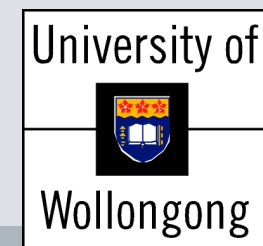




Multi - Modal Stimuli Responsive Materials

Michele Zaroni,
CLARITY, NCSR, Dublin City University



Outline

- ☑ Introduction: Stimuli Responsive Molecules
- ☑ **p-BSP2** Polymer: Synthesis and Properties
- ☑ Photo-Electrochemical Features
- ☑ Surface Study: **AFM**
- ☑ **p-BSP2 - FN** interaction: Photochemical Control
- ☑ Possible Application
- ☑ Conclusion

Stimuli – Responsive Materials

They are molecules that can be switched between different isomers with widely differing property sets.

HOW DO THEY WORK???

- The material is in an inactive initial state.
- An external stimulus converts the structure into the active state.
- When the stimulus is switched off the material returns to its initial conformation.



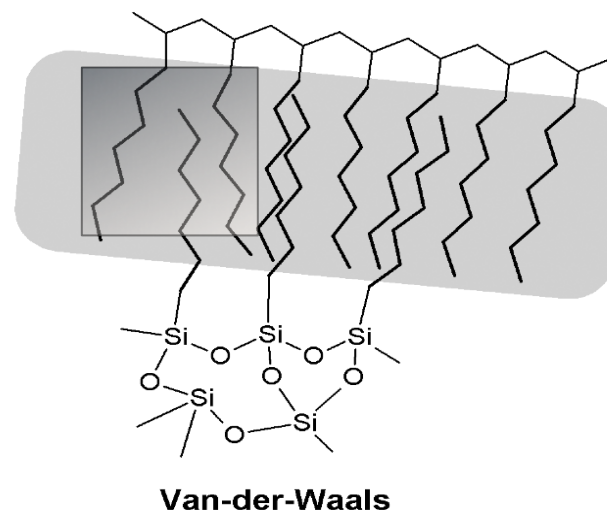
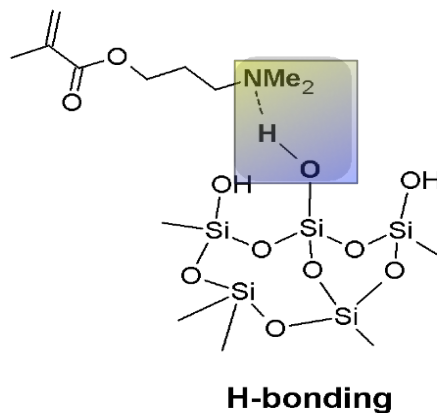
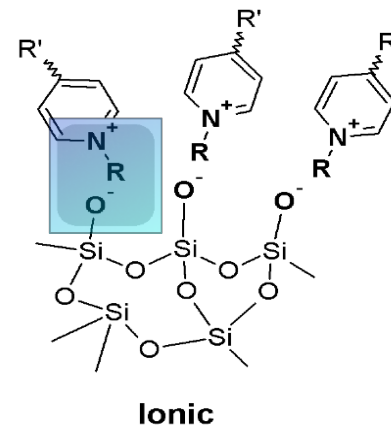
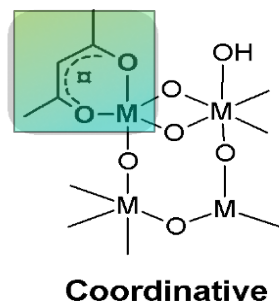
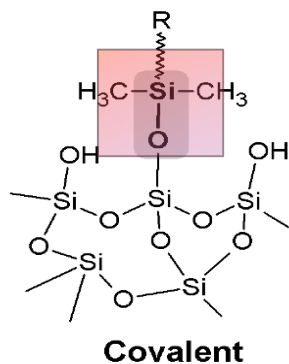
[1] Wu, Y.; Alici, G.; Spinks, G. M.; Wallace, G. G. Synth. Met. 2006,156, 1017.

[2] F. Benito-Lopez, R. Byrne, A.M. Raduta; N.E. Vrana, G. McGuinness and D.Diamond, Lab. Chip, 2010, 10, 195–201

STIMULI RESPONSIVE
MOLECULES

Types of linkage in Common Hybrid Structures

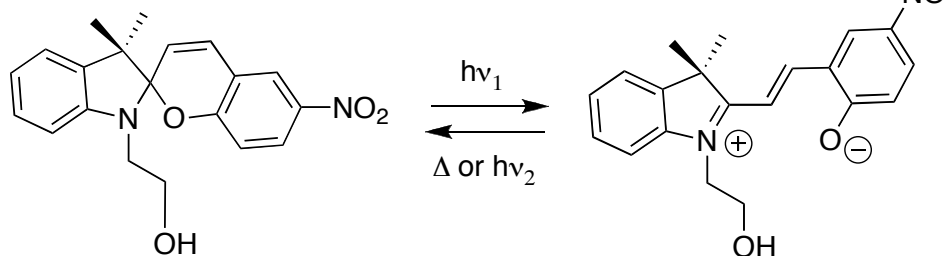
Increasing
Strength of
Interaction



STIMULI RESPONSIVE
MOLECULES

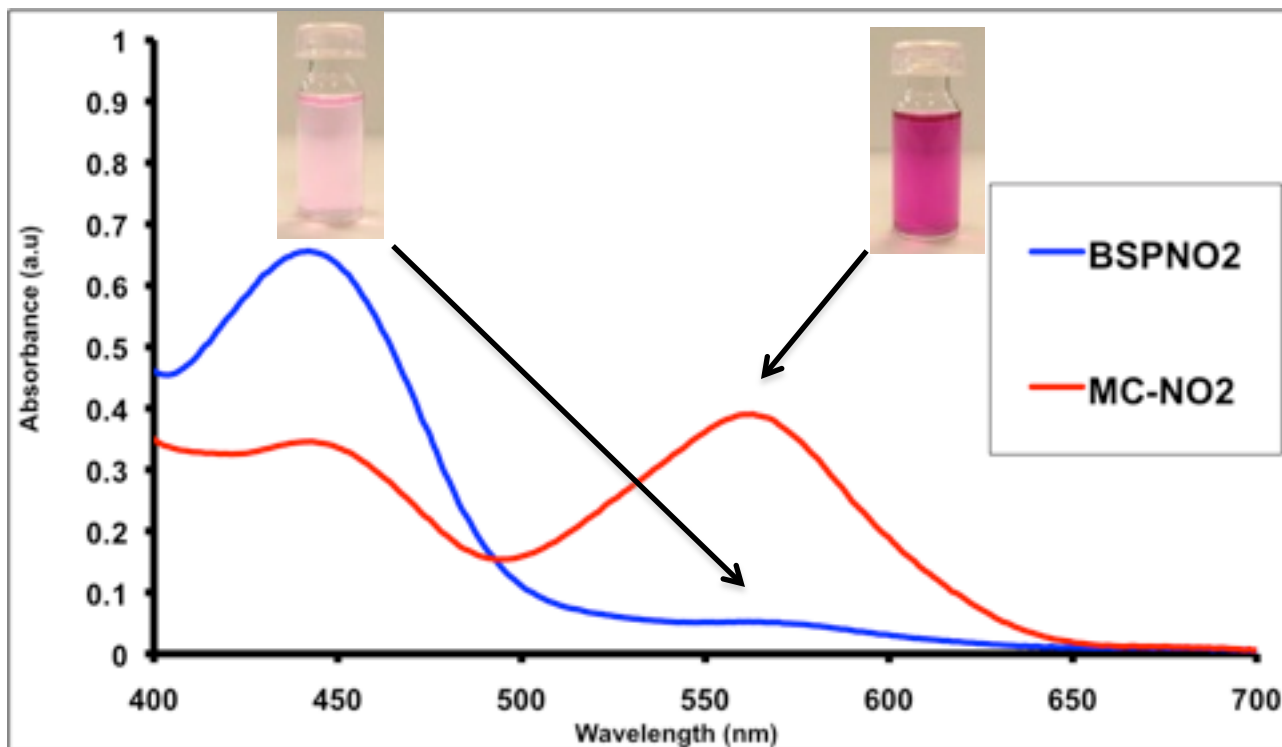
Guido Kickelbick, Hybrid Materials, 2007, Wiley Ed., S.Francisco.

