Dual Control Molecular Switches: a Journey into the Nanoworld of Spiropyran-Functionalized Terthiophene Polymers

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"Considerate la vostra semenza: fatti non foste per viver come bruti, ma pe' seguir virtute e canoscenza".

"Consider well the seed that gave you birth: you were not made to live your lives as brutes, but to be followers of worth and knowledge".

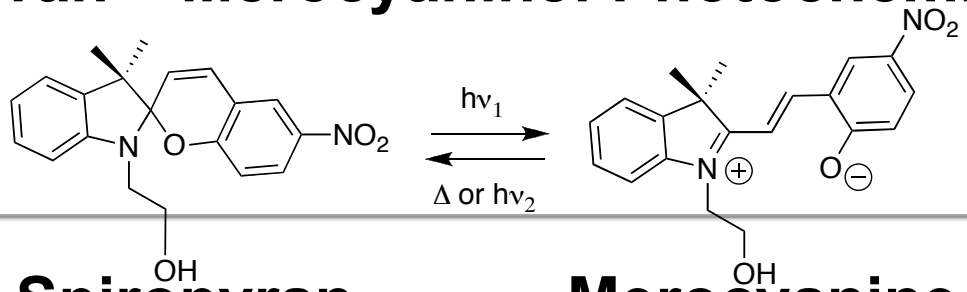
Dante Alighieri, Inferno, Canto XXVI, 118-120.

Outline

- Who is Spiropyran?
- Spiropyran-Terthiophene Polymers: Synthesis
- Photo-Chemical Properties Disclosed to date
- An Interesting Interaction: AFM + Fibronectin
- Potential Applications
- Conclusion and Remarks

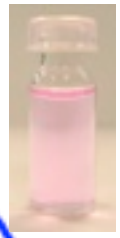
OUTLINE

Spiropyran – Merocyanine: Photochemistry



Spiropyran

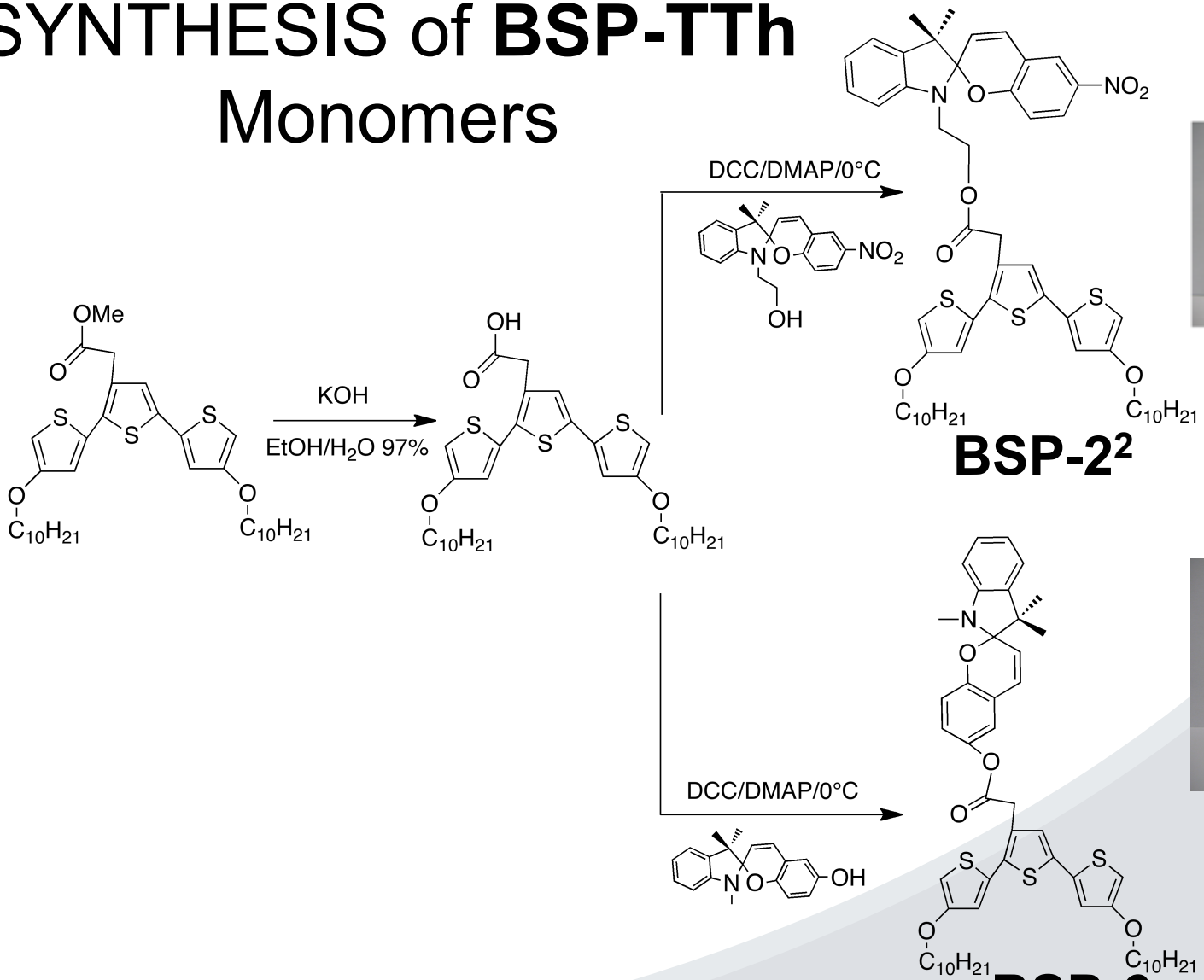
Merocyanine

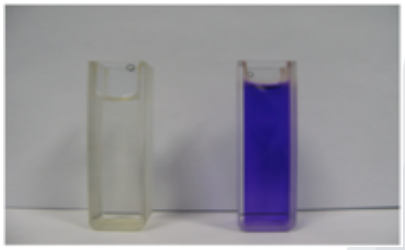


K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, **133** (14), pp 5453–5462

