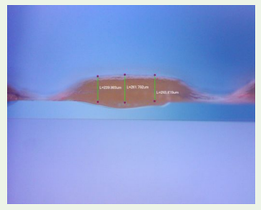
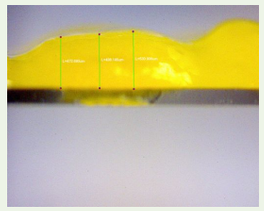
Lines

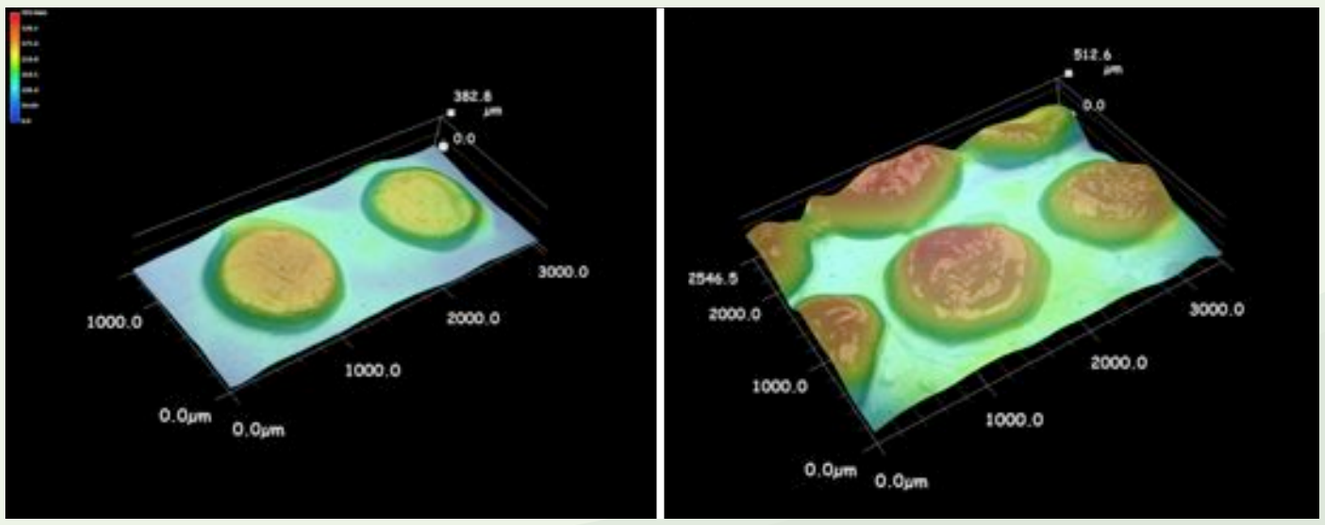


Rings

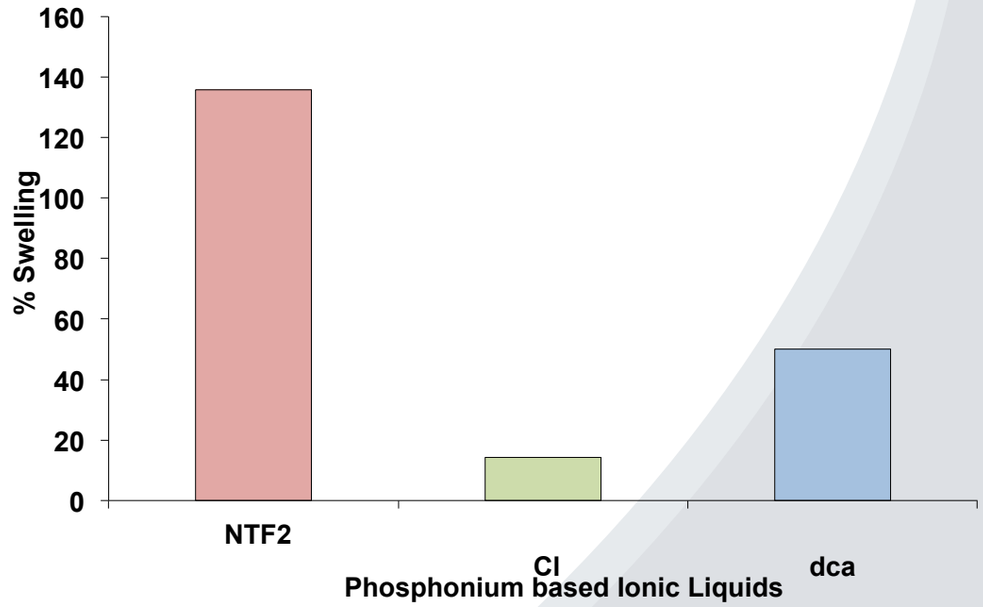
- Change of horizontal dimension.
- Change of vertical dimension (height).
- Time of shrinking.

