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Spirocyclic Polythiophenes-
Hybrid material for bio-sensing applications

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

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Bio-sensing applications

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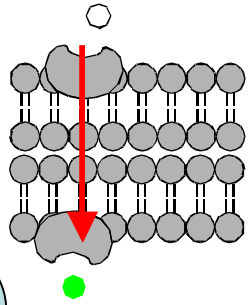


Understanding biochemical pathways

Move towards home/local care
e.g. diabetes-glucose meter

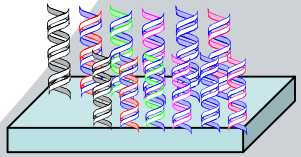
Biochemistry

Health Care Analysis

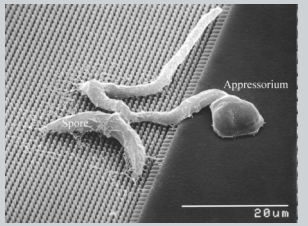
Biosensors

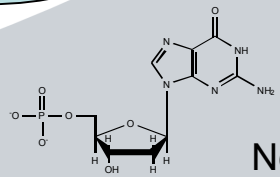
Nanotechnology

Drug Screening



Bio-sensor arrays





New era of drug development
Glyco-proteins

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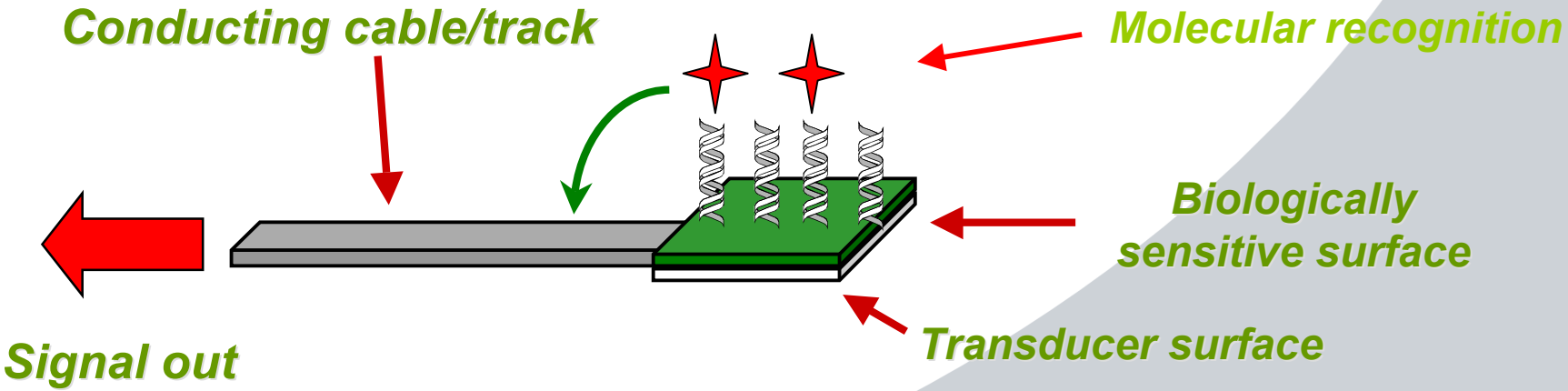
What is a Bio-Sensor?

'a device, consisting of a transducer and a biological element of known molecular properties, that generates a signal related to the concentration of particular biological component in a sample'



In bio-sensors, the sensing surface must interact selectively with a particular biological marker through molecular recognition association such as antibody-antigen, enzyme-substrate, and complimentary DNA sequencing

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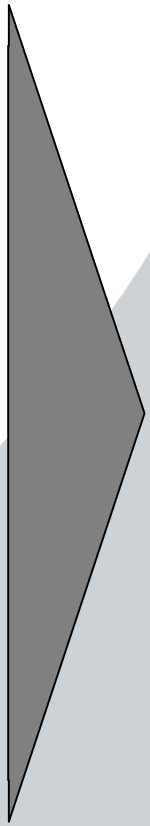
Modes of transduction

- Electroactive surface >> Electrode
- pH change >>Semi-conductor, pH electrode
- Heat >> Thermistor
- Light >> Photon counter
- Mass change >> Piezoelectric device



Output Signal

Conducting polymers are favourable materials for bio-sensing platforms due to their direct and easy deposition on electrodes, control of layer thickness, and redox conductivity

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Biosensors based on Conducting Polymers

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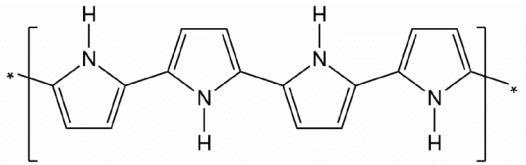
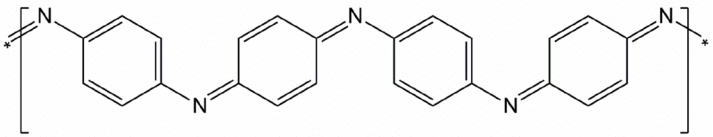
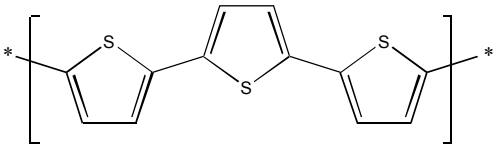
- Polypyrrole



- Polyanaline



- Polythiophene



Active membrane determines sensitivity of electrochemical sensors, the reliability of sensor is thereby linked to quality of chemically active membrane. Immobilisation strategy most important.

•Covalently coupled bio-component – some proteins denature when immobilised
•Cross linked enzymes- enzymes expensive and cross linking should not affect reactivity
•Gelation of bio-components within polymers- leeching of active species

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Design-Biosensing platform

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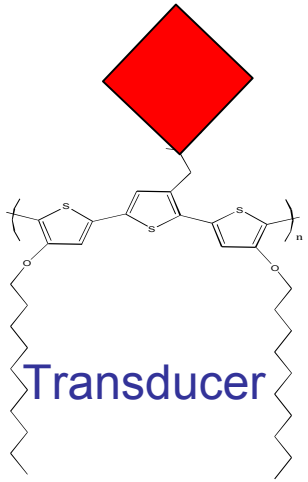
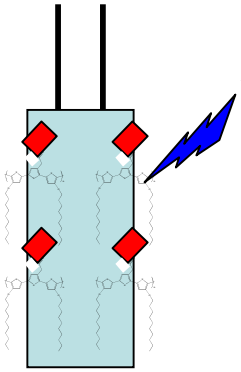
1- Functionalise Terthiophene with photo-switchable material

Photo-reactive Handle

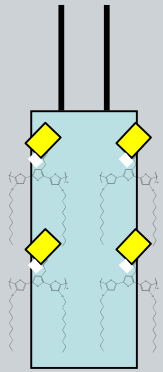


2-Deposit on electrode (ITO)

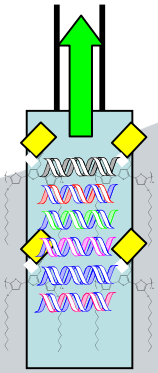


4-Spatial control of reactivity via fibre optic/LED

5-Activated surface binds bio-component



7-Bio-component binds its specific analyte



8-Signal of binding event

9-Photonic irradiation cleans surface, ready for new measurement

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Photoswitchable Material- Spiropyran

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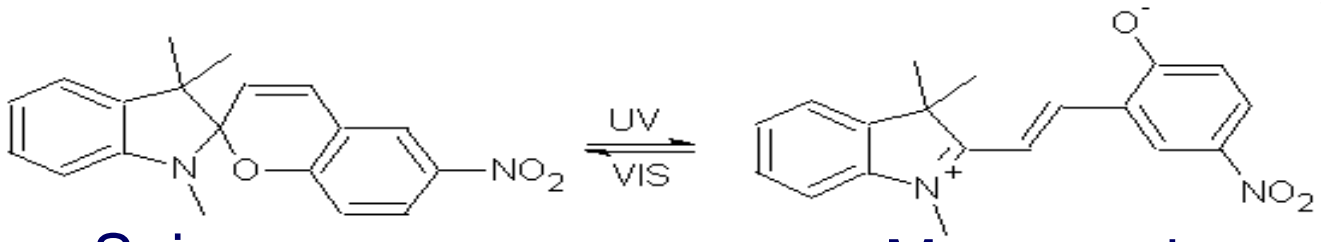
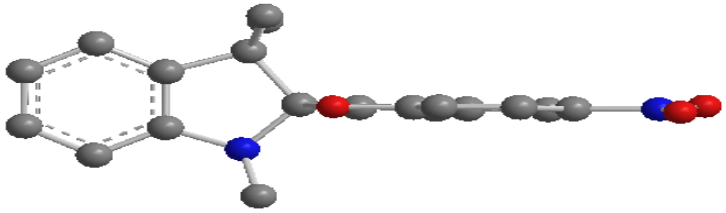
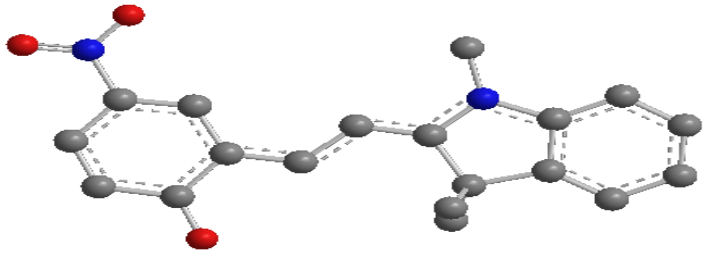
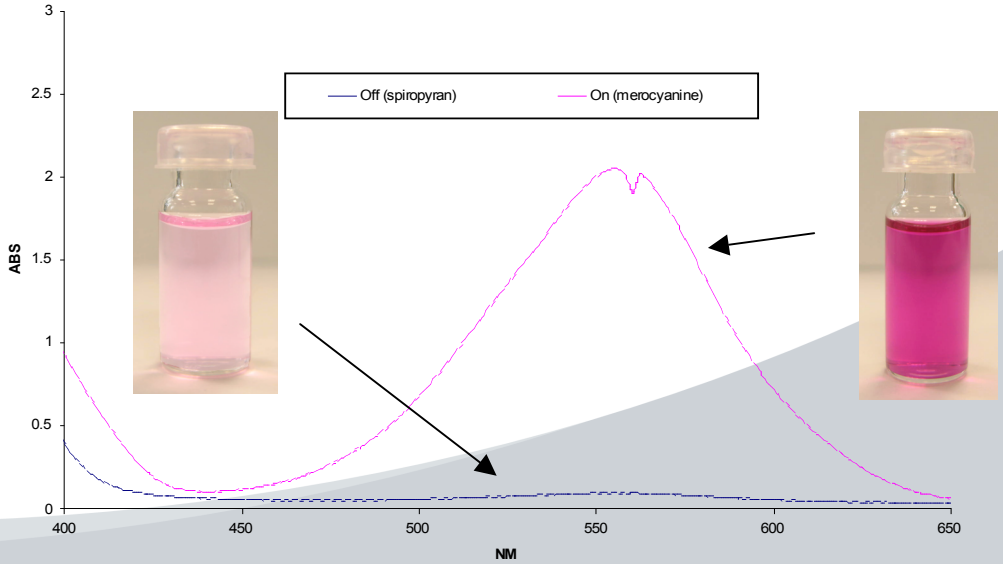


