

Physico – Chemical Properties of New Stimuli Responsive Molecular Switches

**Michele Zanoni,
PhD Candidate,
CLARITY, NCSR, Dublin City University**

“Considerate la vostra semenza: fatti non foste per viver come bruti, ma per 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

- Stimuli Responsive Materials.
- Synthesis of the Hybrid Molecule.
- Electrochemical Features.
- Properties of the Surface.
- Possible applications.
- Conclusion.

OUTLINE

Stimuli Responsive
Materials

Spiropyran

Hybrid Molecule

Current
Applications

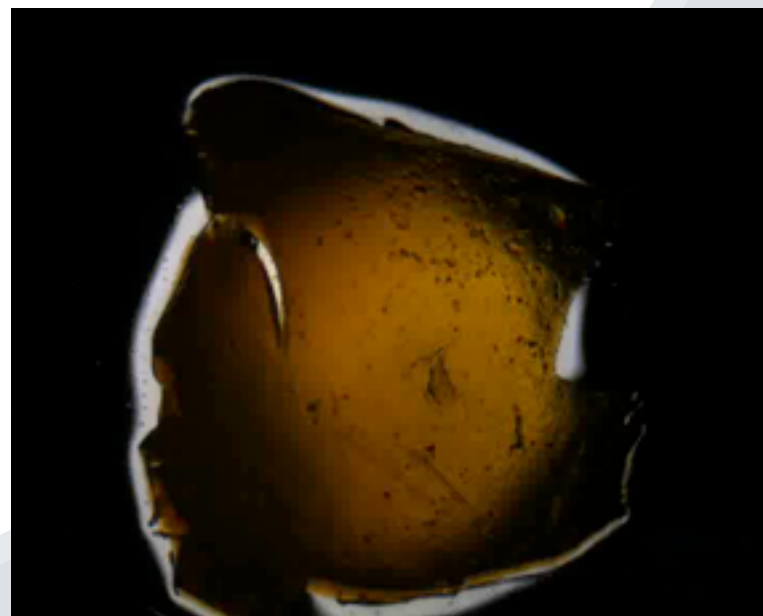
Conclusion

Stimuli – Responsive Materials

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

HOW 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

Outline

STIMULI RESPONSIVE
MATERIALS

Spiropyran

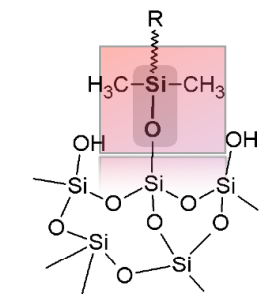
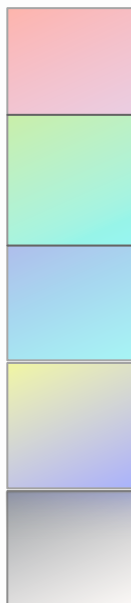
Hybrid Molecule

Current
Applications

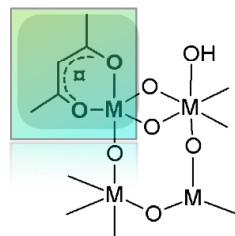
Conclusions.

Types of linkage in Common Hybrid Structures

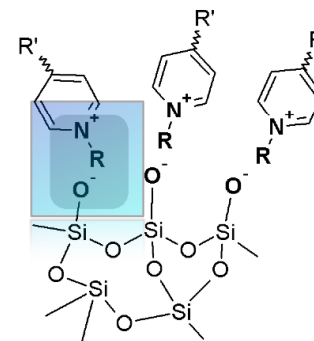
Increasing
Strength of
Interaction



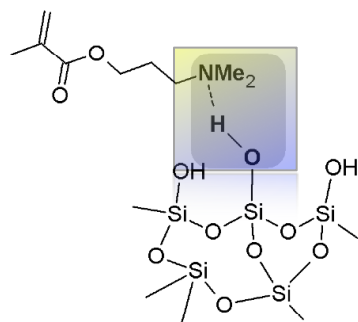
Covalent



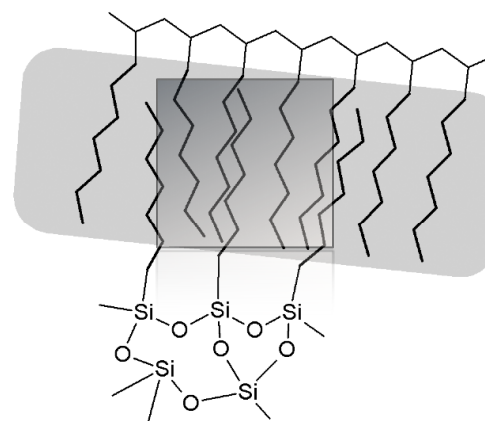
Coordinative



Ionic



H-bonding



Van-der-Waals

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

Outline

STIMULI RESPONSIVE
MATERIALS

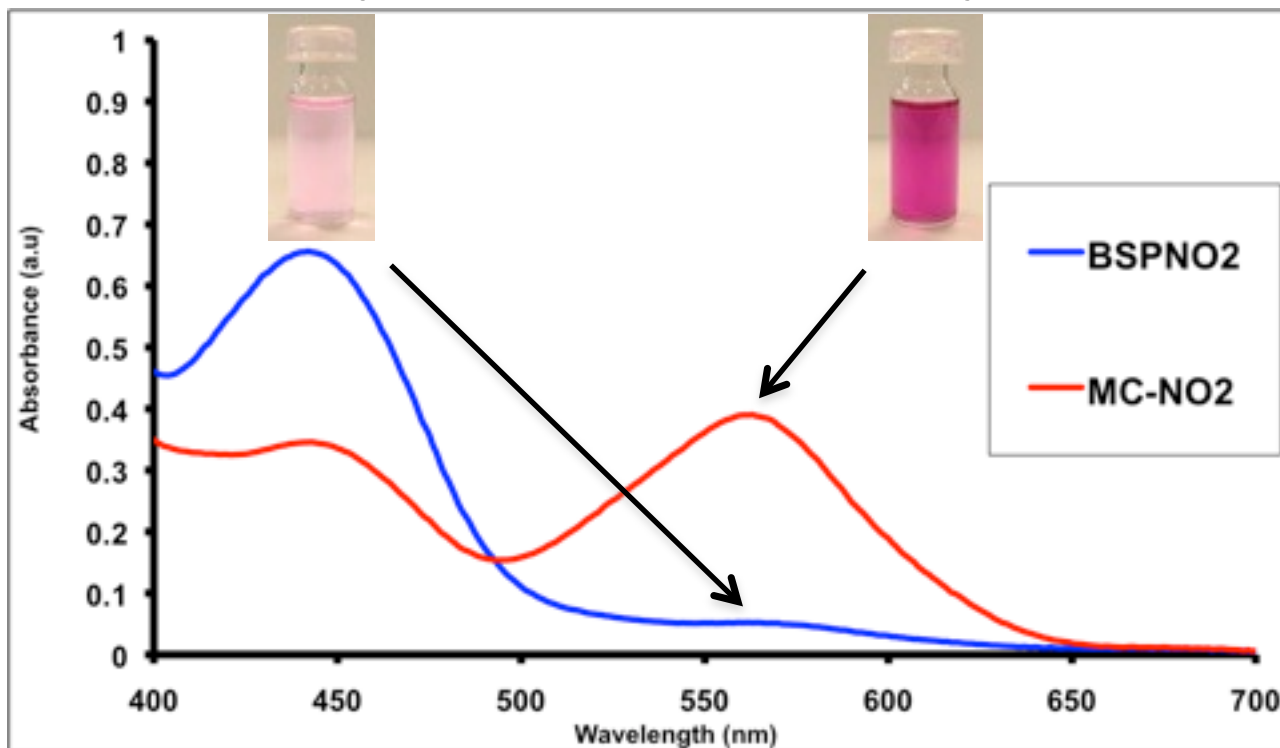
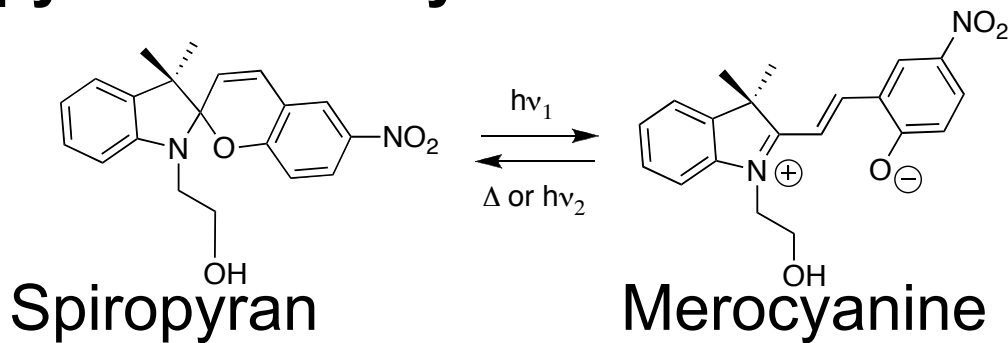
Spiropyran