Photoswitchable microstructures

	Initial		*After 2 hrs in HCl*	*% change*
• $[P_{6,6,6,14}][dca]$		1mM HCl		62.19 %
• $[P_{6,6,6,14}][Cl]$		1mM HCl		14.13%
• $[P_{6,6,6,14}][NTf_2]$		1mM HCl		110.28%



Ionogel microstructures in shrunk (left) and swollen (right) state.

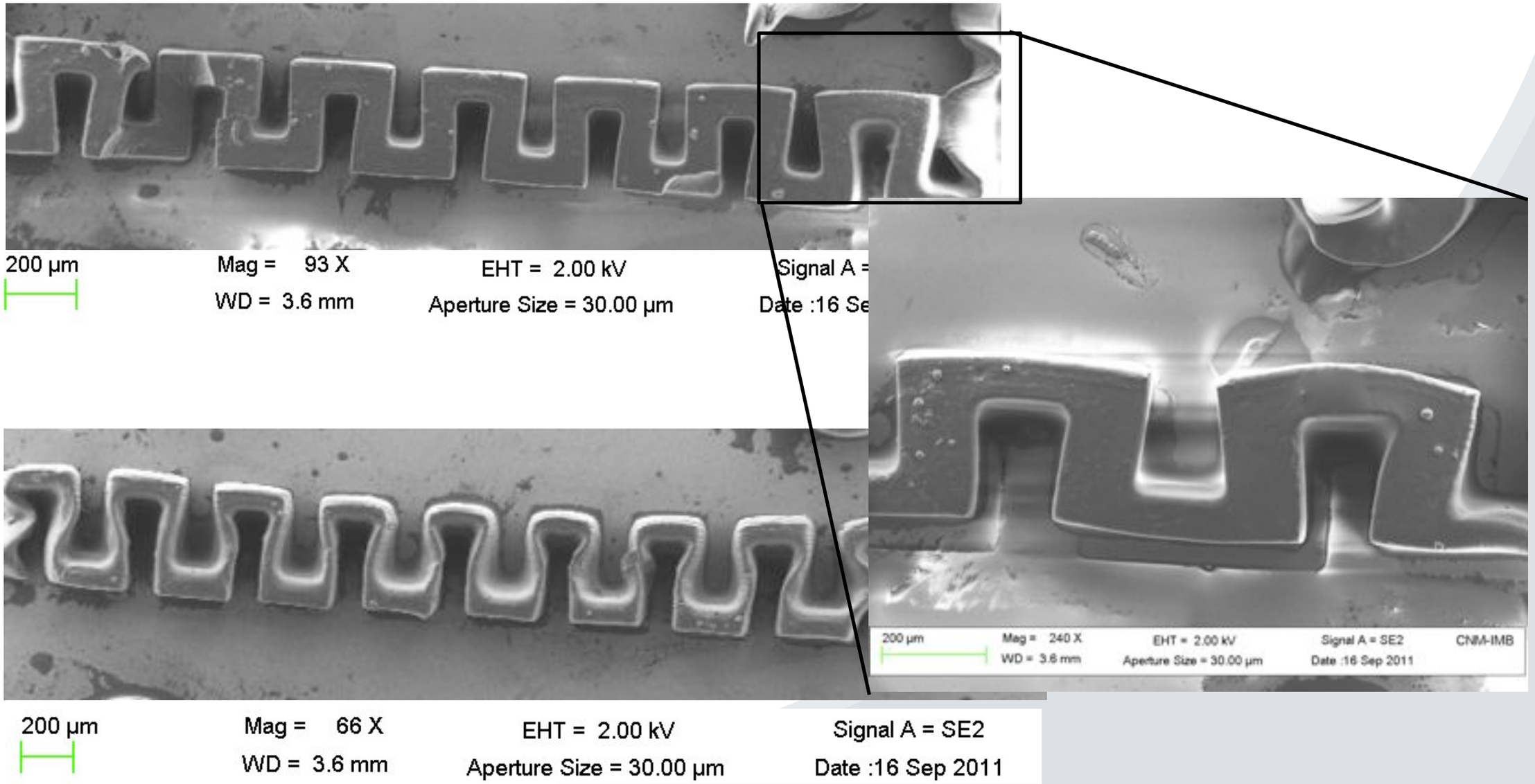