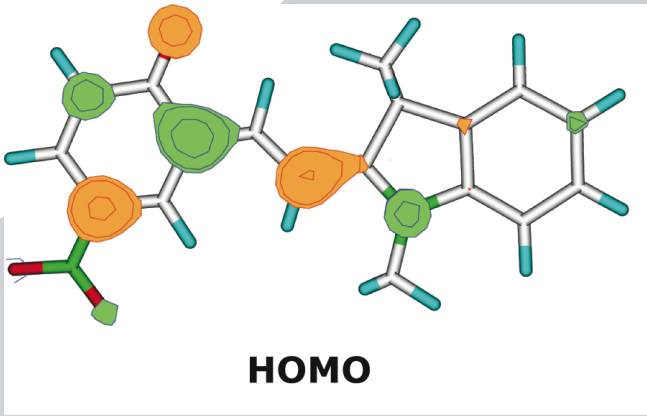
Spiropyran

Merocyanine









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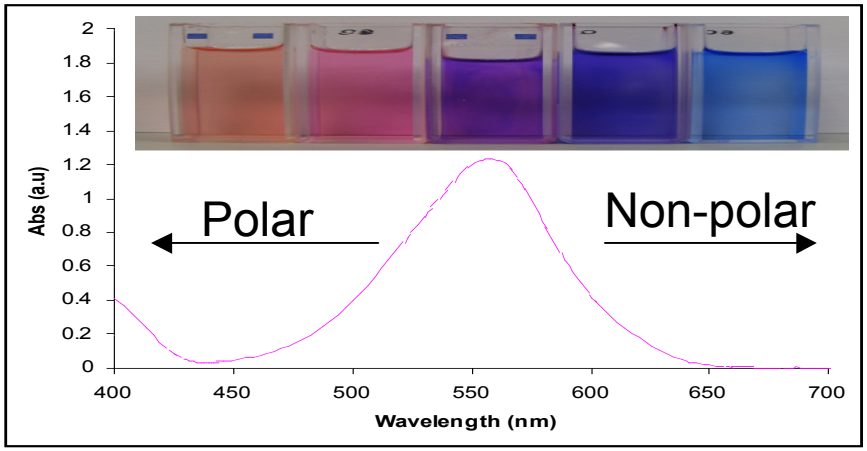
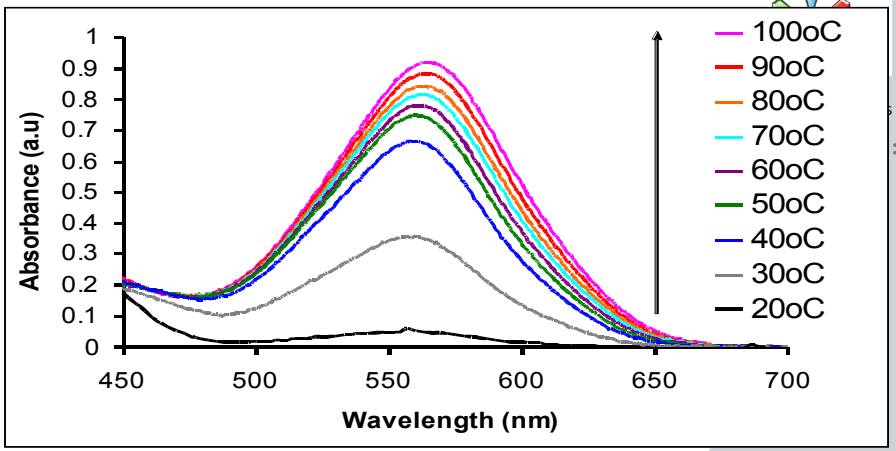
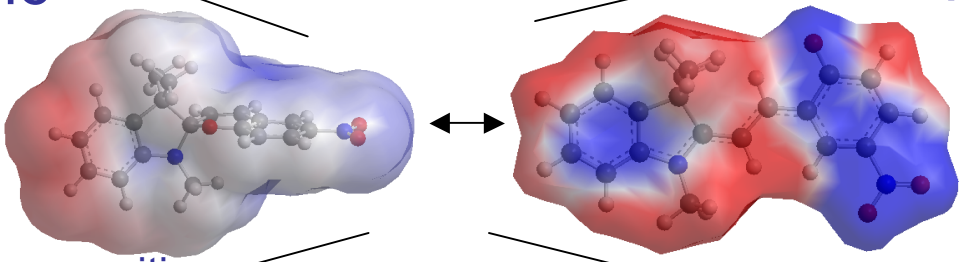