Hybrid Molecule

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Spiropyran – Merocyanine 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

Outline

Stimuli Responsive
Materials

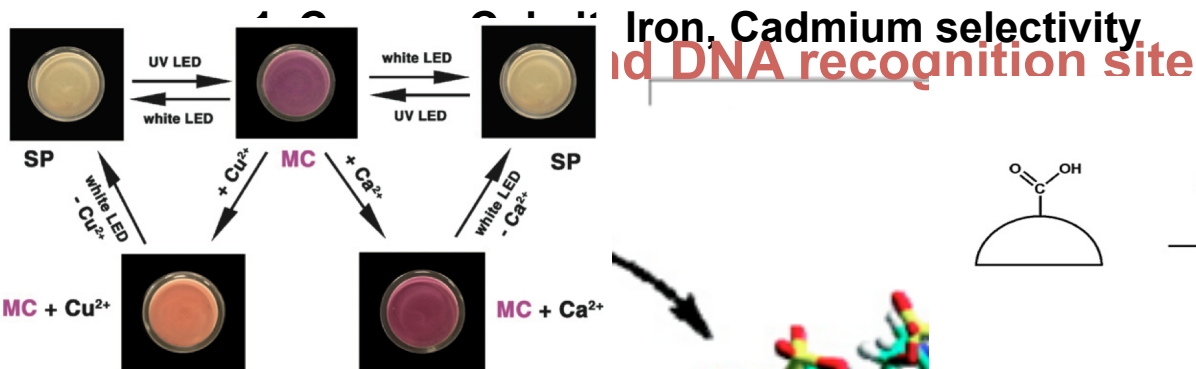
SPIROPYRAN

Hybrid Molecule

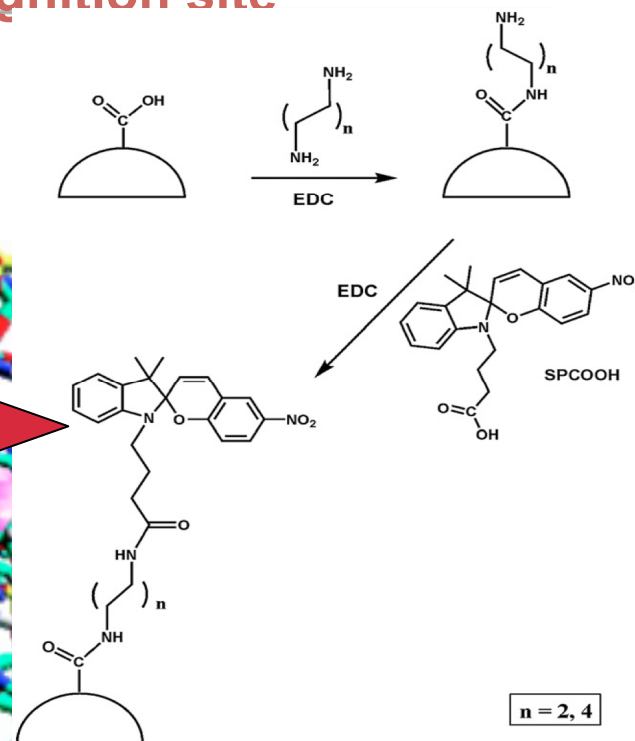
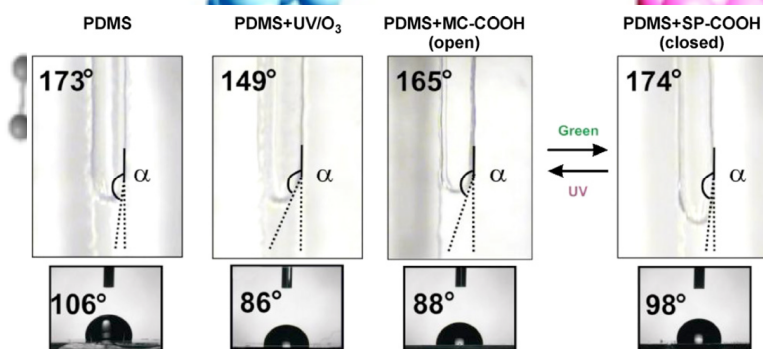
Current
Applications

Conclusions.

Complex Applications



1. Microbeads Systems for optical sensing



2. Functionalisation of Micro-Channels for Micro-Fluidic devices

- [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
 J. Andersson, S. Li, P. Lincoln, and J. Andreasson, *J. Am. Chem. Soc.*, **2008**, 130 (36), 11836-11837.

Outline

Stimuli Responsive
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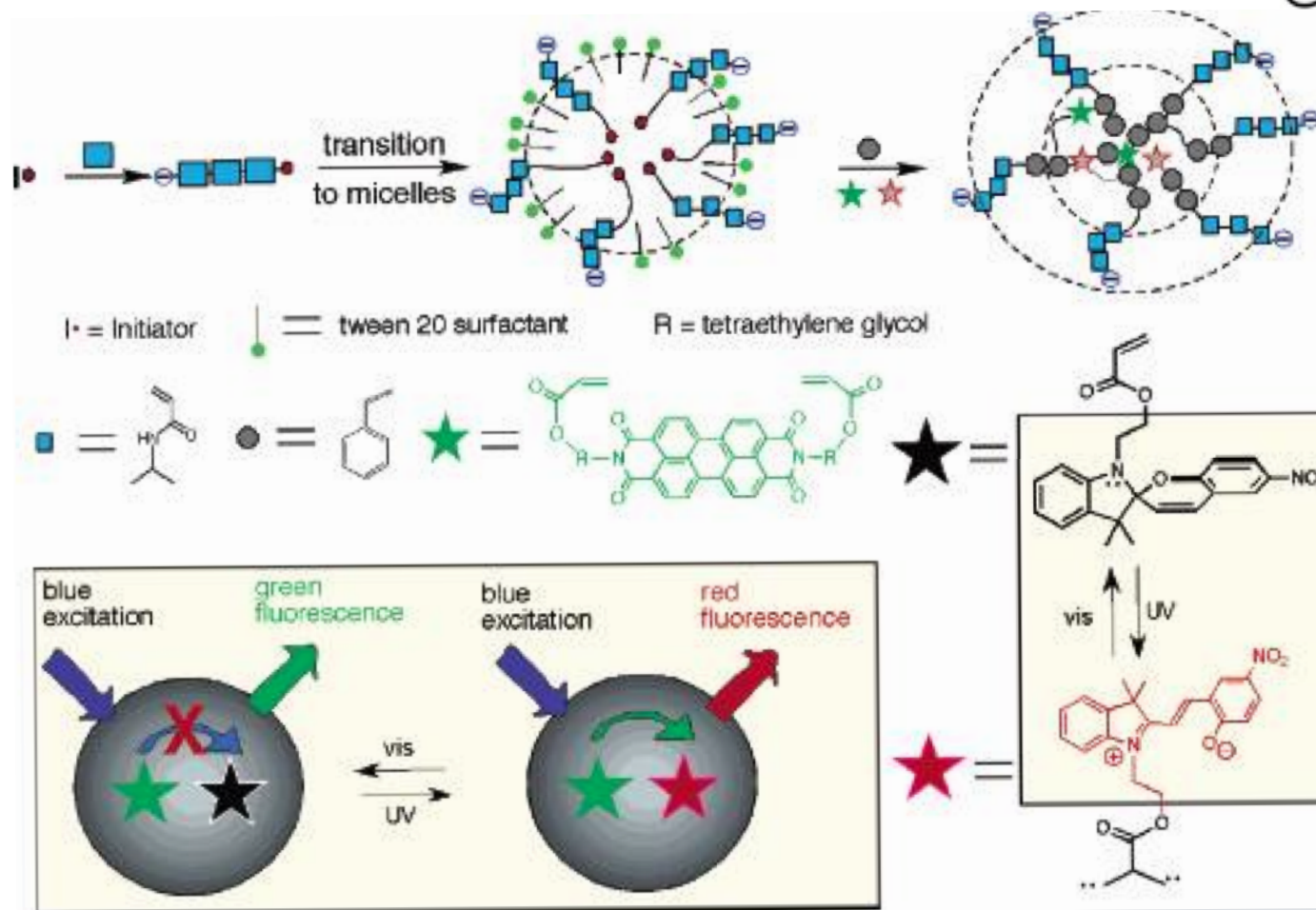
SPIROPYRAN

Hybrid Molecule

Current
Applications

Conclusions.