Percentage of shrinking

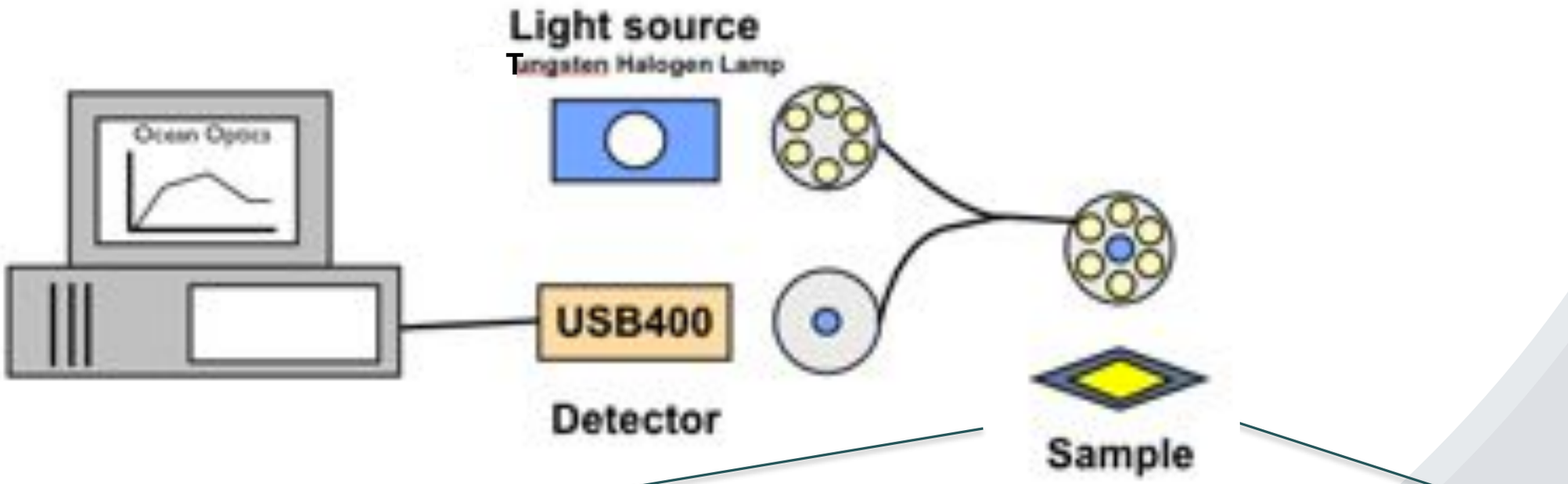
Ionic Liquid	% Shrinking after 15 mins
$[P_{6,6,6,14}][dca]$	31.8
$[P_{6,6,6,14}][Cl]$	6.1
$[P_{6,6,6,14}][NTF_2]$	95.8

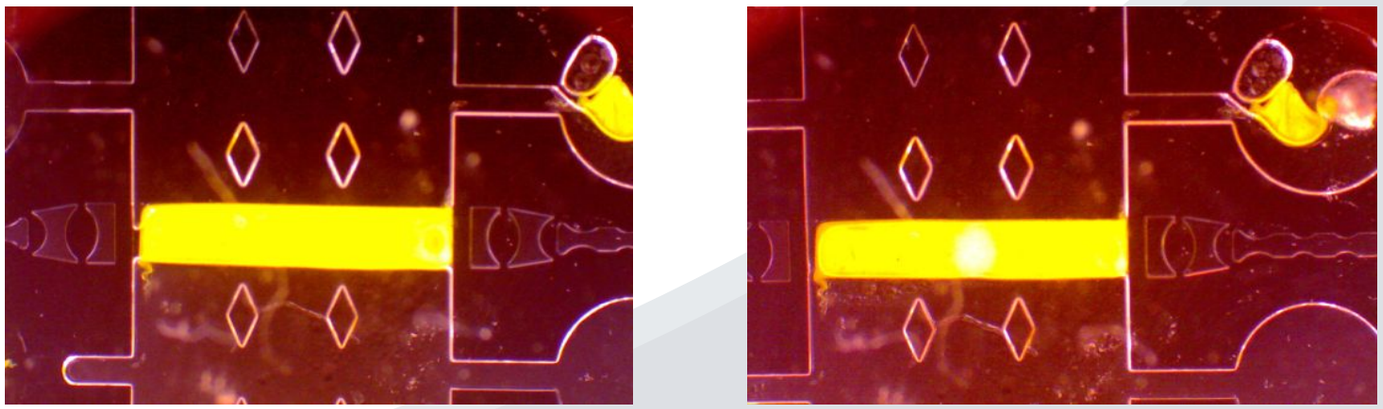
Average volume change percentage after 15 min of white light irradiation