Spiropyran – Merocyanine Photochemistry



Spiropyran

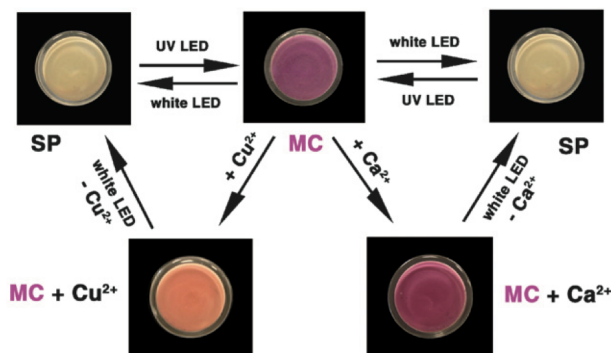
Merocyanine



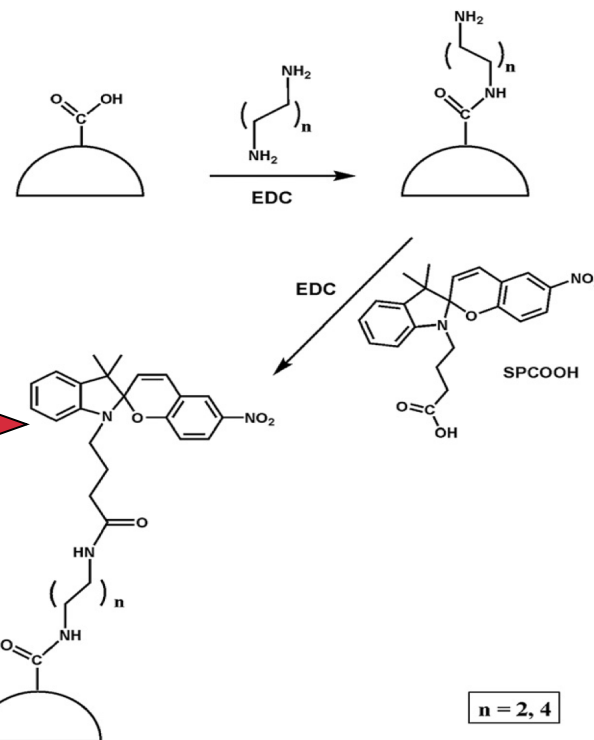
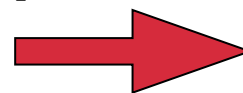
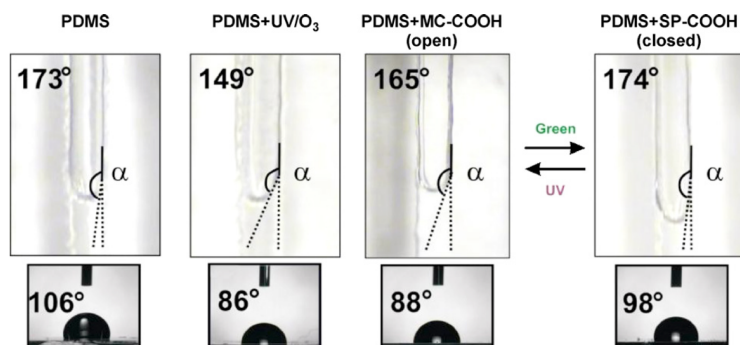
K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, 133 (14), pp 5453–5462

STIMULI RESPONSIVE
MOLECULES

Current Applications



Microbeads Systems for optical sensing [1]

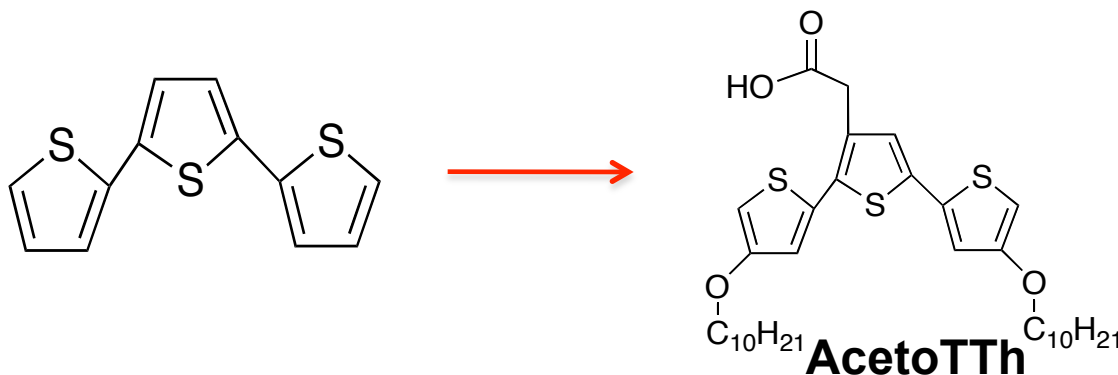


Functionalisation of Micro-Channels for Micro-Fluidic devices [2]

- [1] S. Scarmagnani Z. Walsh, C. Slater, N. Alhashimy, B. Paull, M. Macka and D. Diamond, J. Mater. Chem., 2008, 18, 5063–5071.
 [2] F. Benito-Lopez, S. Scarmagnani, Z. Walsh, B. Paull, M. Macka, D. Diamond, Sensors and Actuators B , 2009, 140, 295–303

STIMULI RESPONSIVE
MOLECULES

Terthiophene: the selected backbone.



- It is a conducting polymer with high environmental stability for both its states, doped and undoped.
- Its structure is versatile [1,2].
- Thanks to its conformation we can tailor the substitution position [3].
- It has multiple applications, such as conductor and organic semiconductor [4].
- It has important reversible optical properties [4].

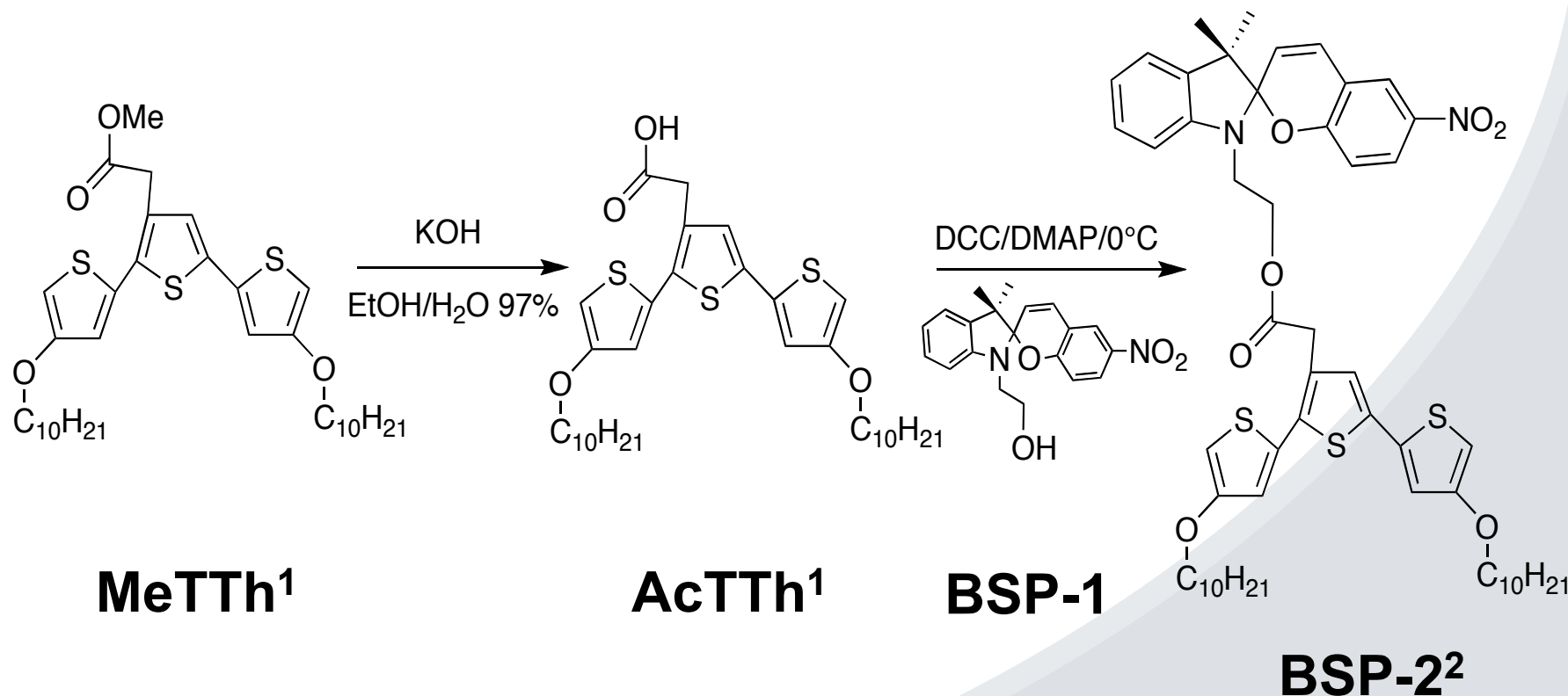
[1] S.Gambhir, K.Wagner, D.L.Officer, Synthetic Metals, 154, 2005, 117-120.

[2] P.Wagner, D.L.Officer, Synthetic Metals, 154, 2005, 325-328.

[3] K.Wagner et al., Macromolecules, 43, 2010, 3817-3827.

[4] J.Roncali, Chem Rev, 92, 1992, 711-38.