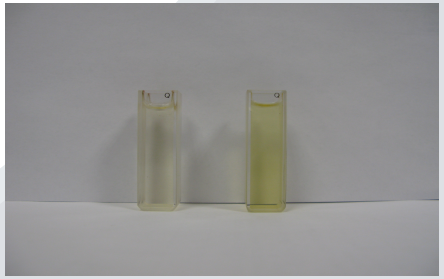
WHO IS SPIROPYRAN?

SYNTHESIS of **BSP-TTh** Monomers





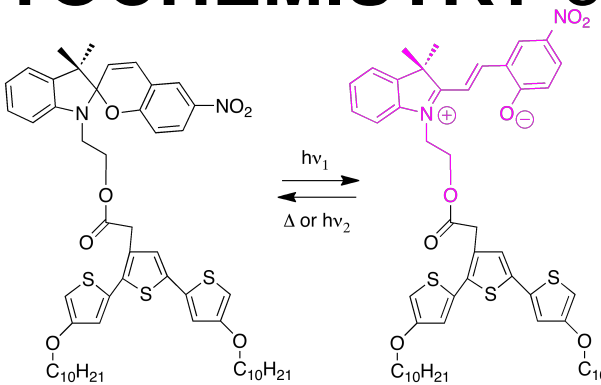
BSP-2 **MC-2**

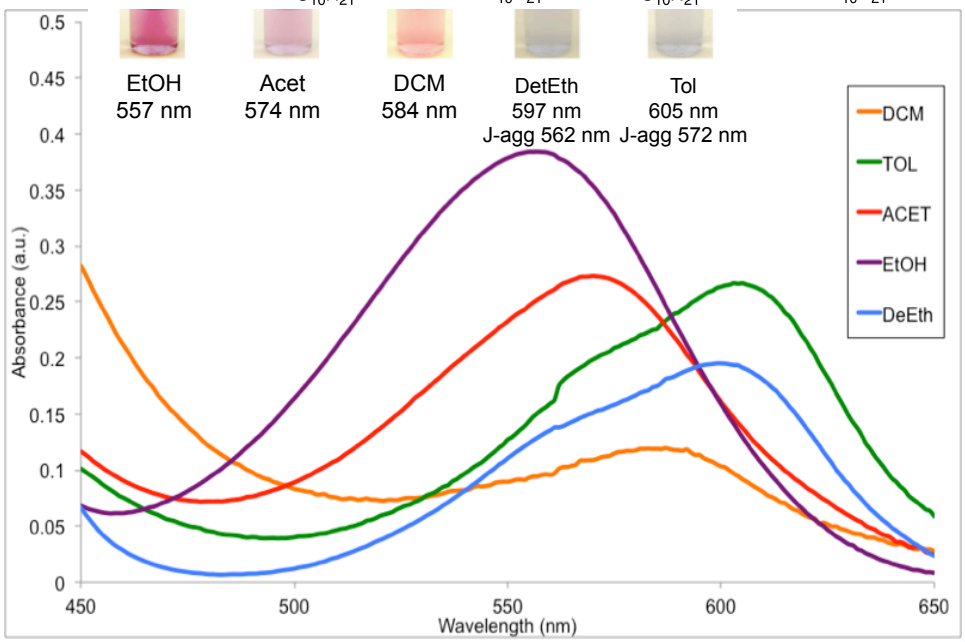


BSP-6 **MC-6**

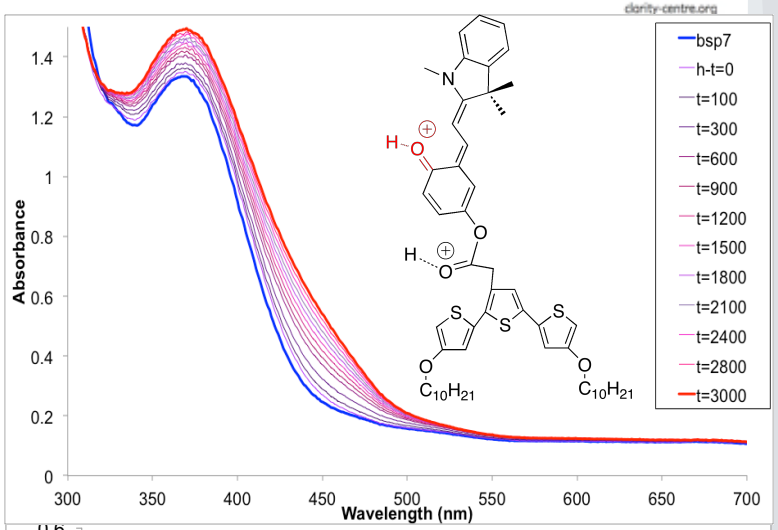
[1] Gambhir, S.; Wagner, K.; Officer, D. L. Synth. Met. 2005, 154, 117–120.
[2] K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, 133 (14), pp 5453–5462