Photoswitchable valve



Photoswitchable valve

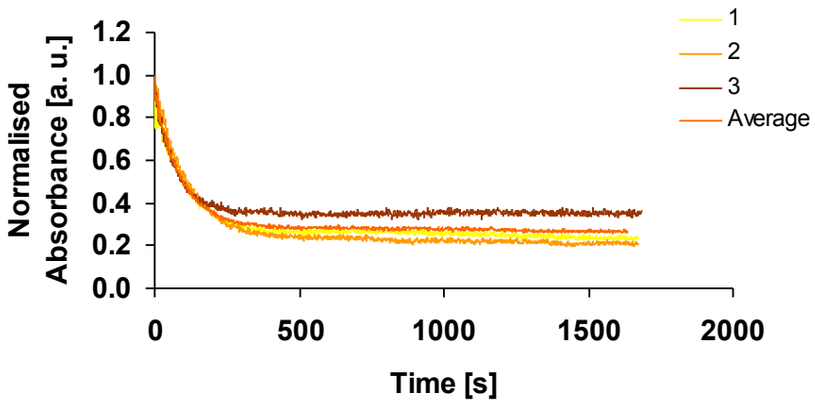




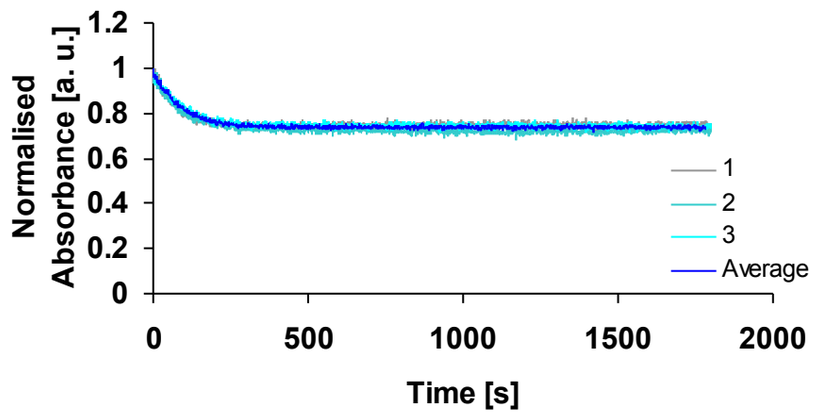
Kinetics - rate of ring closing

λ_{max} = 440 nm

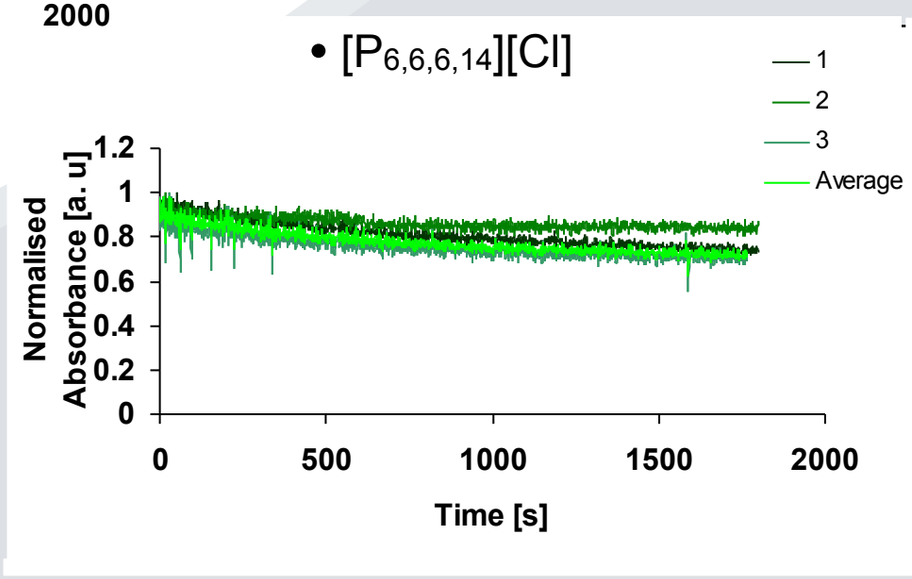