2. Photoswitchable nanoparticles for cell imaging.



[1] Z. Tian, W. Wu, W. Wan, and A. D. Q. Li, *J. Am. Chem. Soc.*, **2009**, 131, 4245–4252.

[2] L. Zhu, W. Wu, M.-Q. Zhu, J.J. Han, J.K. Hurst, and A.D. Q. Li, *J. Am. Chem. Soc.*, **2007**, 129, 3524-3526.

Outline

Stimuli Responsive
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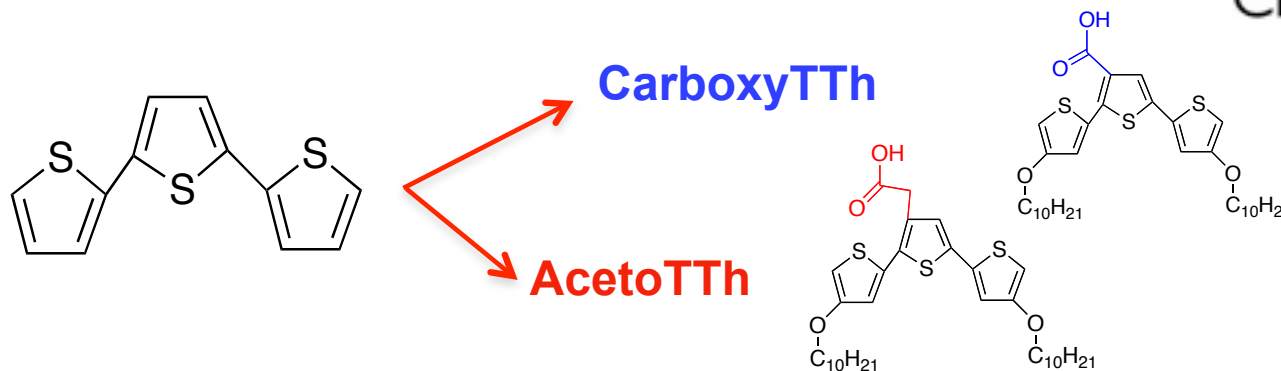
SPIROPYRAN

Hybrid Molecule

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Conclusions.

Terthiophene: the selected backbone.



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

[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.

Outline

Stimuli Responsive
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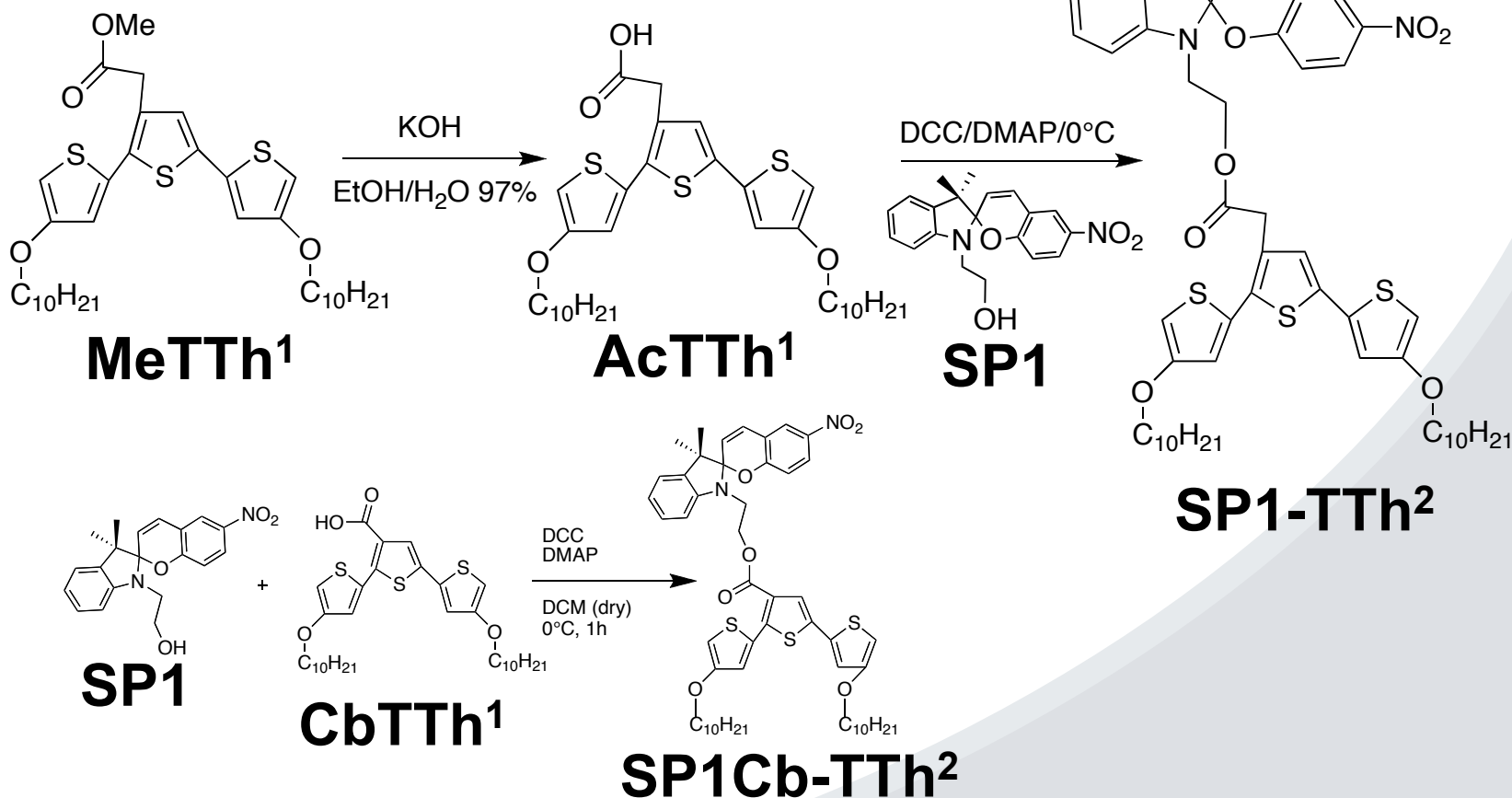
Spiropyran

HYBRID MOLECULE

Current
Applications

Conclusions.

Synthesis of the Monomers



[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

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Stimuli Responsive
Materials

