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SENSOR WEB TECHNOLOGIES

Switchable Materials- The Route to Next Generation Multifunctional Analytical Platforms

Dermot Diamond
CLARITY Centre for Sensor Web Technologies
National Centre for Sensor Research
Dublin City University

presented at

21st International Ion Chromatography Symposium (IICS 2009)
Malahide, Co. Dublin
September 10-11, 2009

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

Tetraester & Tetraphosphine Oxide

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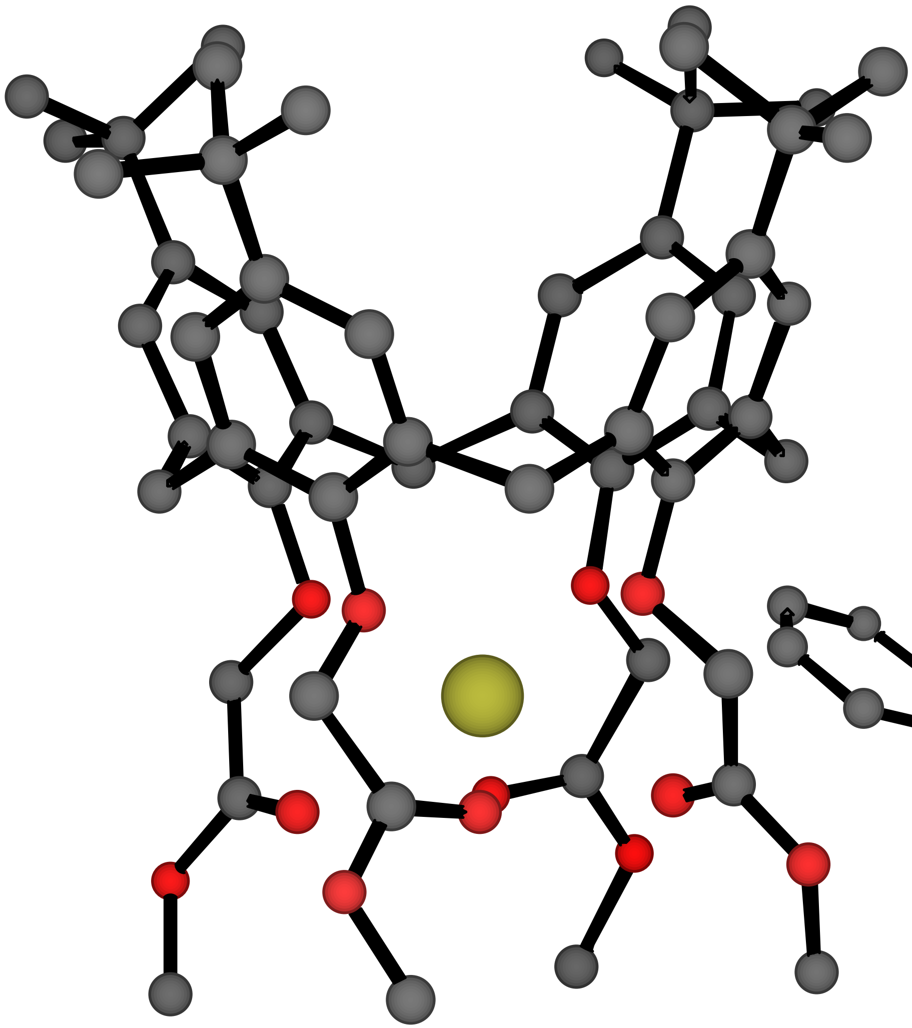
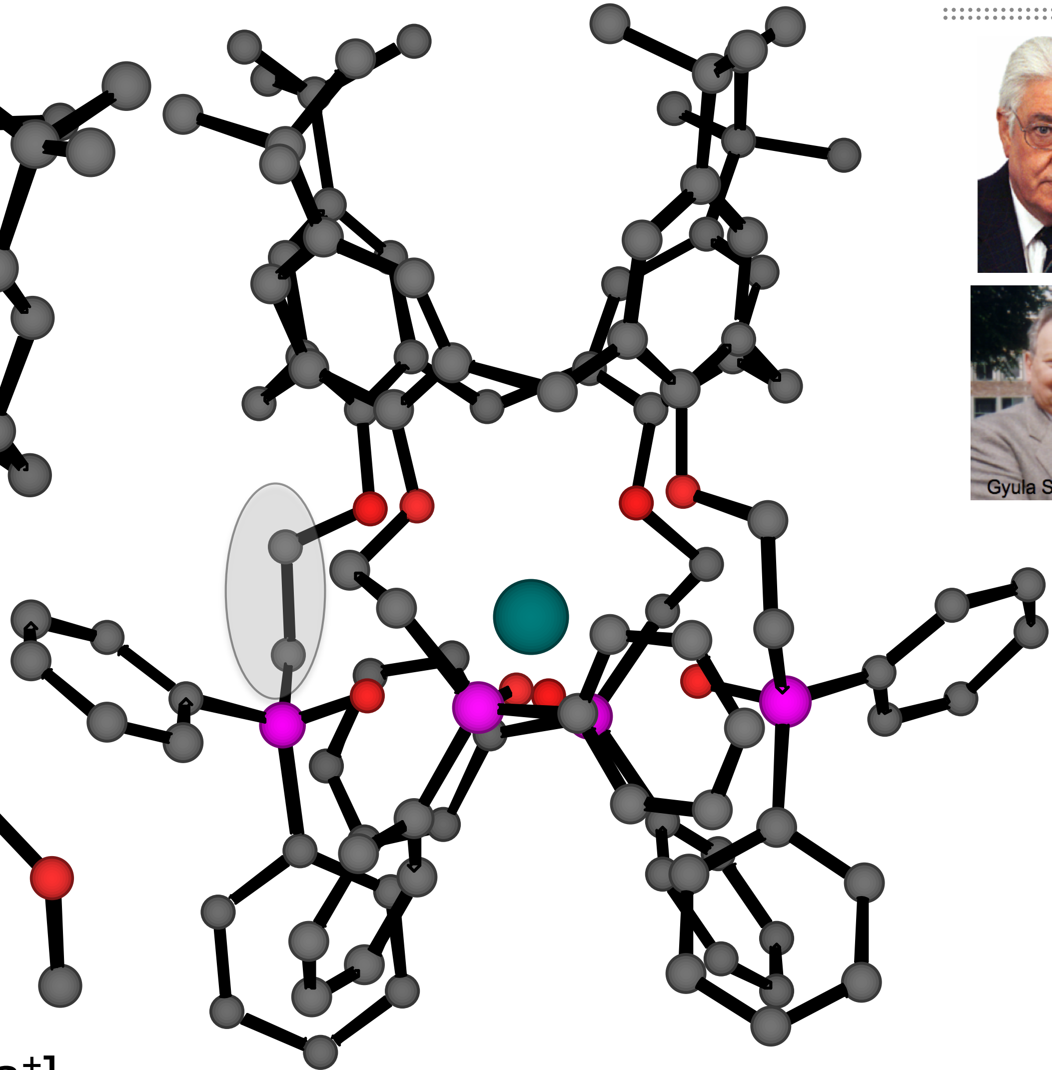


Calix[4]arene Tetraester [Na⁺]



Calix[4]arene Tetraphosphine oxide [Ca^{2}]⁺

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

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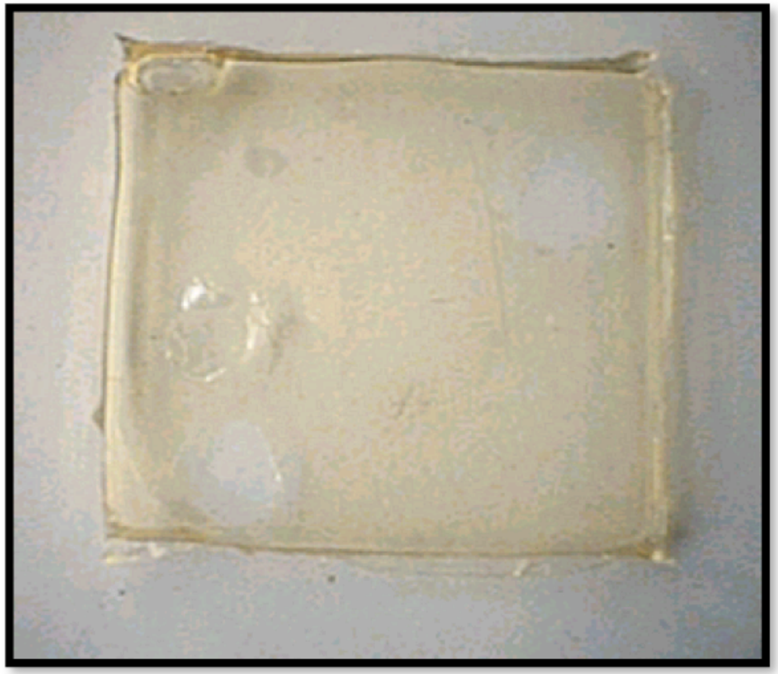
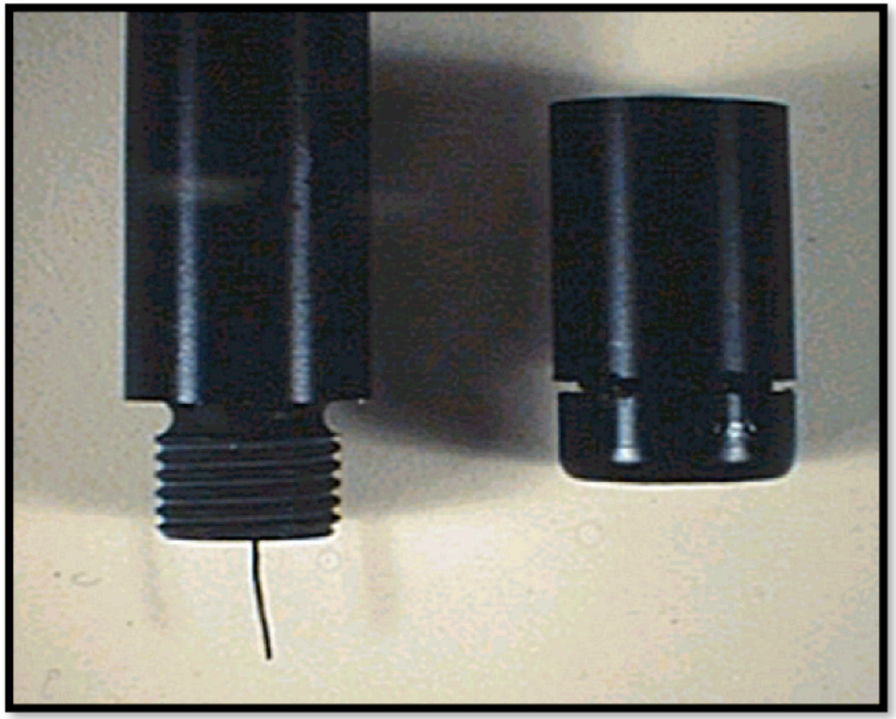
PVC - Membrane ISEs





Typical membrane cocktail (%w/w); PVC:33%, NPOE (plasticiser): 66%; ionophore/exchanger: 1% (ratio at least 2:1 by mole); dissolve in a volatile solvent e.g. THF and cast membrane from this solution