- $[P_{6,6,6,14}][NTf_2]$



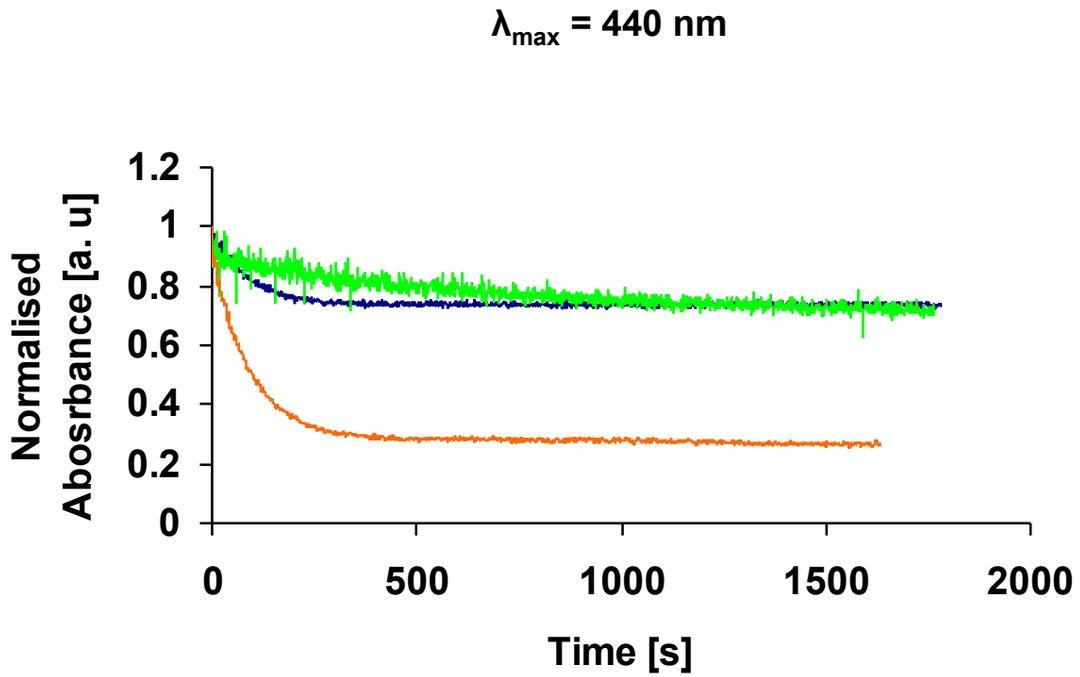
- $[P_{6,6,6,14}][dca]$

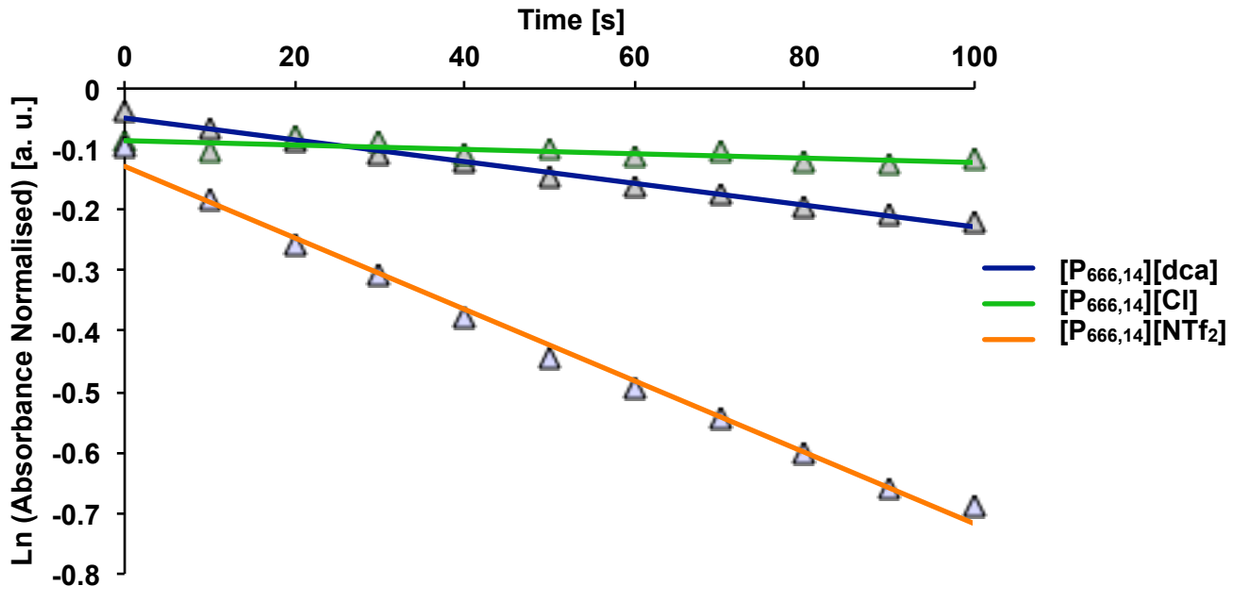


- $[P_{6,6,6,14}][Cl]$



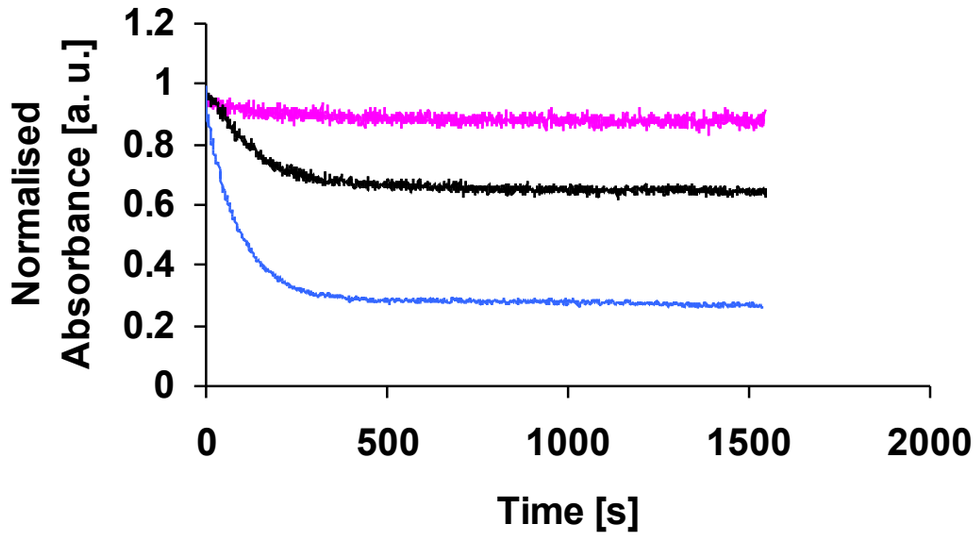