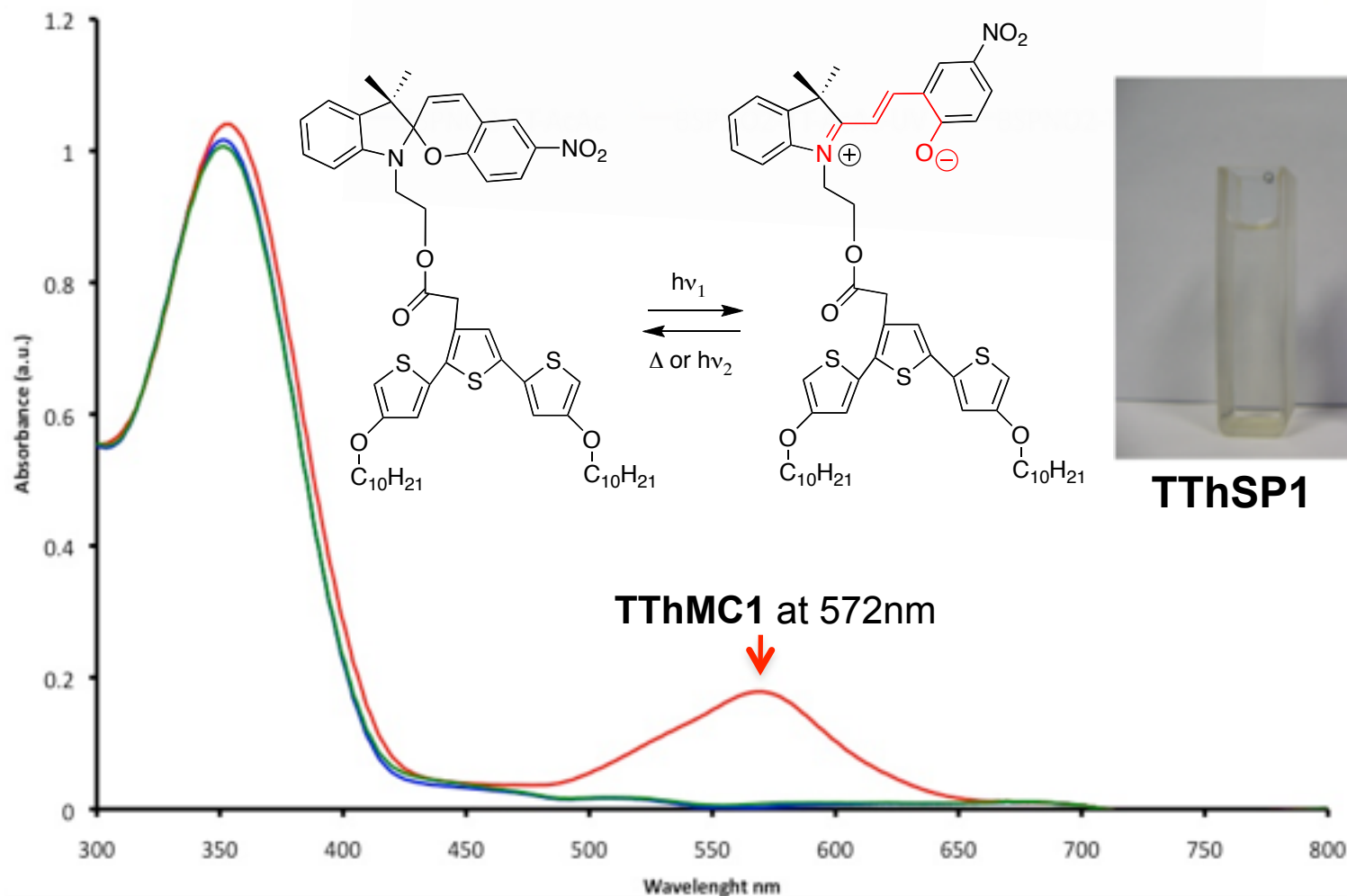
Spiropyran

HYBRID MOLECULE

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Dual control molecule: Photochemistry



TThSP1

TThMC1

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

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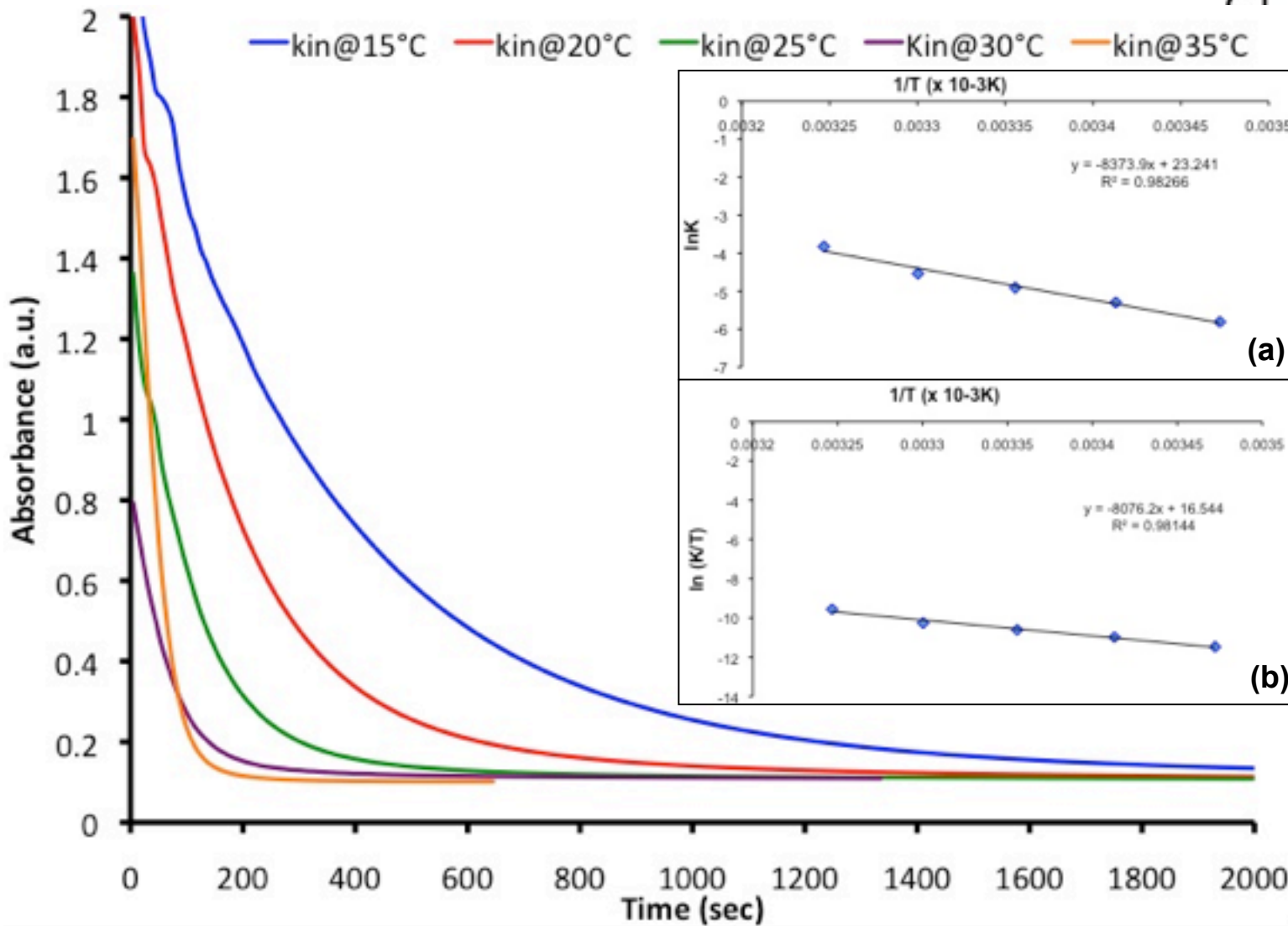
Spiropyran

HYBRID MOLECULE

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Thermochromic Relaxation of TThSP1



Outline

Stimuli Responsive
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Spiropyran

HYBRID MOLECULE

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Variation of Entropy of the Transition State

	BSPNO ₂	BSPNO ₂ acTTh	BSPNO ₂ cbTTh
Average ΔS^\ddagger (J*K ⁻¹ mol ⁻¹)	-66.71	-101.27	-80.20
STD error ΔS^\ddagger	0.7875	0.5644	0.577

- [1] R. Byrne, S. Coleman, K.J. Fraser, A. Raduta, D.R. MacFarlane and D. Diamond, *Phys.Chem.Chem.Phys.*, **2009**, 11, 7286–7291.
 [2] Goerner H., *Phys.Chem.Chem.Phys.*, **2001**, 3, 416-423.

Outline

Stimuli Responsive
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Spiropyran

HYBRID MOLECULE

Current
Applications

Conclusions.

