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

Michele Zanoni[1], *Amy Gelmi*[2], *Michael Higgins*[2], *Klaudia Wagner*[2], *Pawel Wagner*[2], *Sanjeev Gambhir*[2], *Gordon G.Wallace*[2], *David L.Officer*[2] *and Dermot Diamond*[1]

[1] CLARITY Centre for Sensor Web Technologies, National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland.

[2]Intelligent Polymer Research Institute, University of Wollongong, Wollongong NSW 2522, Australia.

Contact: Prof. Dermot Diamond (Dermot.Diamond@dcu.ie)

INTRODUCTION

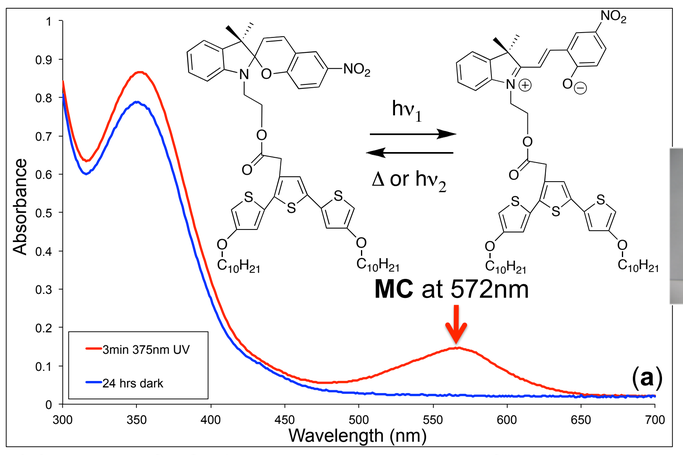
Polythiophenes behave as electrochemical molecular switches and this continues to make their synthesis an interesting subject for the development of new materials with switchable functionalities. Spiropyrans derivatives can be photonically switched between spiropyran and merocyanine derivatives that manifest dramatically different properties. Herein we present the covalent attachment of a spiropyran derivative to terthiophene to generate a new material[1] capable of multi-mode switching (electrochemical and photochemical) between various isomers.

For example, the material's physico-chemical properties can be rapidly switched with complete reversibility by exposure to light or heat sources through mechanisms that can be characterised by first order kinetics. Through the terthiophene moiety, the material can be polymerised without influencing the switching behaviour of the spiropyran moiety.[2] The multi-modal switching behaviour provides additional flexibility for control of the material's properties, for example by using electrochemical switching to assist the reversibility to the system.

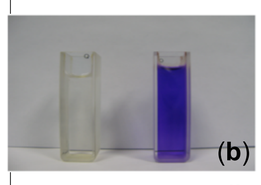
The ability to switch the physico-chemical properties of conducting polymers opens up new possibilities for a range of new applications. Appropriately functionalized materials can provide routes to multi-modal switching, for example in response light and/or electrochemical stimuli; this capability is important in the field of bionics, wherein remote control of the properties of materials opens new possibilities. For example, the ability to actuate a film via photonic stimuli is particularly interesting as it facilitates the modulation of interactions between surface host binding sites and potential guest molecules.[3] In this work, we studied six different poly-terthiophenes: four were functionalized with two different spiropyran photoswitches (p-BSP2, 3, 6, 7) and two with non-photoswitchable carboxylic acid units (p-AcTTh and p-CbTTh). The photochemical activity of these substrates was studied through spectroscopy, electrochemistry and microscopy but of particular interest was the interactions with chemically activated AFM tips with fibronectin (FN) and the adhesion force of the protein to the polymeric surface was measured. Differences in average maximum adhesion force were measured between p-AcTTh and p-BSP2, but after exposure of the p-BSP2 polymer to UV, the average maximum adhesion of the p-MC2 was significantly smaller than both the p-AcTTh and p-BSP2.

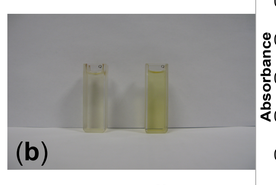
ON DEMAND TUNABLE PROPERTIES OF THE MOLECULAR SWITCHES

PHOTOCHROMISM in SOLUTION



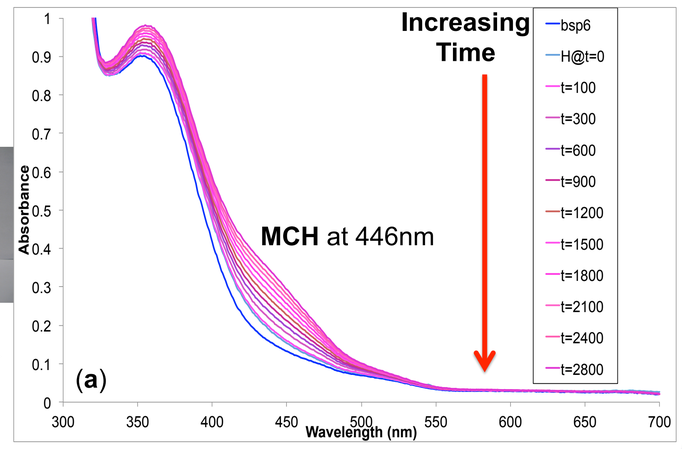
(a) UV-*vis* of **BSP2** with the wavelength of Merocyanine formation **(b)** highlighted (**MC** at 572nm) in Acetonitrile