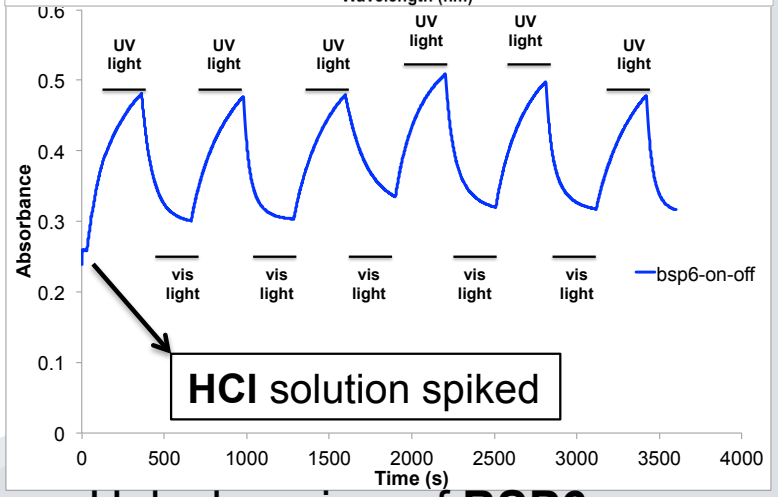
PHOTOCHEMISTRY of the MONOMERS





Solvatochromism of **BSP2**



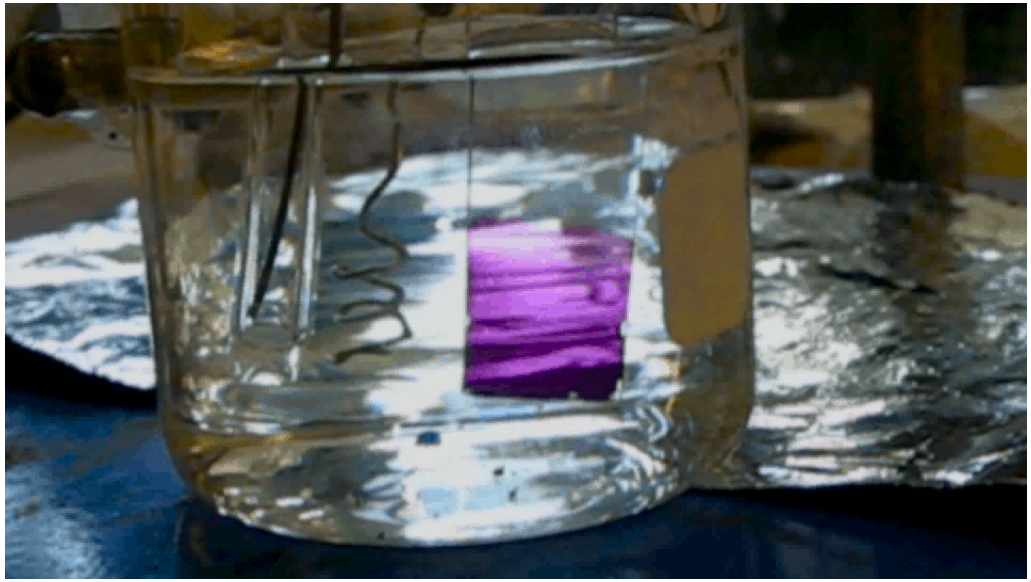


Halochromism of **BSP6**

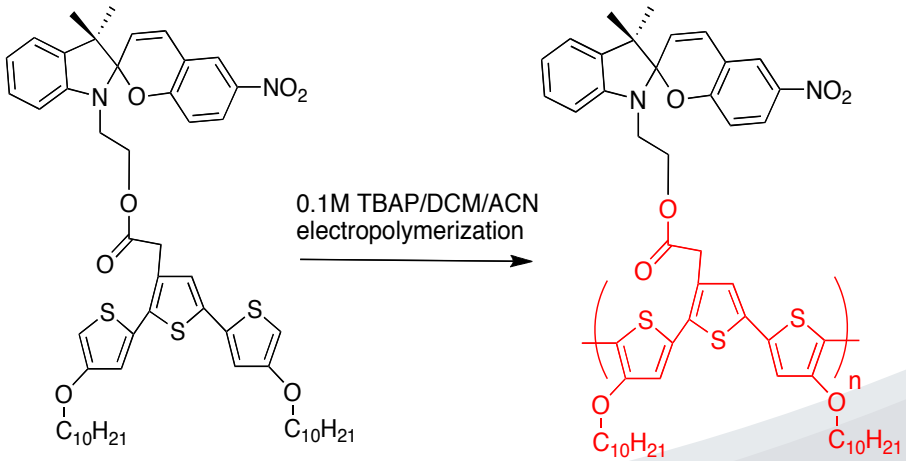
[1] K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, **133 (14)**, pp 5453–5462

[2] M. Zanoni, S. Coleman, K.J. Fraser, R. Byrne, K. Wagner, S. Gambhir, D.L. Officer, G.G. Wallace and Dermot Diamond, Phys. Chem. Chem. Phys., 2012, **14**, 9112–9120