SOLVATOCHROMIC EFFECTS



DCM
583nm



EtOH
552nm



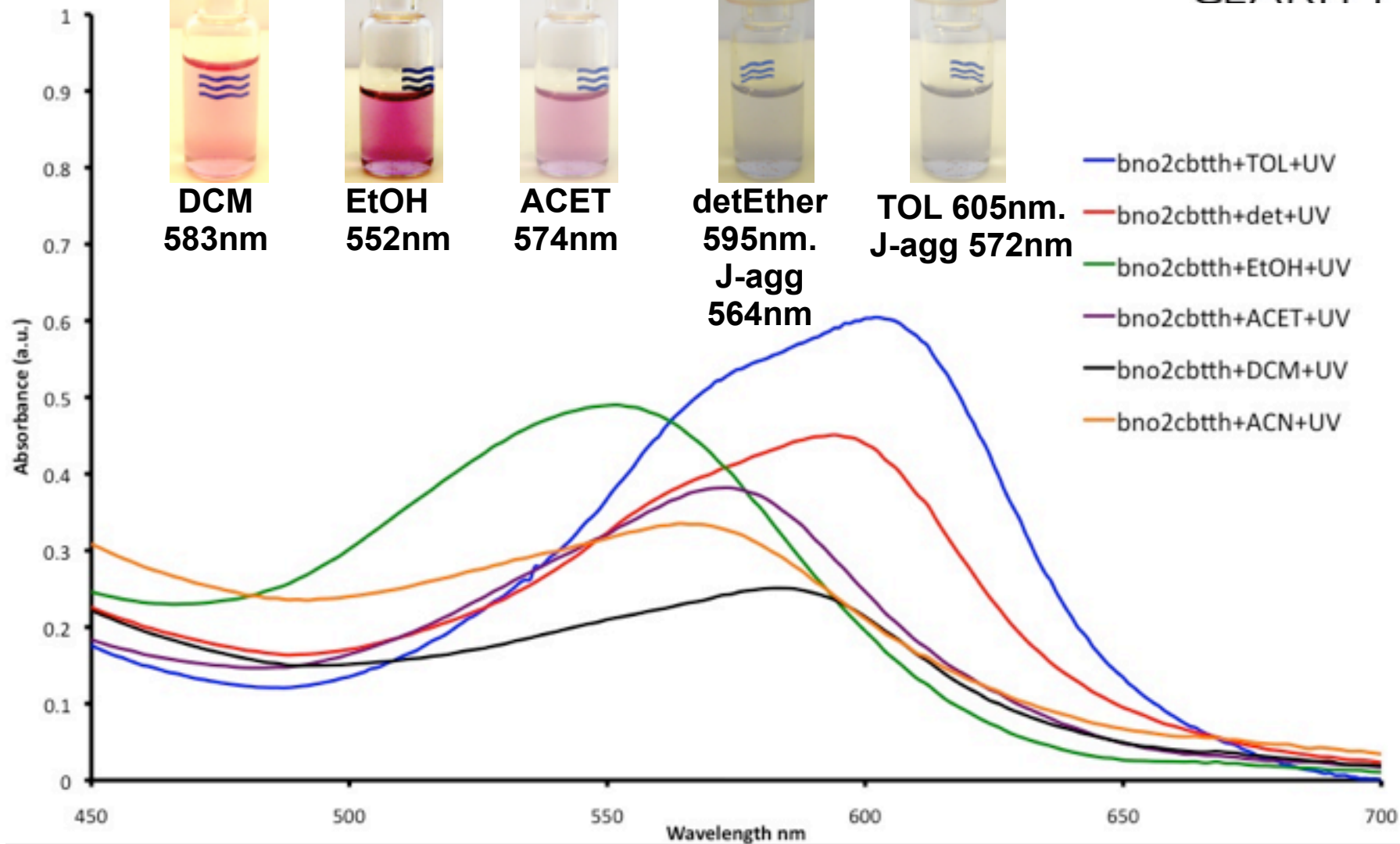
ACET
574nm



detEther
595nm.
J-agg
564nm



TOL 605nm.
J-agg 572nm



Outline

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Spiropyran

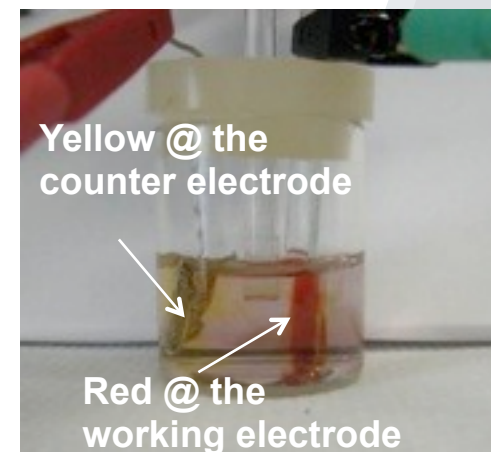
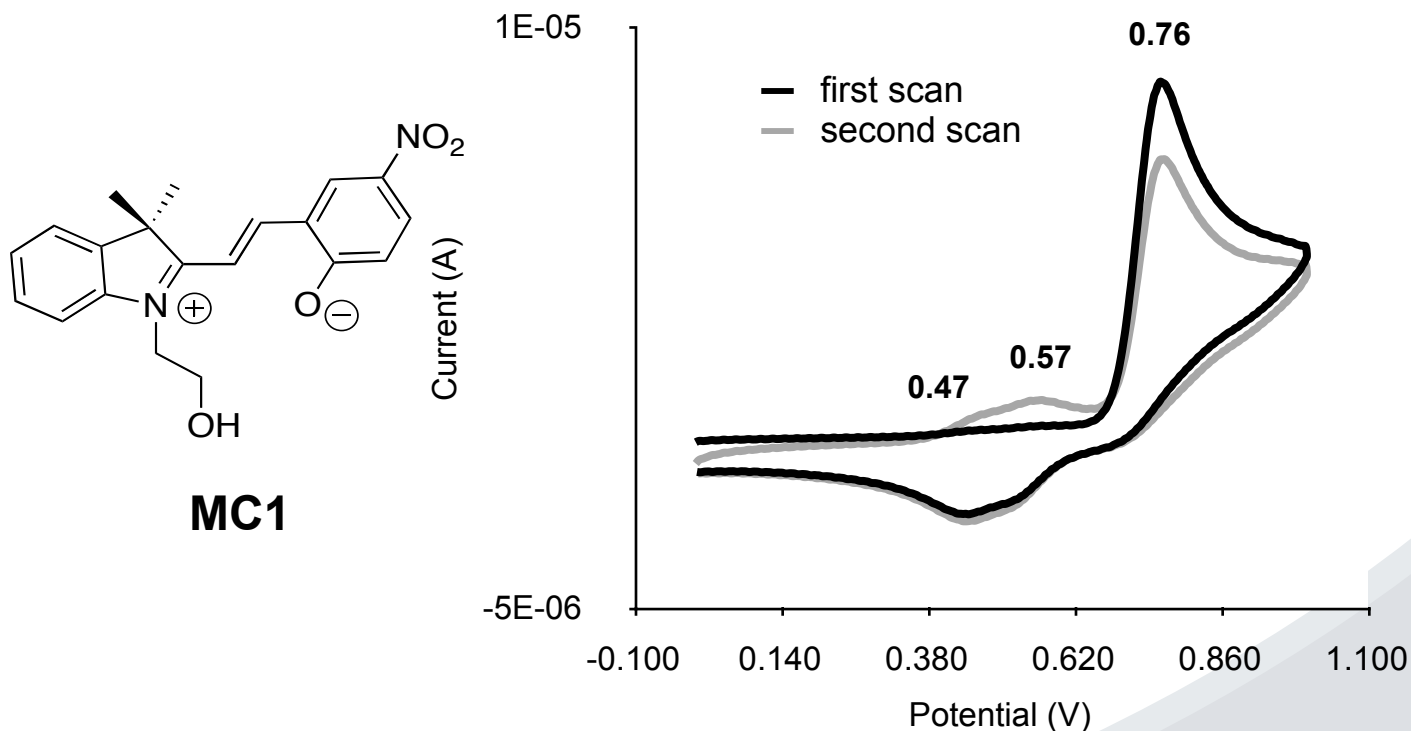
HYBRID MOLECULE

Current
Applications

Conclusions.

New Fascinating properties: Electrochemistry

a) Electrochemistry of $SP1 \rightleftharpoons MC1$



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

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Stimuli Responsive
Materials