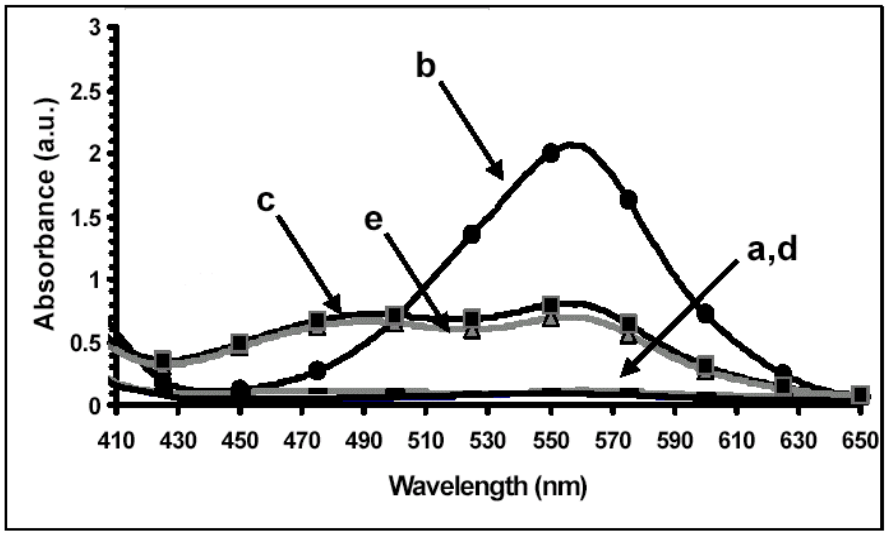
Solvatochromic

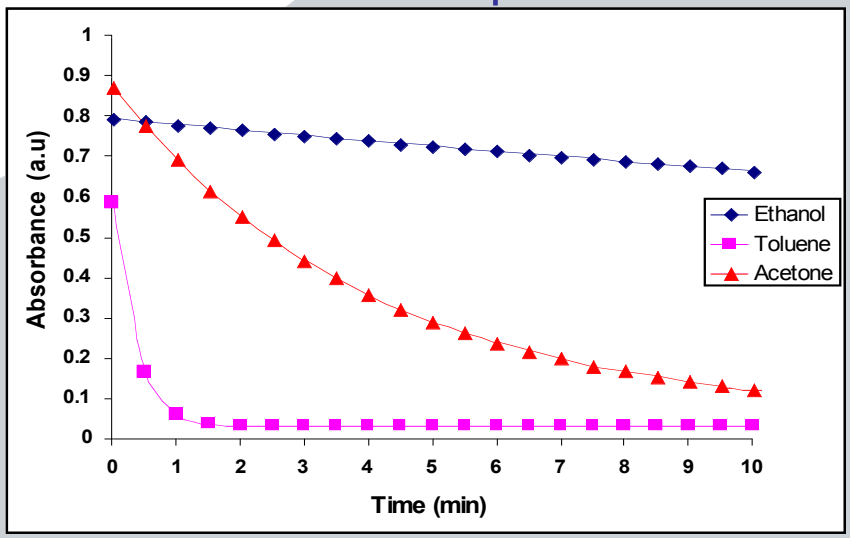
Thermochromic



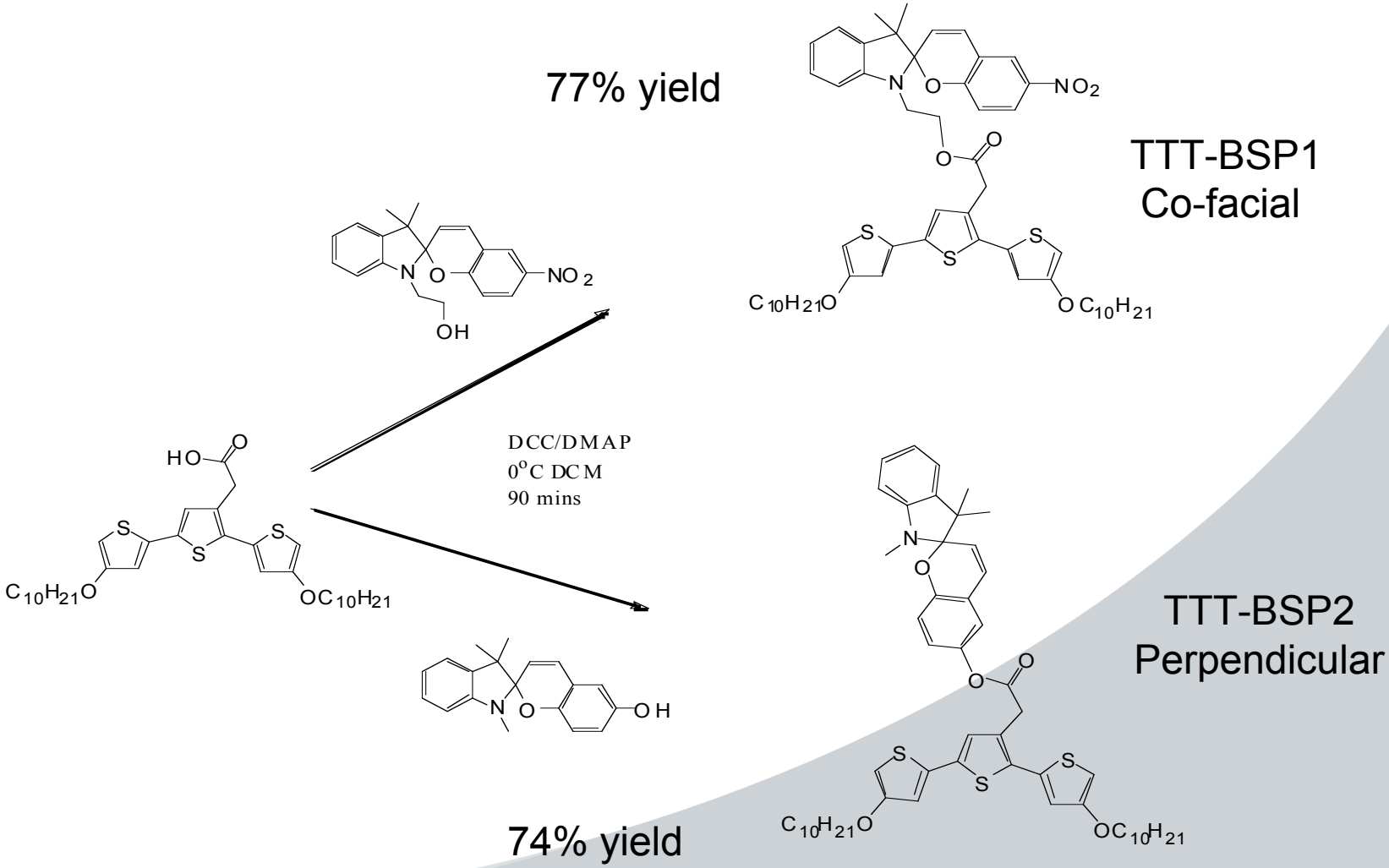
M+,H+ and amino acid recognition

Thermal relaxation dependent on all processes!





Synthesis of photo-switchable monomers



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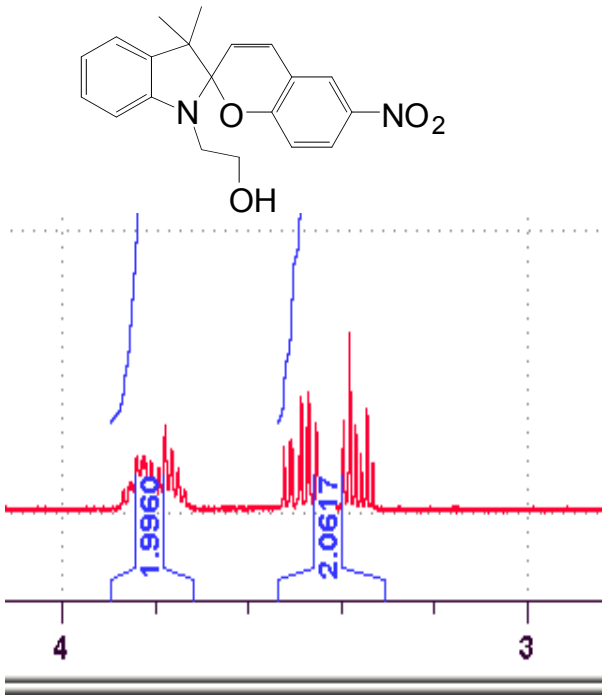
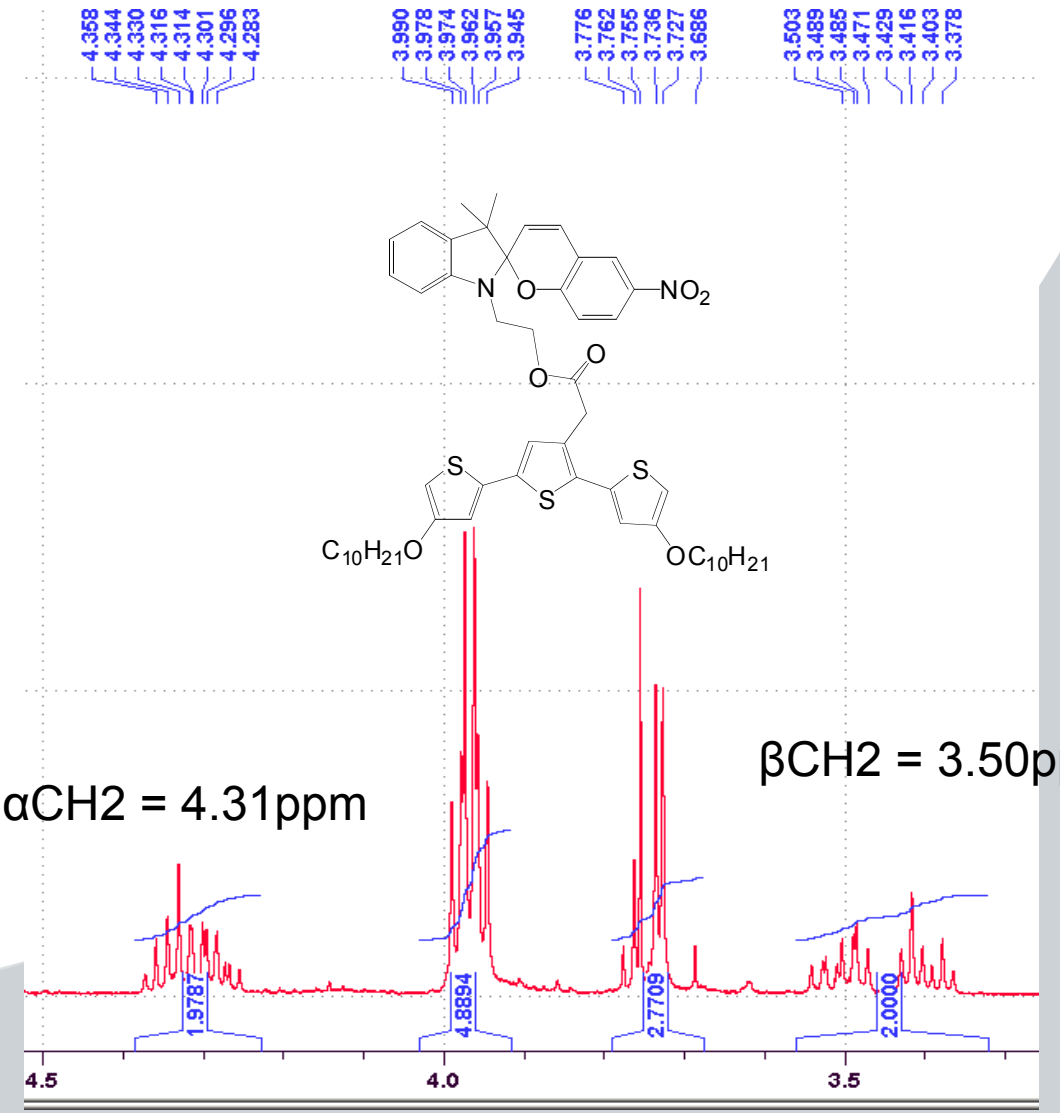
TTT-BSP1 ^{1}H-NMR



αCH2 = 3.86ppm
βCH2 = 3.48ppm



αCH2 = 4.31ppm

βCH2 = 3.50ppm

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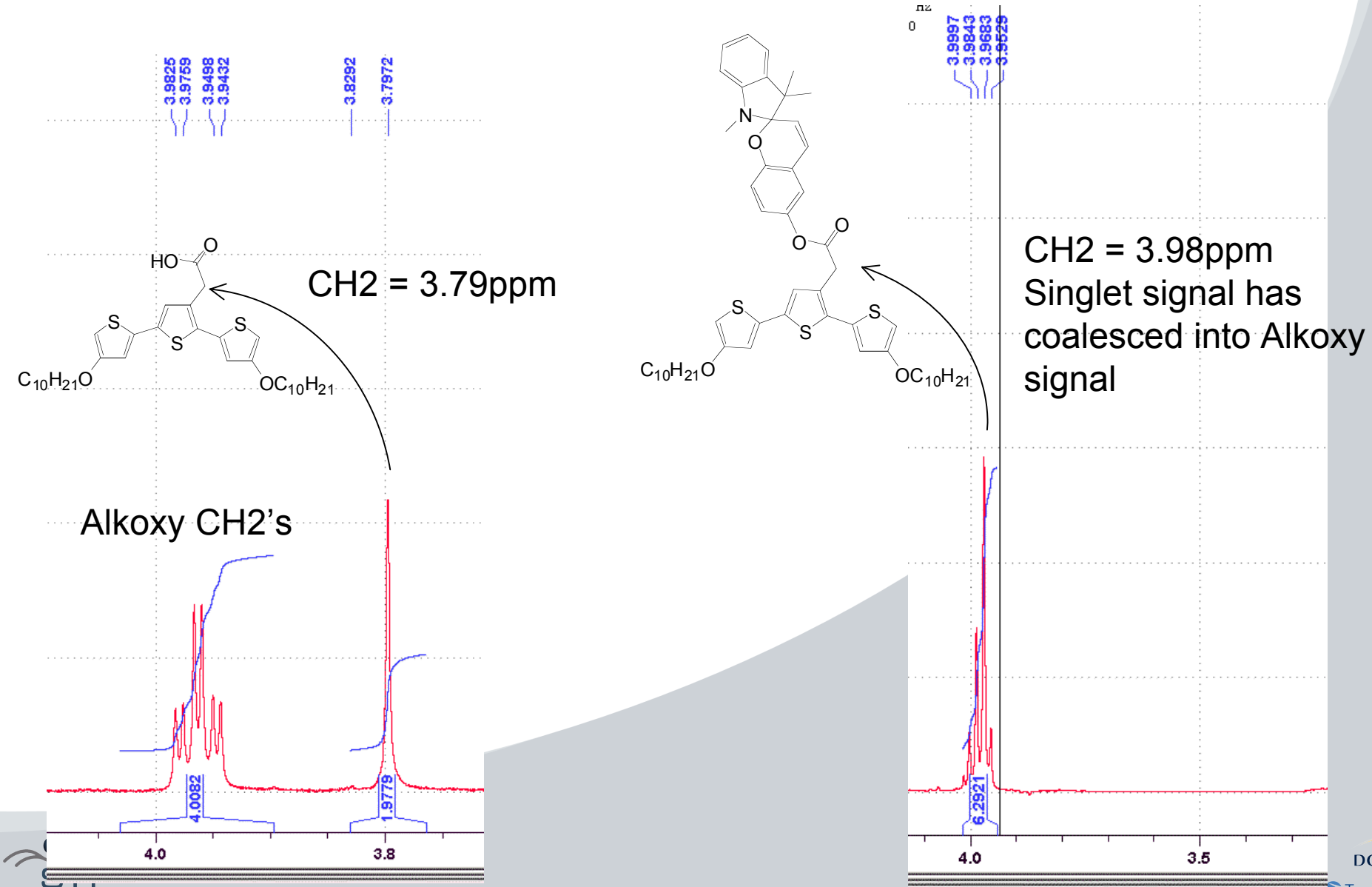
TTT-BSP2 ^{1}H-NMR