Electropolymerisation



Cyclic deposition of p-BSP2 on ITO



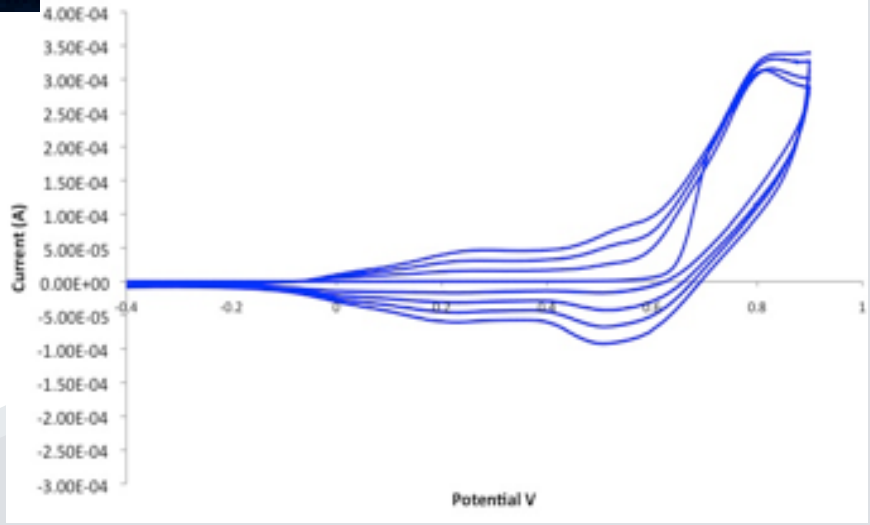


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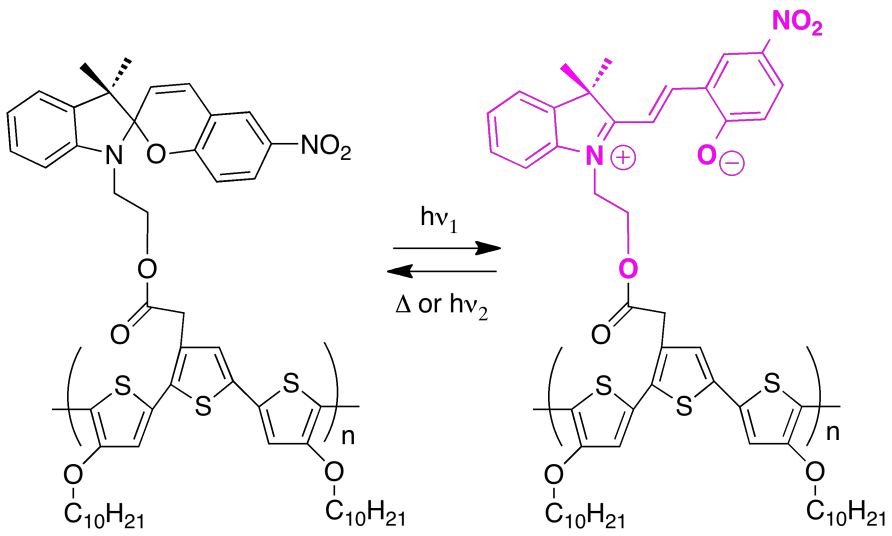
Photo-reversibility of **p-BSP2**

Exposition of **p-BSP2** to different cycles of UV-light at 254nm and White light outside the electrolyte.



