

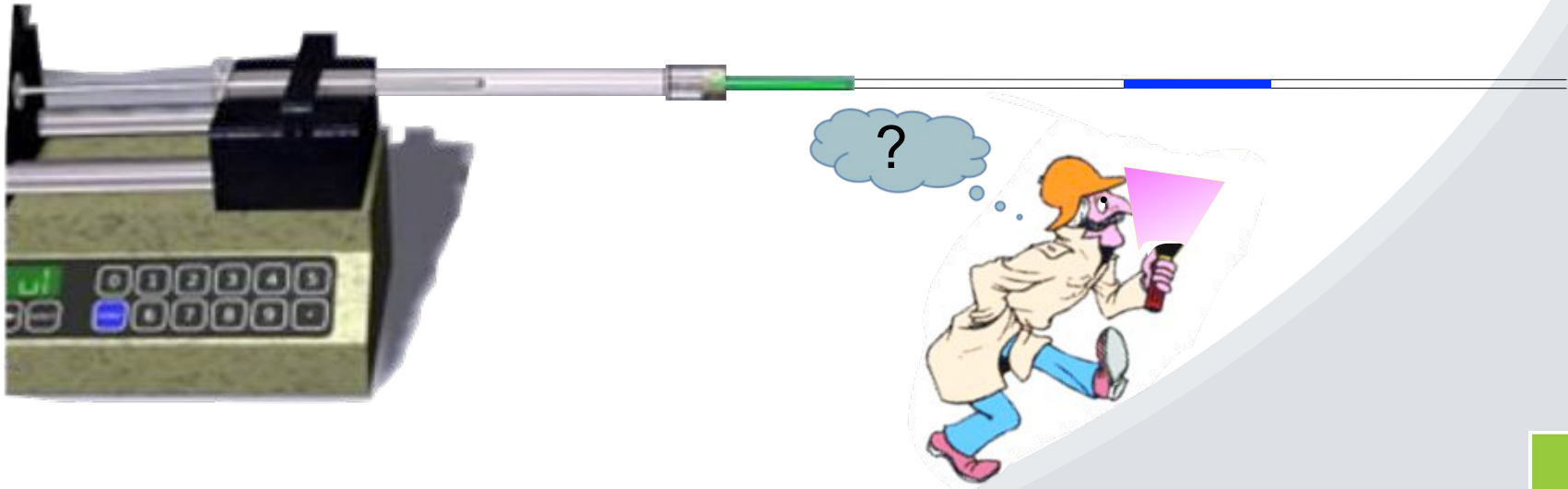
Photo-responsive polymeric structures based on spiropyran

Larisa Florea



CIMTEC 2012

Photo-responsive polymeric structures based on spiropyran



Outline

- Background
- Spiropyran based monomer
- Spiropyran polymeric brushes in micro-capillaries
- Photo-detection of solvents of different polarities
- Conclusions