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Electro-polymerization on ITO

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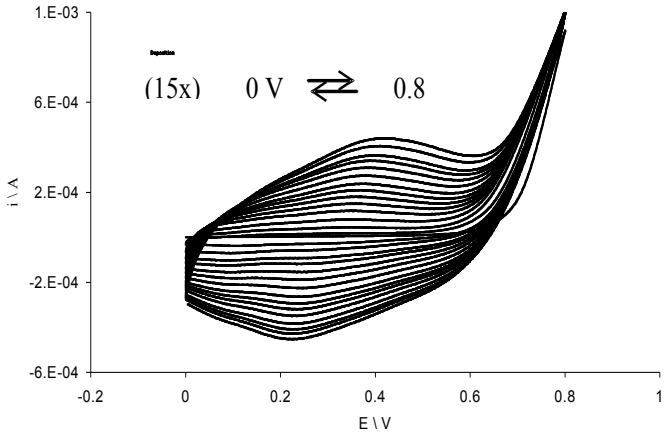
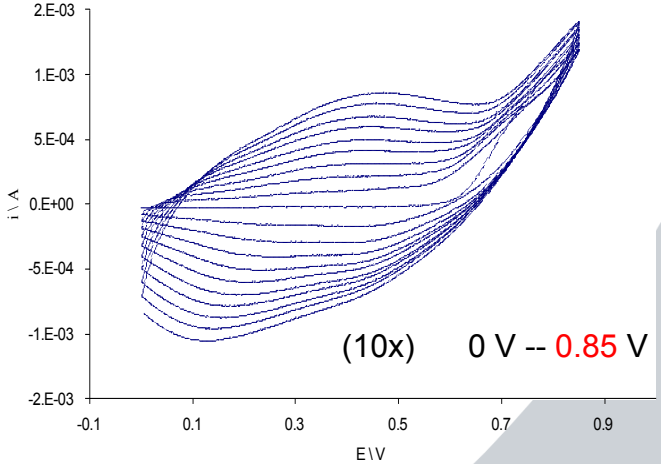
Conditions: 8 mM monomer in 0.1 M TBAP DCM : ACN (2 : 3)

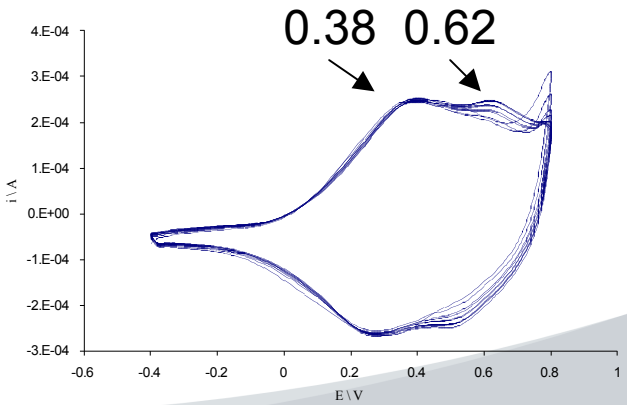
poly(TTT-BSP1)



poly(TTT-BSP2)

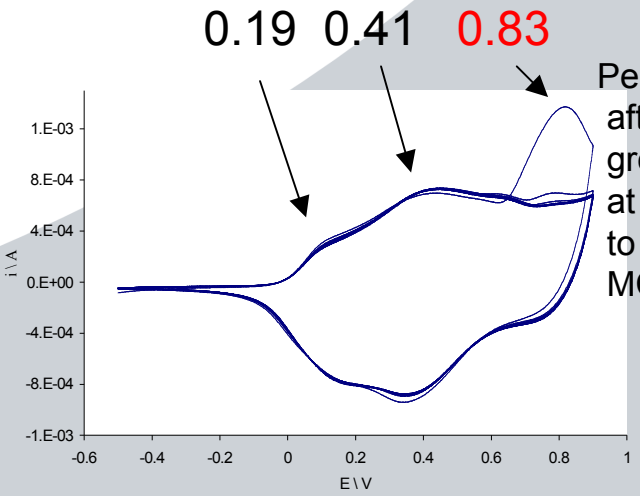


Post CV of the film deposited at 0.8 V, 40 s



(20x) -0.4 V-- 0.8 V

Post CV of the film deposited at 0.75 V, 20 seconds



Peak at 0.83 lost after 2 scans, and growth of peak at 0.71, believed to be protonation of MC isomer.

(10x) -0.5 V 0.9 V

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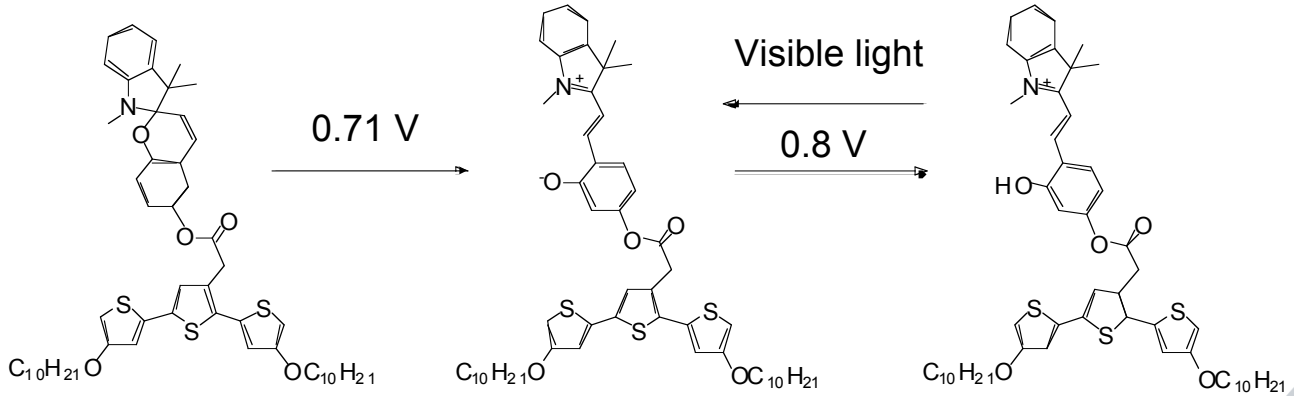
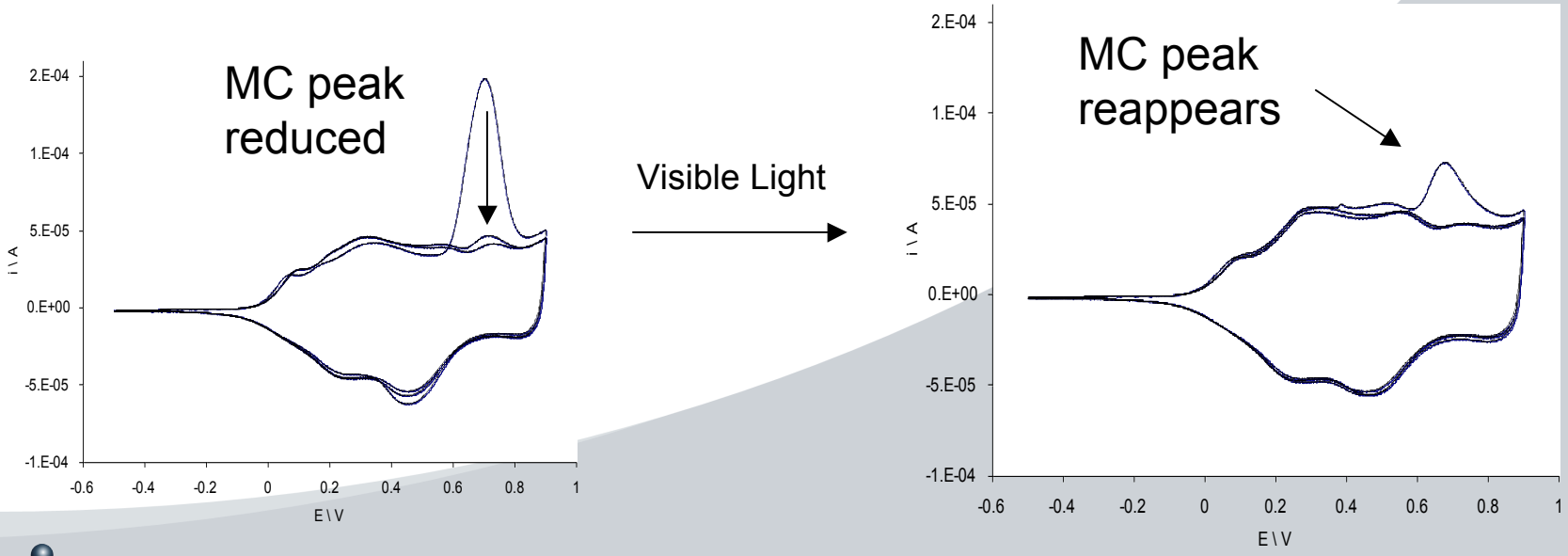
Photo-induced deprotonation of poly(TTT-BSP2)