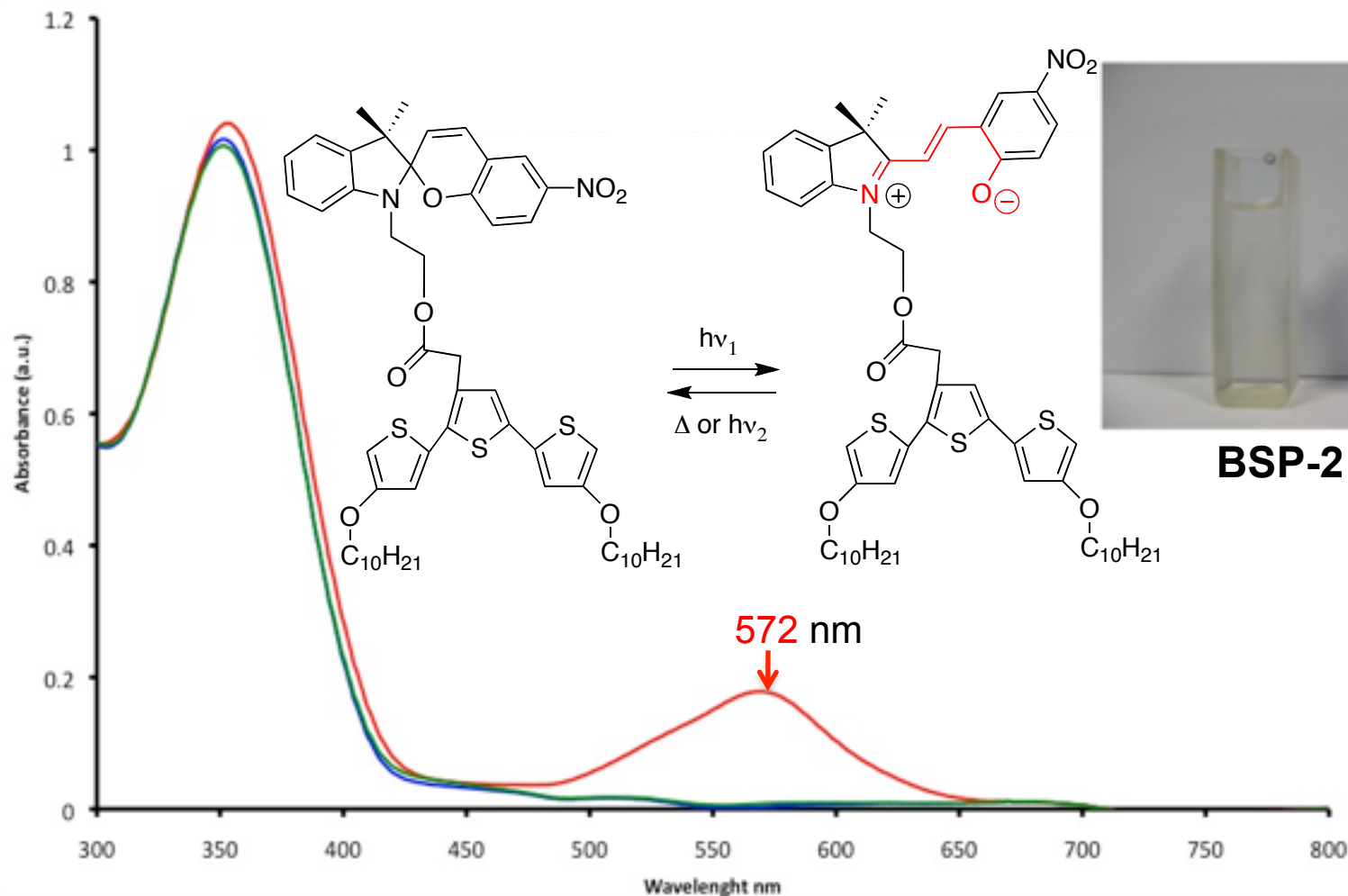
Synthesis of BSP-2



[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

Dual control molecule: Photochemistry

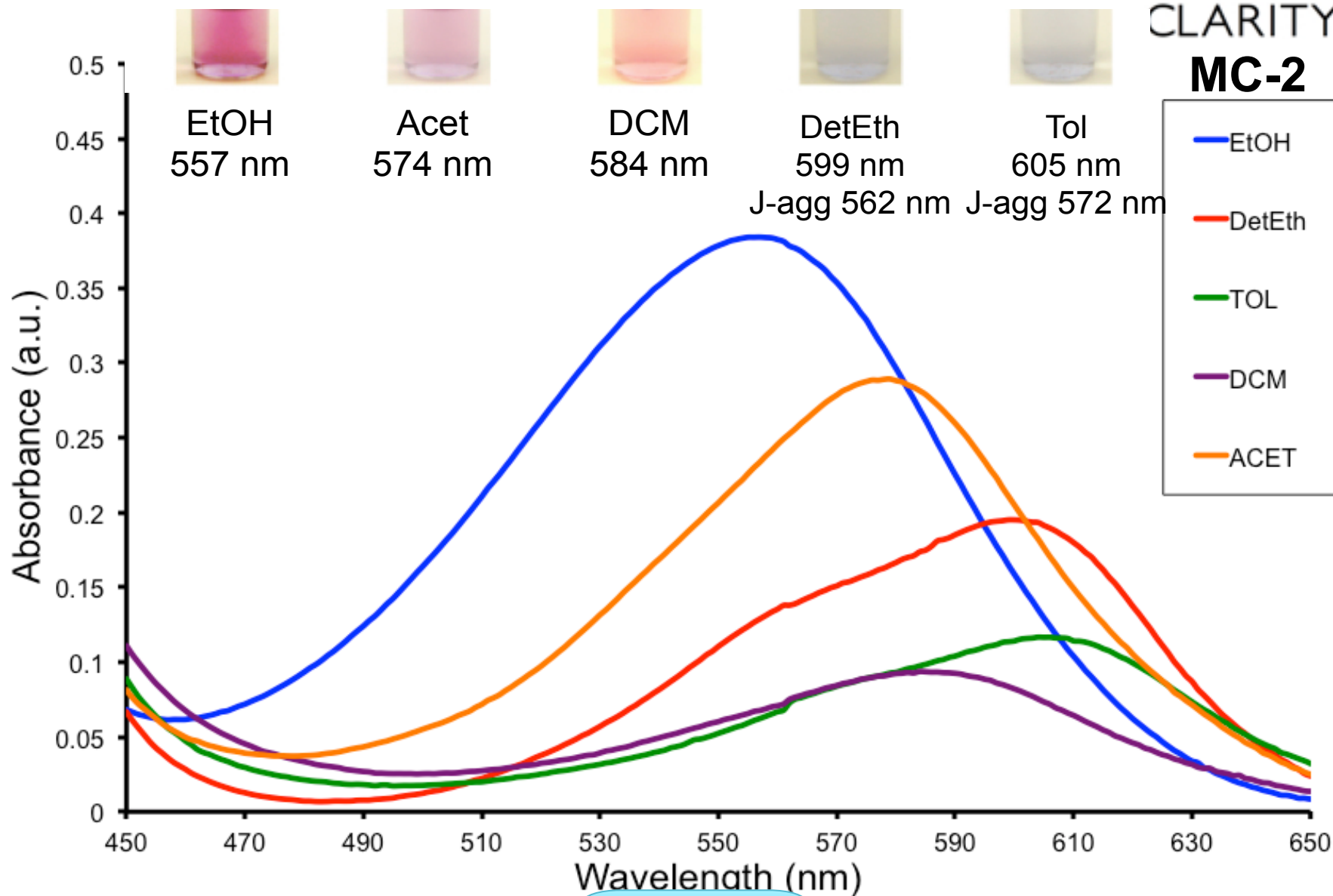


K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, 133 (14), pp 5453–5462

PHOTO-
ELECTROCHEMICAL
FEATURES

SOLVATOCHROMIC EFFECTS