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Molecular Functionality

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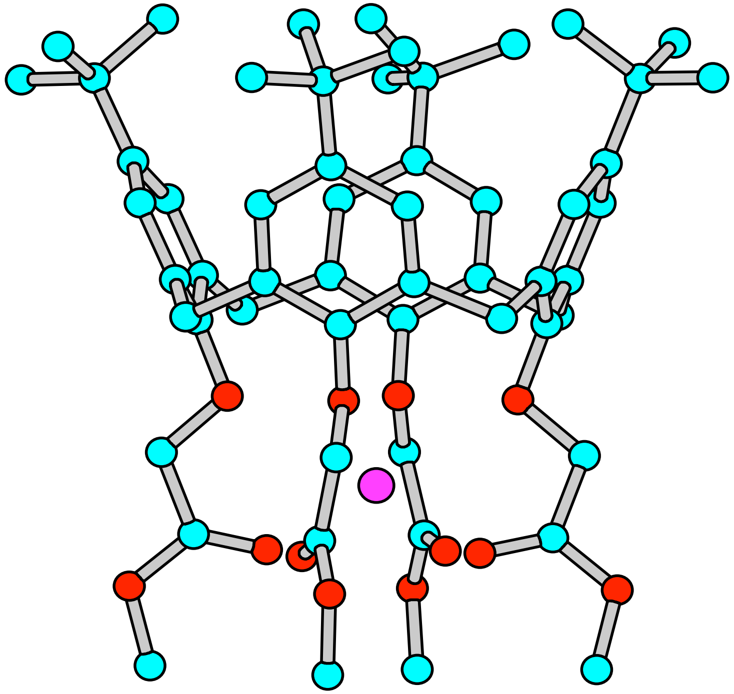


TME:Na+ Side-on View

free

Na+

Surface

Surface

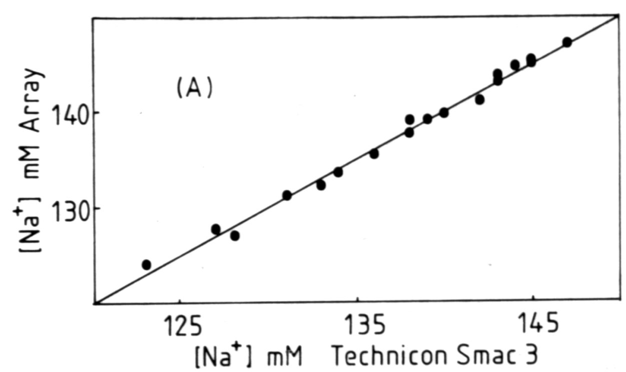
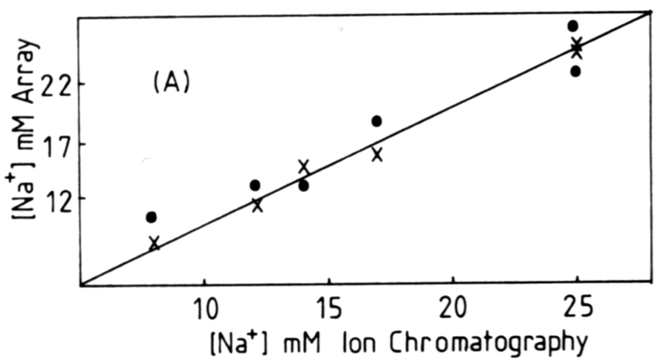


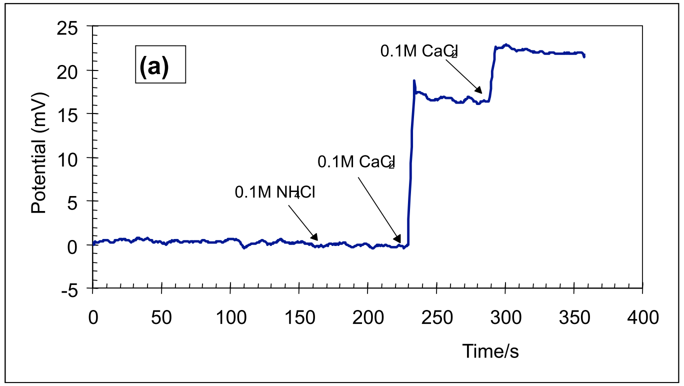
Fig. 3. Comparison of plasma sodium analysis using the array-FIA approach with a SMAC analyser. Good correlation without bias is obtained [5].

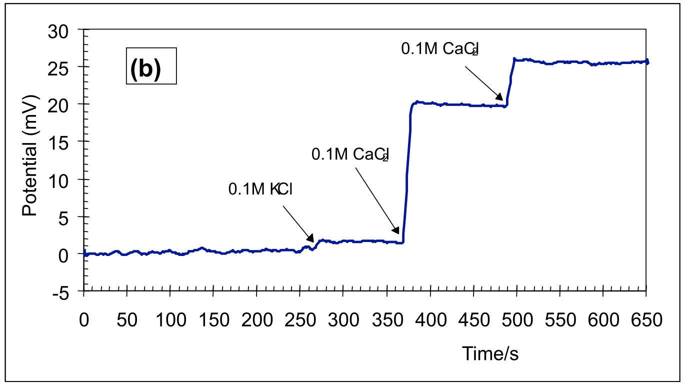


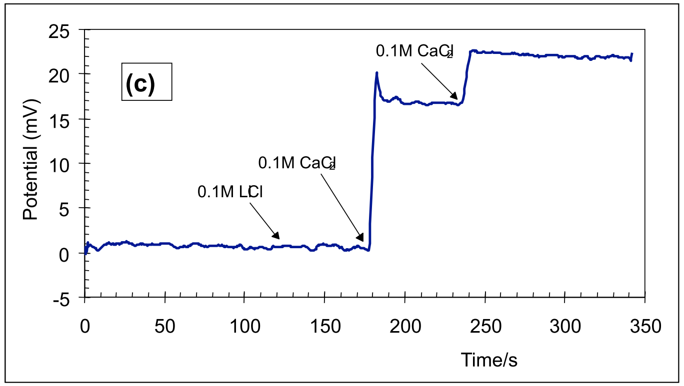
Anal. Chem., *64 (1992) 1721-1728*.

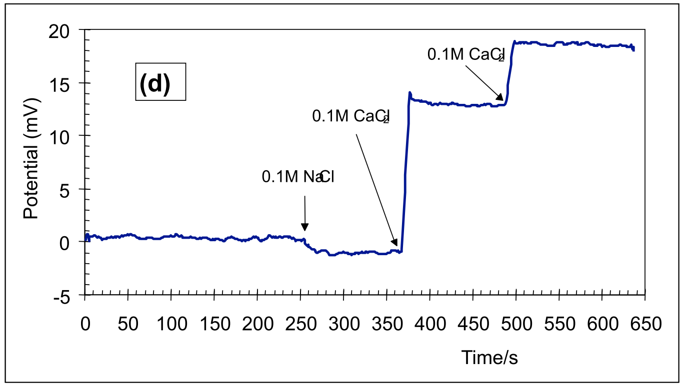
Ligand (and variations of) are used in many clinical analysers for blood sodium profiling

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

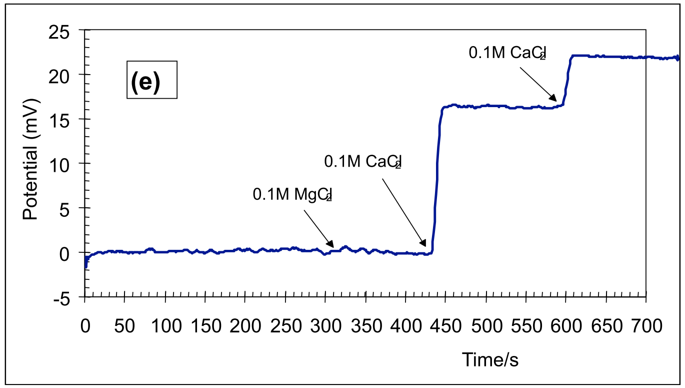








response of TPOL electrode



Calcium-selective Electrode based on a Calix[4]arene Tetraphosphine Oxide, Tom McKittrick, Dermot Diamond, Debbie J. Marrs, Paul O'Hagan and M.Anthony McKervey, Talanta 43 (1996) 1145-1148.

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

Fame at last!!

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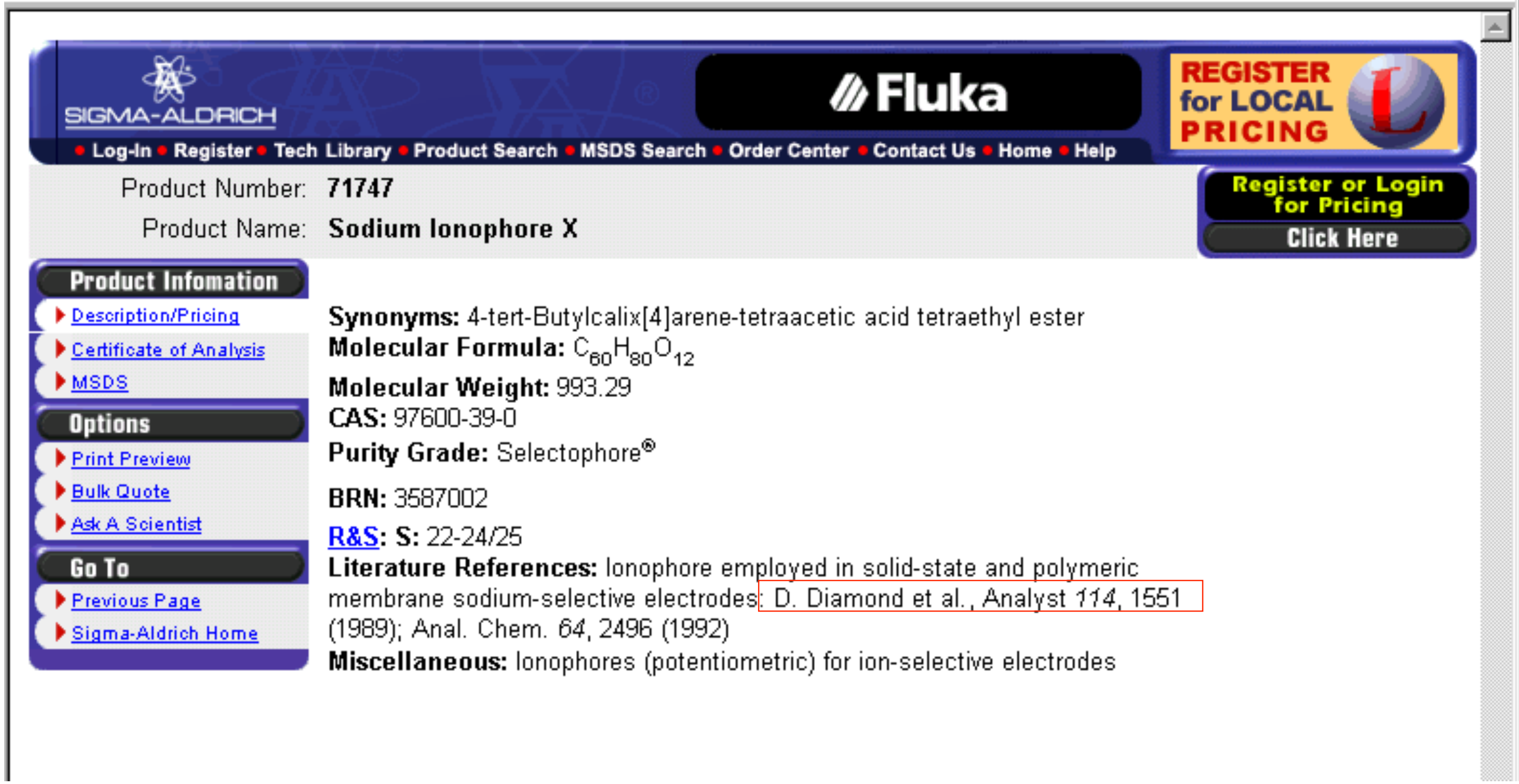

- Best ionophore for sodium

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

Fame at Last!