Kinetics - rate of ring closing

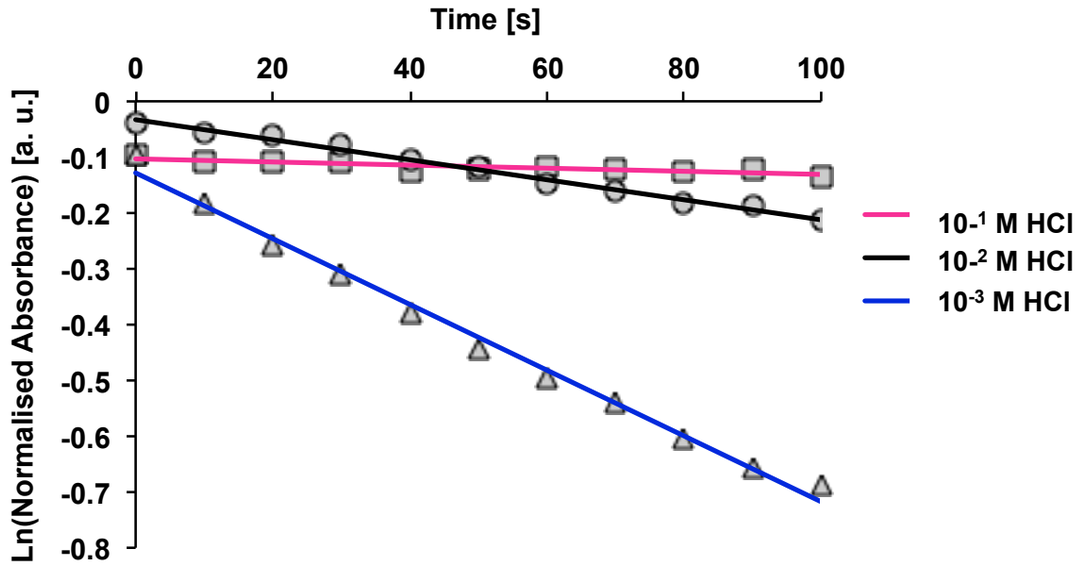




Ionogel	K Value [a. u.]
$[P_{6,6,6,14}][Cl]$	0.0004
$[P_{6,6,6,14}][dca]$	0.0018
$[P_{6,6,6,14}][Ntf_2]$	0.0059