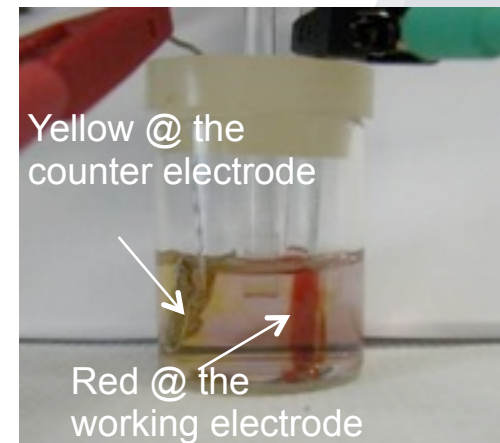
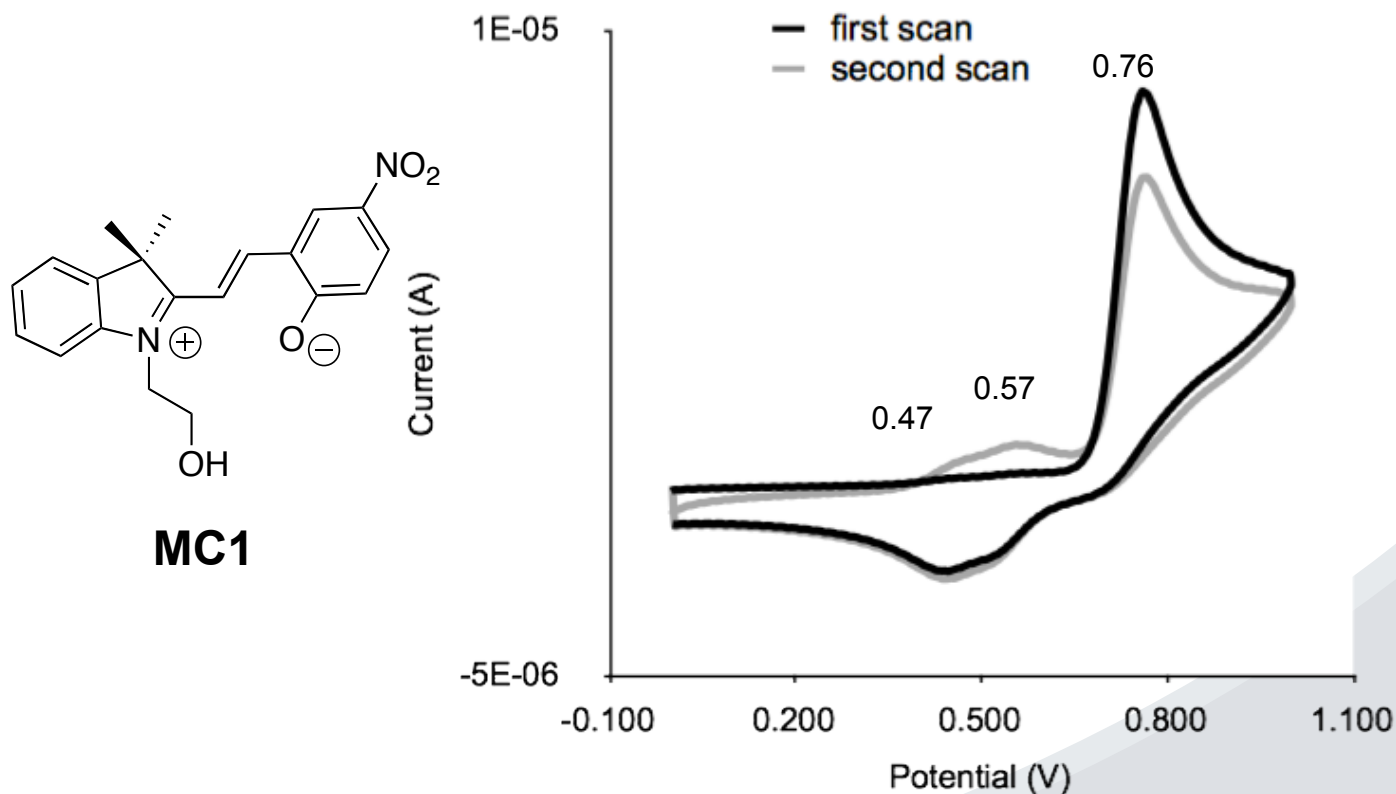
CLARITY
MC-2



Zanoni M. *et al Phys. Chem. Chem. Phys.*, 2012, **14**, 9112-9120

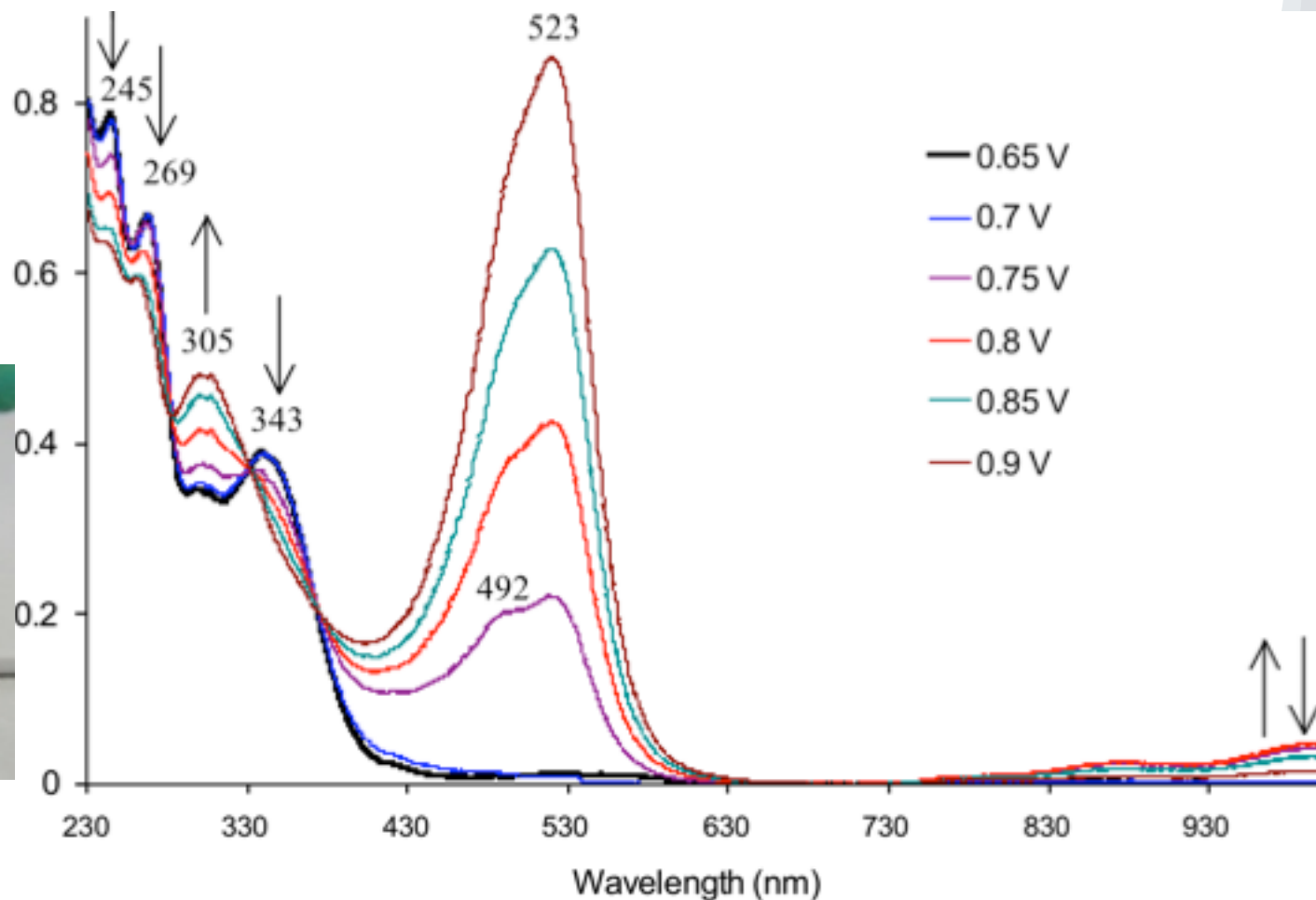
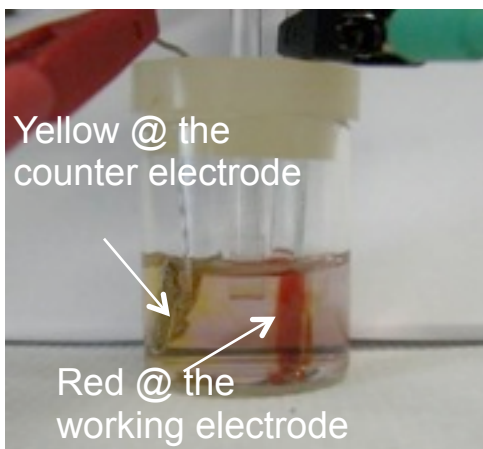
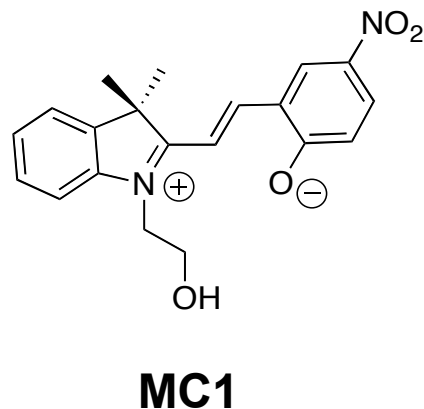
PHOTO-
ELECTROCHEMICAL
FEATURES