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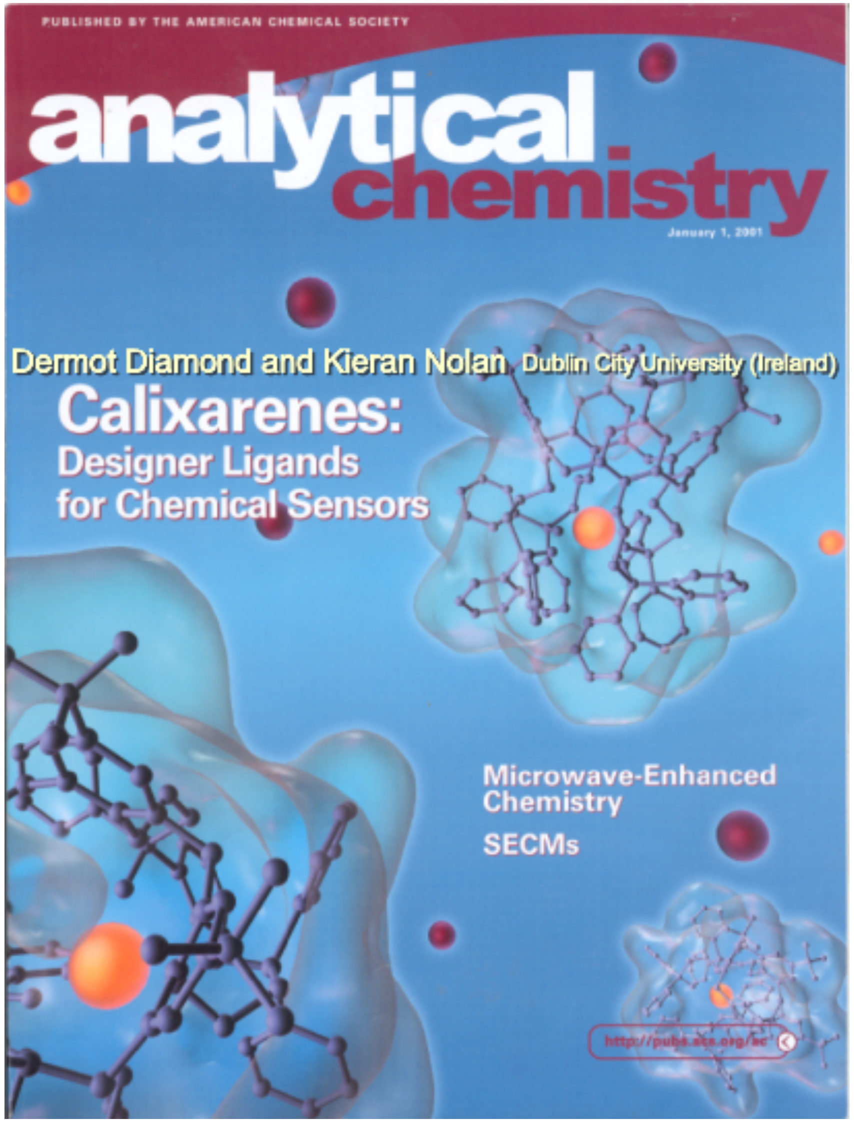

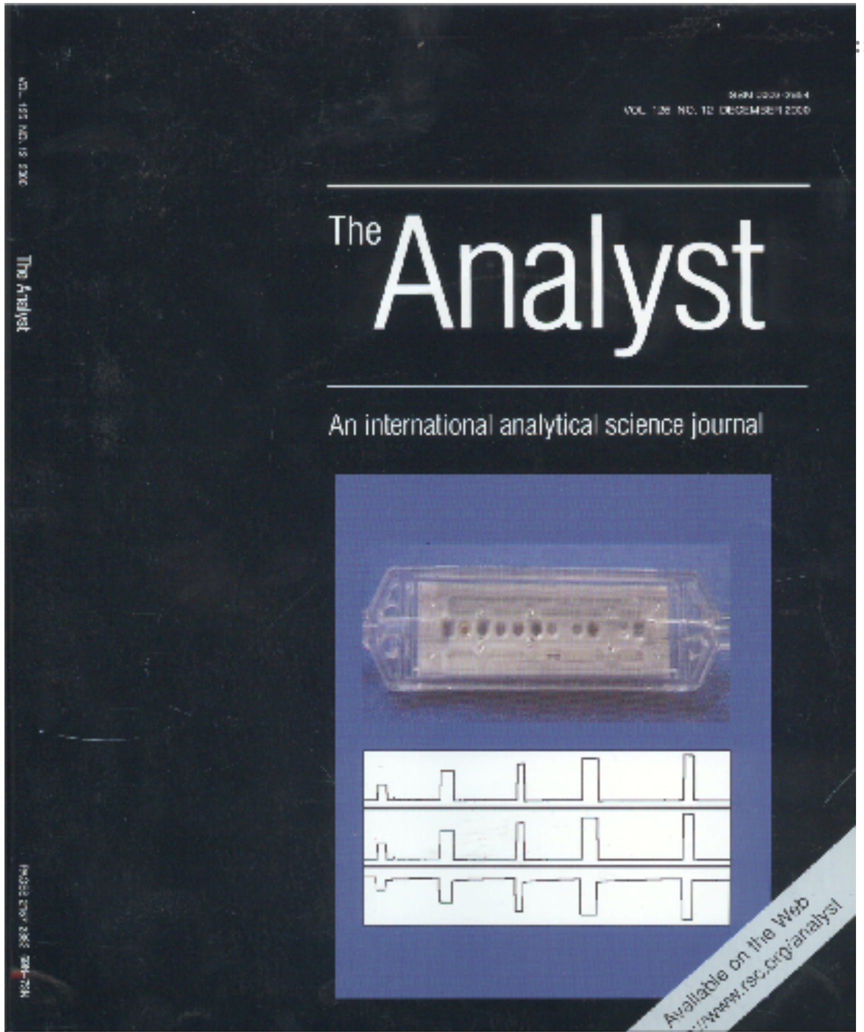

Cover Article: Point-of-Need- Diagnosis of Cystic Fibrosis using a Potentiometric Ion-Selective Electrode Array
Aogan Lynch and Dermot Diamond, NCSR, Dublin City University, Ireland

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

Keynote Article: August 2004, Analytical Chemistry (ACS)

internet scale sensing

Dermot Diamond
Dublin City University
(Ireland)

Incredible advances in digital communications and computer power have profoundly changed our lives. One chemist shares his vision of the role of analytical science in the next communications revolution.

Digital communications networks are at the heart of modern society. The digitization of communications, the development of the Internet, and the availability of relatively inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions of people, places, and objects. Email can instantly transmit complex documents to multiple remote locations, and websites provide a platform for instantaneous notification, dissemination, and exchange of information globally. This technology is now pervasive, and those in research and business have multiple interactions with this digital world every day. However, this technology might simply be the foundation for the next wave of development that will provide a seamless interface between the real and digital worlds.

The crucial missing part in this scenario is the gateway through which these worlds will communicate: How can the digital world sense and respond to changes in the real world? Analytical scientists—particularly those working on chemical sensors, biosensors, and compact, autonomous instruments—are

Dermot Diamond, Anal. Chem., 76 (2004) 278A-286A.

Fundamental Problem: Sensor surface will change with time!

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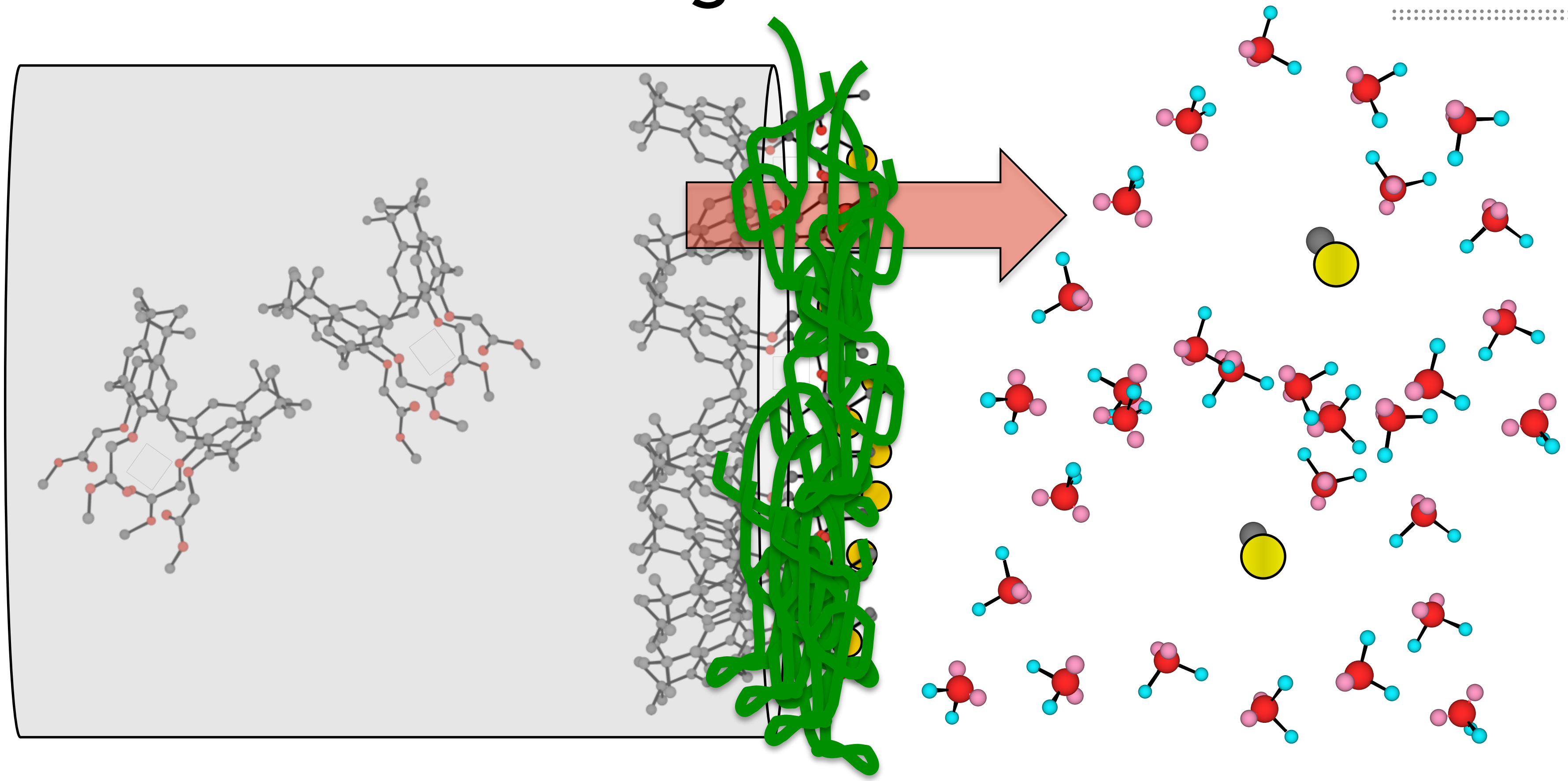

- Surface interactions are critical to signal generation - very susceptible to any process that modifies the surface condition => drift, loss of sensitivity => regular calibration => high cost of ownership
- Leaching, biofouling, physical damage, sample interferents, …..
- Engineers expect a thermistor, we have platforms closer to a washing machine!