Outline

Background

SP-monomer

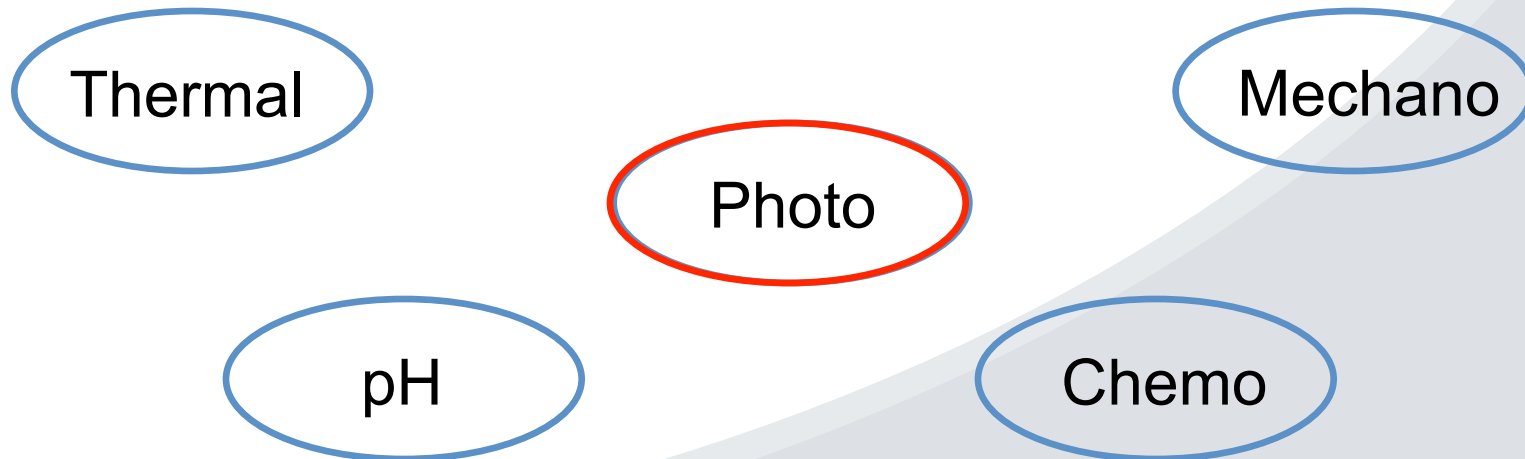
SP-polymer
Brushes

Solvent
Sensing

Conclusions

Stimuli-responsive Materials

Materials whose characteristics can be changed using an external stimulus



Outline

Background

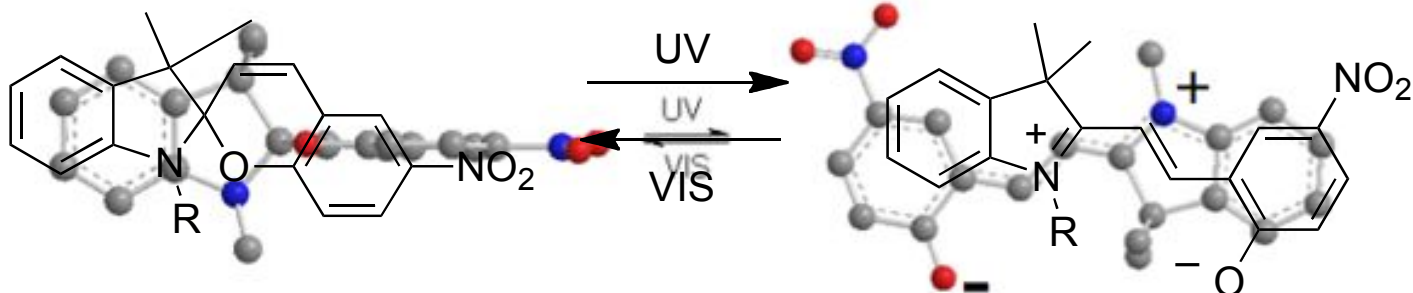
SP-monomer

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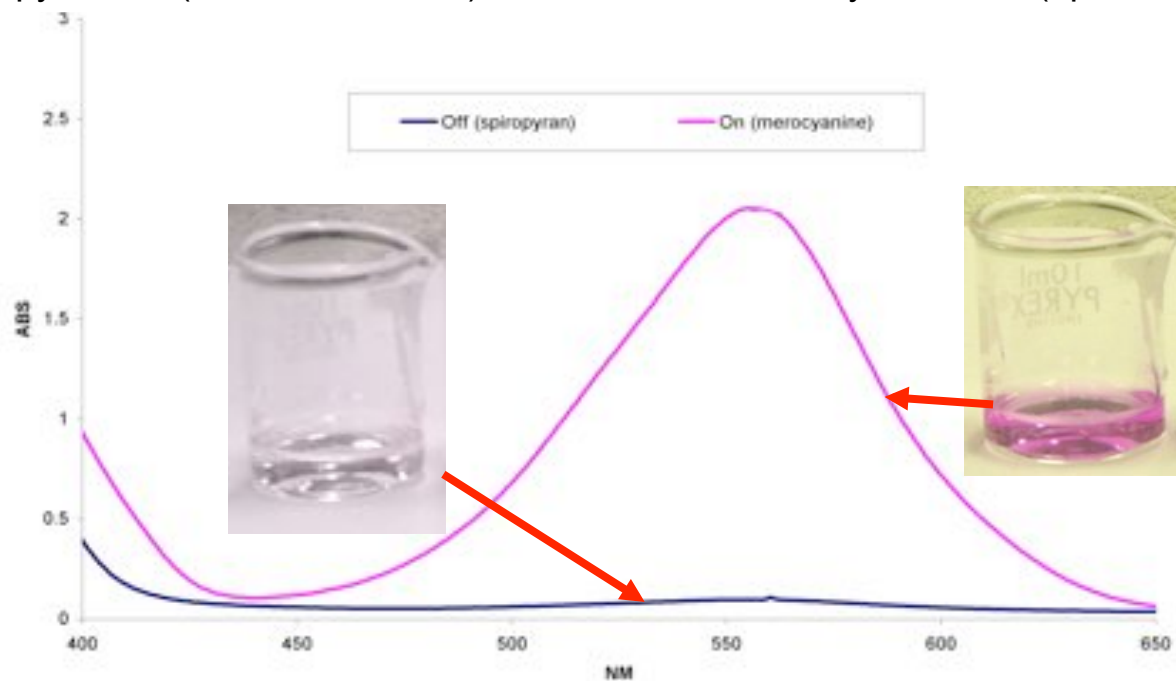
Conclusions

Spiropyran



Spiropyran SP (closed, colorless)

Merocyanine MC (open, colored)



Outline

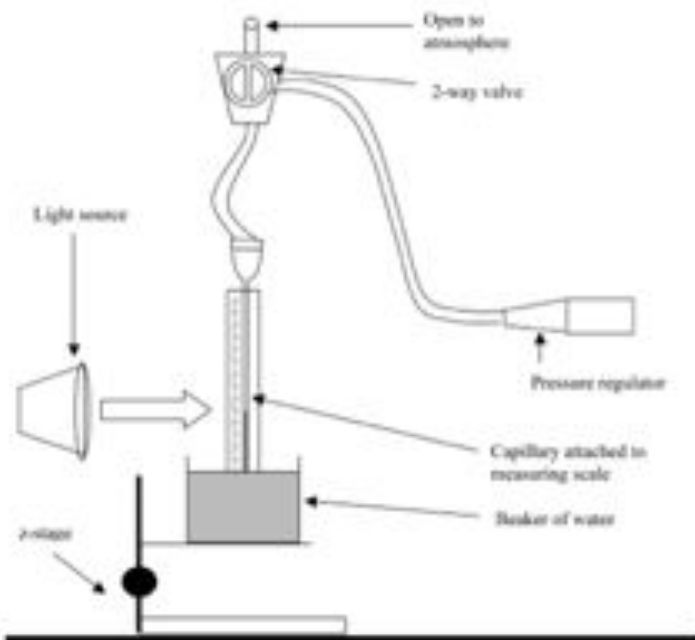
Background

SP-monomer

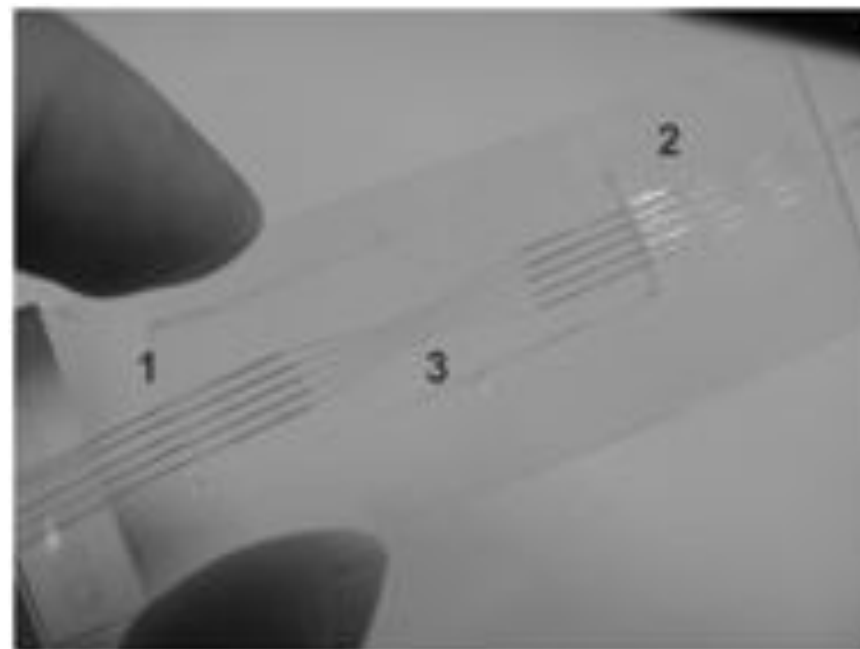
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Experimental setup for measurement of capillary rise in a spiropyran monolayer functionalised capillary [1].



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

Outline

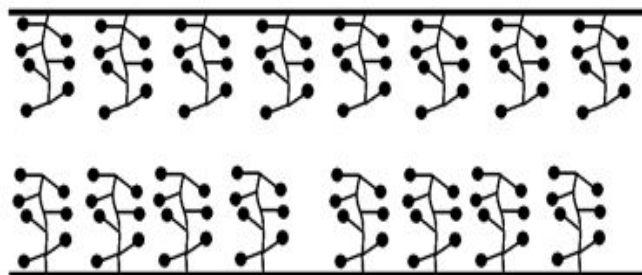
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- polymer brushes
- high loading of spiropyran molecule
- 3D arrangement