p-BSP2 **p-MC2**

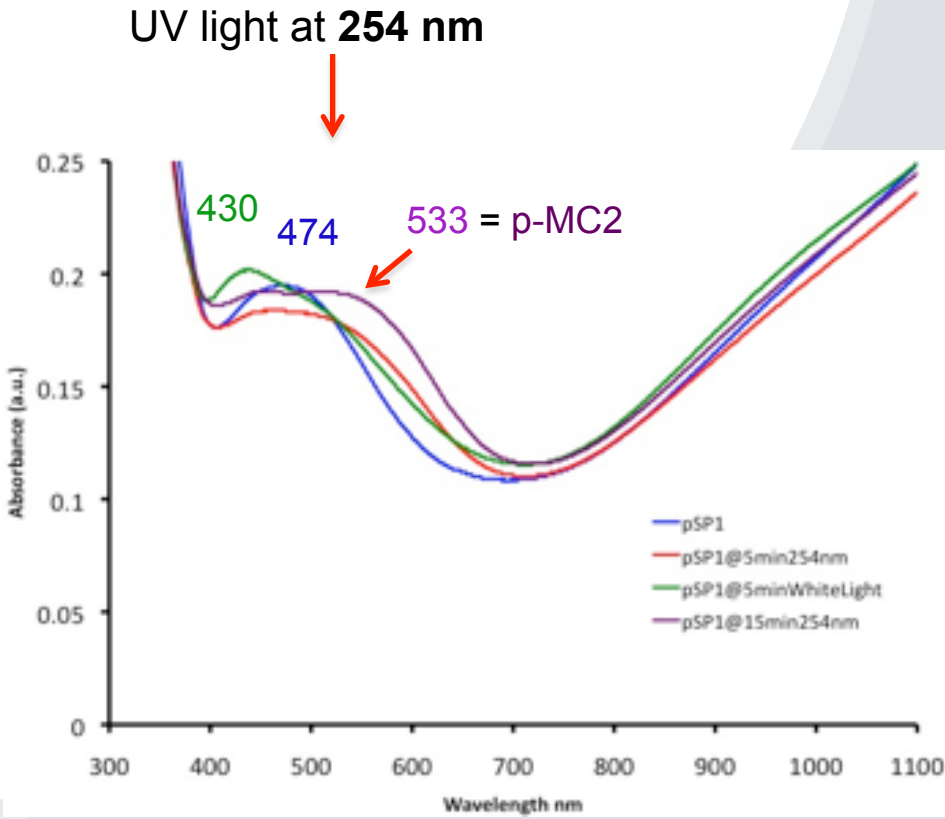


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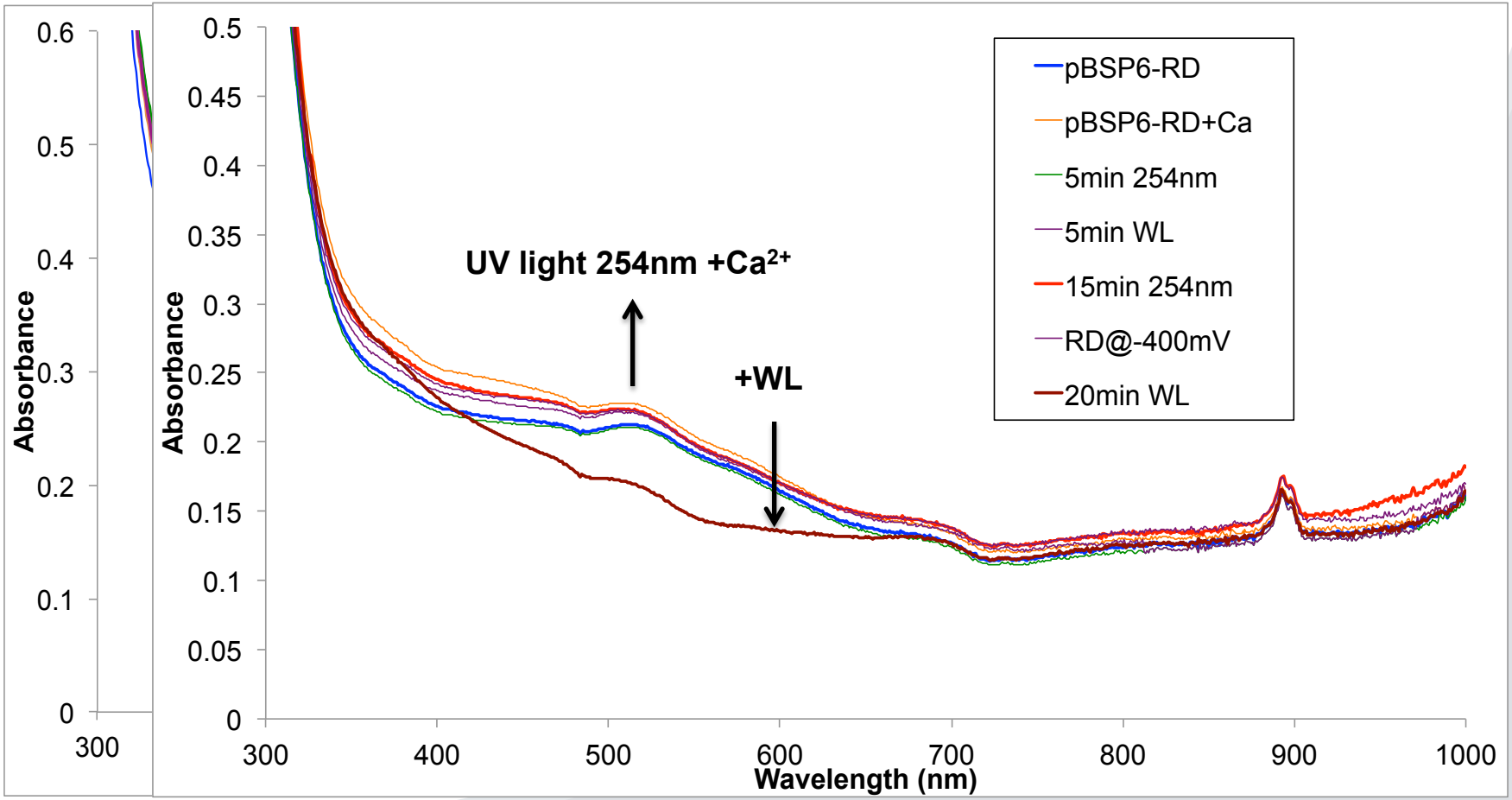
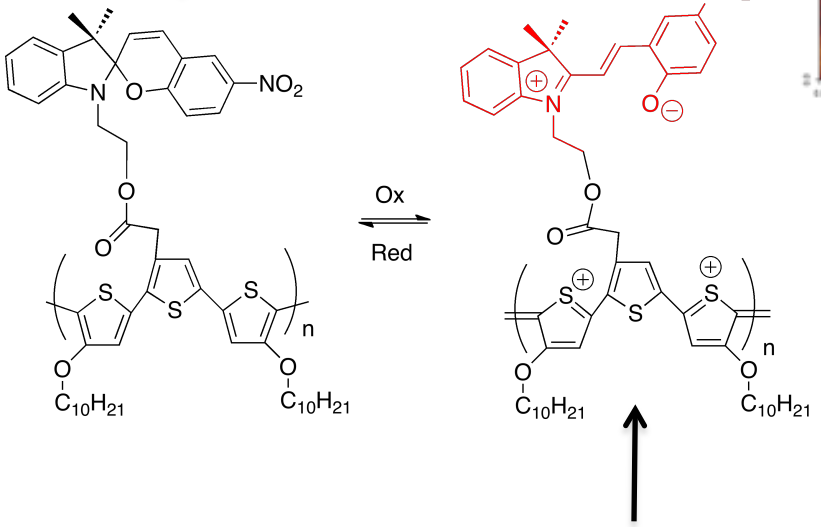
Photo-manipulated ligand activity of **p-BSP6**