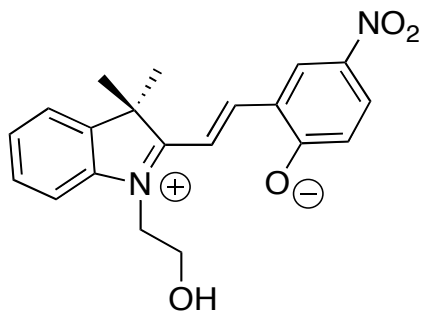
Spiropyran

HYBRID MOLECULE

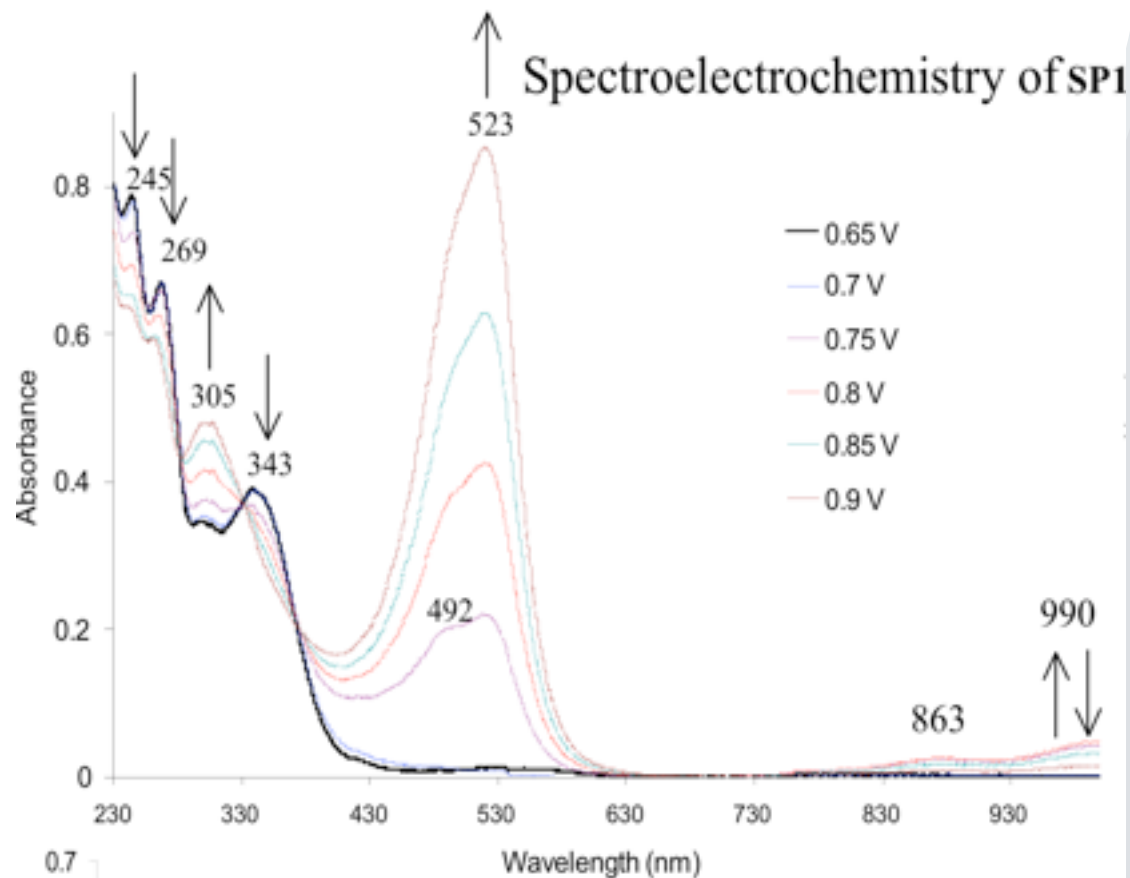
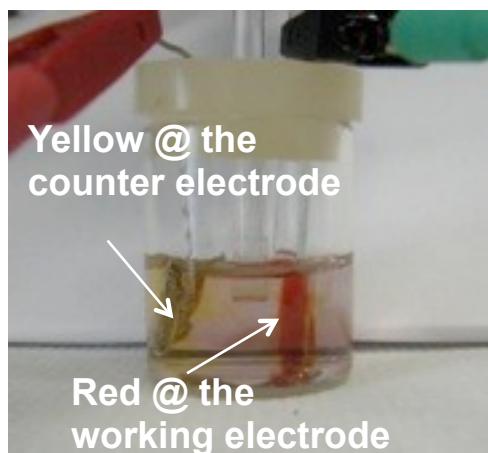
Current
Applications

Conclusions.

a) Electrochemistry of **SP1** ⇌ **MC1**



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

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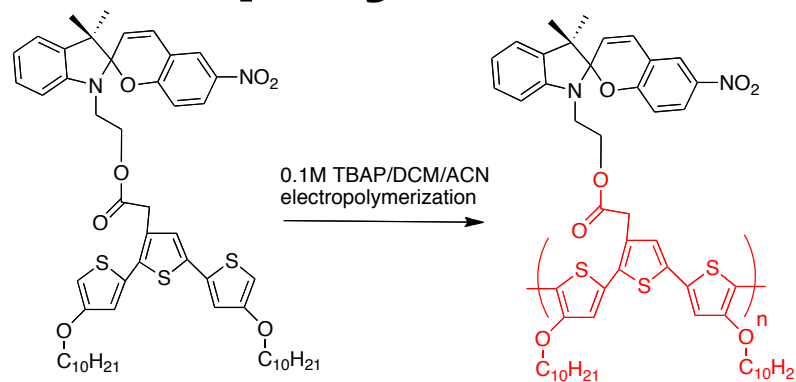
Spiropyran

HYBRID MOLECULE

Current
Applications

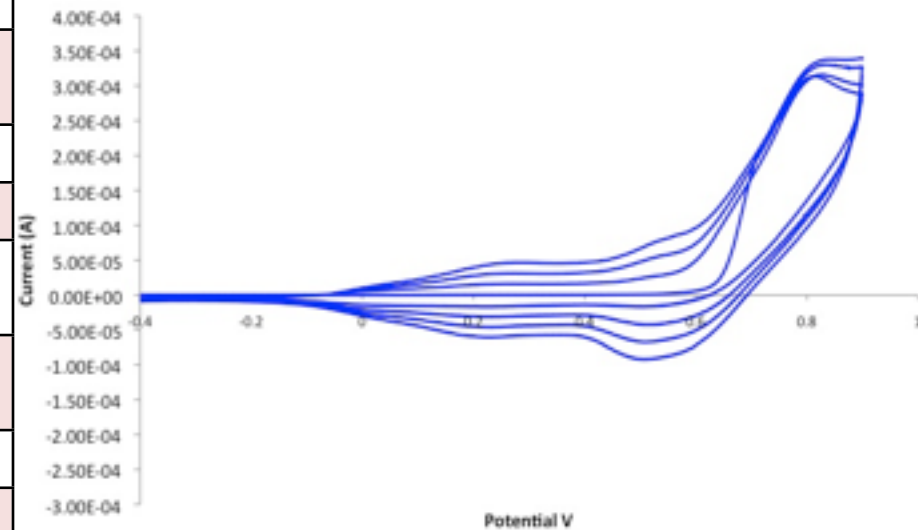
Conclusions.

Electropolymerisation



Cyclic deposition of pTTh-SP1

Monomer Concentration	8mM solution of monomer in DCM +ACN, 2:3
Electrolyte	0.1M solution of TBAP buffer in DCM+ACN, 2:3
Working electrode	ITO, PET-ITO
Counter electrode	Pt wire
Reference electrode	Ag/AgCl with AgNO ₃ 10mM non aqueous.
Scan range	Cyclic deposition From -0.4V to 0.9V
Sensitivity	0.05V per sec
Sweep segments	8



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Outline

Stimuli Responsive
Materials

Spiropyran

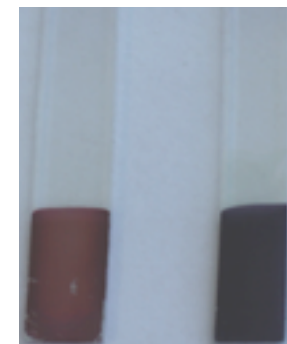
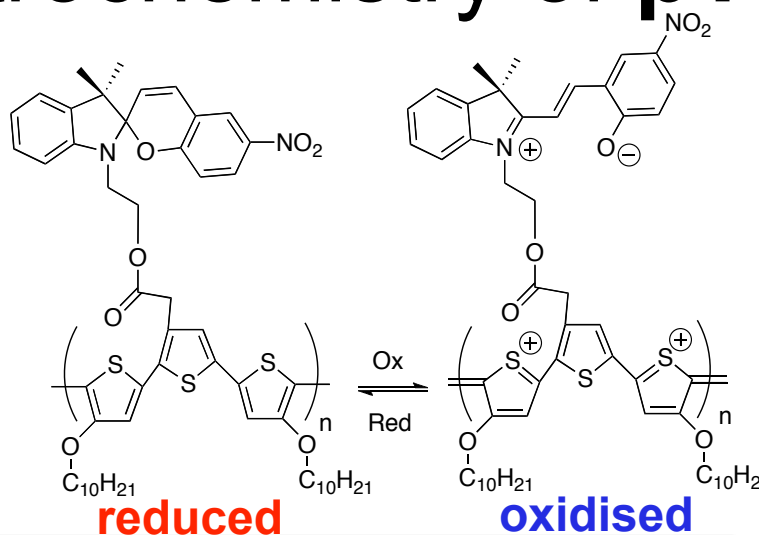
HYBRID MOLECULE

Current
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Conclusions.