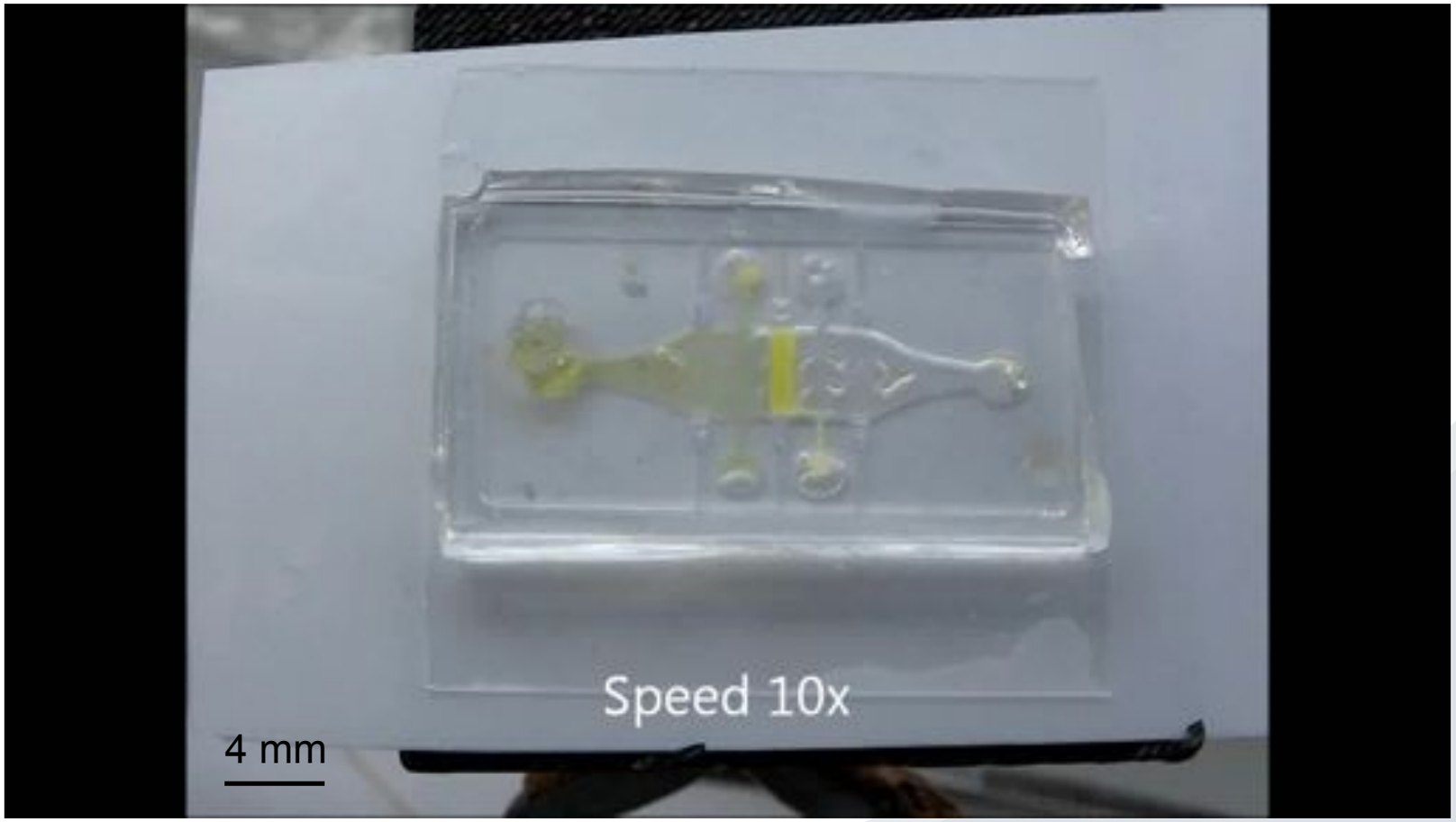
Kinetics - various HCl concentrations





Concentration [Moles]	K Value [a. u.]
10^{-1}	0.0003
10^{-2}	0.0018
10^{-3}	0.0059

Performance of the microvalve



Valve actuation under white light irradiation

Conclusions

Functionality

- Optimatization of the fabrication of photoswitchable ionogel microstructures.
- Successful fabrication of the hybrid PDMS/glass microchip incorporating microvalve.
- Study of the kinetics of valve actuation showed the fastest response of the $[P_{6,6,6,14}][NTf_2]$ based ionogel, k=0.0059.
- Analysis of the influence of the HCl concentration showed the fastest ionogel response for 10^{-3} M HCl.

List of outputs

Publications

- **M. Czugala *et. al***., *Optical sensing system based on wireless paired emitter detector diode device and ionogels for lab-on-a-disc water quality analysis,* Lab Chip, 23 (2012) 5069
- B. Ziółkowski[1], **M. Czugala[1]**, D. Diamond, *Integrating stimulus responsive materials and microfluidics – The key to next generation chemical sensors*, JIMSS, 2012
- **M. Czugala *et. al***., *CMAS: fully integrated portable Centrifugal Microfluidic Analysis System for on-site colorimetric analysis* (in preparation).