Electrochemistry of **BSP1** $\rightleftharpoons$ **MC1**



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

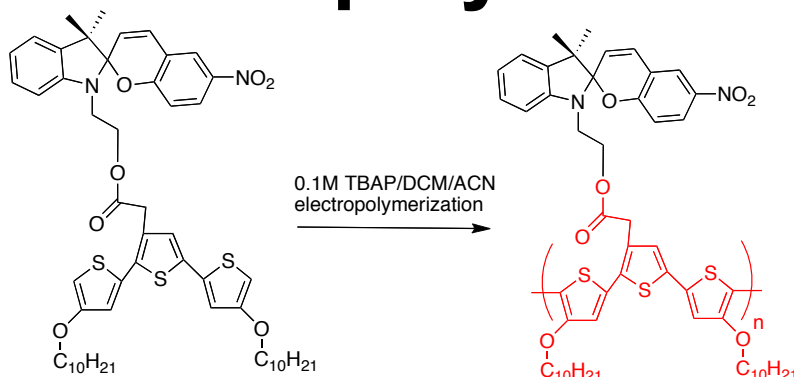
Spectroelectrochemistry of **BSP1** $\rightleftharpoons$ **MC1**



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

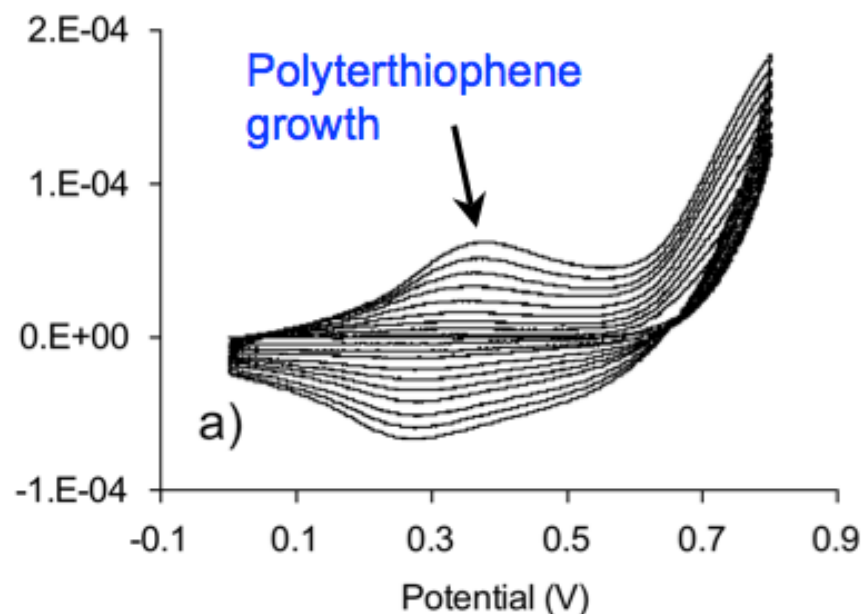
PHOTO-
ELECTROCHEMICAL
FEATURES

Electropolymerisation



Cyclic deposition of **p-BSP2** on ITO

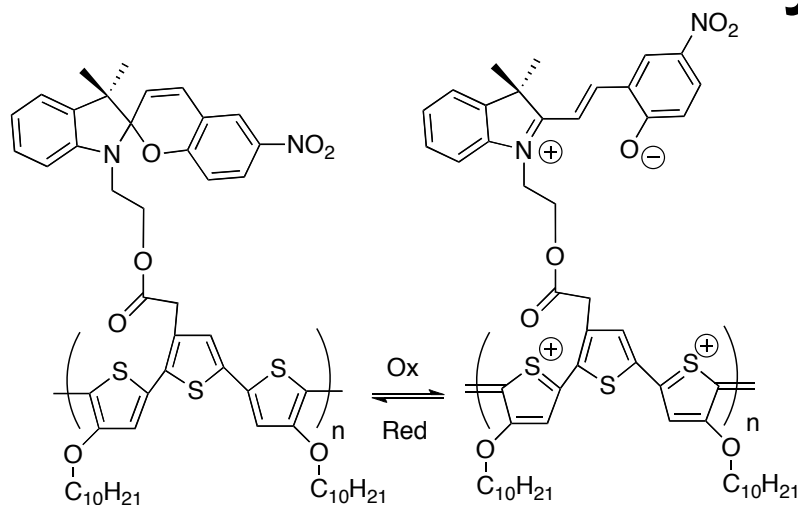
Monomer Concentration	8mM solution of BSP-2 in DCM+ACN, 2:3
Electrolyte	0.1M solution of TBAP buffer in DCM +ACN, 2:3
Working electrode	ITO
Counter electrode	Pt
Reference electrode	Ag/AgCl, AgNO ₃ 10mM n.a.
Scan range	Cyclic deposition From 0V to 0.8V
Rate	0.05V per sec
Sweep segments	8



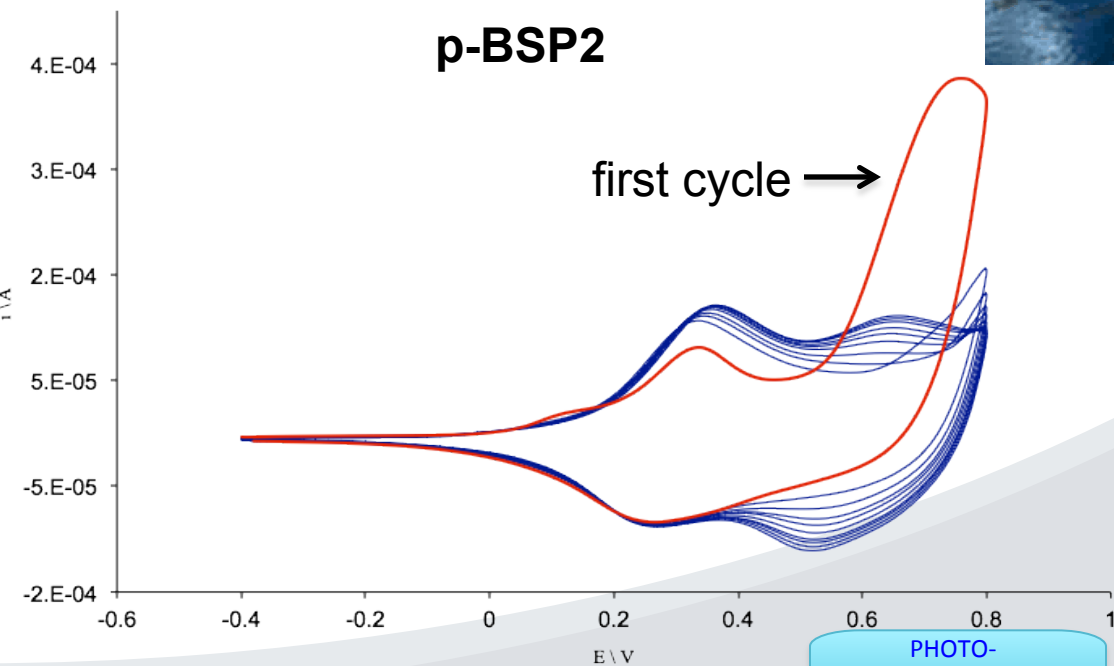
K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, 133 (14), pp 5453–5462