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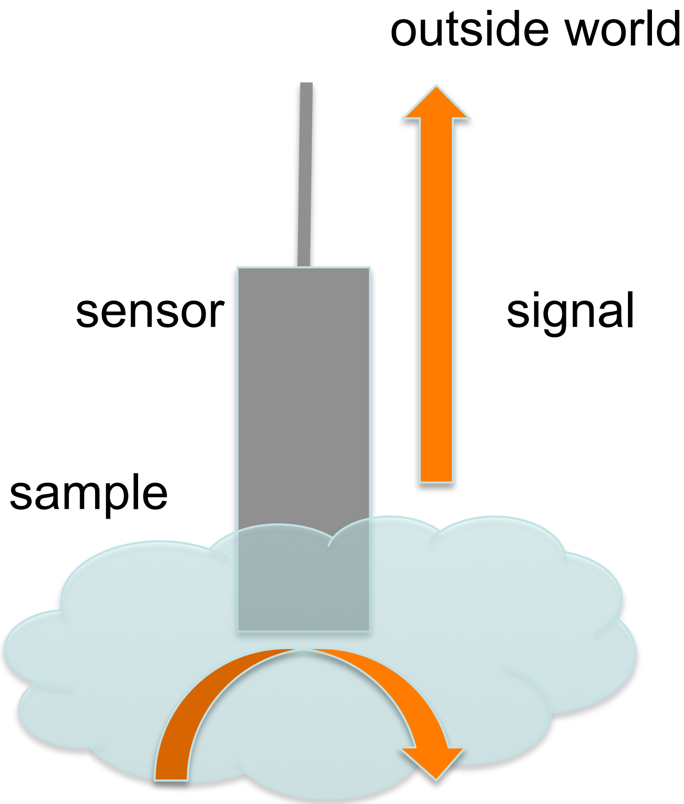
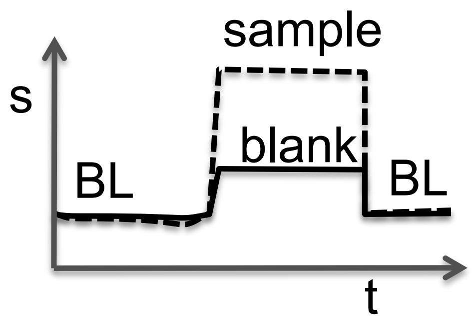
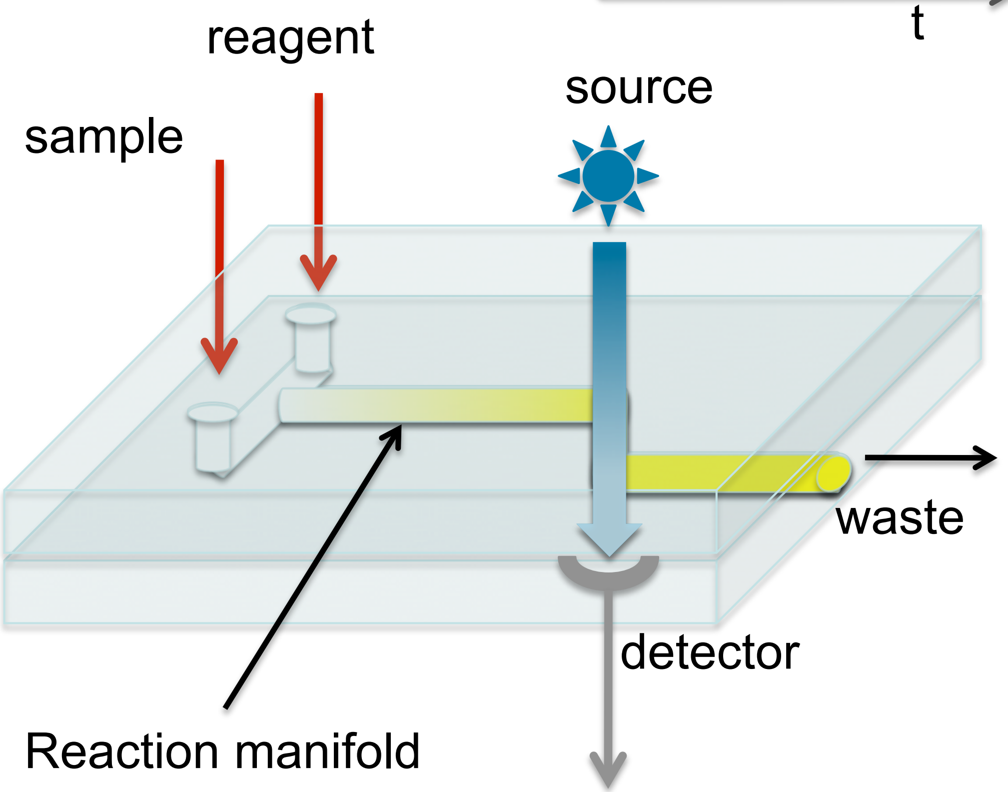
Direct Sensing vs. Reagent Based LOAC

Direct Sensing



LOAC Analyser





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

Adaptive (Stimulus-Responsive) Materials

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- Materials that possess 'multiple personalities' or characteristics
- Can switch reversibly between these via a stimulus (chemical, electrochemical, photochemical.....)
- Properties change dramatically e.g. chemical binding behaviour, surface charge/polarity, porosity, permeability, dimensions, colour.....

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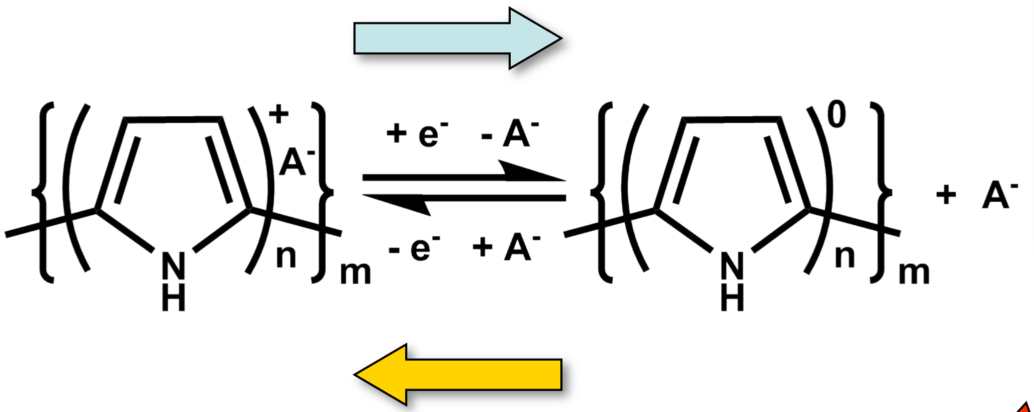
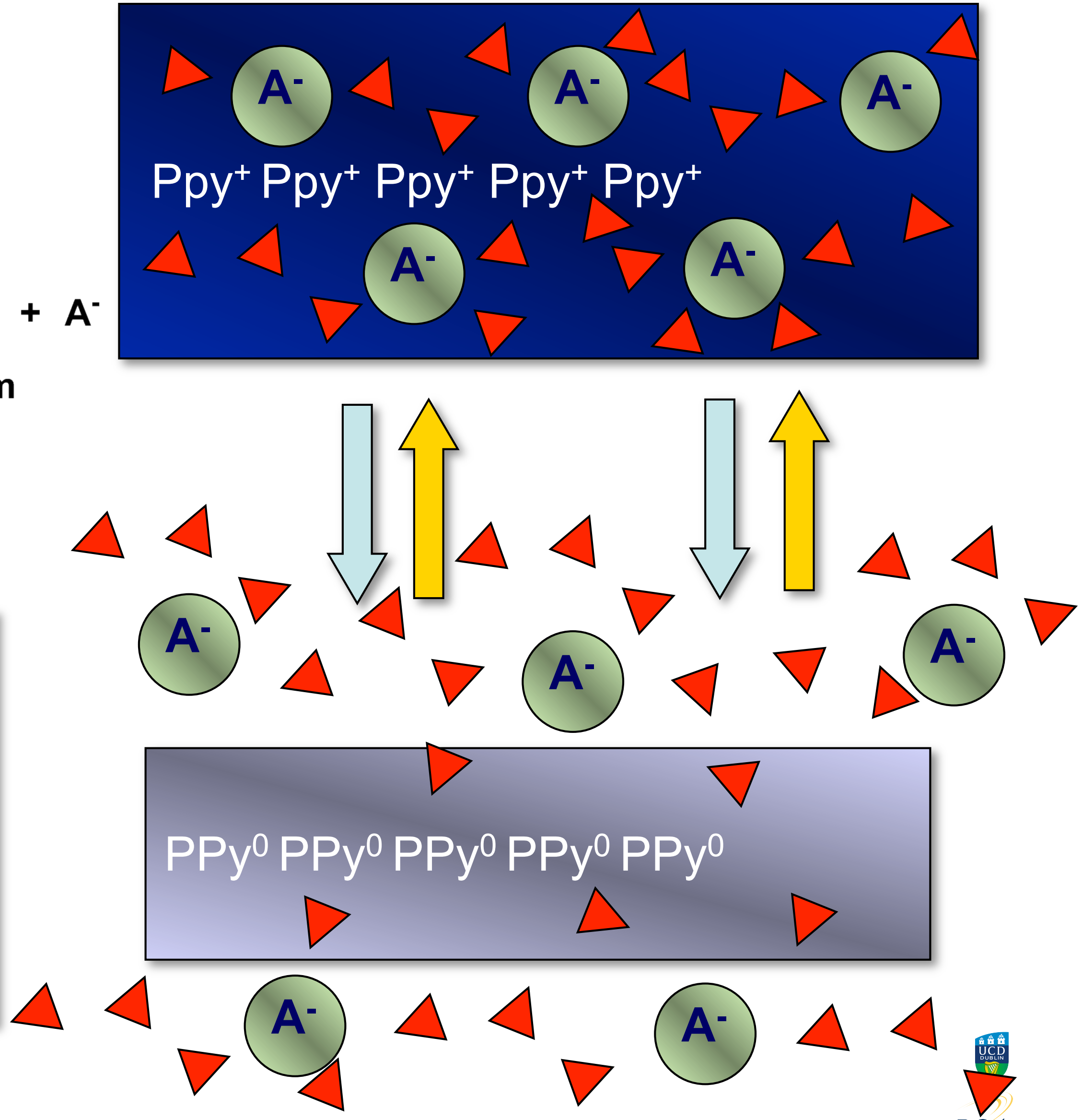
UCD DCU Tyndall

Switchable Materials: Soft Polymer Actuators





Principle can be used to make soft polymer (biomimetic, artificial muscle) actuators such as **'benders'**

(multi-laminated structures designed so that an outer PPY layer expands as the inner contracts to produce a bending movement)

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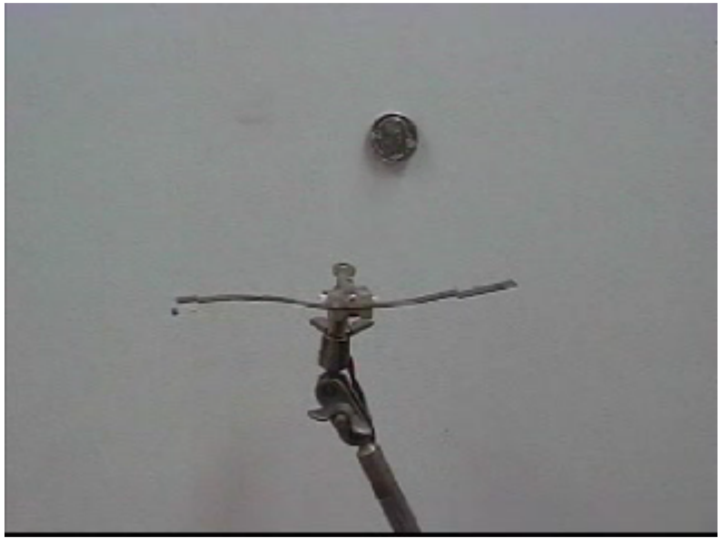
‘Artificial Muscle’ – Mobile Platforms