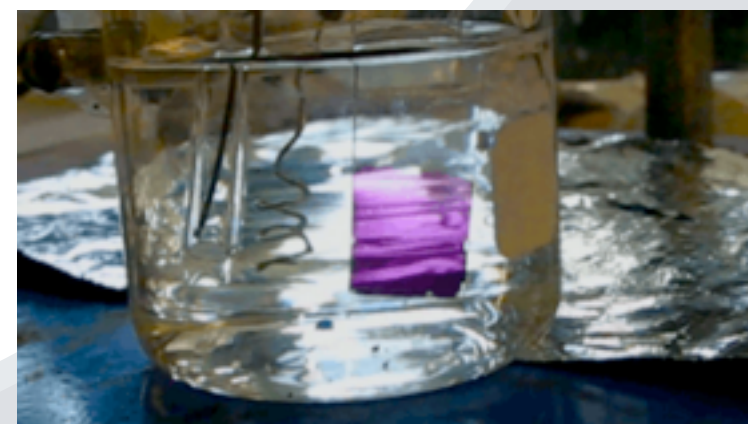
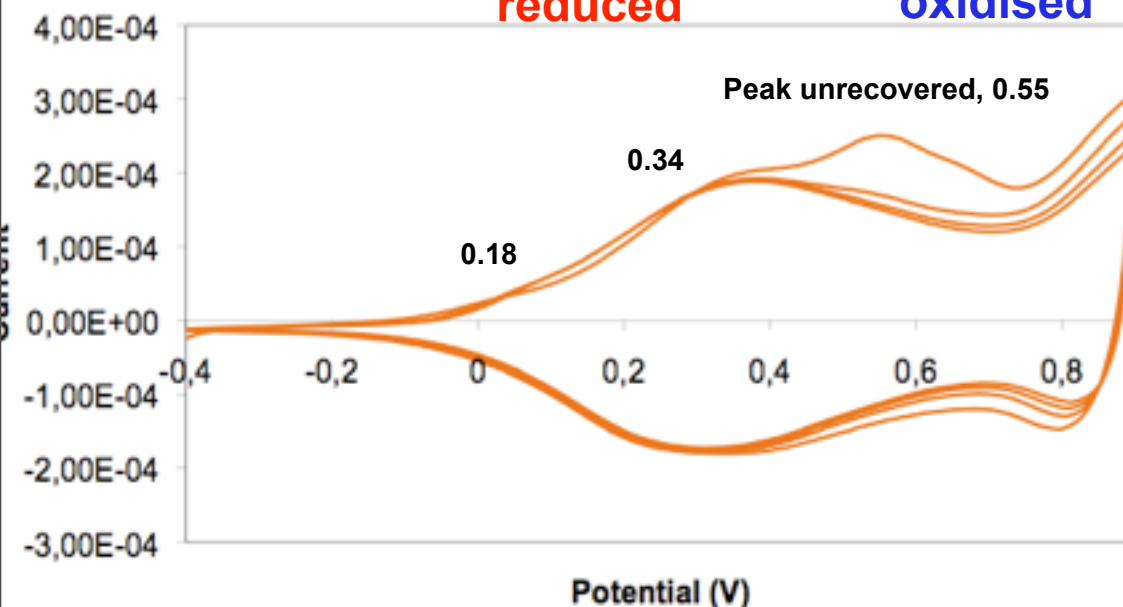
b) Electrochemistry of pTTh-SP1

pTTh-SP1



reduced

oxidised



Outline

Stimuli Responsive
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Spiropyran

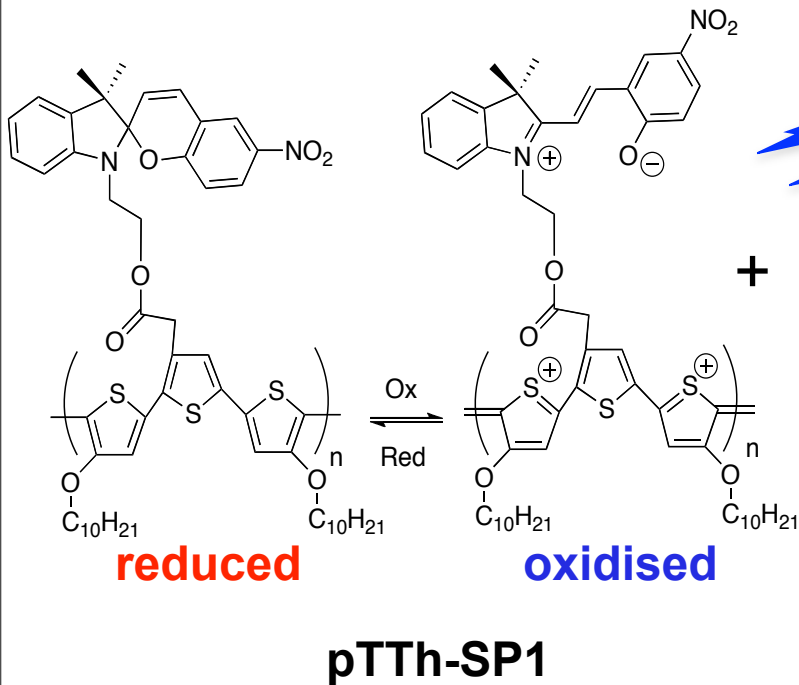
HYBRID MOLECULE

Current Applications

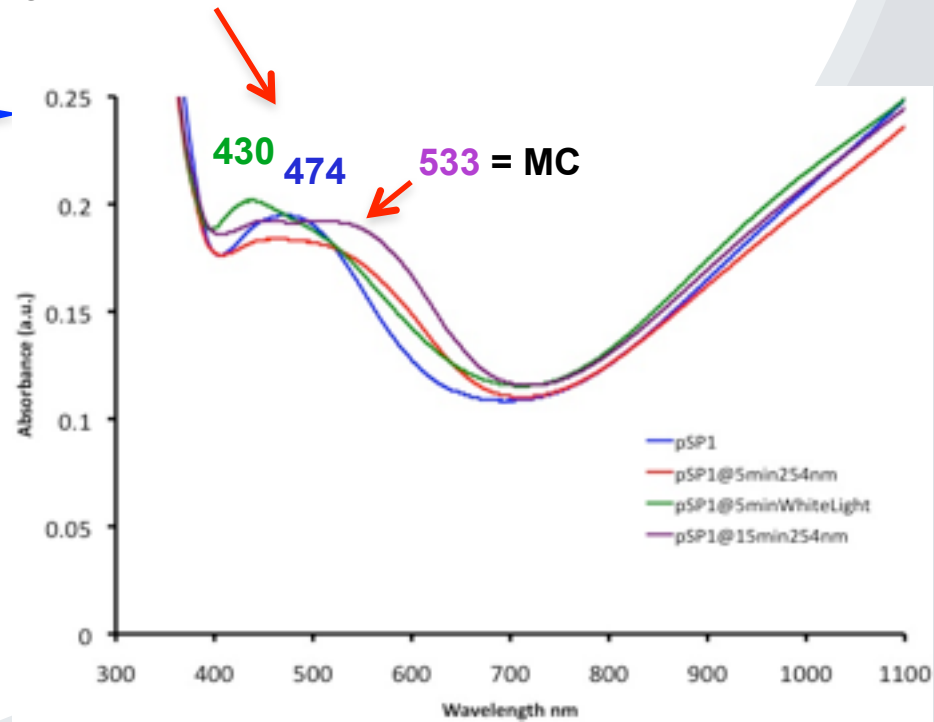
Conclusions.

Photochemical reversibility of pTTh-SP1

Exposition of **p-TTh-SP1** to different cycles of UV-light at 254nm and White light **outside the electrolyte**.