PHOTO-
ELECTROCHEMICAL
FEATURES

Electrochemistry of p-BSP2



p-BSP2

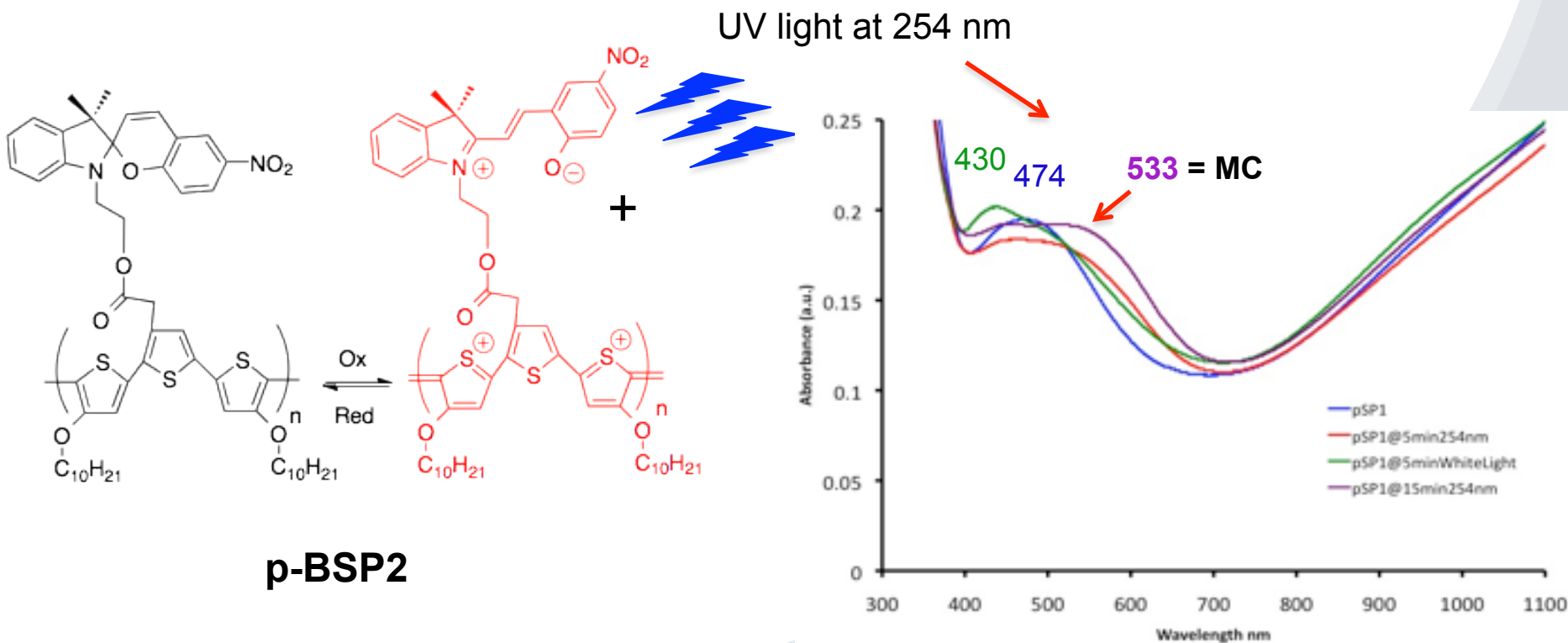


Reduced

Oxidised

Photochemical reversibility of p-BSP2

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

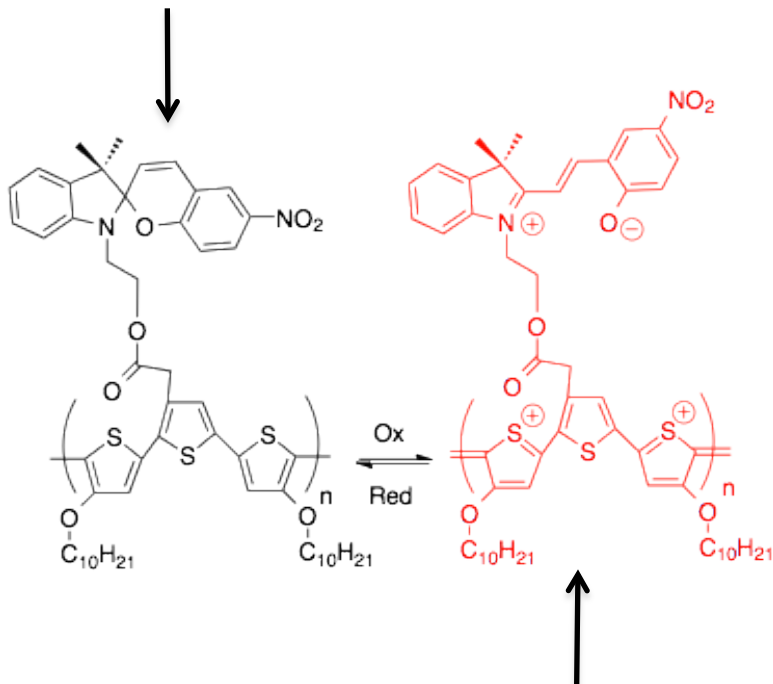


K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, J. Am. Chem. Soc., 2011, 133 (14), pp 5453–5462

PHOTO-
ELECTROCHEMICAL
FEATURES

AFM and SEM measurements

p-BSP2 at
reduced state

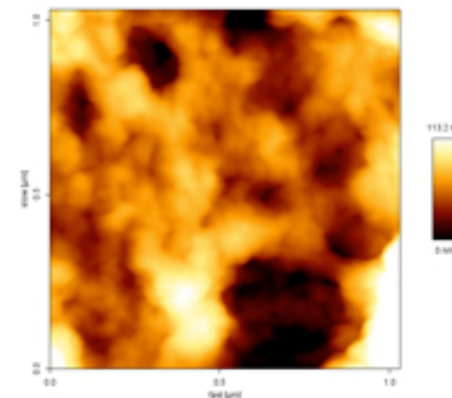
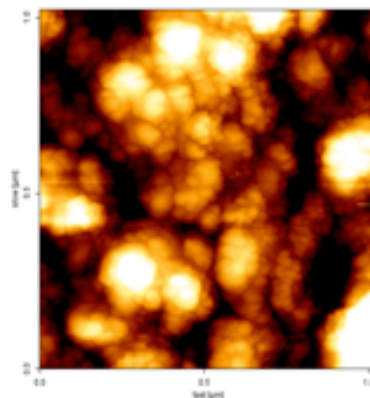


p-BSP2 at
oxidised state

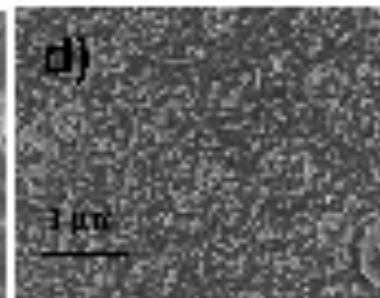
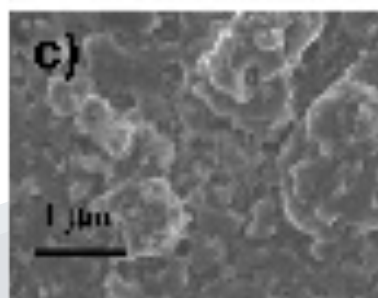
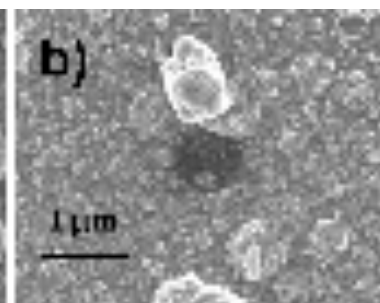
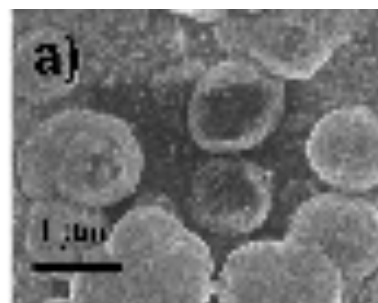
oxidised

AFM

reduced



SEM

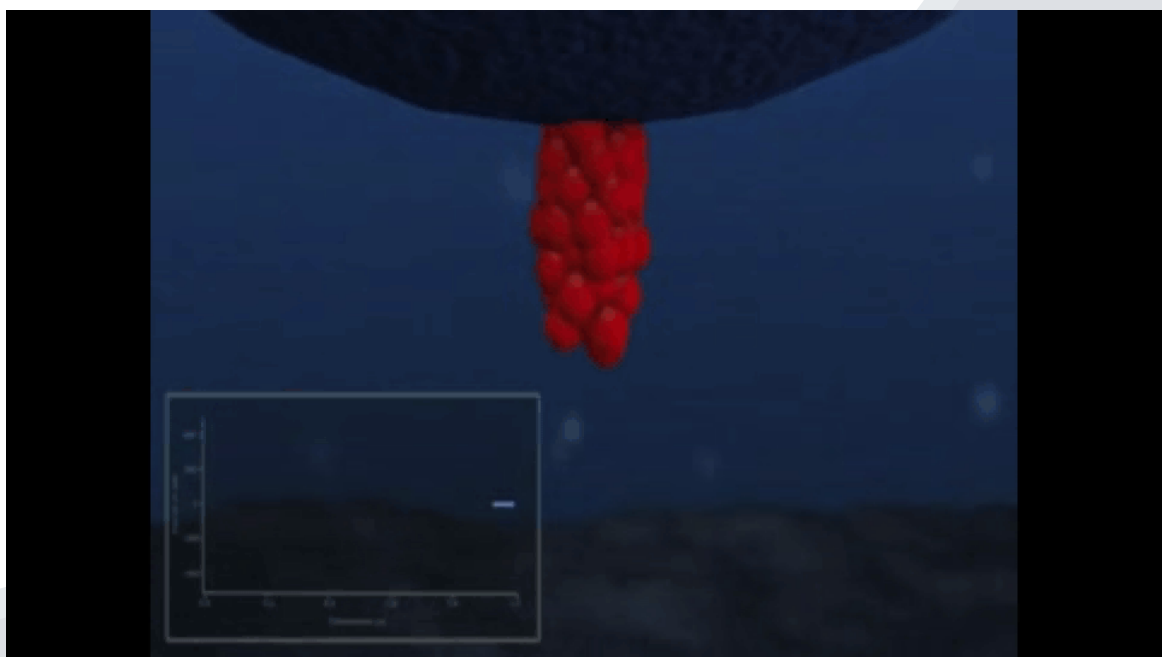
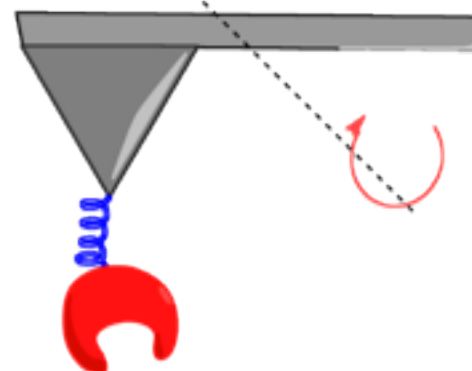
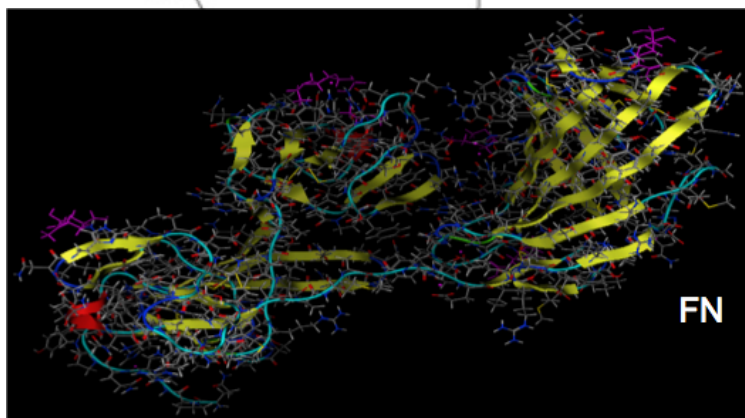
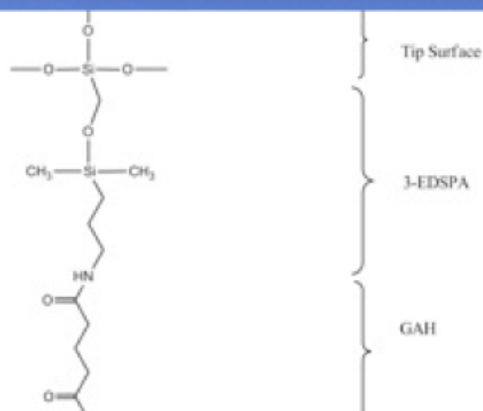