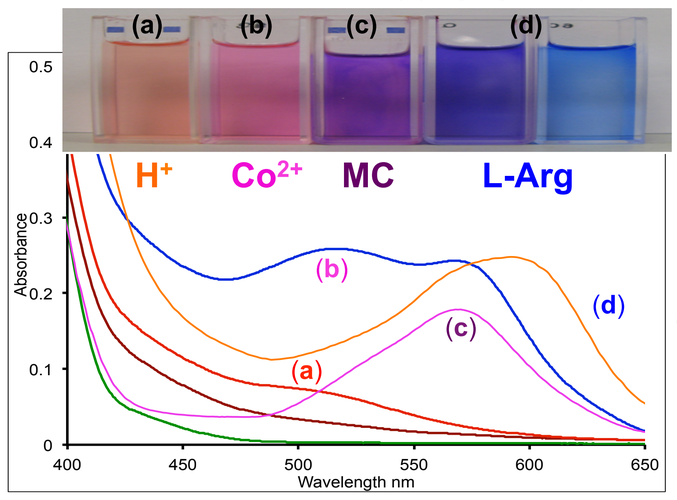


The dramatic differences in colour is due to the different substitution arrangement for **BSP2** and **BSP6**, in particular the replacement of the NO_2 group at position 6 (**BSP2**) on the spiropyran with a terthiophene derivative (**BSP6**).

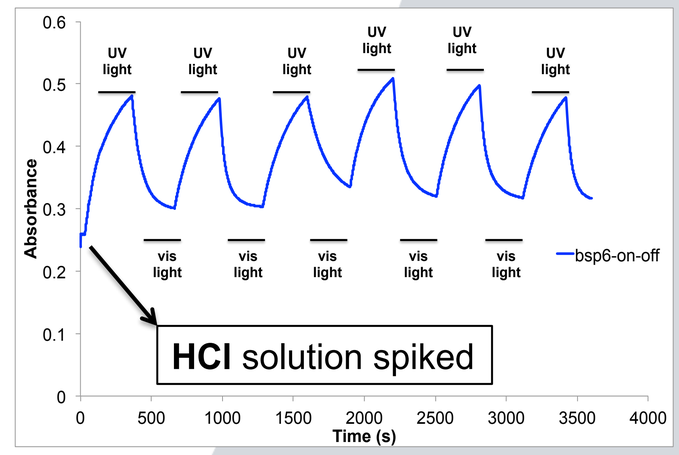
PHOTODYNAMIC HALOCHROMISM



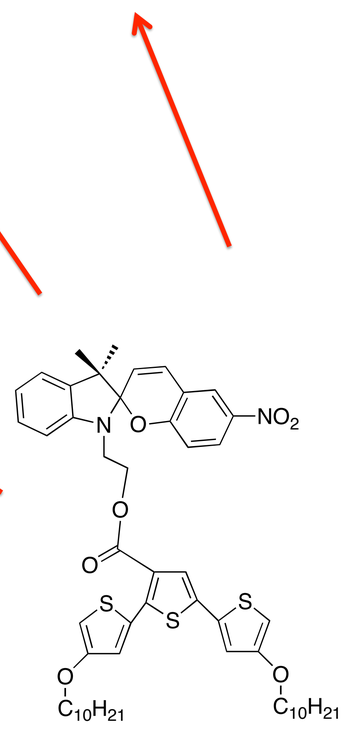
To a 10^{-4} M solution of **BSP6** in ACN were added 160µl of 0.1M solution of HCl. The spectra of formation of **MCH6** were obtained at 20^0C over 2800sec.



Ligand Activity in solution for **BSP2** with miscellaneous species

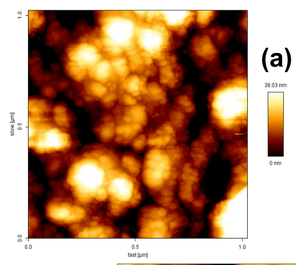


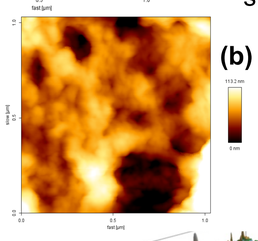
Protonation (UV LED assisted) and de-protonation (white LED assisted) study on **MCH6**. λ max = 446 nm.