Exposition of **p-BSP6** to a 10^{-4}M solution of **Ca^{2+}** and to several cycles of UV-light (**254nm**) and White light inside the quartz cuvette.



SURFACE STUDY

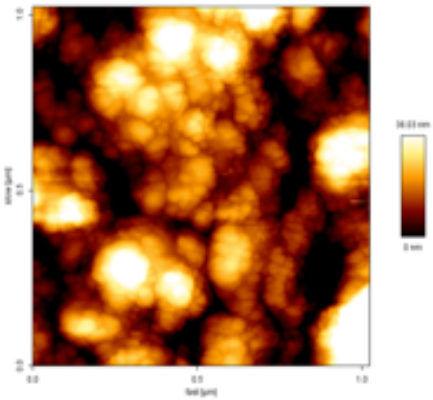
pBSP2 in the reduced state



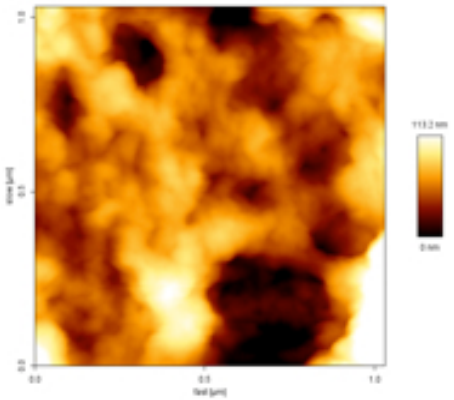
pBSP2 in the oxidised state

AFM

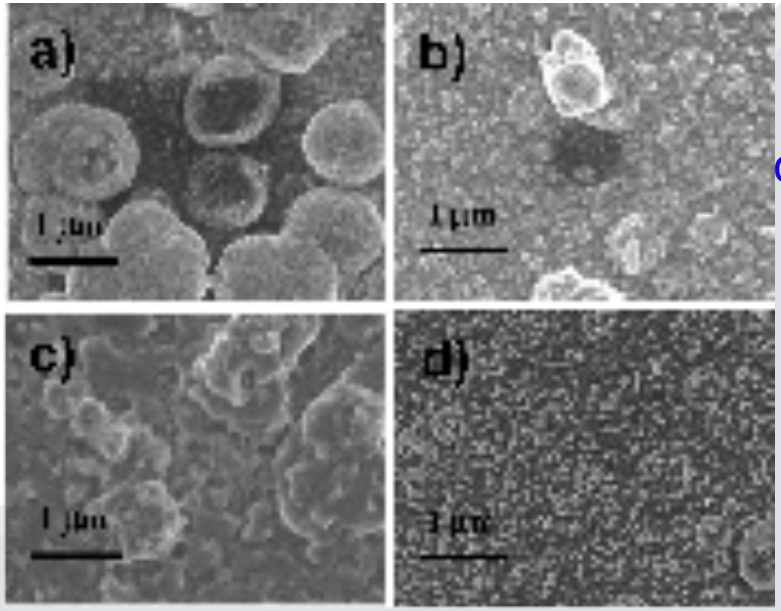
oxidised



reduced



SEM

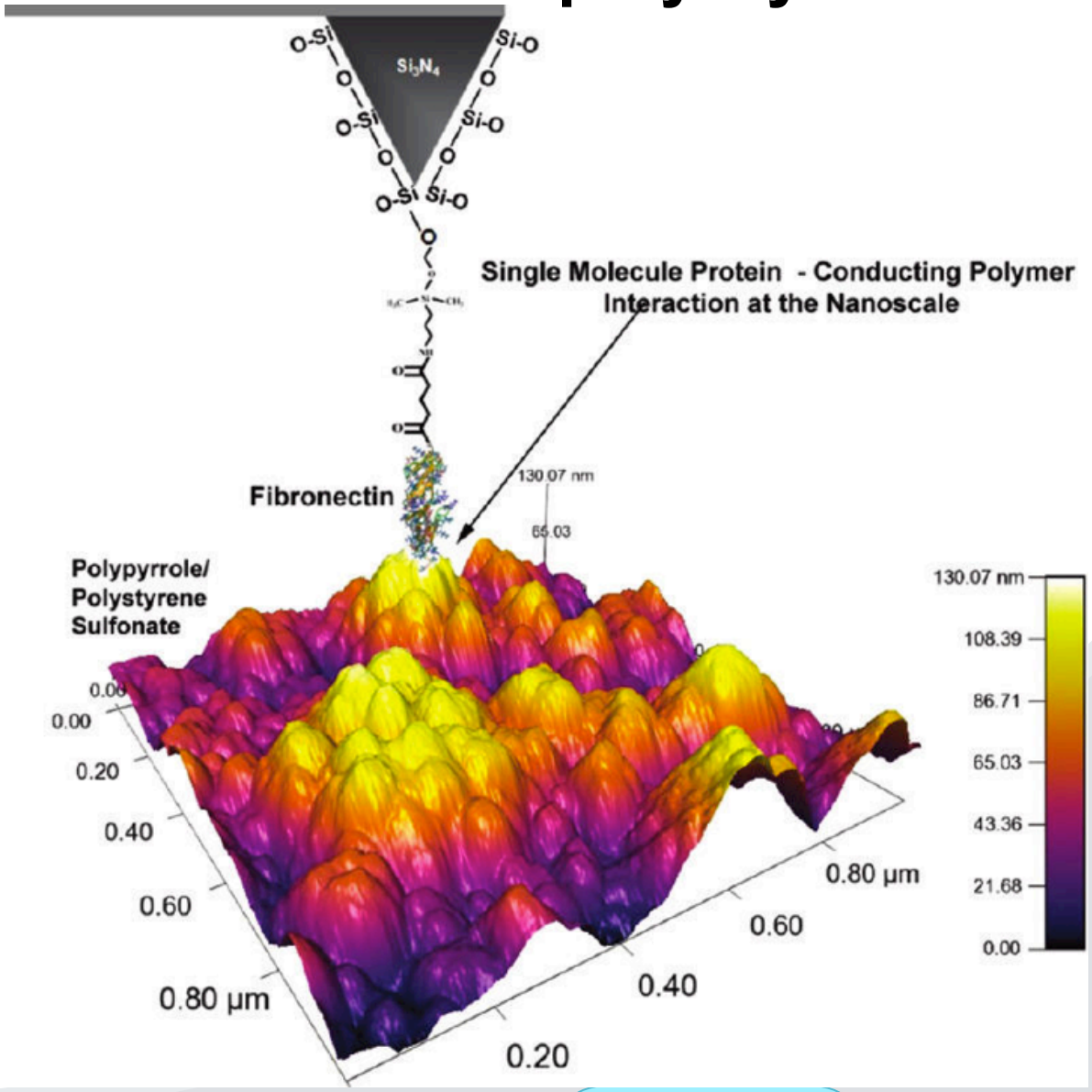


oxidised

reduced

AFM and FIBRONECTIN

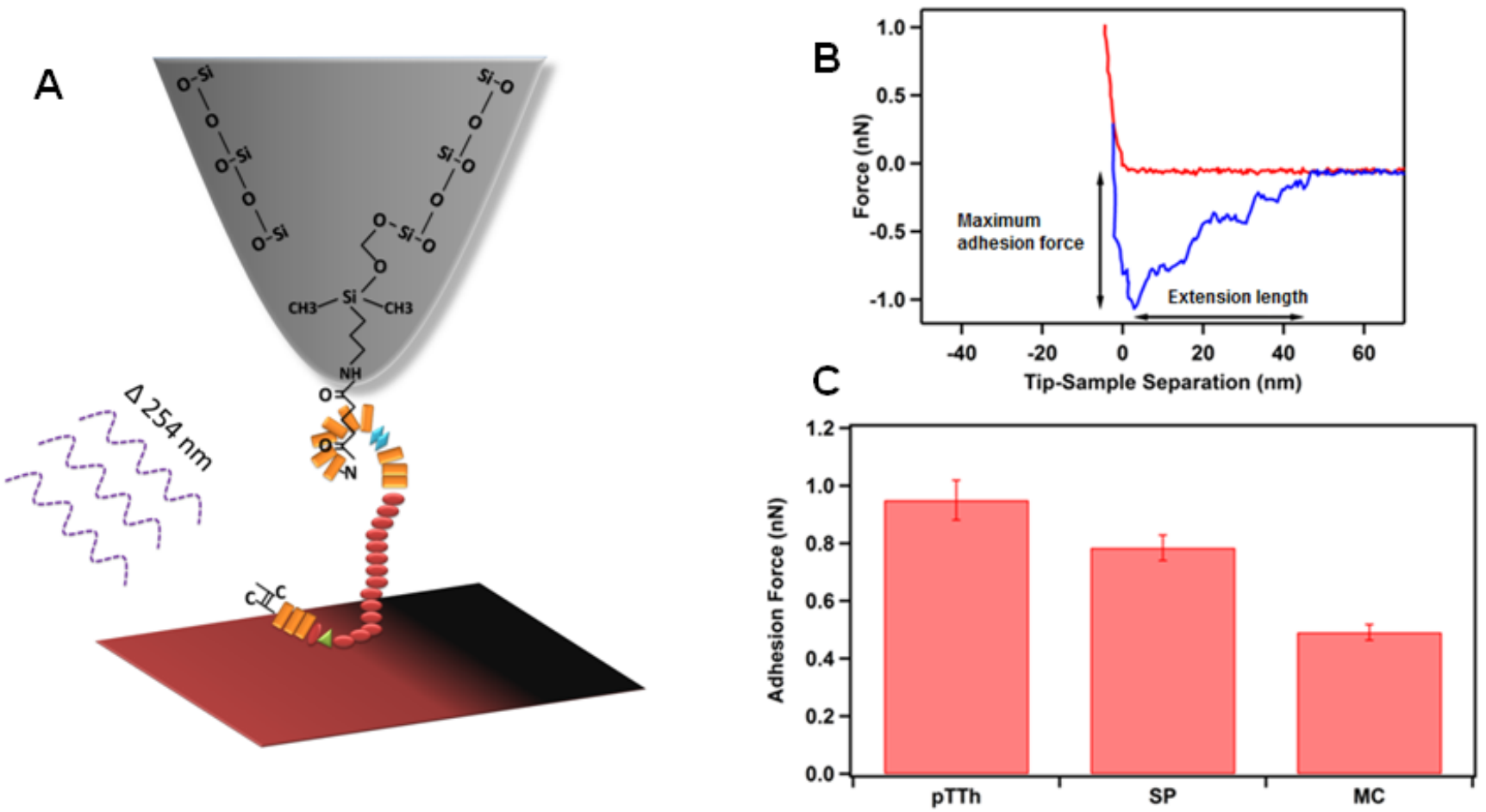
FN Interaction with **poly-Pyrrole**



M. Higgins *et al.,* Chem. Mater. 2012, 24, 828-839

AFM and FIBRONECTIN

Photochemically Induced Interactions between **Fibronectin** and **pBSP2**



Gelmi A, Zanoni M. *et al.,* JMatChemB, Manuscript Accepted, 2013

AFM and FIBRONECTIN

CONCLUSIONS