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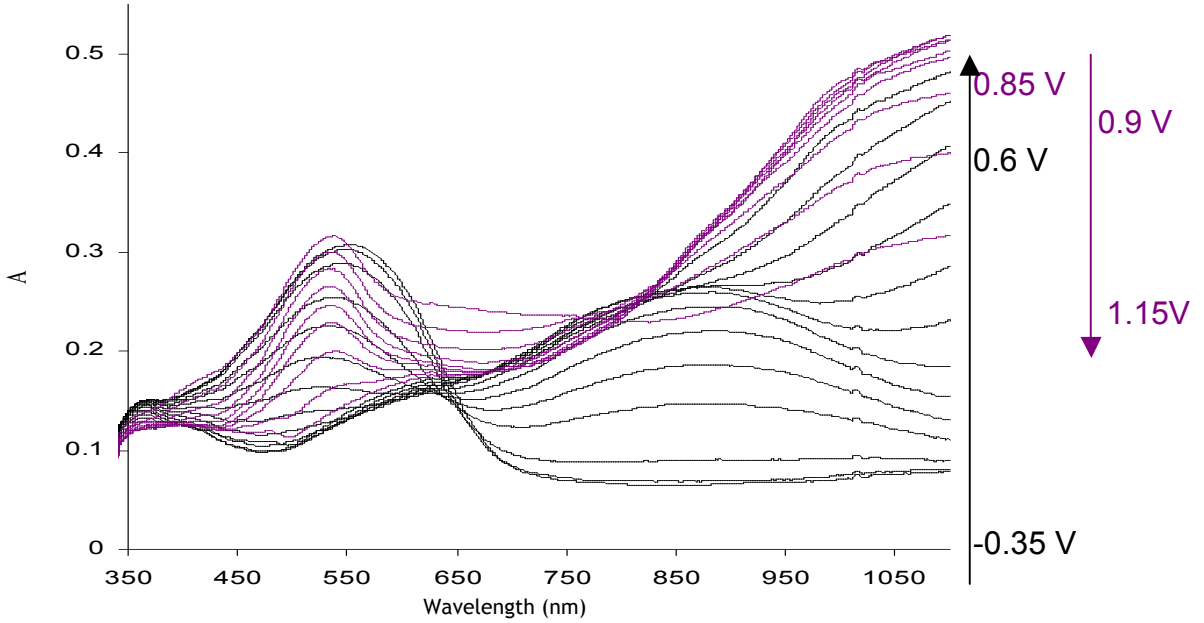
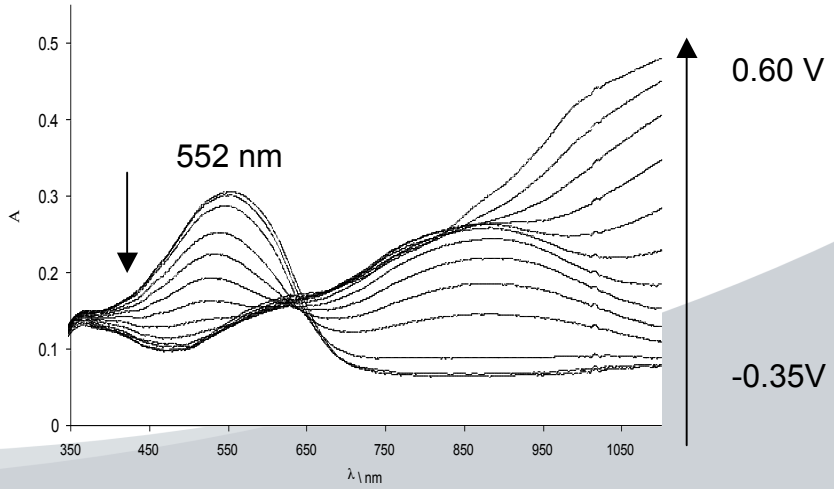
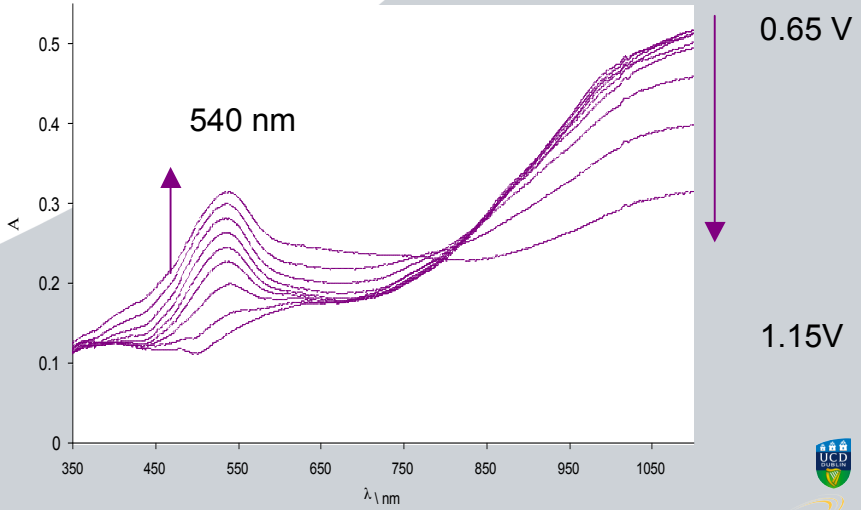
Spectrelectrochemistry poly(TTT-BSP1)



At 0.65V, the BSP ring starts to open to the MC isomer 540 nm





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Spectrelectrochemistry poly(TTT-BSP2)

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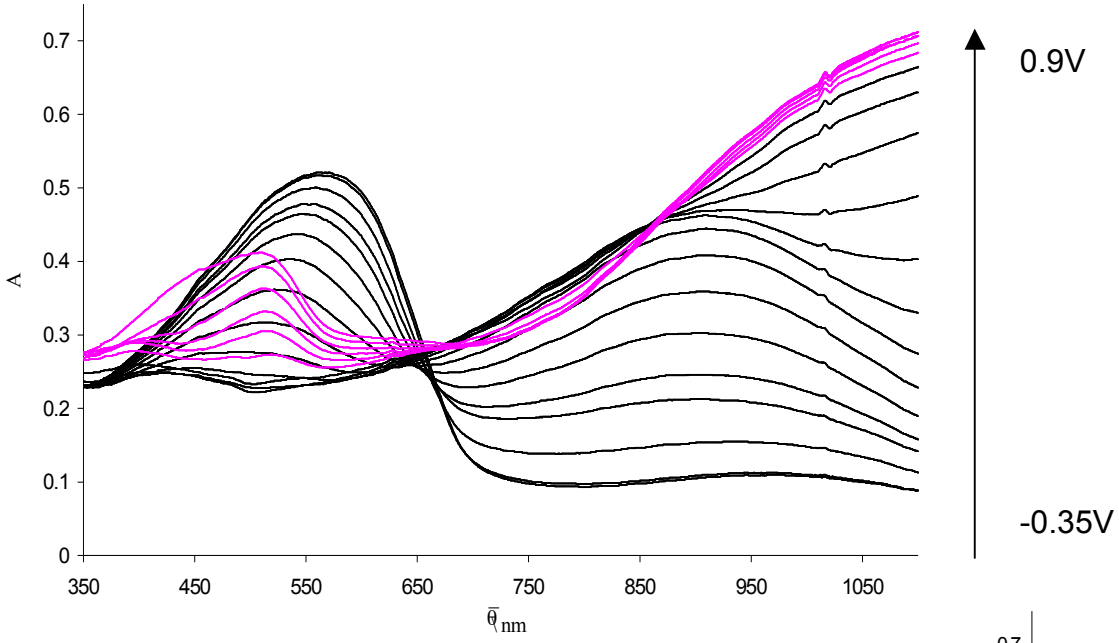
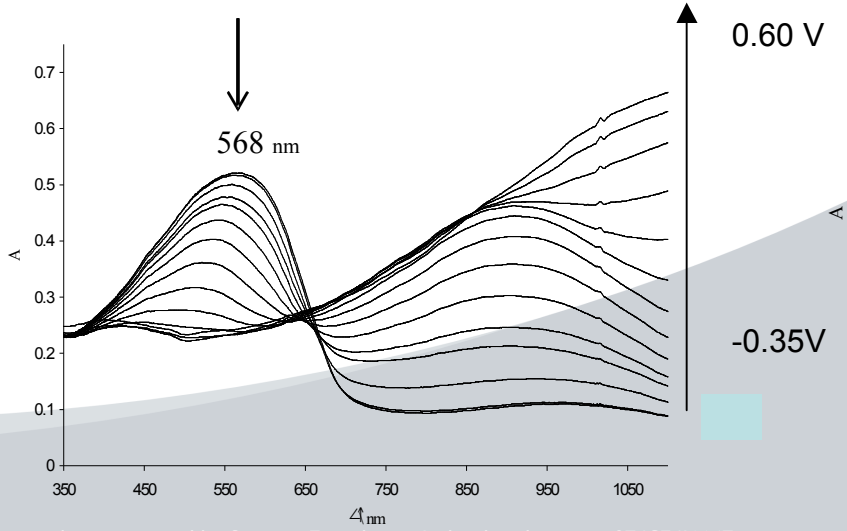
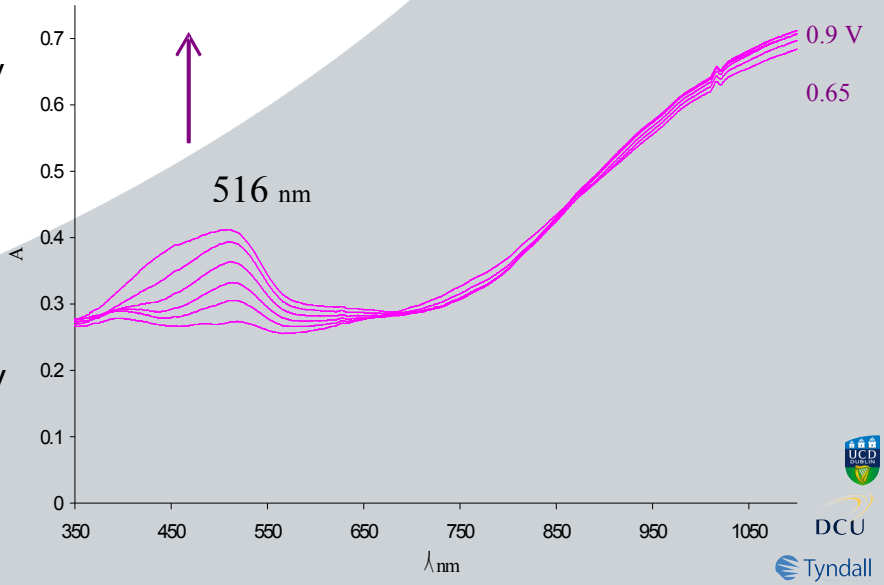