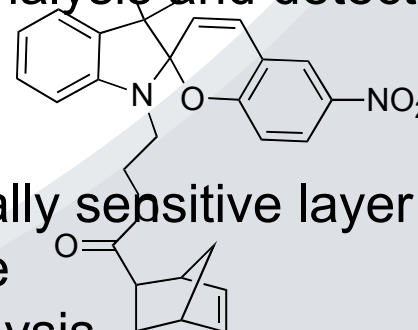
↑ - spiropyran molecule

Synthesis of Spiropyran Monomer

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



SP

SP-M

Outline

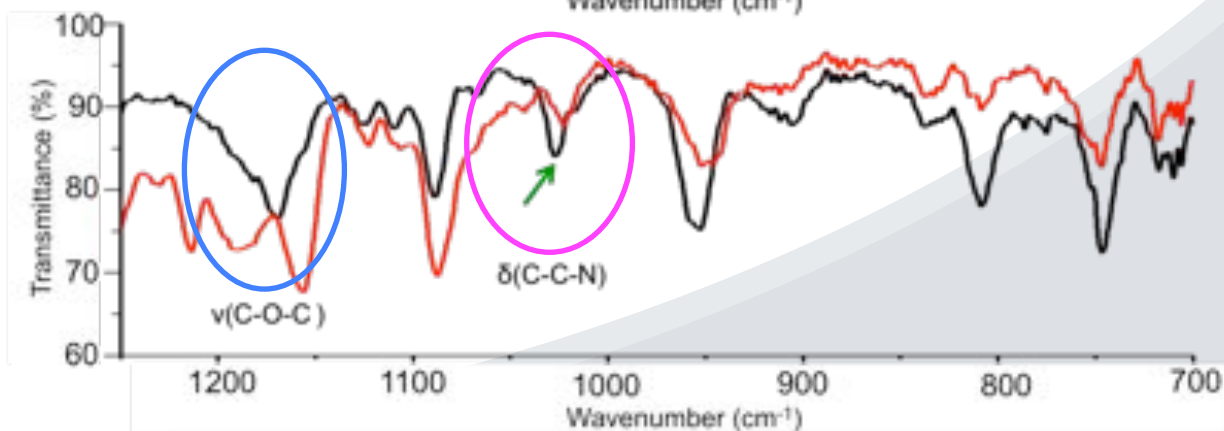
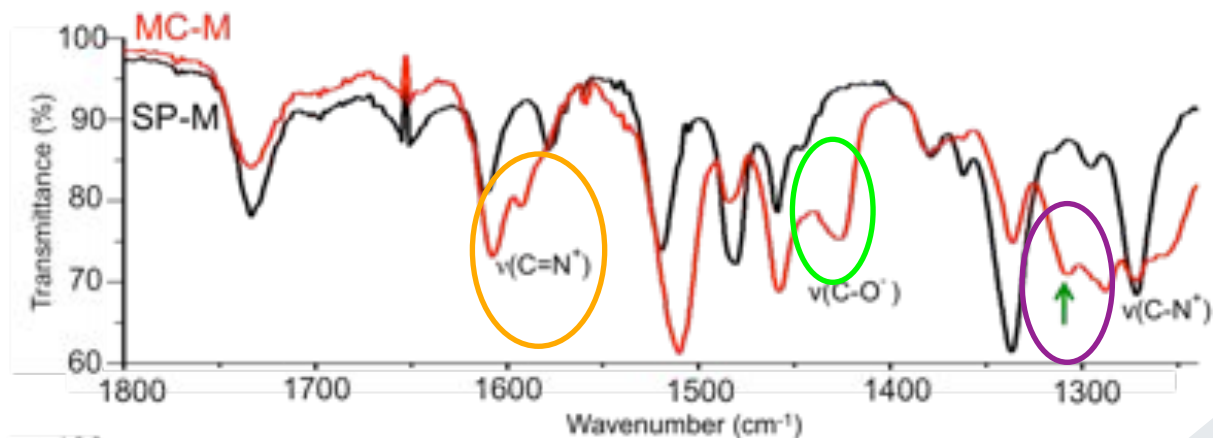
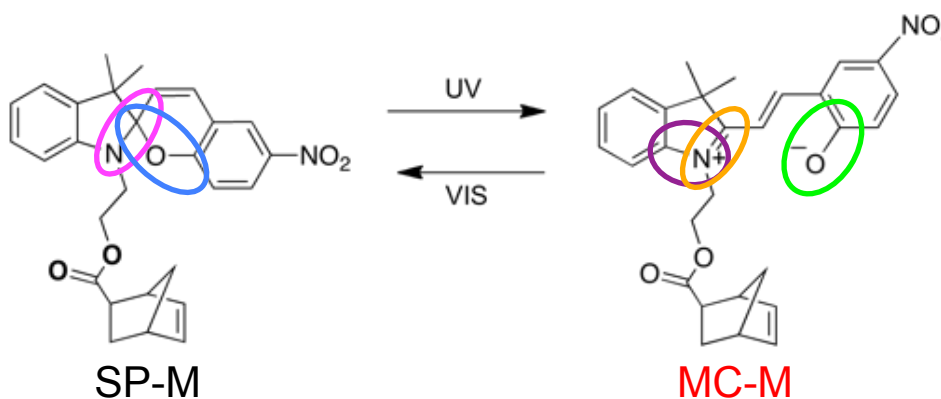
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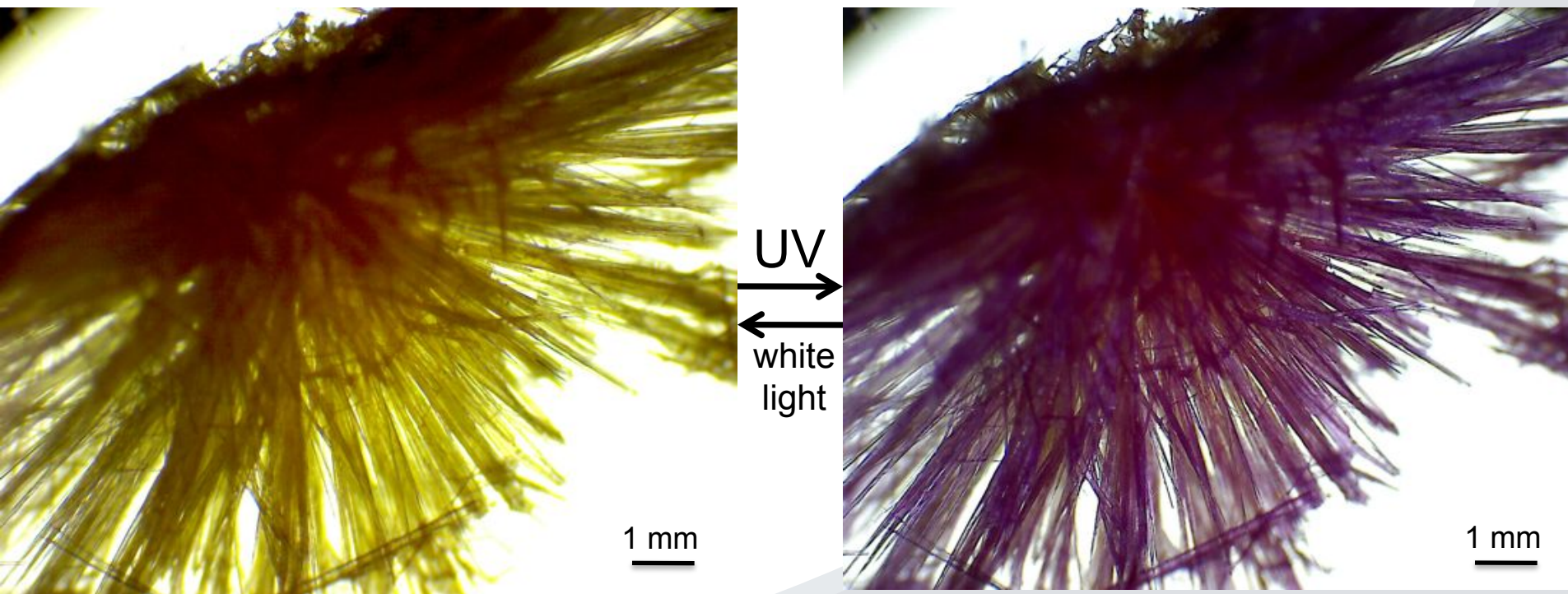
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Spiropyran-norbornene monomer