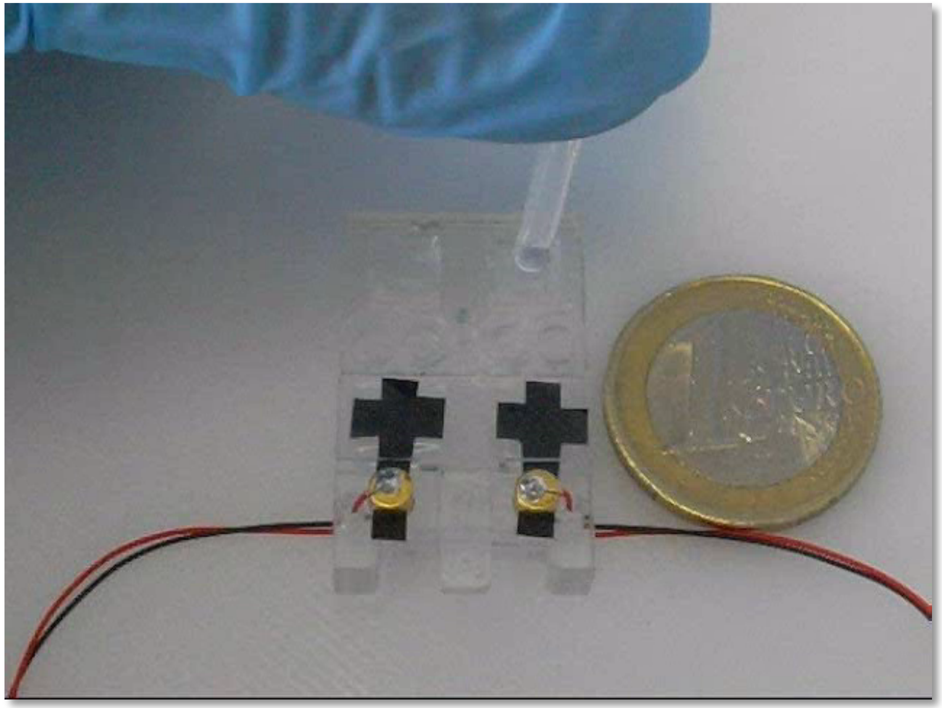
- Conducting polymer fibre bundles contained within polymer ‘skin’
- Mobile electrolyte solution
- Polarisation of the bundles causes movement of ions and associated water molecules due to charge compensation
- Causes swelling or contraction
- Effect can be translated into bending by laminating two oppositely polarised layers with a flexible porous inactive intermediate layer – soft pumps and valves!



Videos from Moshen Shahinpoor’s website at www.unm.edu/~amri

This work is supported by Scienc

Polymer Micropumps and Valves



Daniel Kim and Kim Lau

- Low power, low cost components are vital for realisation of next generation micro-dimensioned analytical platforms
- Based on polypyrrole CP 'benders'
- Soft polymer actuators more attractive for integrated ufluidics manifolds
- 'lego' approach – detector block will slot in

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

Soft Polymer Actuators

- Can be used to provide pumping and valving functions
- Can be fully integrated into microfluidic manifolds
- In principle are more reliable in micro-scale than conventional ‘hard’ materials
- Could drive down the cost and complexity of ‘analyser’ platforms

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Photoswitchable Materials

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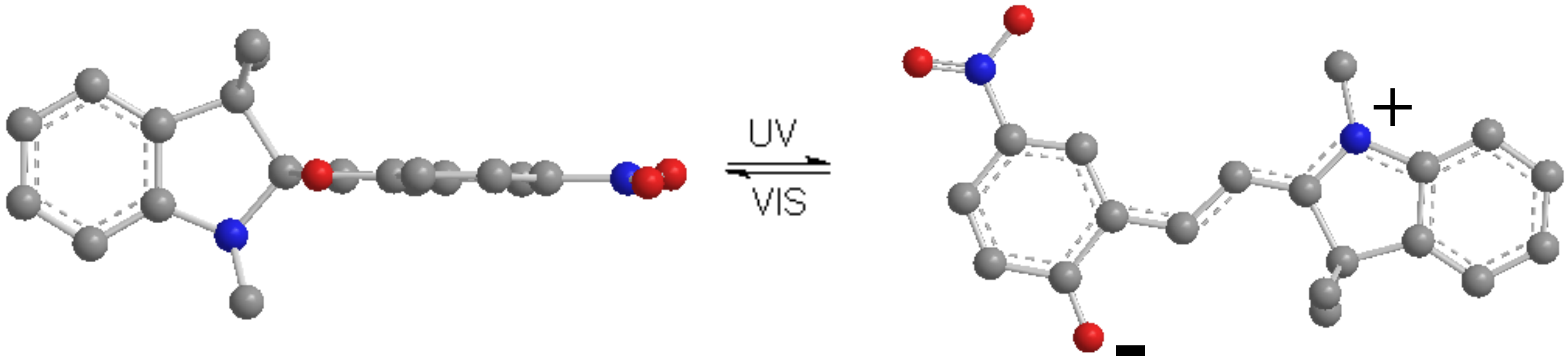

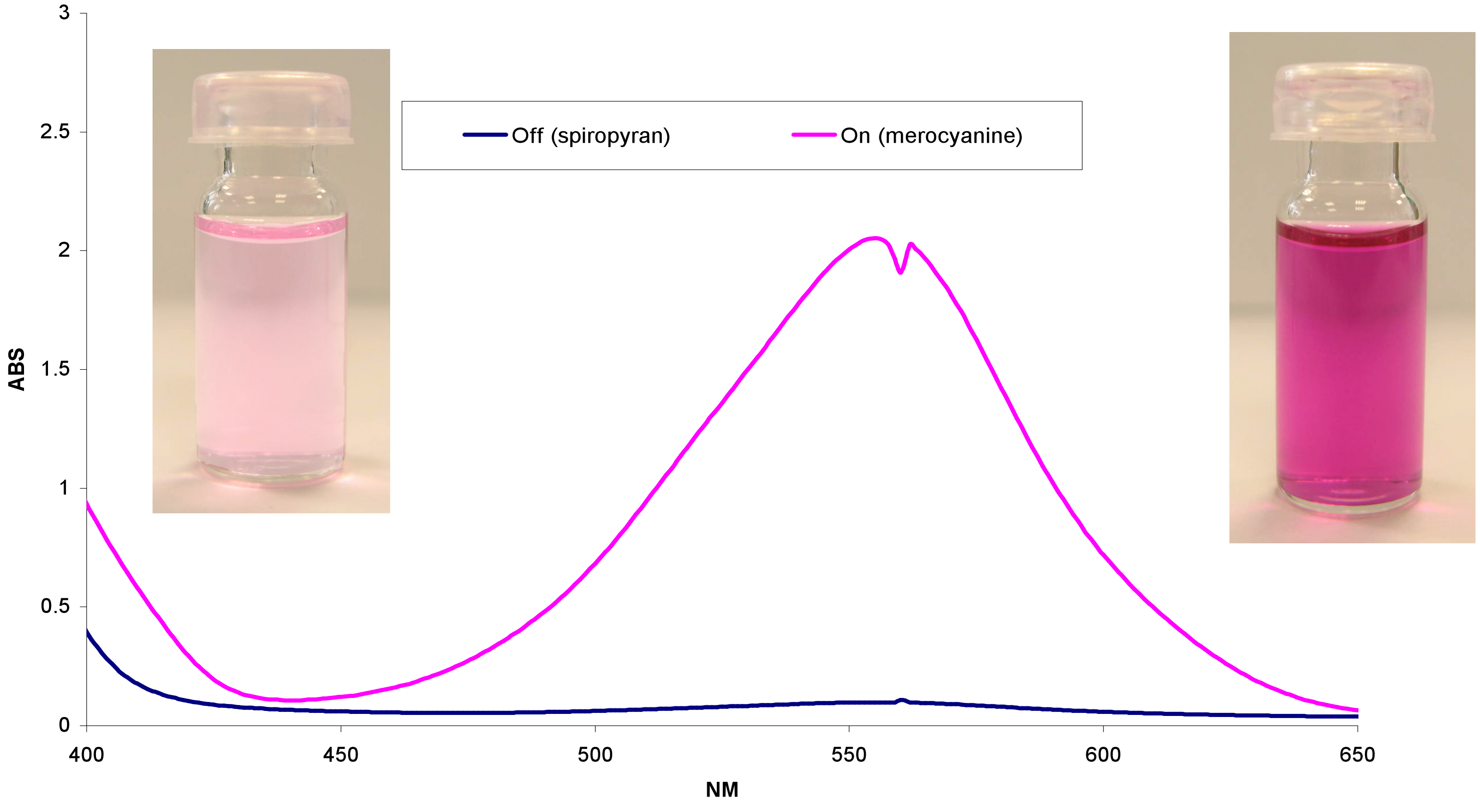

This work is supported by Science Foundation Ireland under grant 07/CE/I1147

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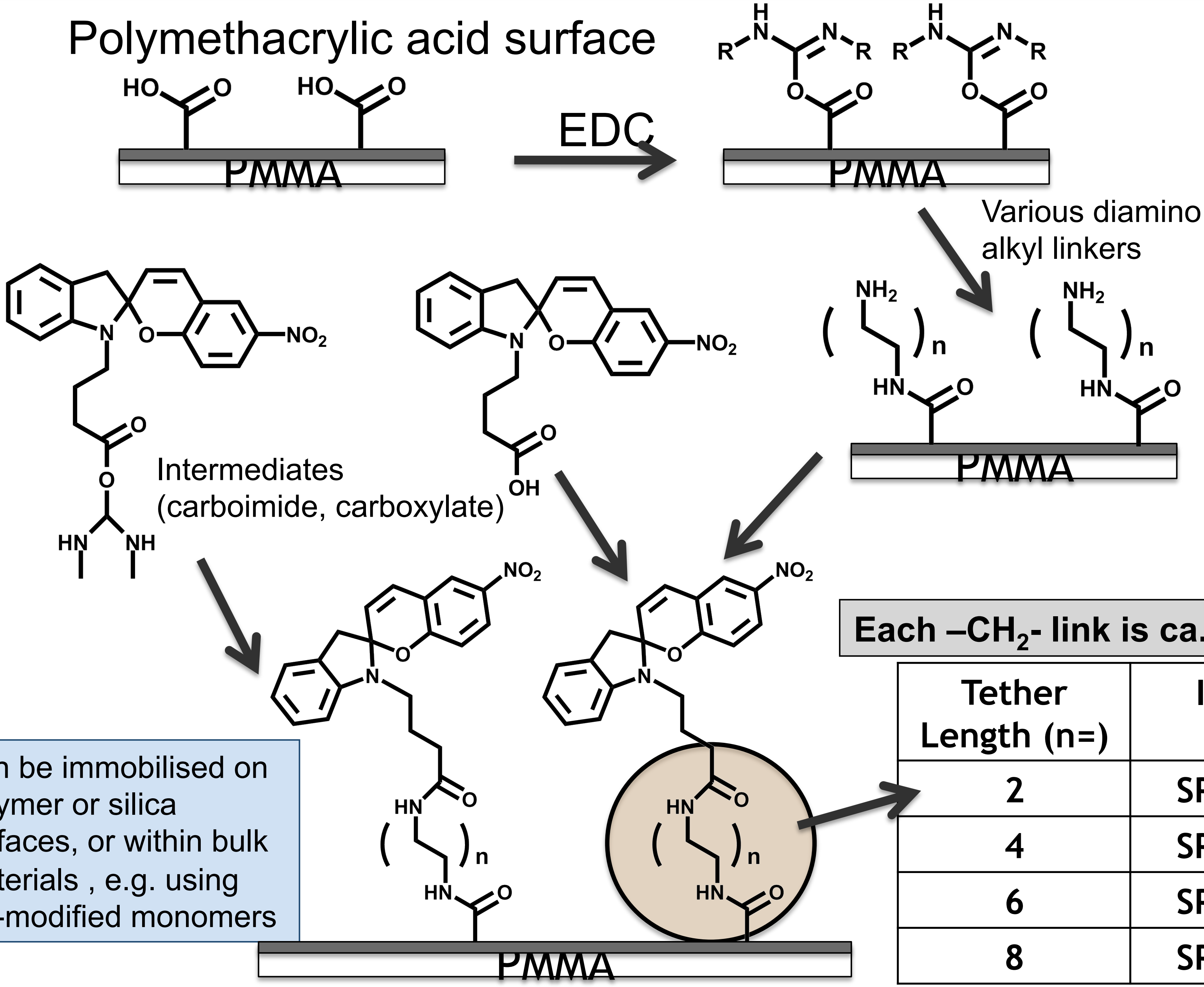
Polymethacrylic acid surface