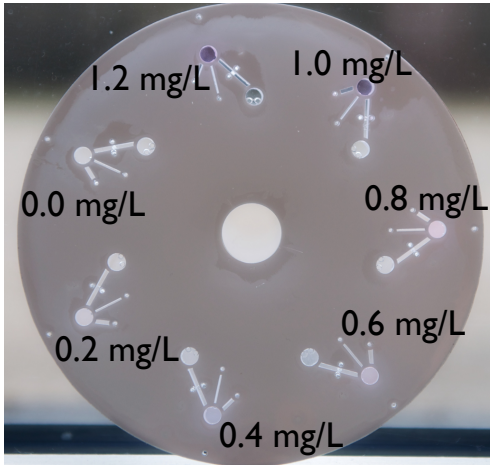
- A new Class of Dual-Control Stimuli Responsive Materials has been Synthesized and Characterised
- Photo - Electrochromic Properties Have Been Studied
- **p-BSP2** Presents Photo-Actuation and Photo-Reversibility
- **p-BSP6** Reacts with Agents Dissolved in Solution
- **p-BSP2** is Able to Generate Lipophilic Interactions with a Fundamental Protein: **FN**
- The Process is Reversible and Repeatable Over Time

CONCLUSION

Future Applications: Few IDEAS!

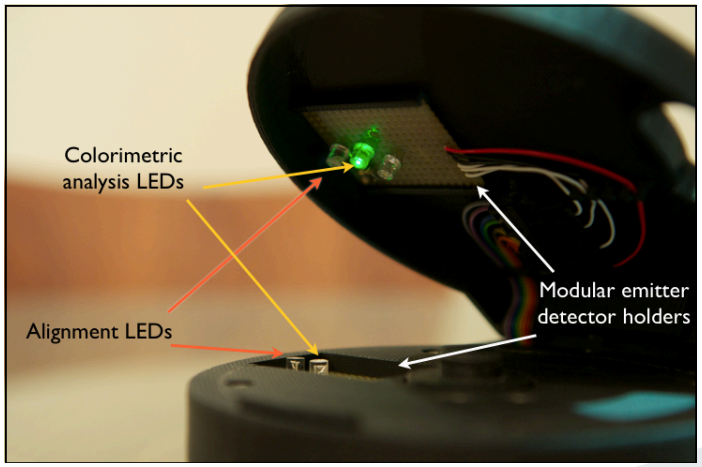
CLARITY
clarity-centre.org

µfluidics??



Soft actuator??

Benito-Lopez F. *et al.*, LabChip, 2010



Czugala M. *et al.*, LabChip, 2013

Sensor / Biosensor??

FUTURE APPLICATIONS

Special Thanks to:

- Prof. Dermot Diamond and Dr. Robert Byrne (**DCU**)
- Prof. Gordon G. Wallace and Prof. David L. Officer (**IPRI**)
- Dr. Klaudia Wagner, Dr. Michael Higgins, Dr. Pawel Wagner, Dr. Sanjeev Gambhir, Dr. Paul Molino and Dr. Amy Gelmi (**IPRI**)
- The **SG07 crew,** Dr. Kevin J. Fraser, Dr. Fernando Benito-Lopez (**DCU**)

- ✓ **Prof. Dermot Diamond (DCU, Ireland)**

Materials Science and the Sensors Revolution - Re-Inventing Chemical Sensing for Remote Long-Term Deployments (today at 16.30)

- ✓ **Michael Higgins (IPRI, UOW, Australia)**

  High speed dynamics of Protein Interactions with Conducting Polymers (today at 16.15)

- ✓ **Vincenzo Fabio Curto (DCU, Ireland)**

  Ionic Liquids in biosensors: influence of hydrated choline based ILs on the bio-functionality of Lactate Oxidase (Tomorrow at ~15.30)

Don't Miss Them!!

AND YOU ALL FOR YOUR ATTENTION!!!