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Solid-state photochromism



Outline

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SP-monomer

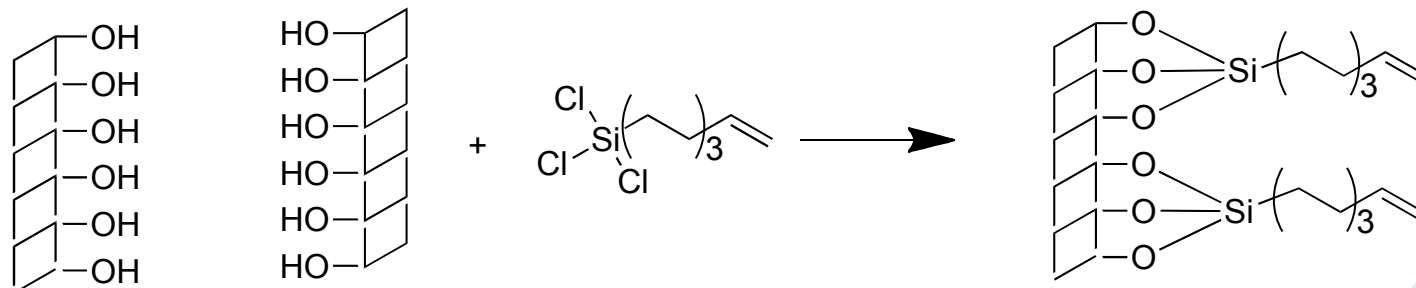
SP-polymer
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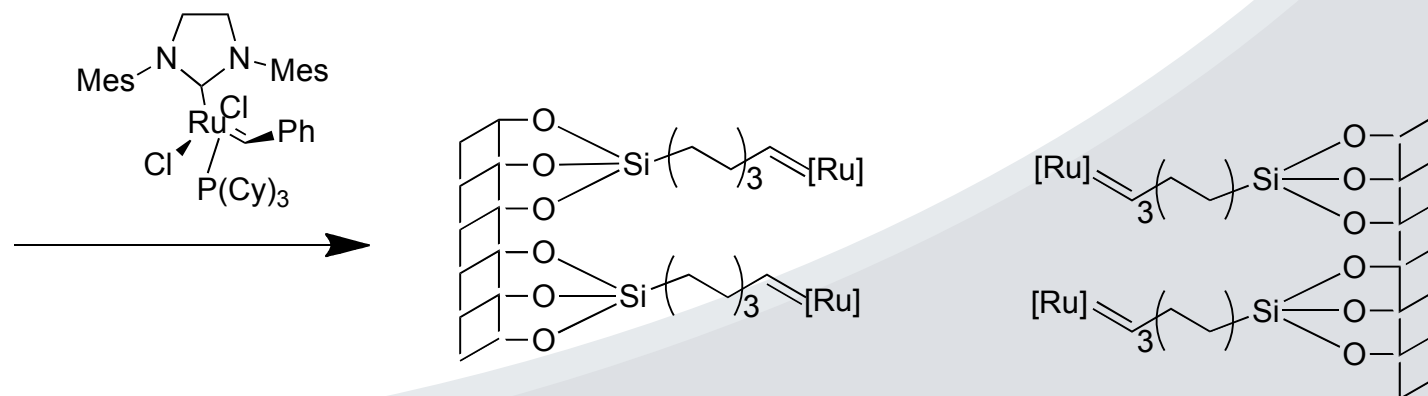
Conclusions

Spiropyran polymeric brushes in micro-capillaries

Silanisation



Attachment of the catalyst



Outline

Background

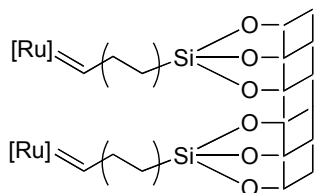
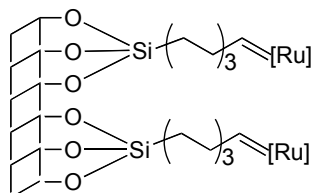
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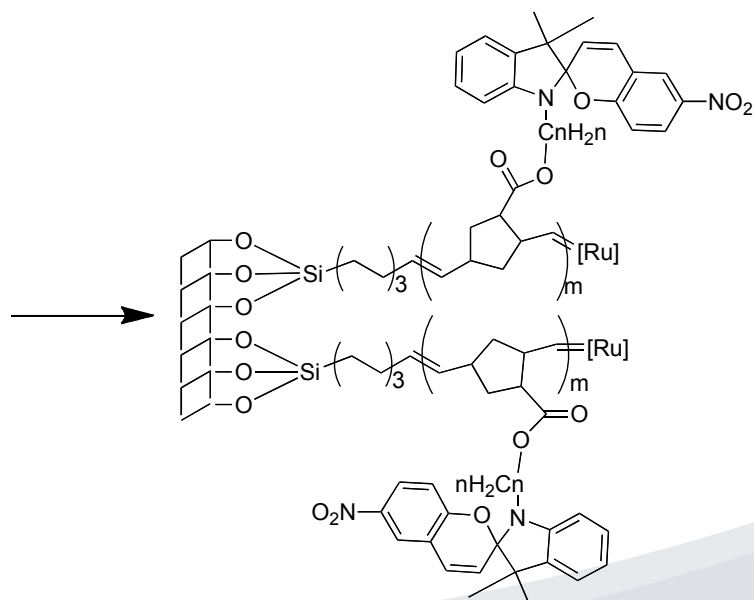
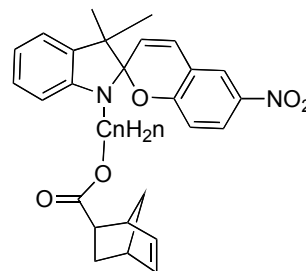
Solvent
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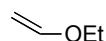
Spiropyran polymeric brushes in micro-capillaries



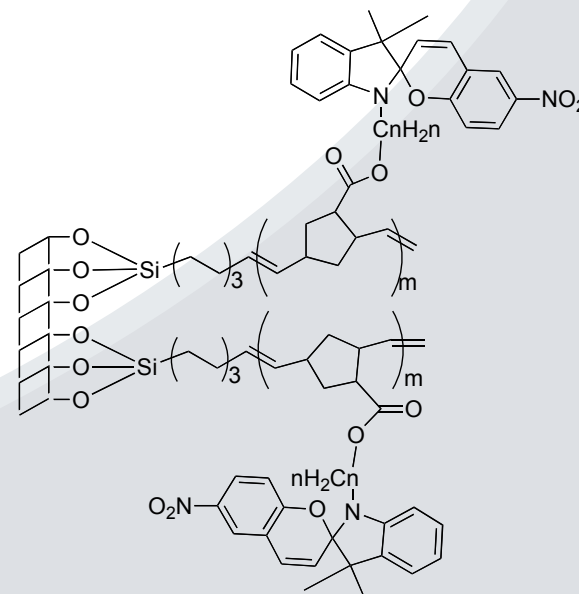
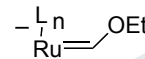
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+



Termination



III.