UV light at **254 nm**



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

Outline

Stimuli Responsive
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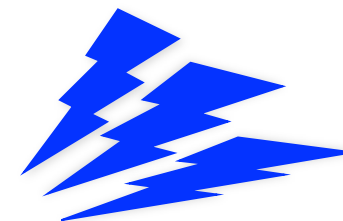
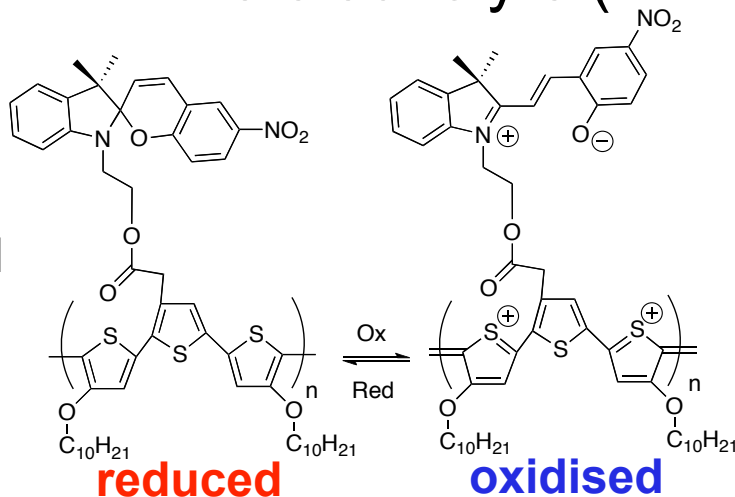
HYBRID MOLECULE

Current
Applications

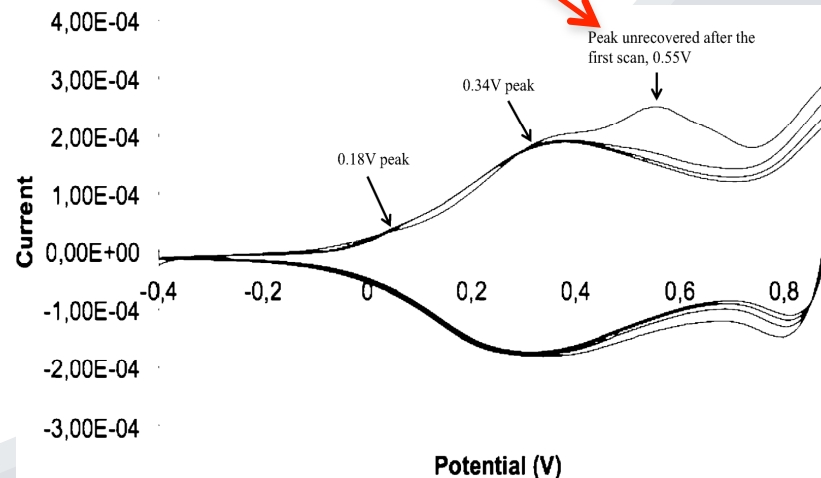
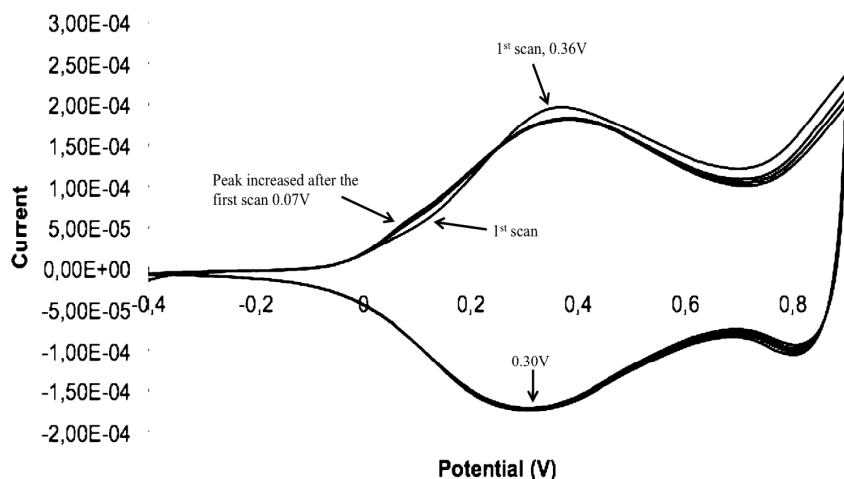
Conclusions.

UV light exposure during Cyclic Voltammetry in the electrolyte (TBAP).

pTTh-SP1



UV light at 254 nm



K. Wagner, R. Byrne, M. Zaroni, 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

Outline

Stimuli Responsive
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Spiropyran

HYBRID MOLECULE

Current
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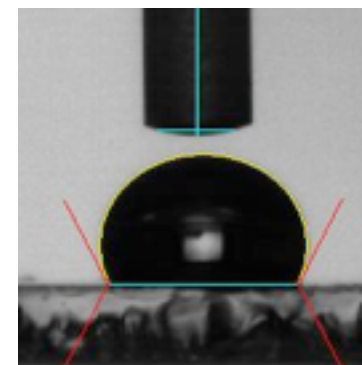
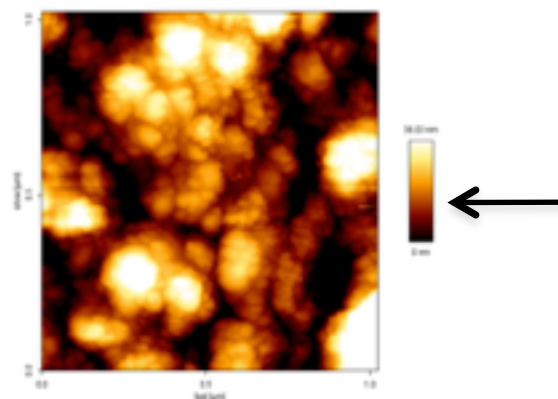
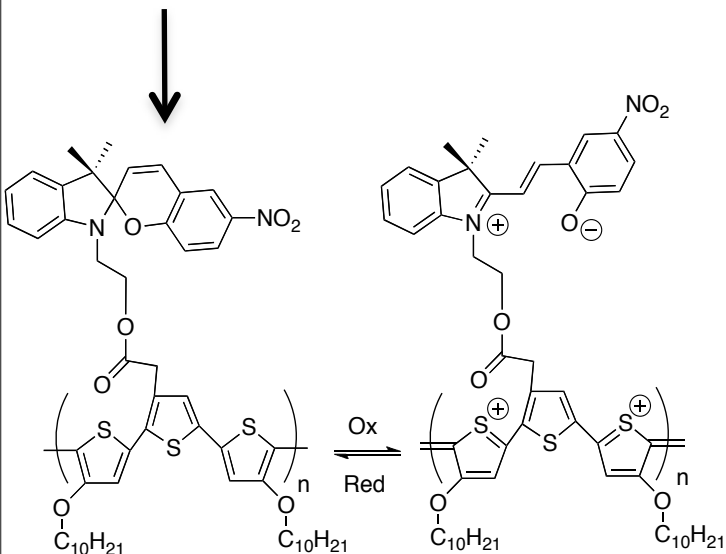
Conclusions.

AFM and Contact Angle + Electrochemistry

pTTh-SP1

reduced

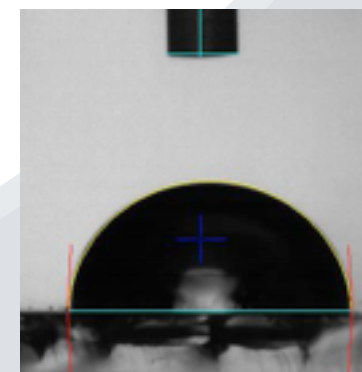
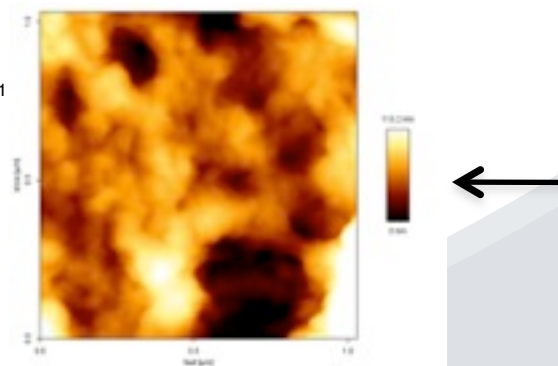
TTh-SP1 at reduced state



Potential: -0.4V
Contact angle: 114.34°

oxidised

TTh-SP1 at oxidised state



Potential: 0.8V
Contact angle: 87.01°

Outline

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TTh-SP1 as Molecular Actuator



Outline

Stimuli Responsive
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Spiropyran

Hybrid Molecule

CURRENT
APPLICATIONS

Conclusions.

CONCLUSION

- A new Category of **Stimuli Responsive Materials** was synthesised and characterised.
- The Molecule Shows Intriguing Properties Deriving from the Combination of **Spiropyran** and **Terthiophene**.
- Spectrochemical Techniques showed the Dual Control-Features of this Polymer.
- **p-TTh-SP1** shows Innovative Photochemical Response under UV Light Exposure.
- This Multiswitchable Polymer Can Be the Platform for Portable Analytical Devices and Biocompatible Systems.

Outline

Stimuli Responsive
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Hybrid Molecule

Current
Applications.

CONCLUSIONS

Special Thanks to:

Prof. Dermot Diamond and Dr. Robert Byrne.
Prof. Gordon G.Wallace and Prof. David L. Officer.
Dr. Klaudia Wagner, Dr. Sanjeev Gambhir.
Dr. Kevin J. Fraser and Dr. Fernando Benito-Lopez.



AND TO YOU ALL FOR YOUR ATTENTION