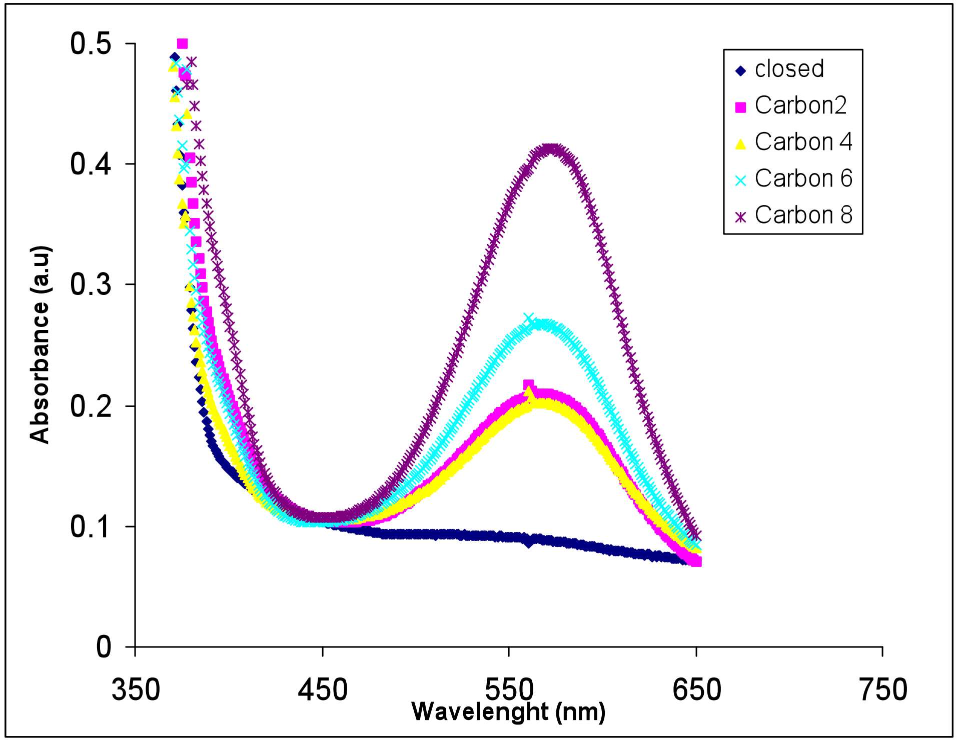
Can be immobilised on polymer or silica surfaces, or within bulk materials , e.g. using SP-modified monomers

Each –CH_2- link is ca. 1.5 Å

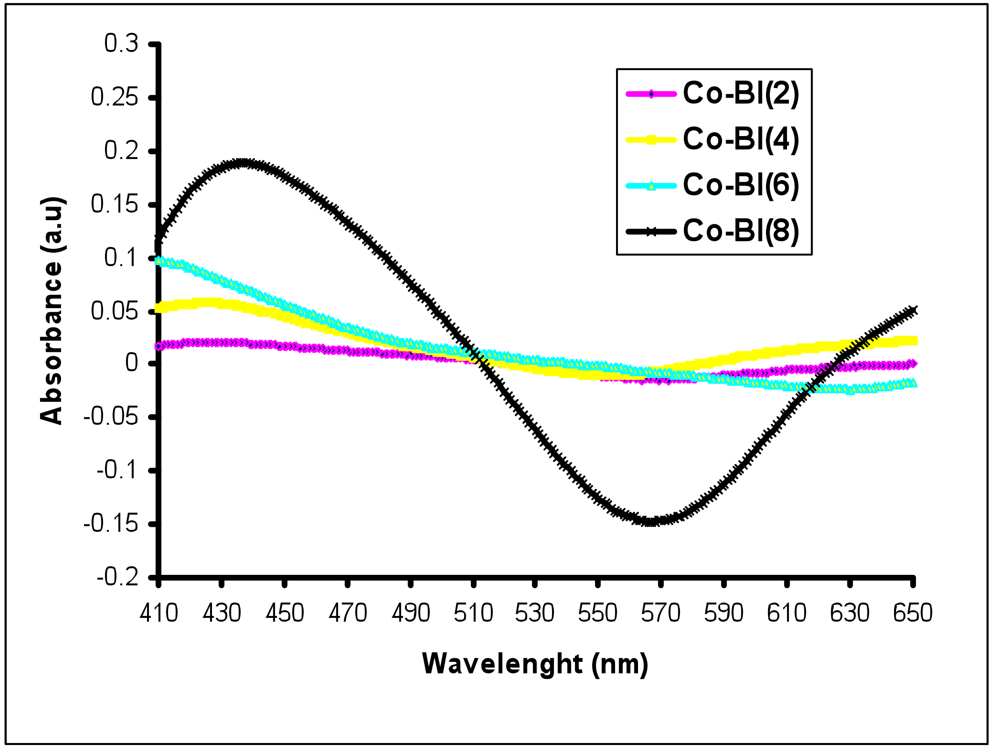
Tether Length (n=)	ID
2	SP-2
4	SP-4
6	SP-6
8	SP-8

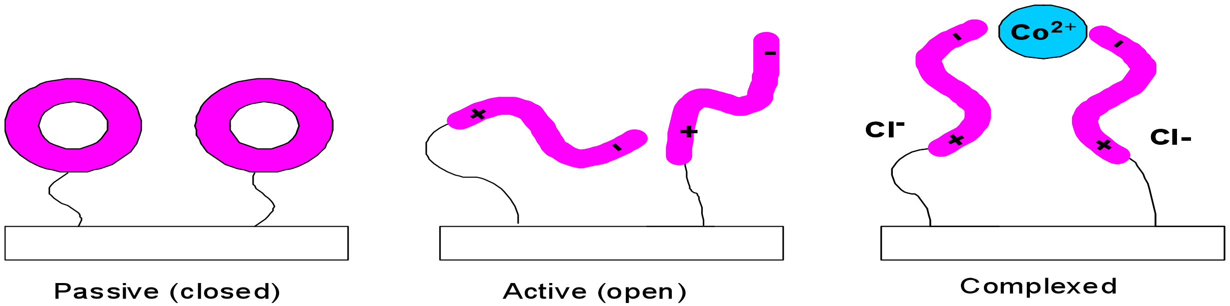
Importance of Linker Length

SP-MC Switching



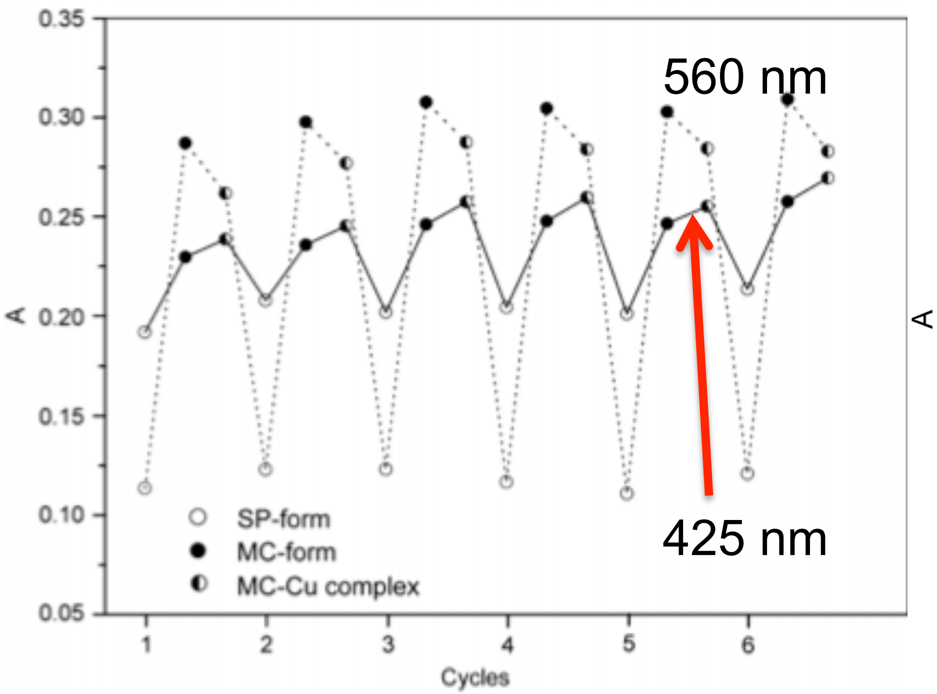
Co^{2+}-Complexation

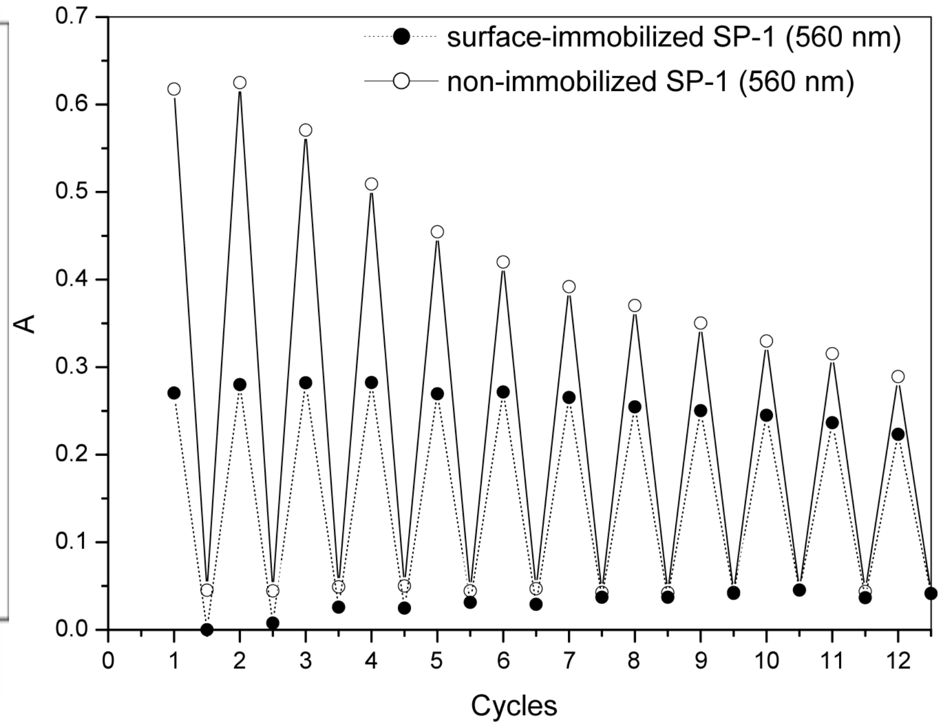




This work is supported by Science Foundation Ireland under grant 07/CE/I1147

Detection of switching between SP/MC/MC-Cu2+ states using the 'Discophotometer





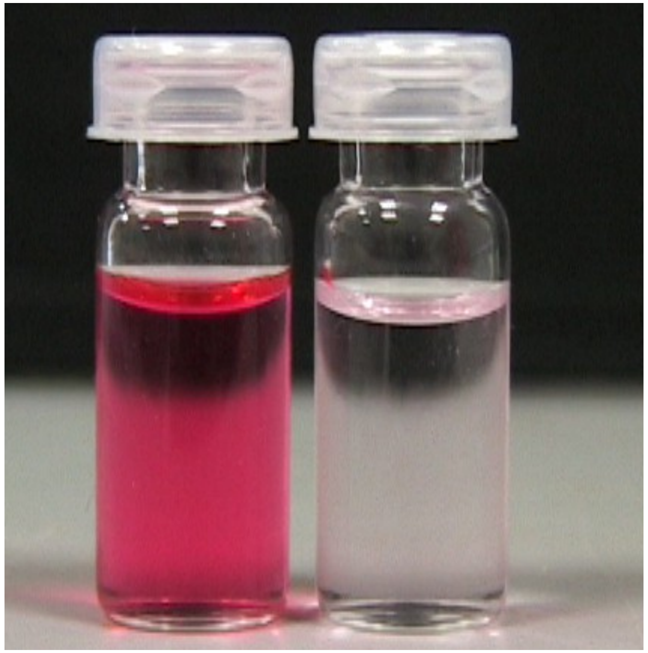
Photonic Modulation of Surface Properties: A Novel Concept in Chemical Sensing, Aleksandar Radu, Silvia Scarmagnani, Robert Byrne, Conor Slater, King Tong Lau and Dermot Diamond, J. Phys.D; Appl. Phys., 40 (2007) 7238-7244.