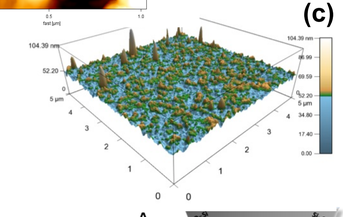
Structure of the monomers **BSP2** and **BSP6**

AFM PROFILING AND FORCE MEASUREMENTS





AFM images of **(a) p-BSP2** at reduced state; **(b)** at oxidized state; **(c)** Topography of **p-BSP2.**



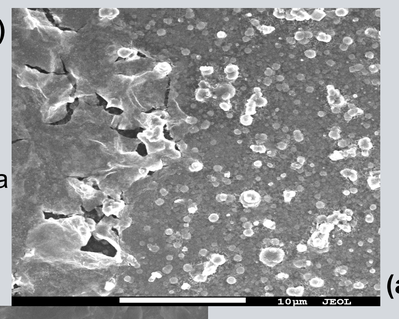
(A) Diagram of AFM tip functionalized with FN interacting with **pBSP2** stimulated with UV (λmax 254 nm). **(B)** Example force curve analysis, extension (red) and retraction (blue). **(C)** Average adhesion forces for as-grown **pTTh** (n=228), **BSP** (n=200) and **MC** (n=150).

Fibronectin is a glycoprotein:

1. Binds integrins, collagen, fibrin and proteoglycans
2. Fundamental for effective cell adhesion
3. Important for cell growth
4. Essential for cell migration

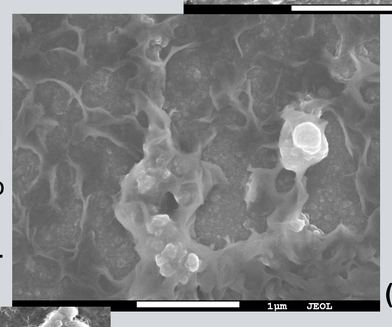
SEM SURFACE STUDY

SEM surface study of **(a) p-BSP6** after synthesis; **(b)** at reduced state (1µm); **(c)** oxidized (1µm)**.**



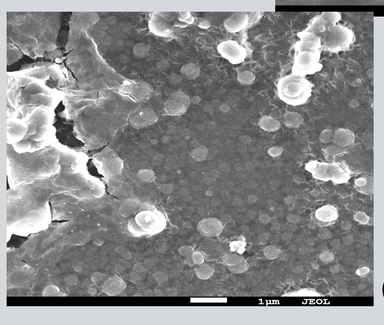
(a)

The morphology of the fresh **p-BSP6** (**a**) shows a globular structure, with features approximately 1 µm in diameter present on the polymer surface.



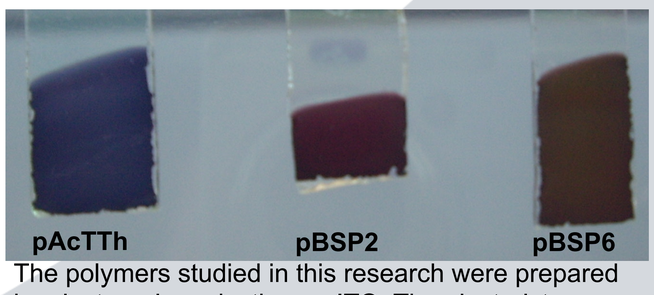
(b)

Oxidation of the polymer to 0.85V (**b**) gave a film with an entirely different morphology with a distinctive webbed and close-packed structure. A reduced film to -0.4V (**c**) showed a globular conformation comparable to the one of the freshly polymerized film.



(c)

ELECTROCHEMISTRY



The polymers studied in this research were prepared by electropolymerisation on ITO. The electrolyte was TBAP 0.1M in Acetonitrile.

REFERENCES

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, *Journal of the American Chemical Society*, 2011, **133**, 5453-5462.
2. M. Zanoni, S. Coleman, K. J. Fraser, R. Byrne, K. Wagner, S. Gambhir, D. L. Officer, G. G. Wallace and D. Diamond, *Physical Chemistry Chemical Physics*, 2012, **14**, 9112-9120.
3. A. Gelmi, M. Zanoni, M.J. Higgins, S. Gambhi, D. L. Officer, D. Diamond, G.G. Wallace, *Accepted Manuscript in J. Mat. Chem. B*, 2013

CONCLUSIONS

The target of this work was the analysis of the surface interactions between two different adaptive materials and an important biological agent like fibronectin. The technique used to probe the intensity and the nature of these interactions was **AFM**. Atomic Force Microscopy tips functionalized with **human FN** appear to show the presence of adhesion forces between **FN** and the hybrid conducting polymer in exam. The results were reproducible and showed higher interactions with the **BSP2** isomer than **MC2**. The molecules demonstrated a specific activity when stimulated by a variation of the surrounding chemical environment and these features were reversible and reproducible over time.

This work is supported by Science Foundation Ireland under grant 07/CE/I1147