At 0.6V, the BSP ring starts to open to the MC isomer 516 nm





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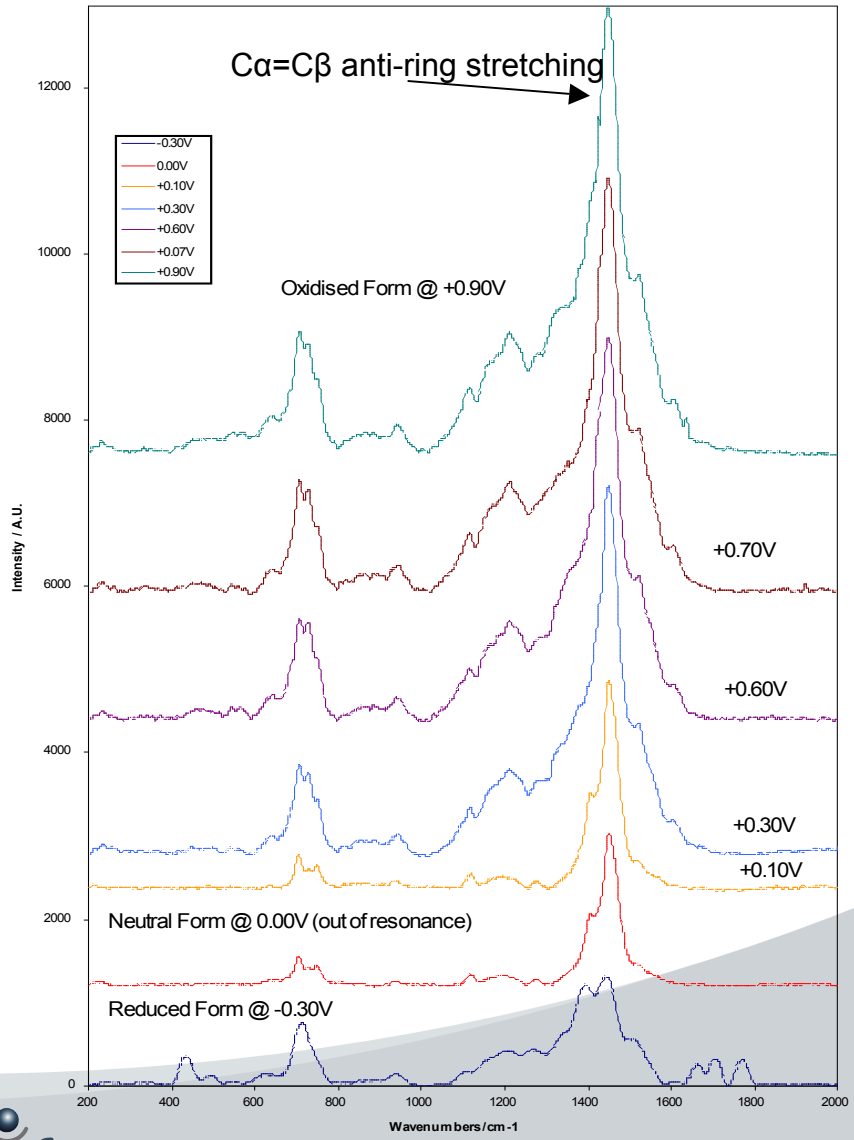
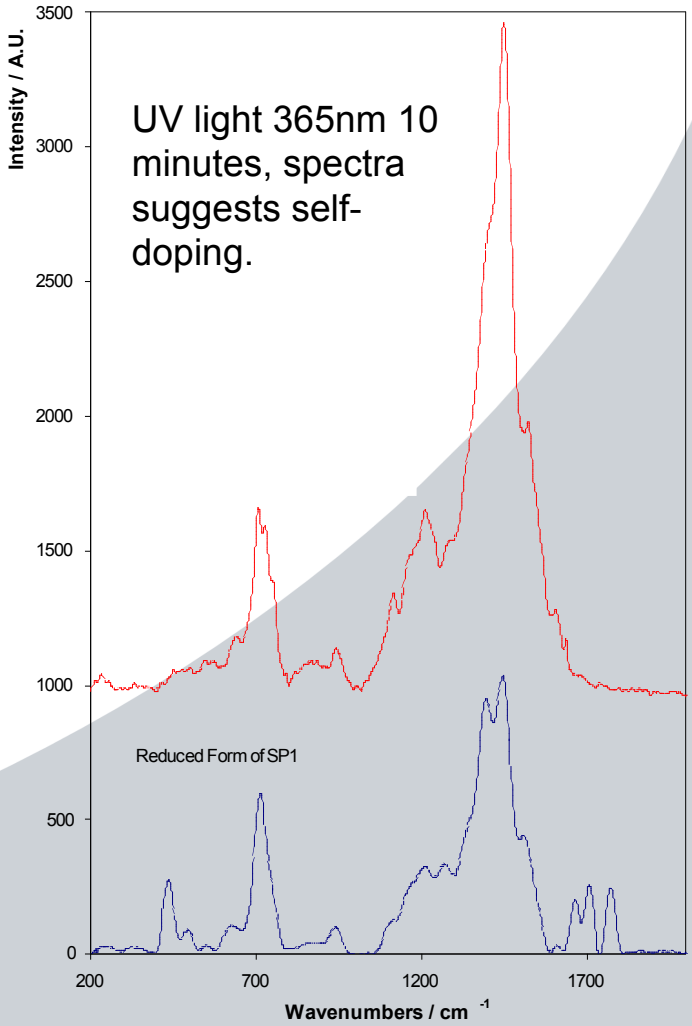
Raman Spectrelectrochemistry-TTT-BSP1





Raman excitation 638.21 nm

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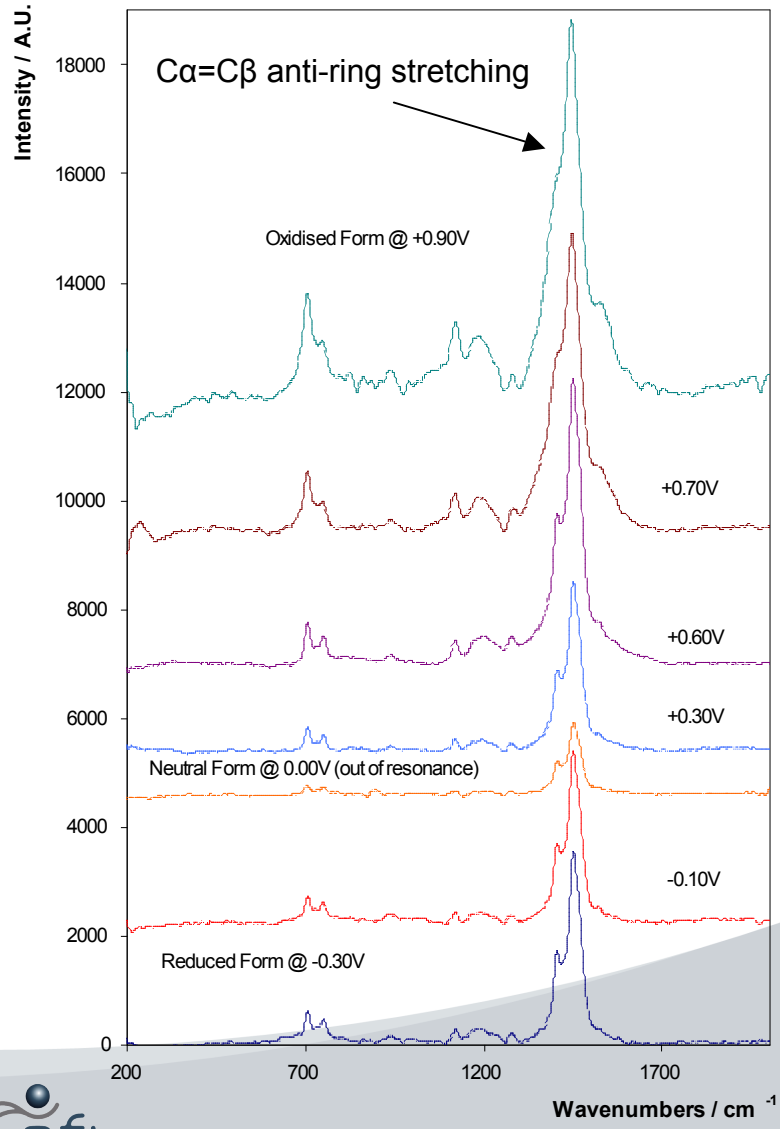
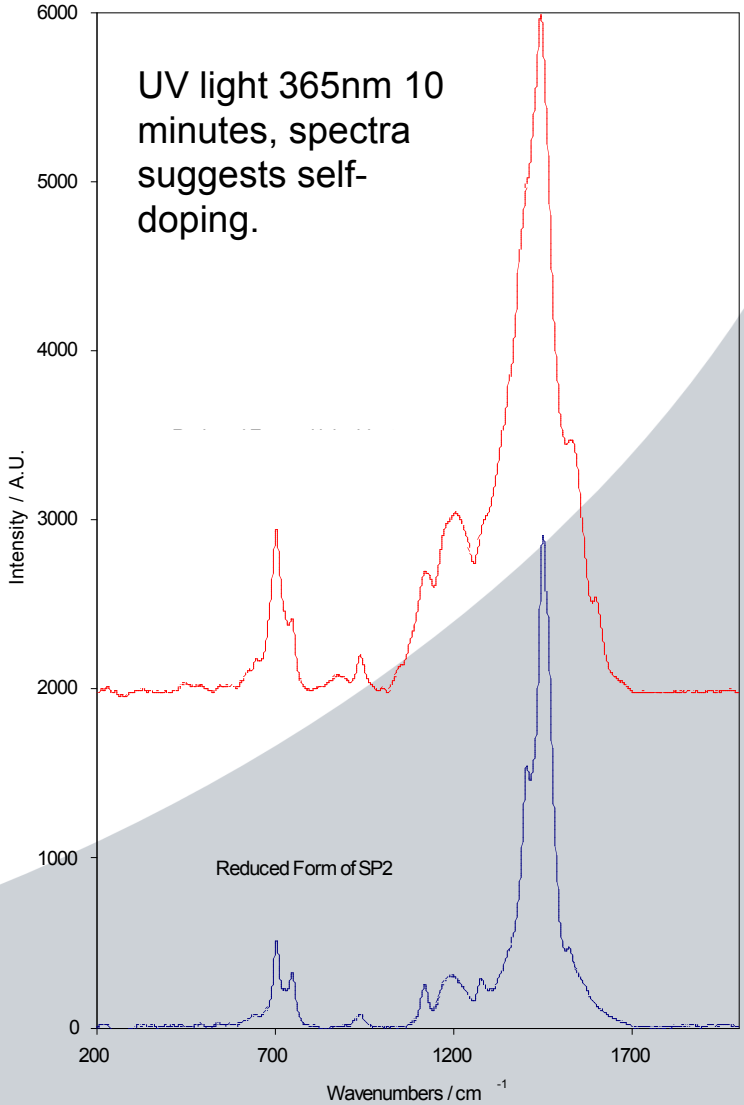
Raman Spectrelectrochemistry-TTT-BSP2