oxidised

reduced

SURFACE
PROPERTIES

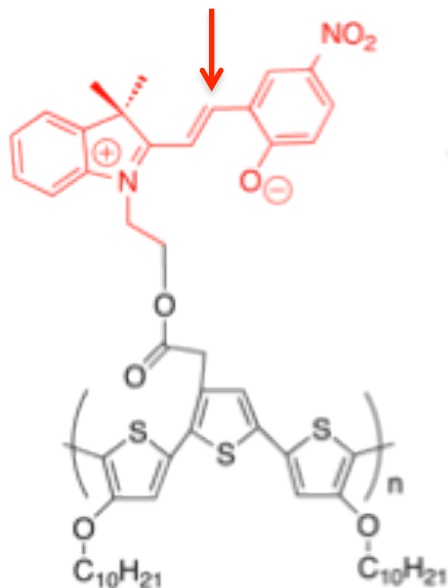
AFM Cantilever Functionalization with FN



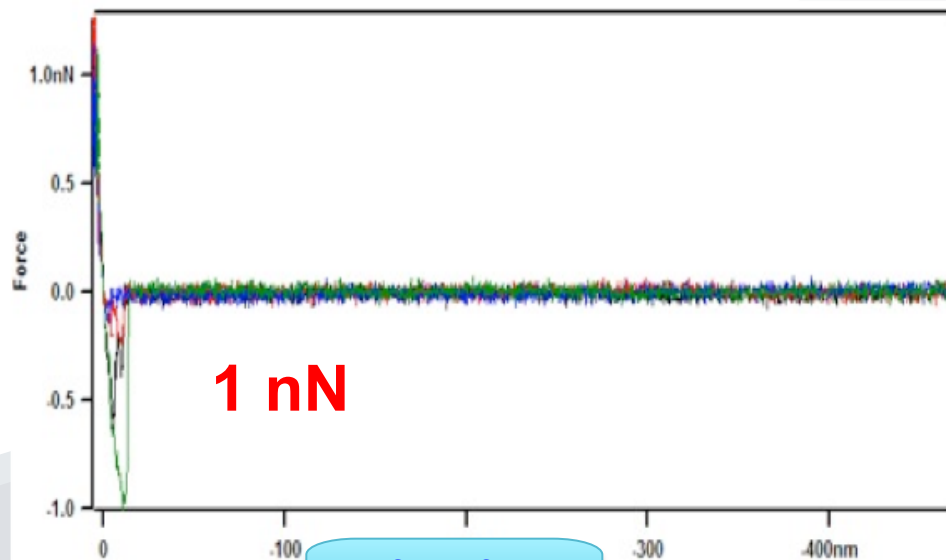
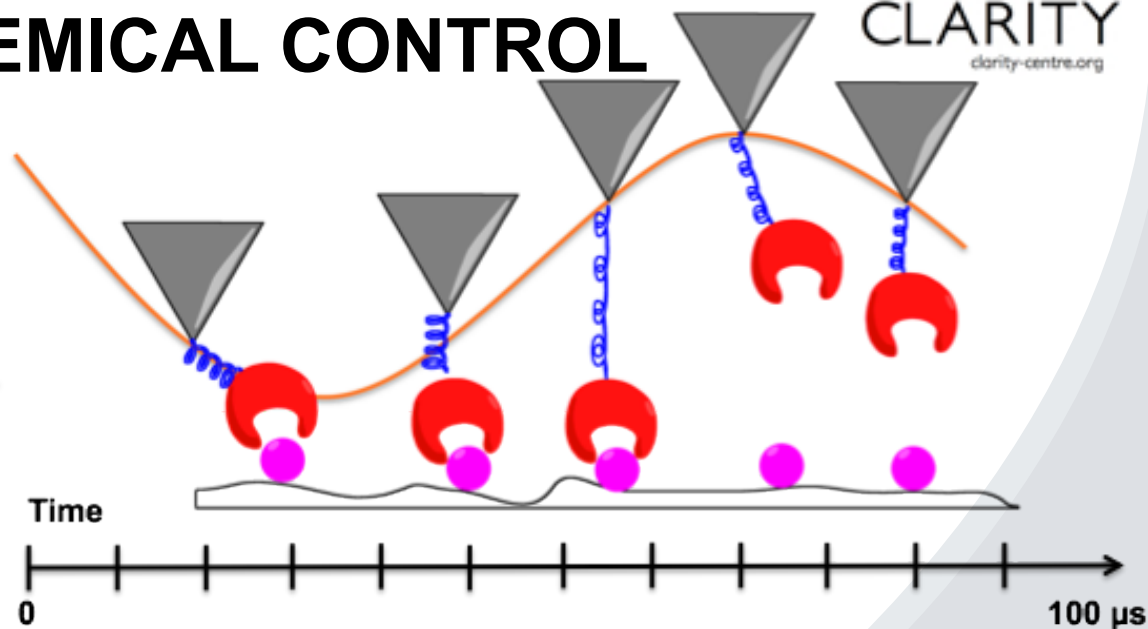
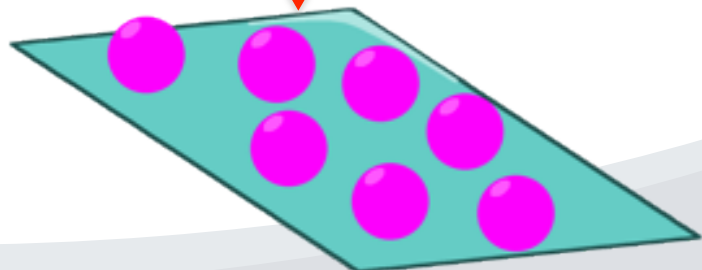
SURFACE
PROPERTIES