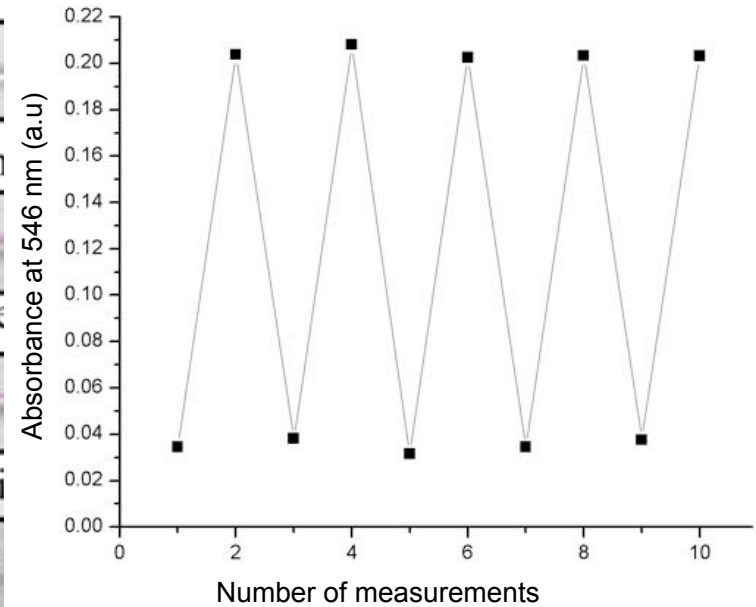
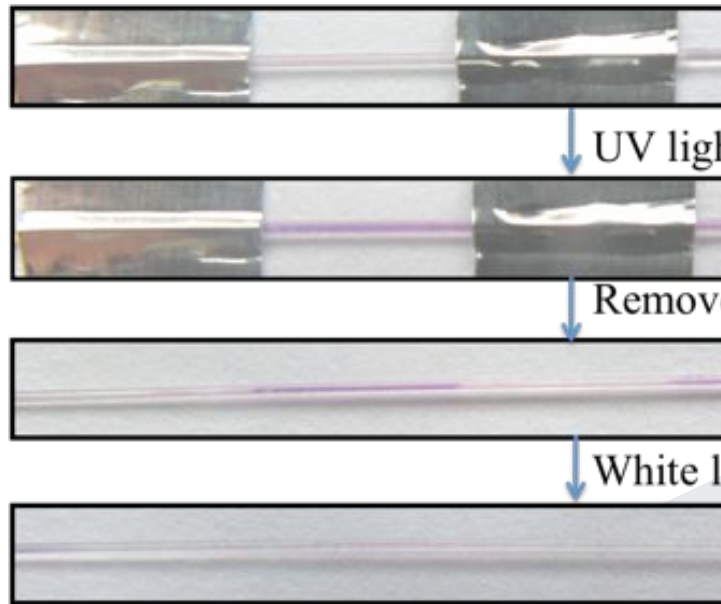
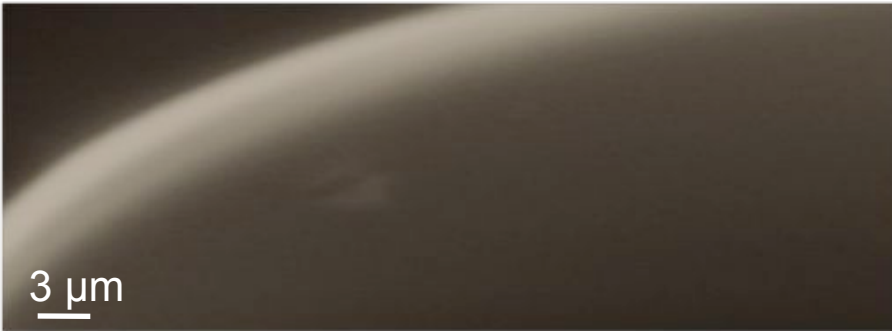
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L. Florea, A. Hennart, D. Diamond, F. Benito-Lopez, Sens. Actuators B: Chem., 2011, DOI:10.1016/j.snb.2011.12.055

Outline

Background

SP-monomer

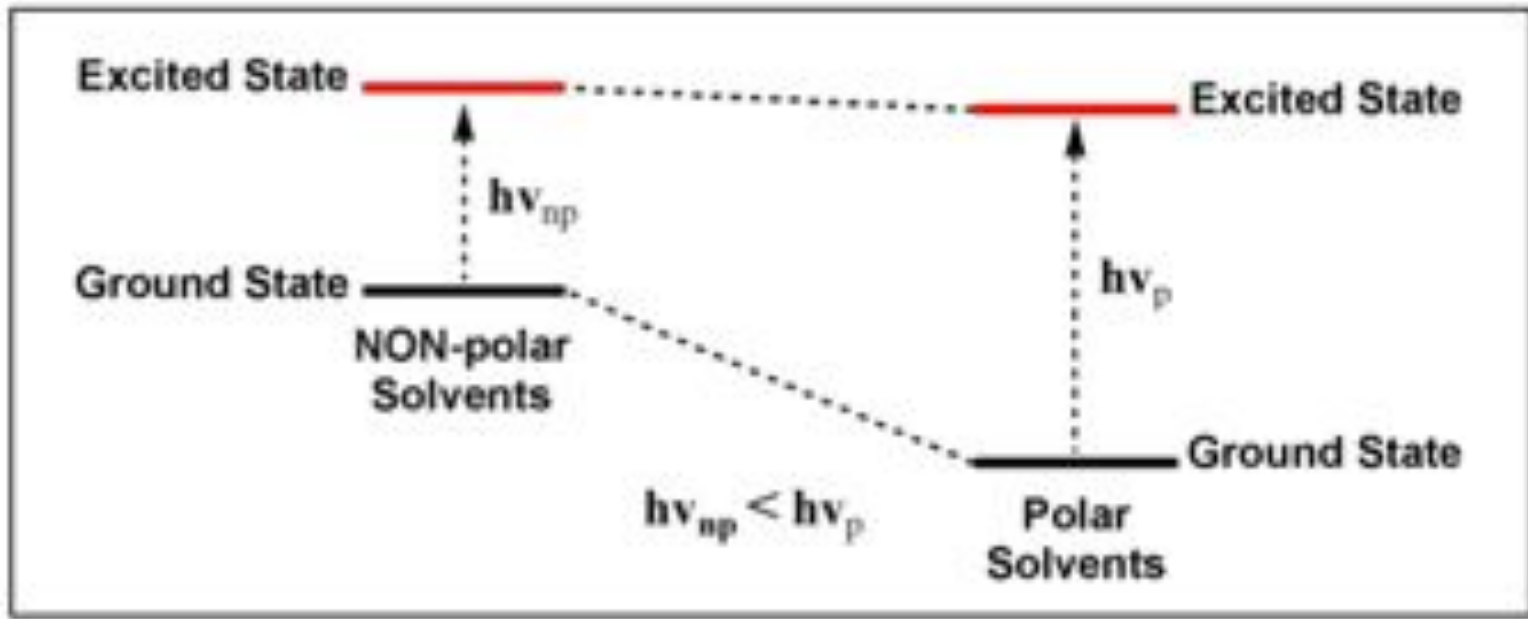
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Solvatochromic Properties

The colour of the MC form depends on the difference in polarity between the photo-excited MC form and the conjugated zwitterionic ground state [1]