Raman excitation 638.21 nm

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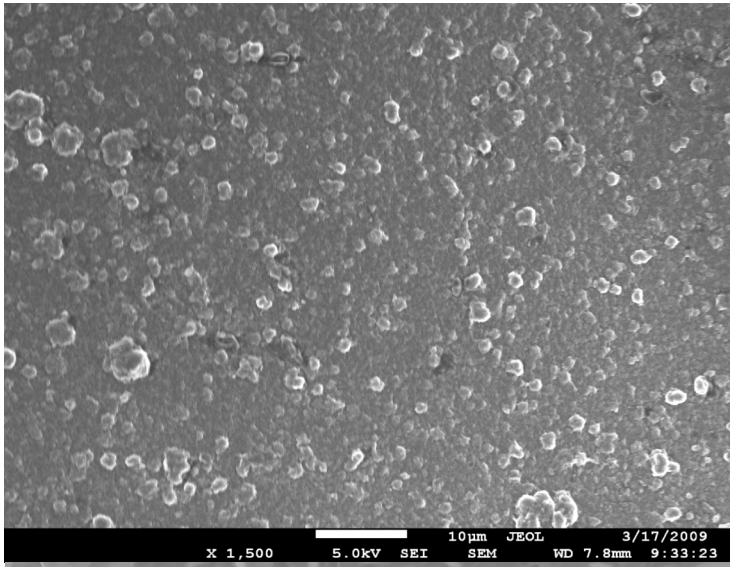
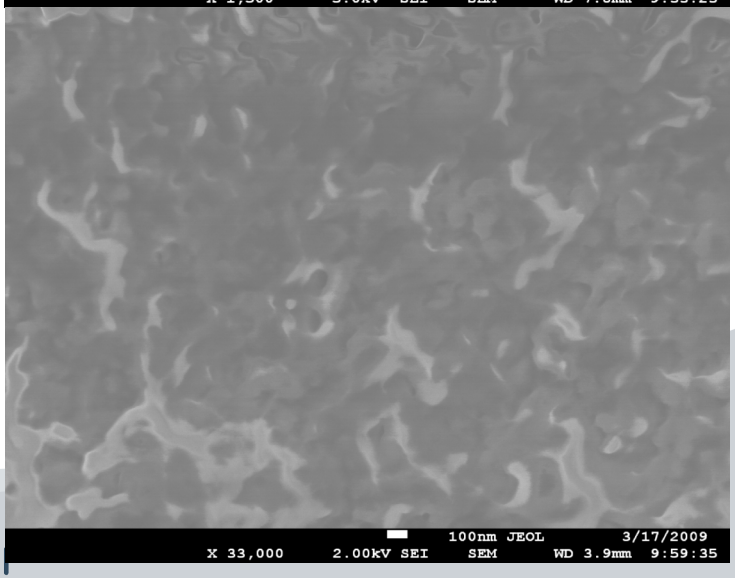
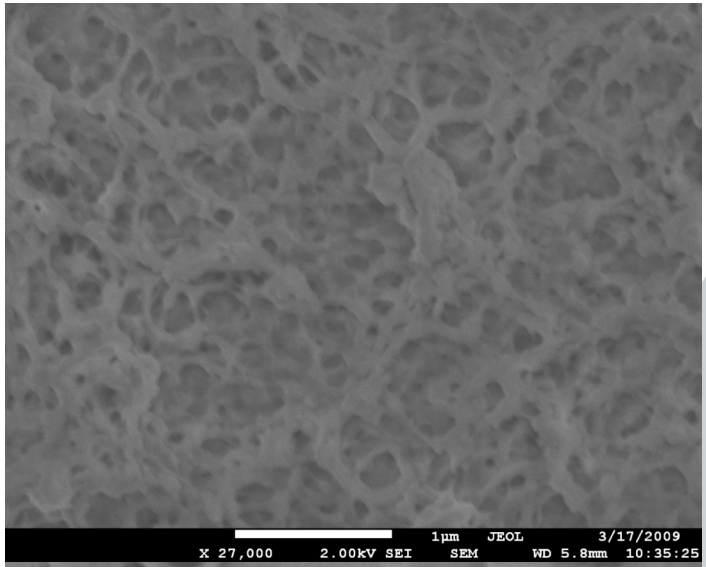
SEM images of TTT-BSP2

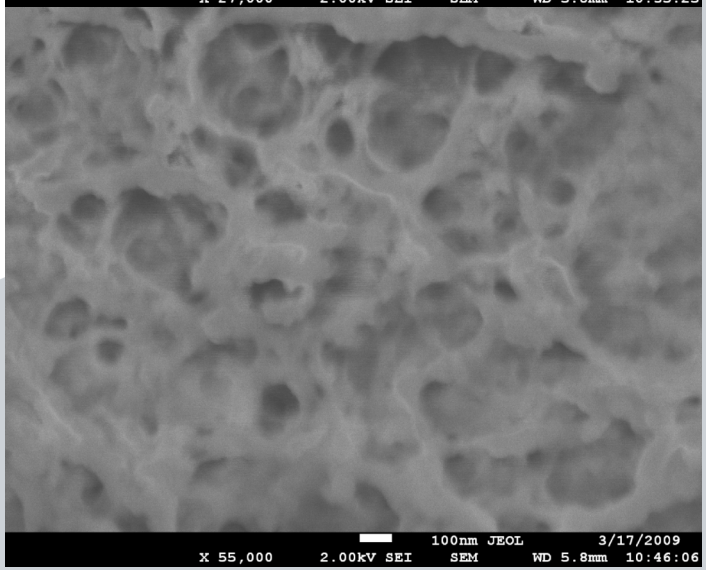
Reduced polymer-nodular features





Oxidised polymer- porous webbed structure





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AFM imaging poly(TTT-BSP2)

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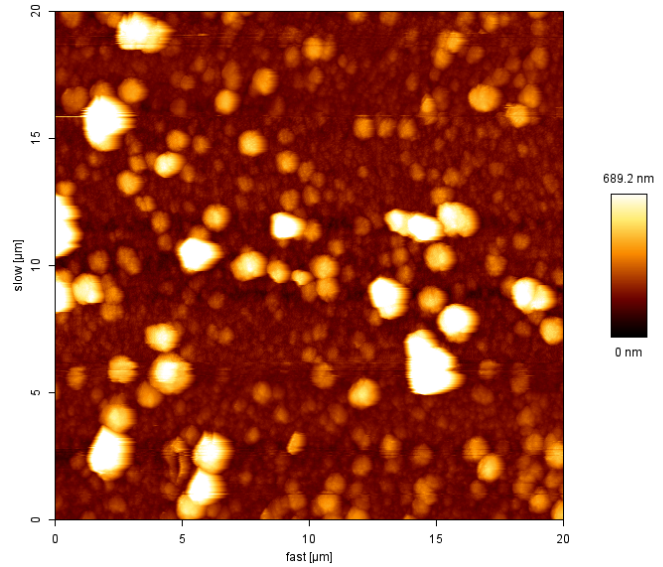
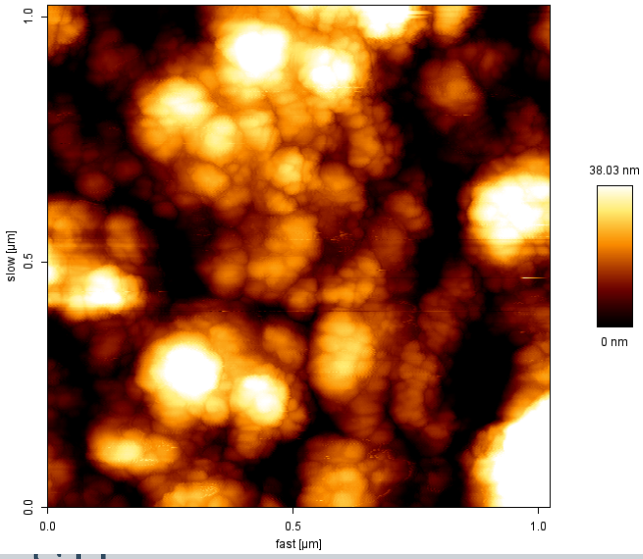
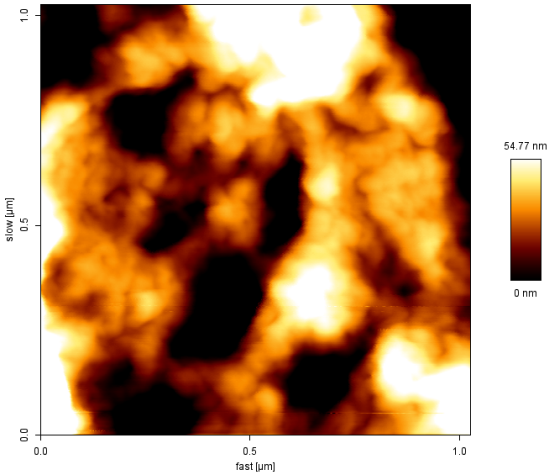
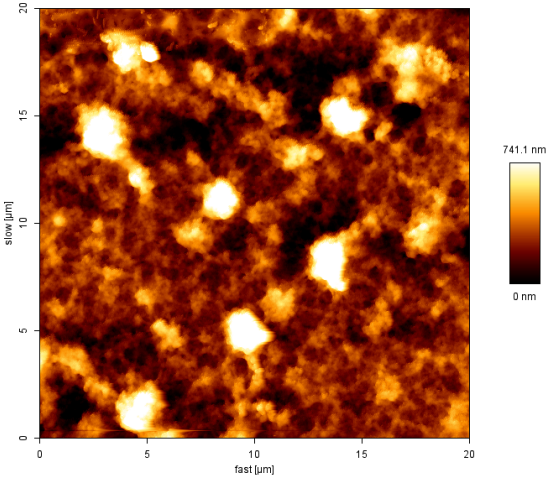
Reduced polymer-nodular structure