Conferences

- **MicroTAS 2012**, The 16th International Conference on Miniaturized Systems for Chemistry and Life Sciences, 28 OCt - 1 Nov, 2012, Okinawa *(ORAL)*
- **2nd International Symposium on Functional Nanomaterials**, 6-7 Sept 2012, Dublin, Ireland
- **ICEST2012**, 6th International Conference on Environmental Science and Technology 2012, June 25-29, 2012, Houston, USA *(ORAL)*

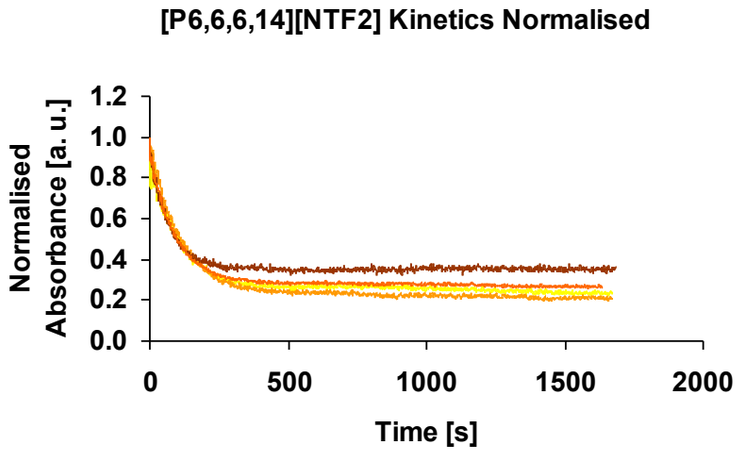
Courses

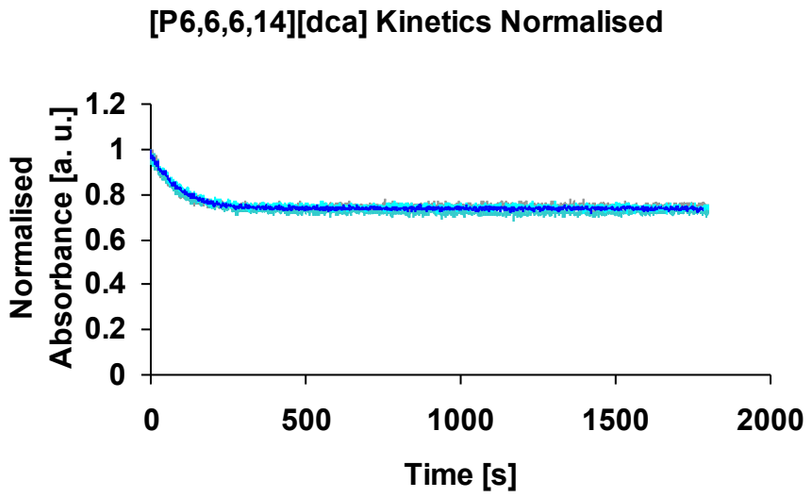
- Cambridge **Certificate in Advanced English (CAE)** - granted with grade B, Dublin, Ireland.
- **DCU Microsoft StudySmart** - Microsoft Word Course, Dublin, Ireland.
- **CMA Analytical Workshop 2012,** Dublin, Ireland.

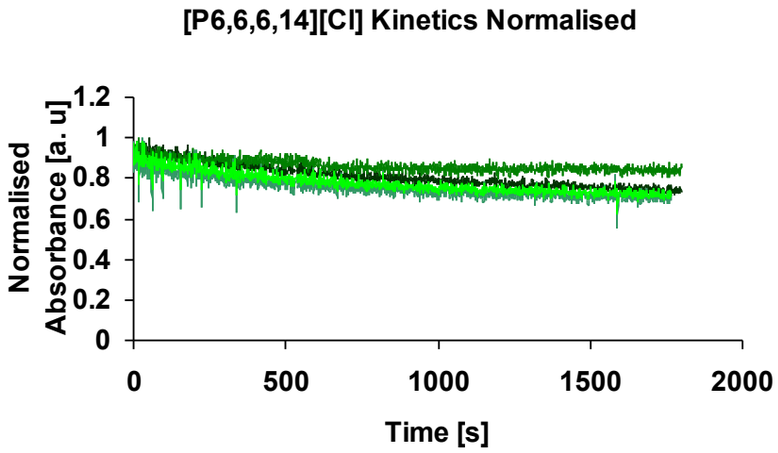
Acknowledgements

- Claire O'Connel
- Dr. Andreu Llobera
- Dr. CHAVI??
- Dr César Fernández Sánchez,
- Prof. Dermot Diamond
- Dr. Fernando Benito-Lopez
- Adaptive Sensors Group, Dublin City University
- Marie Curie ITN funded by the EC FP7 People Program
- Science Foundation of Ireland under grant 07/CE/I1147

Thank you for your attention!


[P6,6,6,14][NTF2] Kinetics Normalised
Normalised Absorbance [a. u.]
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Time [s]


[P6,6,6,14][dca] Kinetics Normalised
Normalised Absorbance [a. u.]
1.2
1
0.8
0.6
0.4
0.2
0
0
500
1000
1500
2000
Time [s]


[P6,6,6,14][Cl] Kinetics Normalised
Normalised Absorbance [a. u]
1.2
1
0.8
0.6
0.4
0.2
0
0
500
1000
1500
2000
Time [s]