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

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

Outline

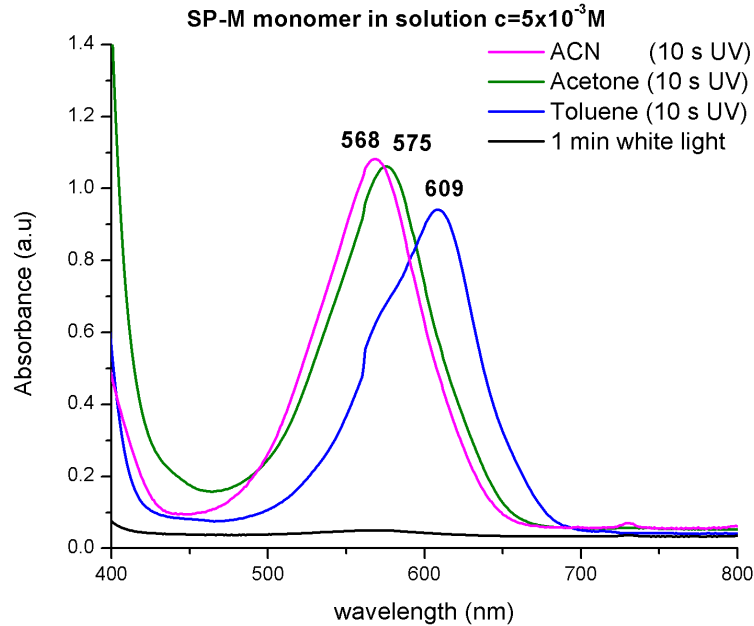
Background

SP-monomer

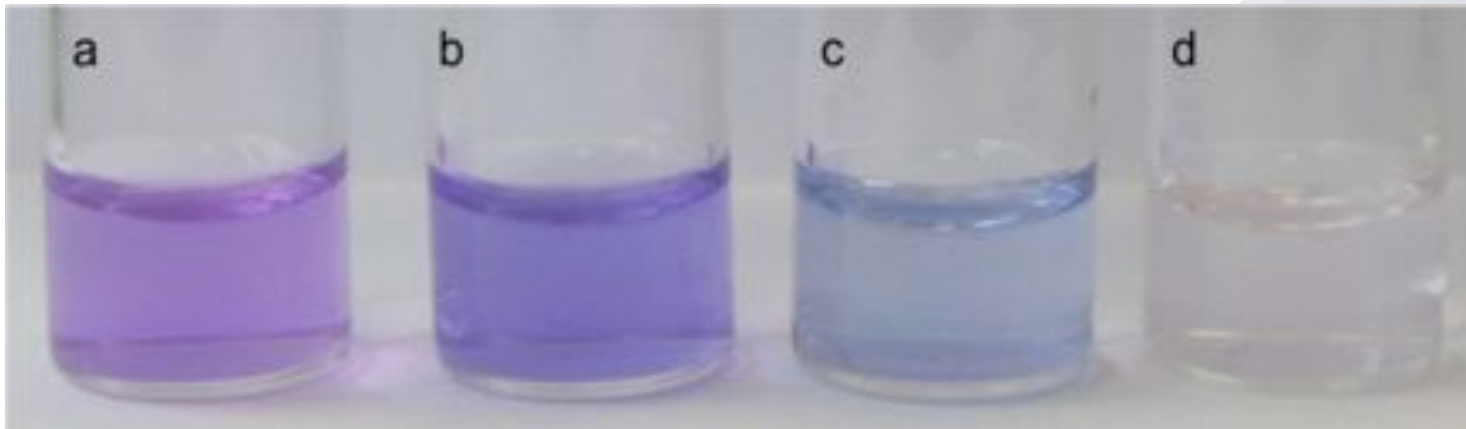
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- a – ACN
- b – Acetone
- c – Toluene
- d – after 1 min white light



Outline

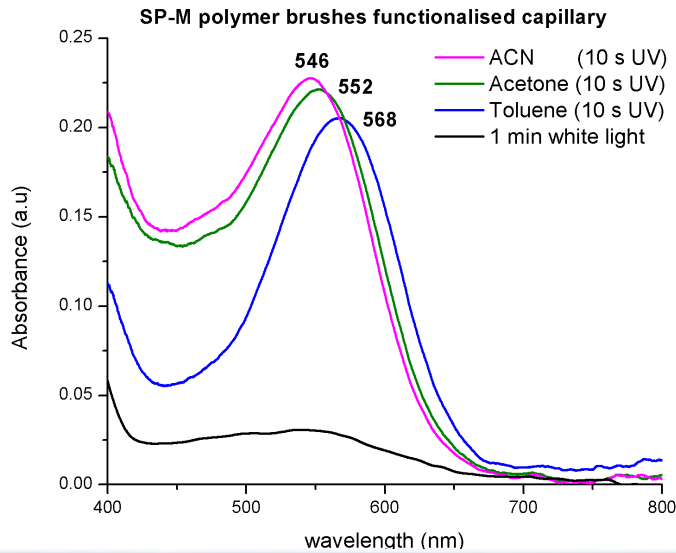
Background

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- 1 – ACN
- 2 – Acetone
- 3 – Toluene
- 4 – after 1 min white light



Outline

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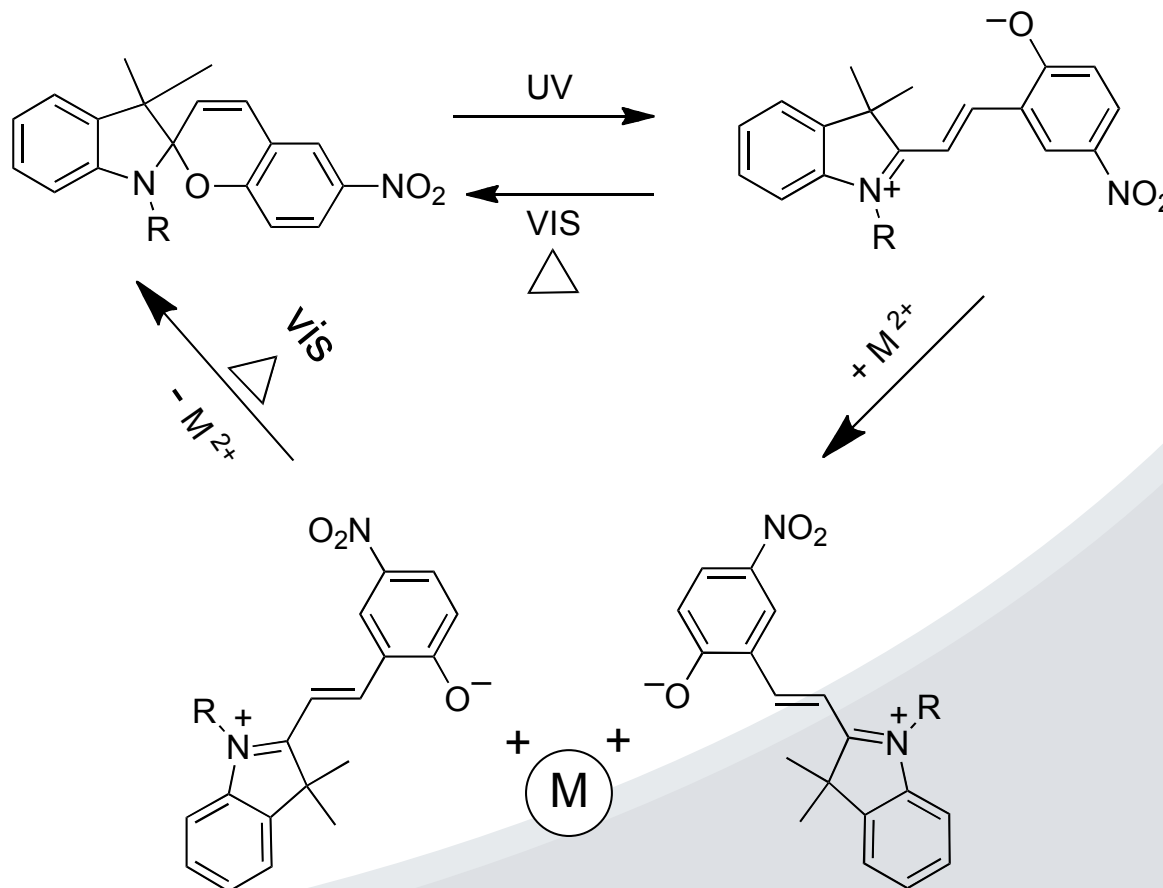
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Metal ions sensing, binding and releasing