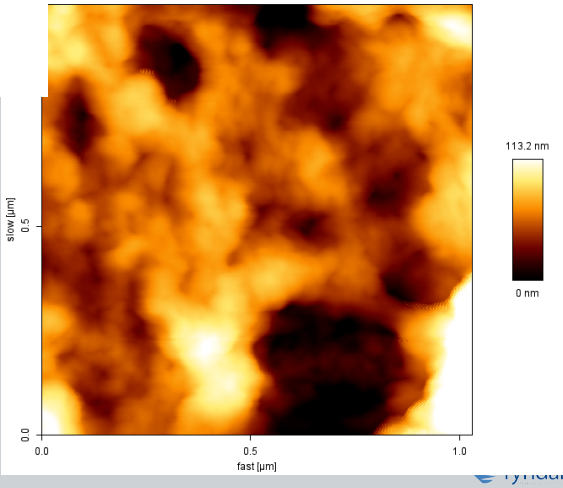




Oxidised polymer-Porous structure

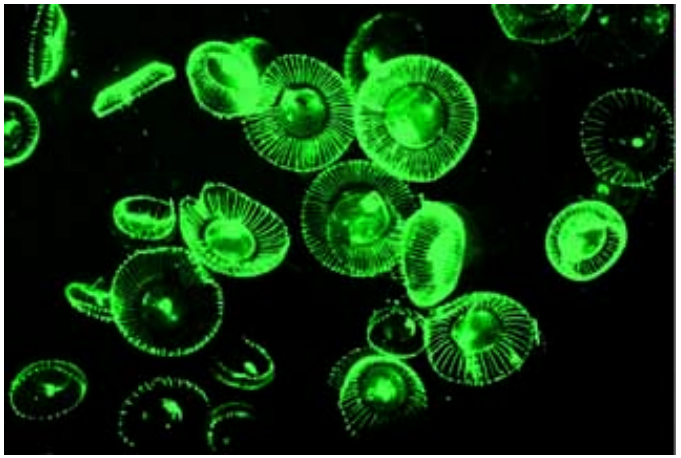


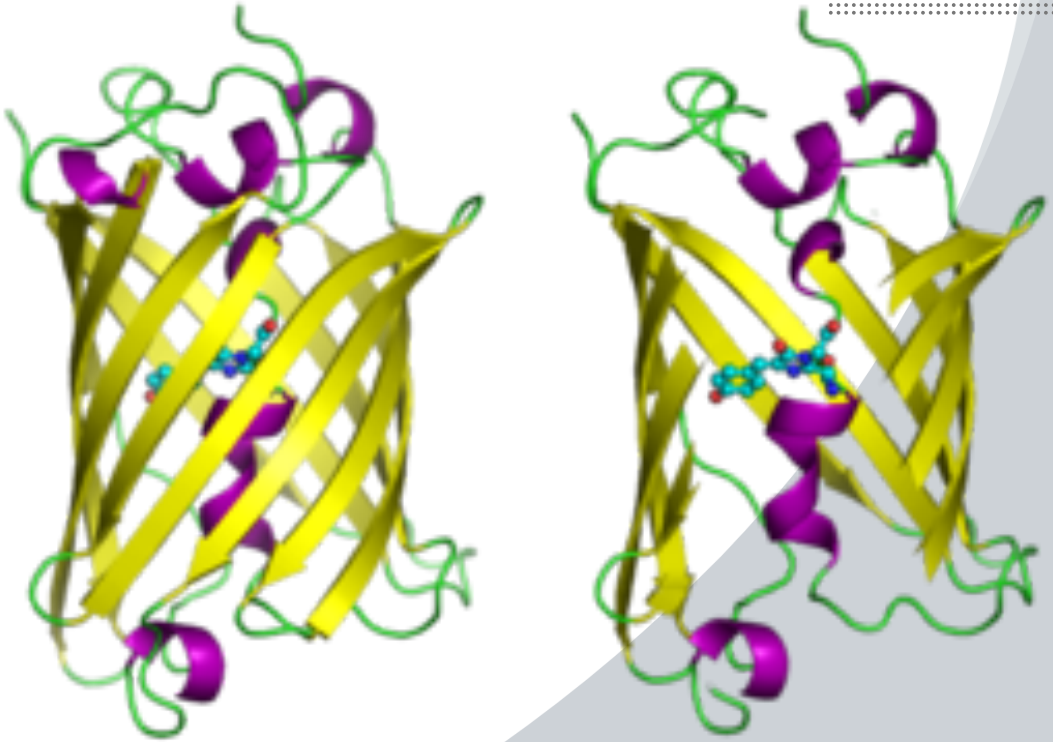




This work is supported by Science Foundation Ireland under grant 07/CE/I1147

Capture and release of glyco-protein GFP

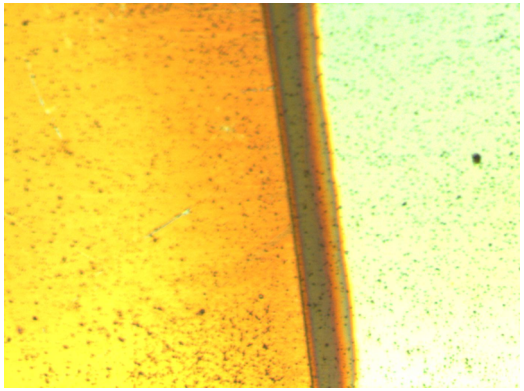




- The jellyfish species Aequorea contains the highly fluorescent glyco-protein GFP.
- GFP folds to protect its fluorescent inner core, this results in a non-polar interior and highly charged exterior.
- Perfect candidate for proof of concept due to proteins robustness and ease of detection.

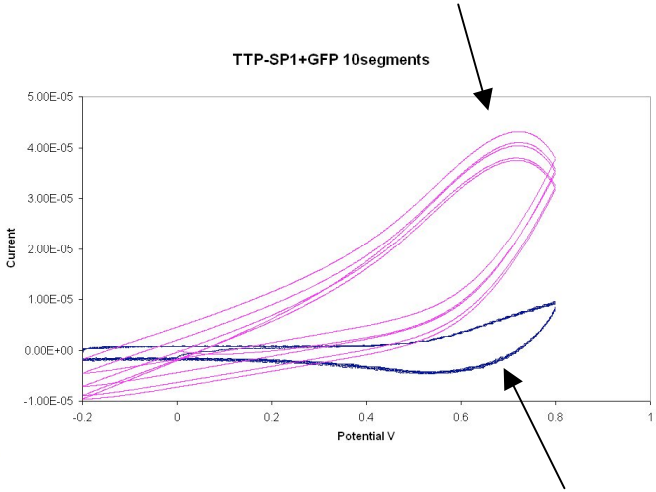
This work is supported by Science Foundation Ireland under grant 07/CE/I1147

Optical release of GFP with spatial control

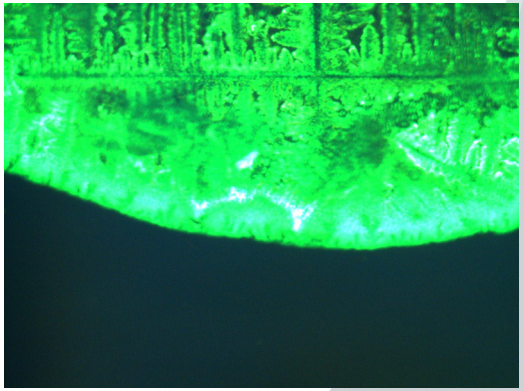


(1) poly(TTT-BSP1) on ITO

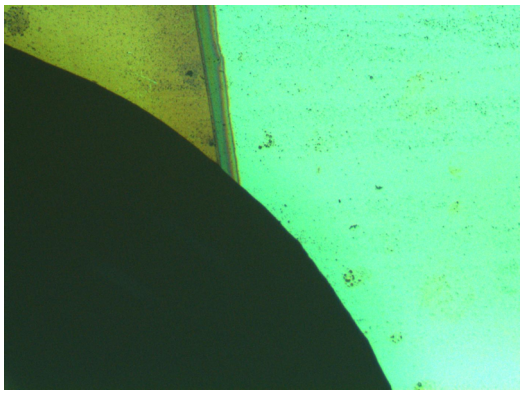
poly(TTT-BSP1) on ITO



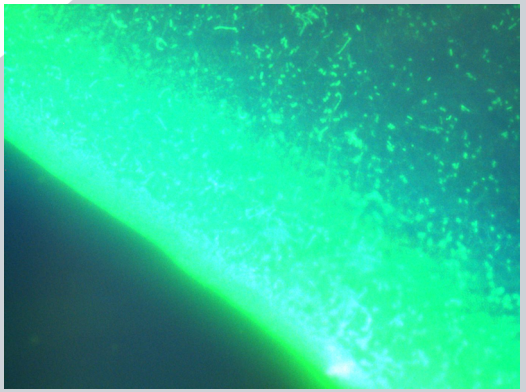
After addition of GFP to buffer



(3) Substrate washed with buffer and irradiated with 470 nm



(2) 0.8V + 1mg/ml of GFP 10mins
Photo mask placed in front of ITO substrate, irradiation of 550nm for 10 minutes



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Conclusions

- Synthesis of new photo and electrochromic terthiophene polymers
- UV-vis and Raman analysis of electrochemical switching
- Polymer morphology changes drastically upon photo and/or electric stimuli
- Initial experiments show capture/release functionality

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

Acknowledgements

- Science Foundation Ireland
- Dermot Diamond
- David Officer and Gordon Wallace
- Klaudia, Lynn, Michael, and Sanjeev

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