p-BSP2 and FN Interaction: PHOTOCHEMICAL CONTROL

Exposure to 254nm UV
light for 10 minutes prior
the AFM detection



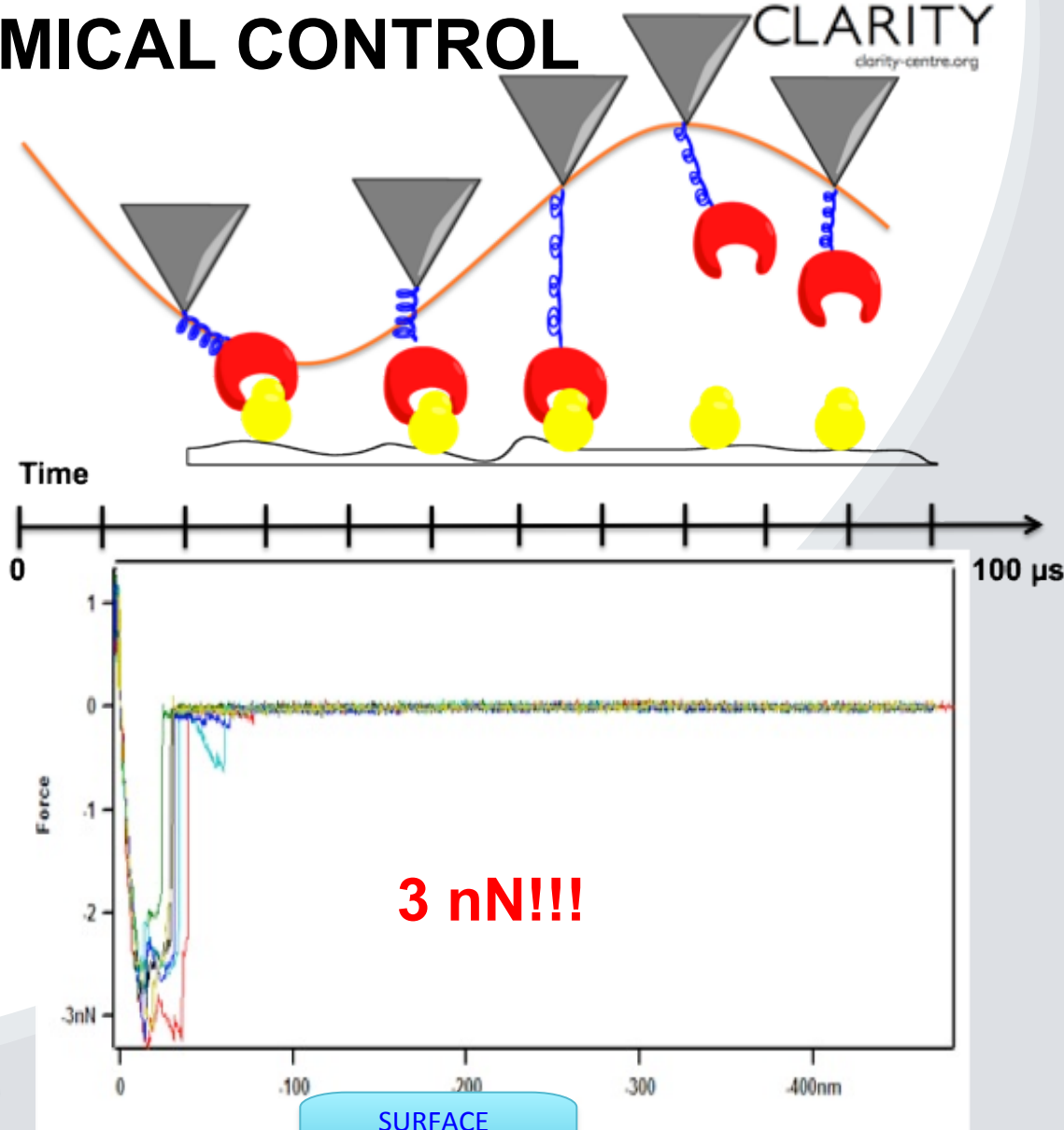
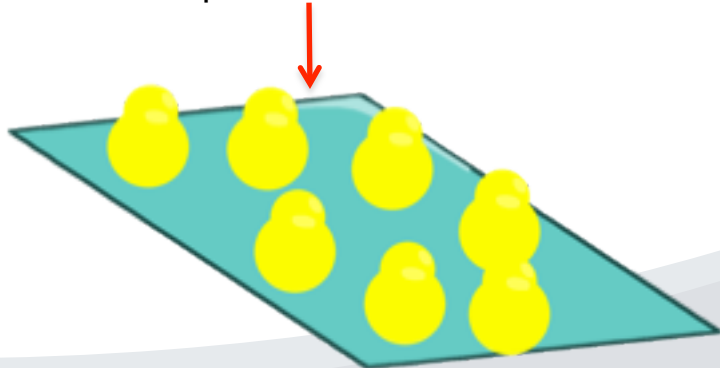
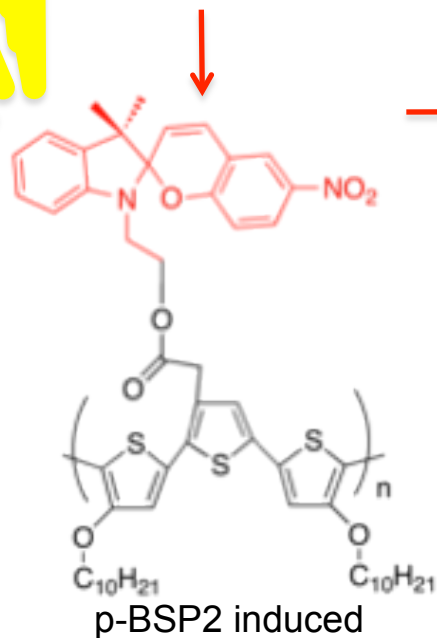
p-MC2 induced



SURFACE
PROPERTIES

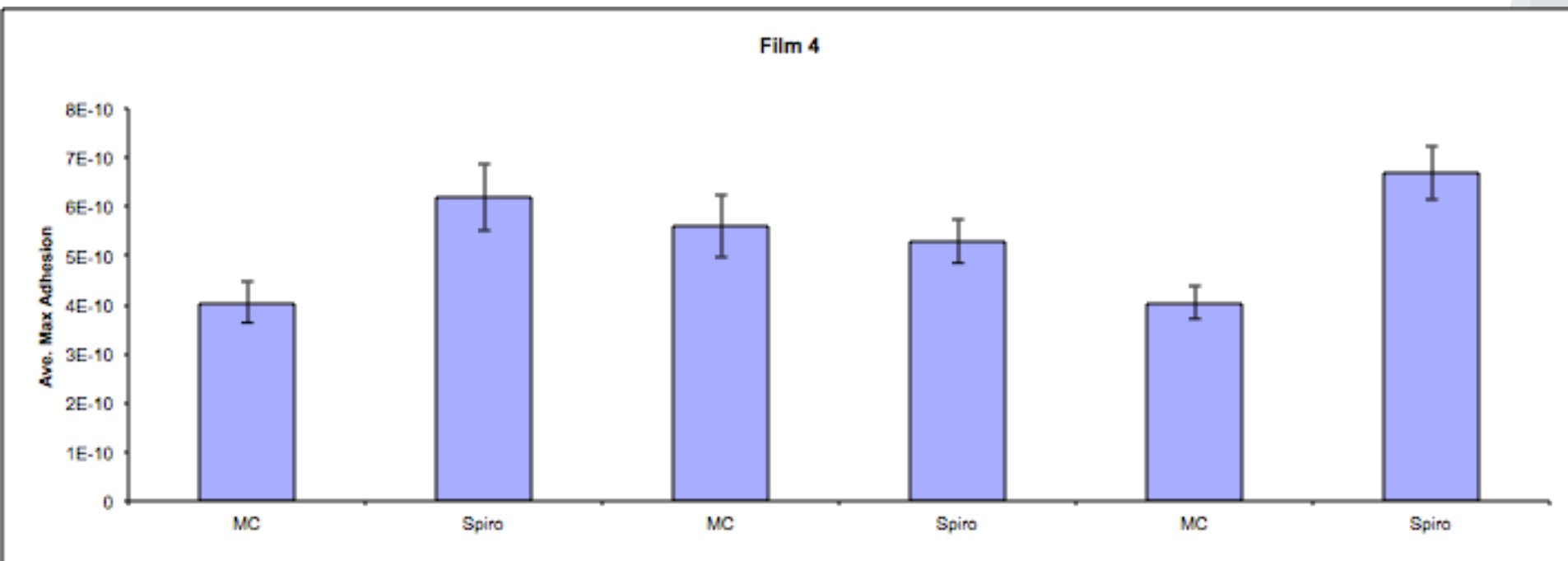
p-BSP2 and FN Interaction: PHOTOCHEMICAL CONTROL

Exposure to white light for
10 minutes prior the AFM
measurement



SURFACE
PROPERTIES

p-BSP2 and FN Interaction: PHOTOCHEMICAL CONTROL



	Average Max Adhesion	Std Error
p-BSP2	9.56E-10	6.91E-11
p-MC2	7.73E-10	4.02E-11

SURFACE
PROPERTIES

p-BSP2 as Molecular Actuator



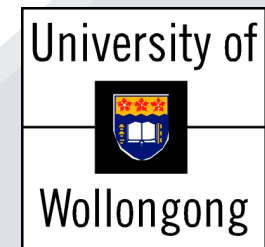
POSSIBLE
APPLICATION

CONCLUSION

- ☑ A new Class of Stimuli Responsive Moieties was prepared
- ☑ The Molecule Shows Intriguing Properties Deriving from Equal Contribution of Spiropyran and Terthiophene
- ☑ Spectrochemical Techniques showed the Dual Control-Features of this Polymer
- ☑ **p-BSP2** shows Innovative Photochemical Response under UV Light Exposure
- ☑ This Multiswitchable Polymer Can Be the Platform for Portable Analytical Devices and Biocompatible Systems

ACKNOWLEDGEMENTS

- Prof. Dermot Diamond and Dr. Robert Byrne (**DCU**).
- Prof. Gordon G. Wallace and Prof. David L. Officer (**IPRI**)
- Dr. Klaudia Wagner, Dr. Michael Higgins, Mrs. Amy Gelmi and Dr. Paul Molino (**IPRI**).
- Dr. Kevin J. Fraser (**DCU**).



AND TO YOU ALL FOR YOUR ATTENTION!!!