Absorbance measured at 560 nm for cyclical switching between SP and MC when for surface immobilized (full circles) and non-immobilized (open circles) SP-1.

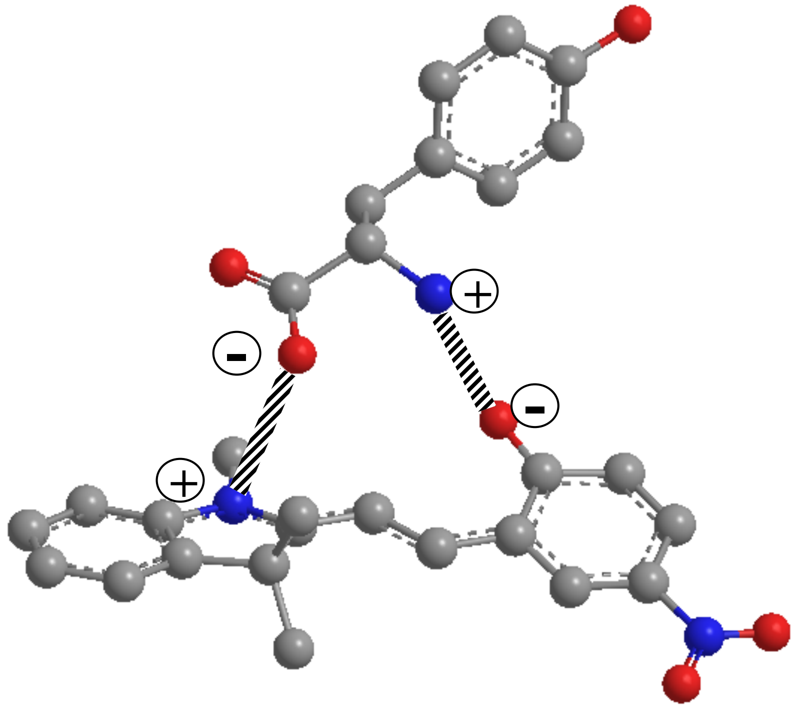
A. Radu et al. Journal of Photochemistry and Photobiology A:Chemistry 206 (2009) 109–115.

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

Merocyanine Interaction with Amino Acids



A strongly coloured solution of merocyanine and tyrosine in a 4:1 acetonitrile:water mixture. The merocyanine was formed by illuminating spiropyran (1:1 mole ratio to tyrosine) for 1 minute with a UV-LED. The picture was taken after 100 hours storage in the absence of light. (top, right): The control experiment without tyrosine shows almost complete decoloration, i.e. return to spiropyran form.



Energy minimised structures (Chem 3-D Ultra, V. 9.0, Cambridgesoft) suggests complementary binding of tyrosine to the merocyanine zwitterion which stabilises the coloured merocyanine form.

Key: carbon atoms – grey, oxygen atoms – red, nitrogen atoms – blue (hydrogen atoms not shown for clarity)

Chemo/Bio-Sensor Networks, Robert J Byrne and Dermot Diamond, Nature Mater., 5 (2006) 422-424.

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

Photocontrolled DNA Binding

J|A|C|S
COMMUNICATIONS

Published on Web 08/13/2008

Photoswitched DNA-Binding of a Photochromic Spiropyran

Johanna Andersson, Shiming Li, Per Lincoln, and Joakim Andréasson*

Department of Chemical and Biological Engineering, Physical Chemistry, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

Received March 17, 2008; E-mail: a-son@chalmers.se

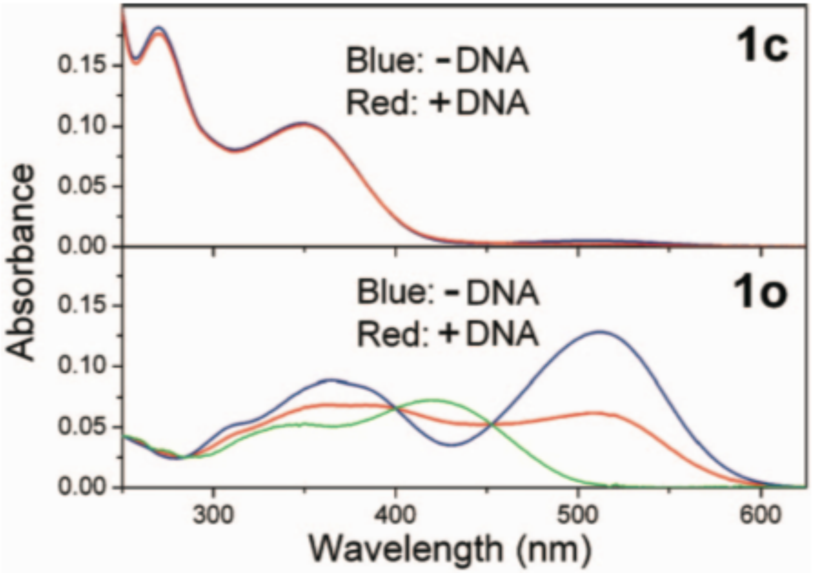
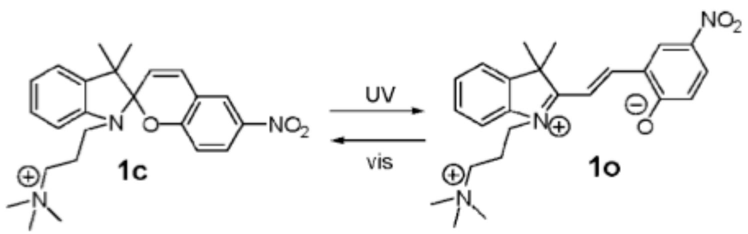


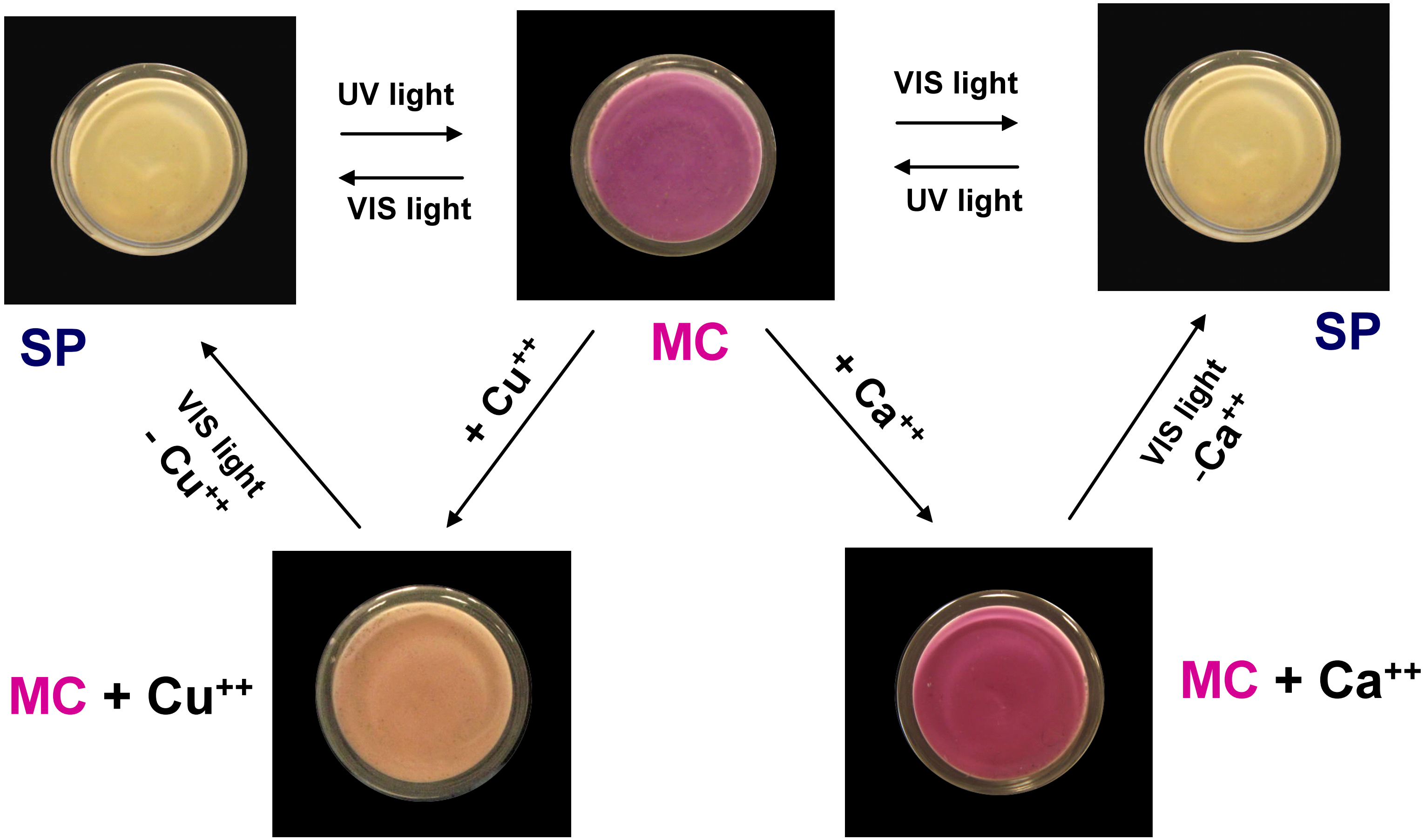
Figure 1. Absorption spectra of **1c** (top panel) and **1o** (lower panel) in the absence (blue lines) and presence (red lines) of calf-thymus DNA. The contribution from DNA to the overall absorption has been subtracted for ease of comparison. Likewise, the contribution from **1c** has been subtracted from the spectra of **1o** shown in the lower panel. The green line corresponds to a sample of 100% **1o** bound to DNA as the contribution from unbound **1o** has been corrected for (see Supporting Information for details). The total concentration of **1** was ~1.5 × 10^{-5} M. The concentration of DNA was 11.6 × 10^{-5} M, and the NaCl concentration of the solution was 8.6 × 10^{-3} M.

Chart 1. Structures of Photochromic Spiropyran **1**



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

Functionalised Microbeads: optically controlled selective binding of metal ions



Polystyrene Beads-Based System for Optical Sensing using Spiropyran Photoswitches, Silvia Scarmagnani, Zarah Walsh, Conor Slater, Nameer Alhashimy, Brett Paull, Mirek Macka and Dermot Diamond, J. Mater. Chem., 2008, 18, 5063 – 5071

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

Changing EOF in CE using Light!