Outline

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SP-monomer

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I. Solution studies

SP-M sol in ACN

20 s UV light

+ Ni²⁺

+ Cd²⁺

+ Co²⁺

+ Cu²⁺

+ Zn²⁺



Outline

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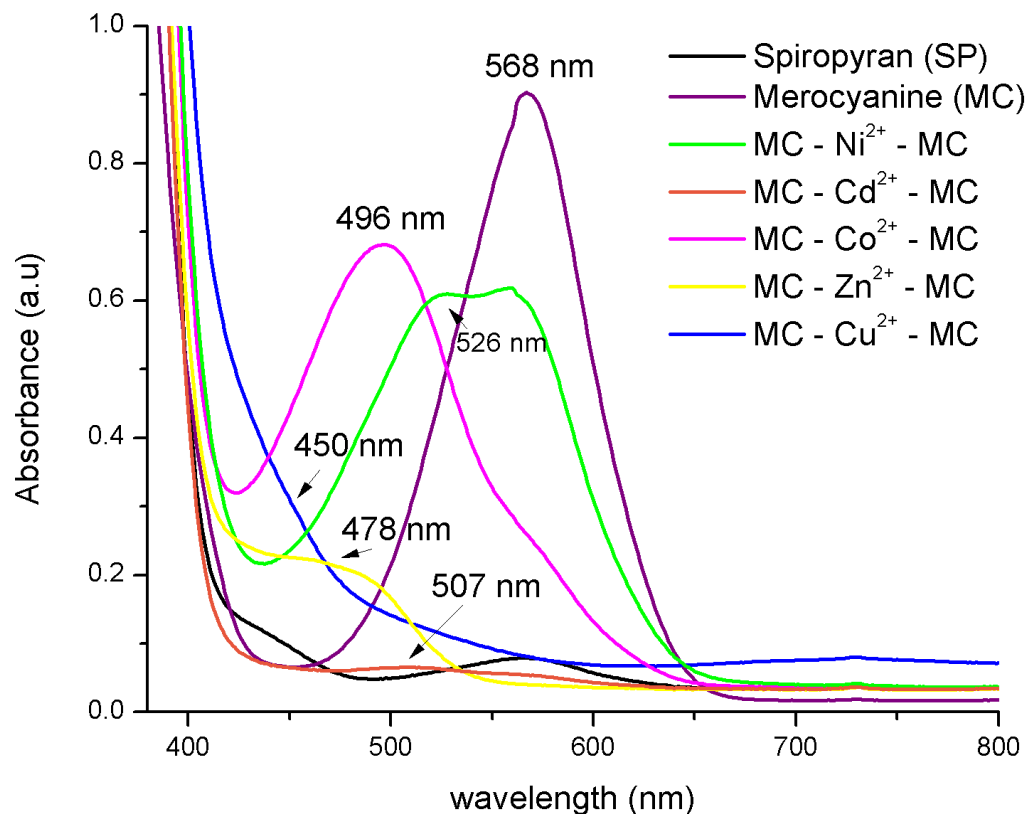
SP-monomer

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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

Outline

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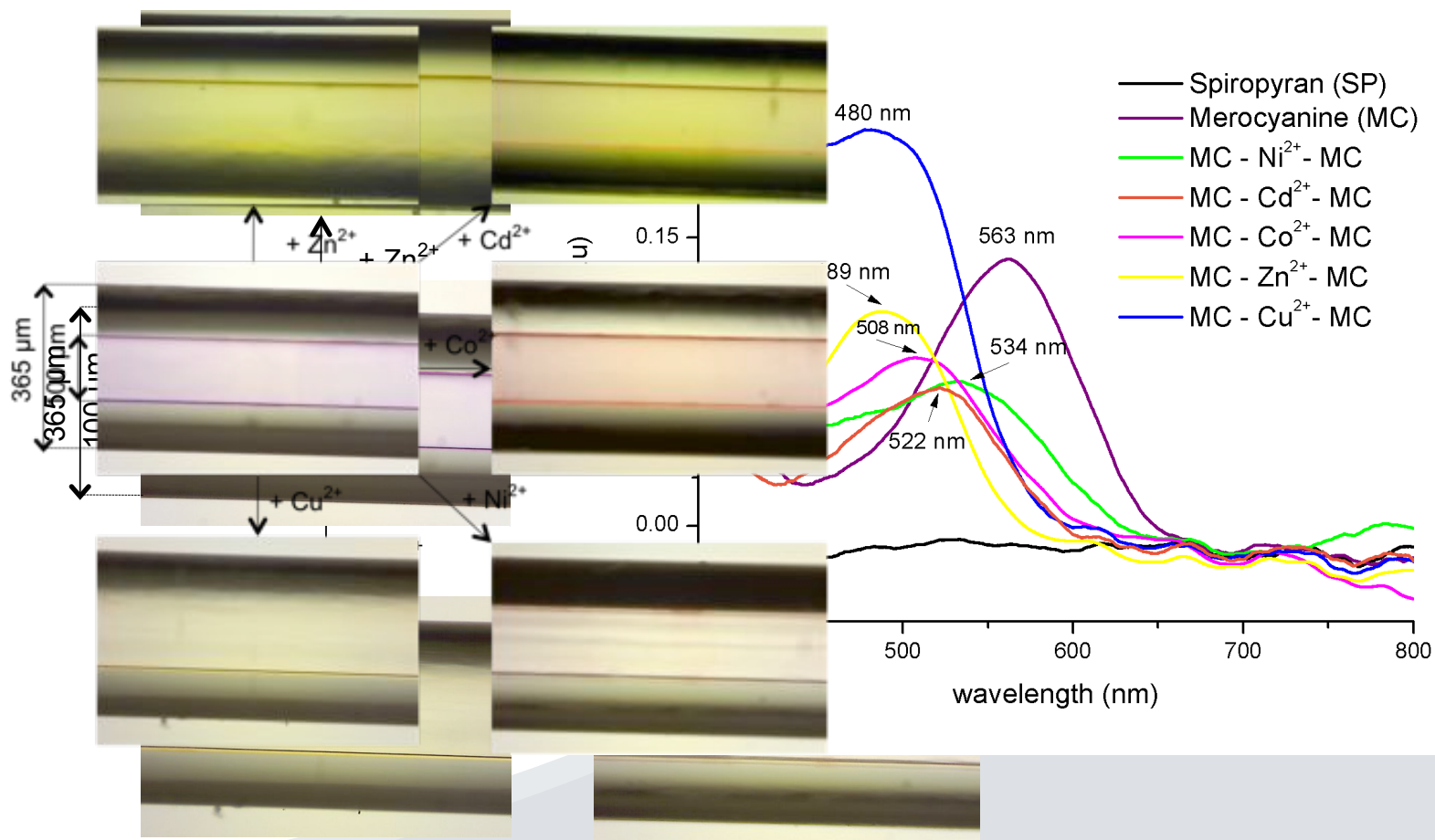
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II. Capillary coatings



Outline

Background

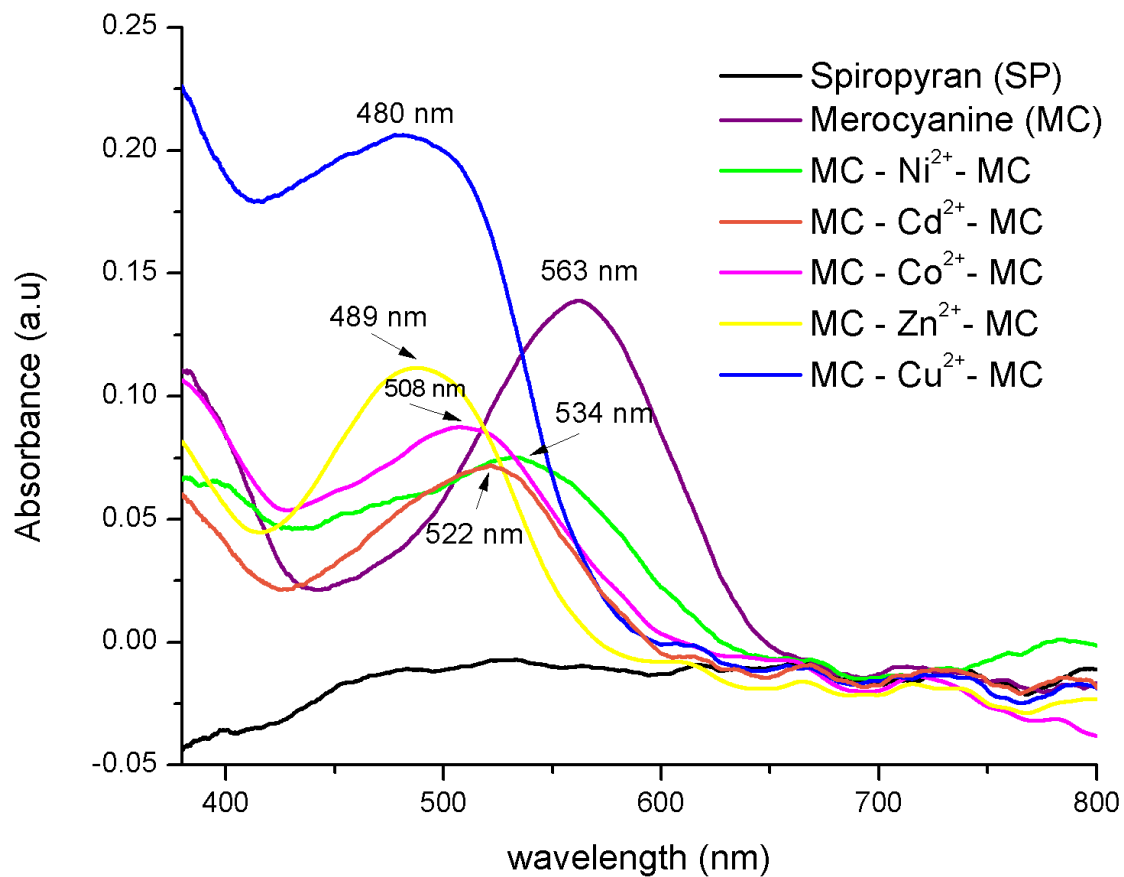
SP-monomer

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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

Outline

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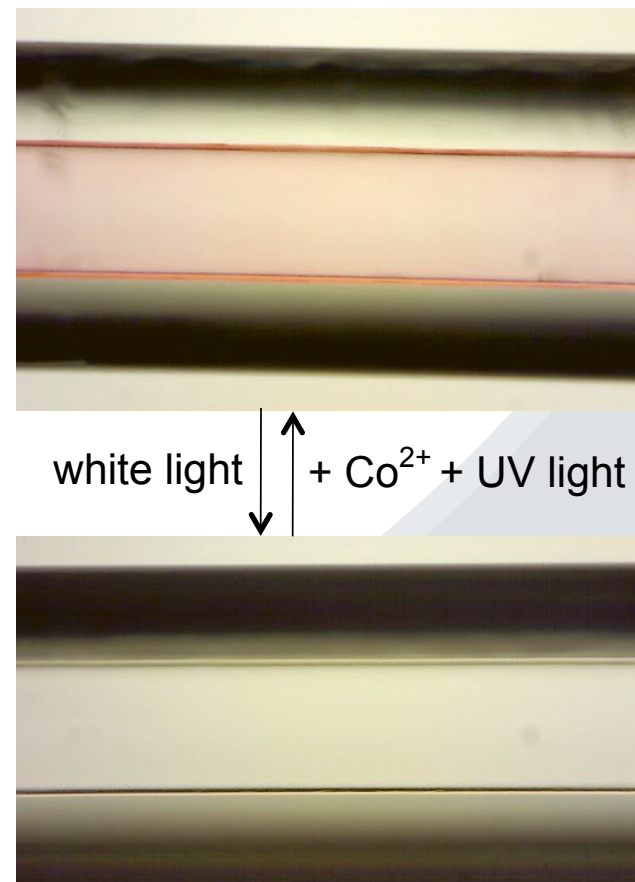
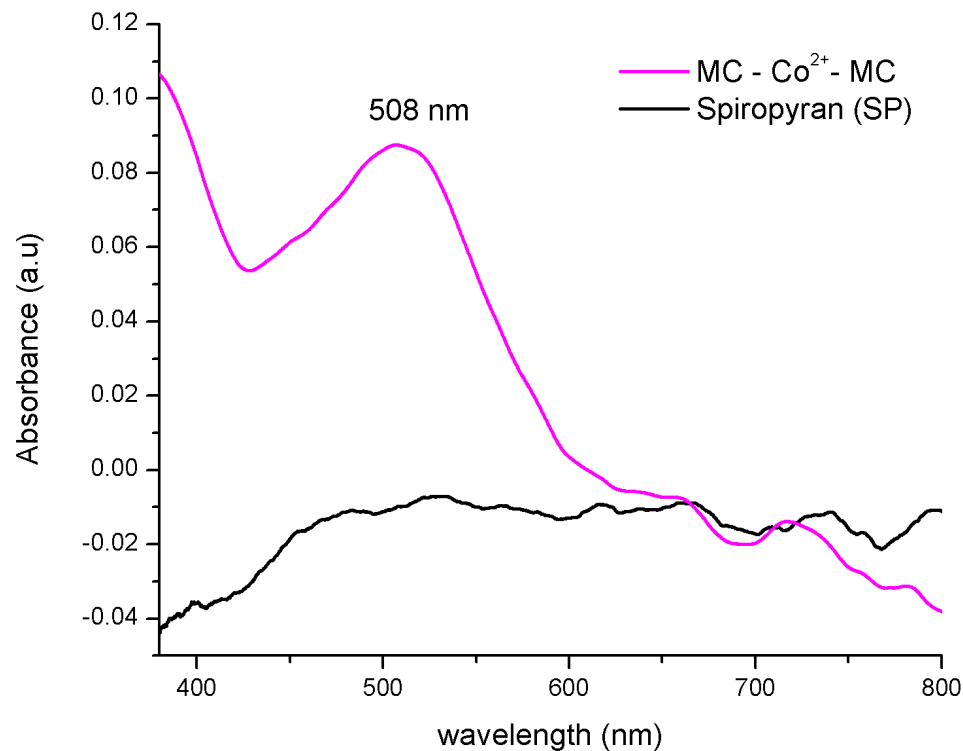
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Metal ions binding and releasing



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Conclusions

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

Acknowledgments

- Prof. Dermot Diamond
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Thank you for your attention !!





Questions ?