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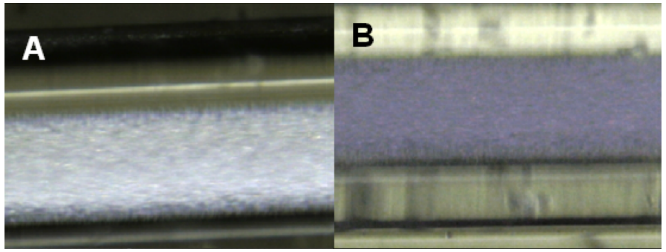
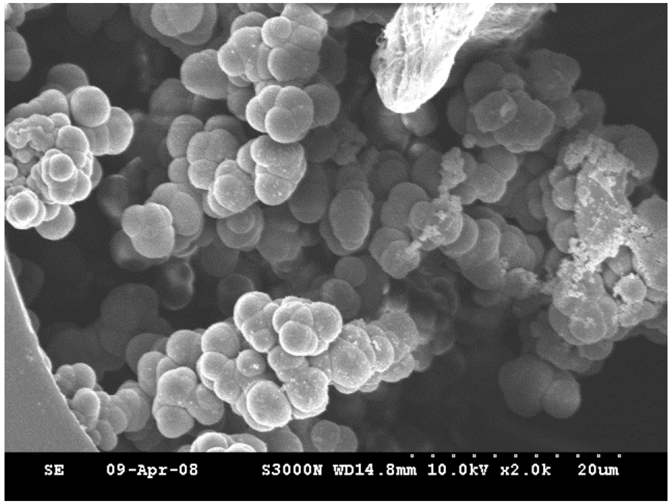
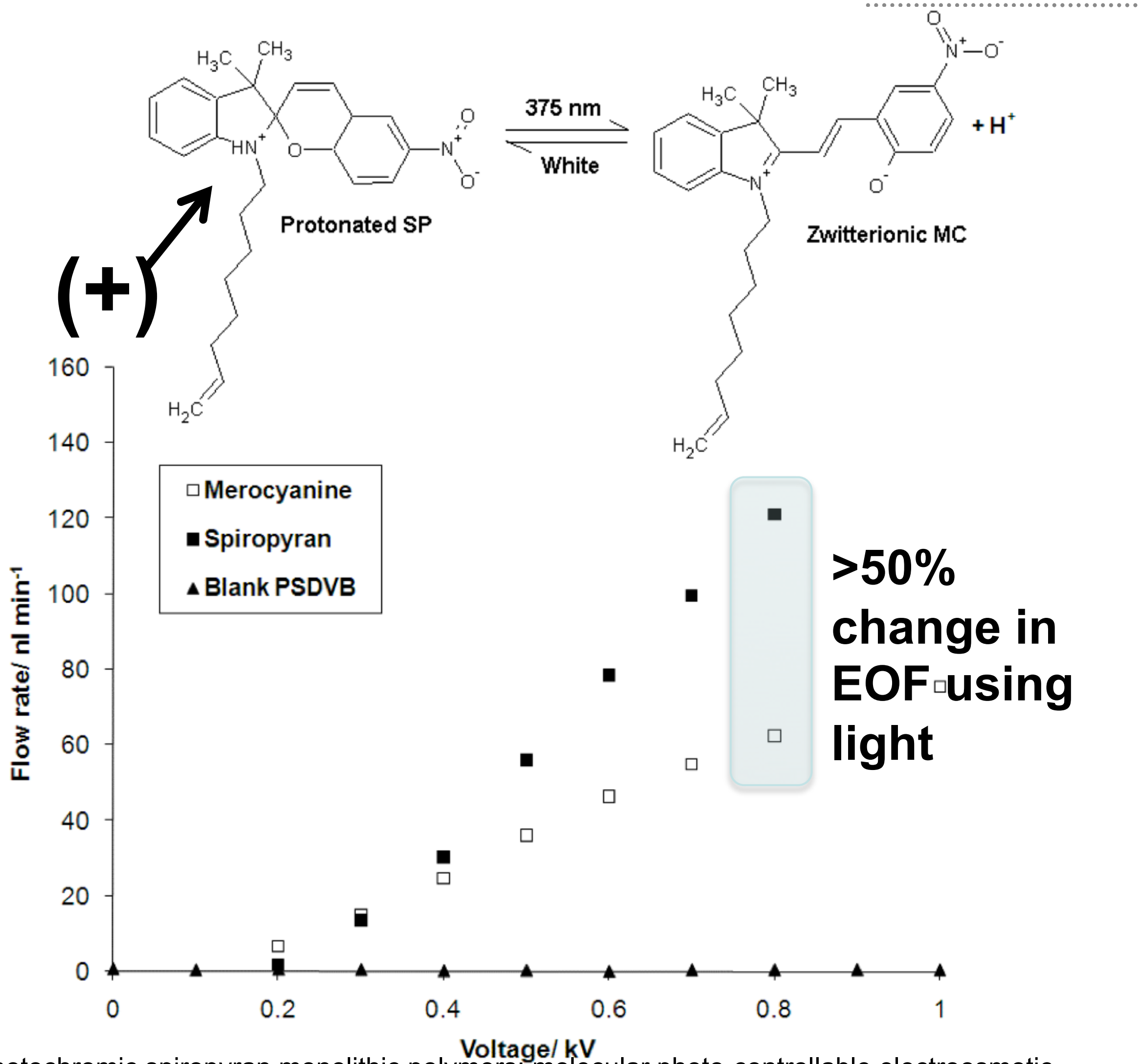


Optical microscope images of poly (spiropyran-*co*-divinylbenzene) monoliths in both the spiropyran (A) and merocyanine (B) forms.



Scanning electron micrograph of the monolithic poly (spiropyran-*co*-divinylbenzene) within the PTFE coated fused silica capillary; channel dimensions 8mm x 0.4mm x 0.4mm



Photochromic spiropyran monolithic polymers: molecular photo-controllable electroosmotic pumps for micro-fluidic devices, Zarah Walsh, Silvia Scarmagnani, Fernando Benito-Lopez, Silvija Abele, Fu-Qiang Nie, Conor Slater, Robert Byrne, Dermot Diamond, Brett Paull and Mirek Macka, J. Mater. Chem., 2009, submitted for publication

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

Polymer based photoactuators

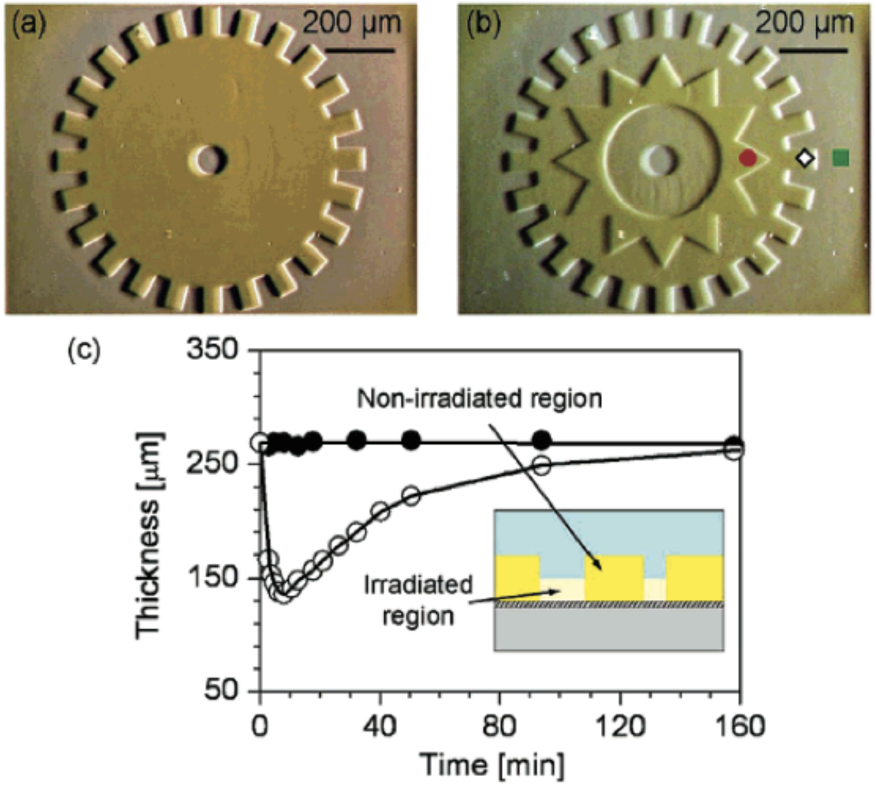
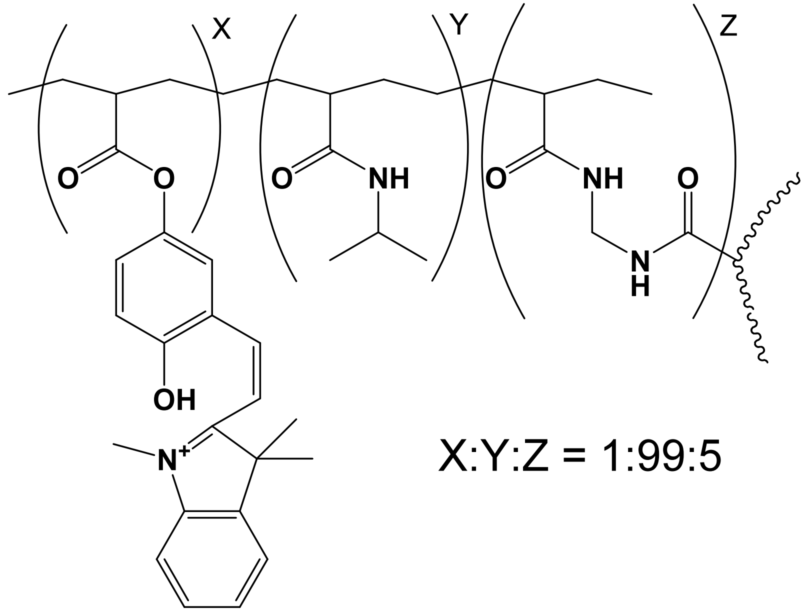


Figure 3. (a, b) Images of the pSPNIPAAm hydrogel layer just after the micropatterned light irradiation. Duration of irradiation was (●, red) 0, (◊) 1, and (■, green) 3 s. (c) Height change of the hydrogel layer in (●) non-irradiated and (○) irradiated region as a function of time after 3 s blue light irradiation.



X:Y:Z = 1:99:5

Polymer developed by by Kimio Sumaru et al[1]

1) *Chem. Mater.*, **19** (11), 2730 -2732, 2007.

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

Photo-actuator polymers as microvalves in microfluidic systems

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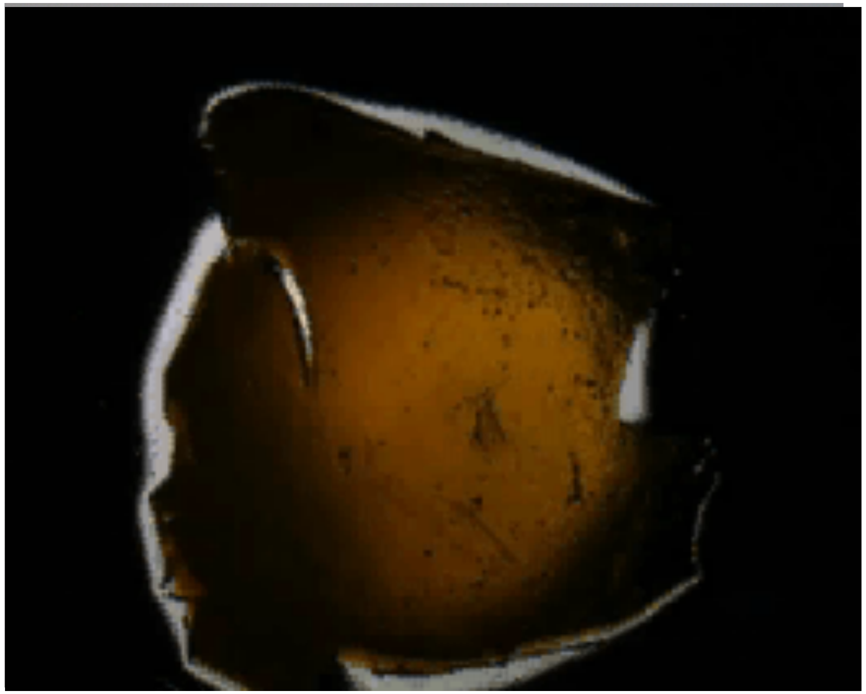
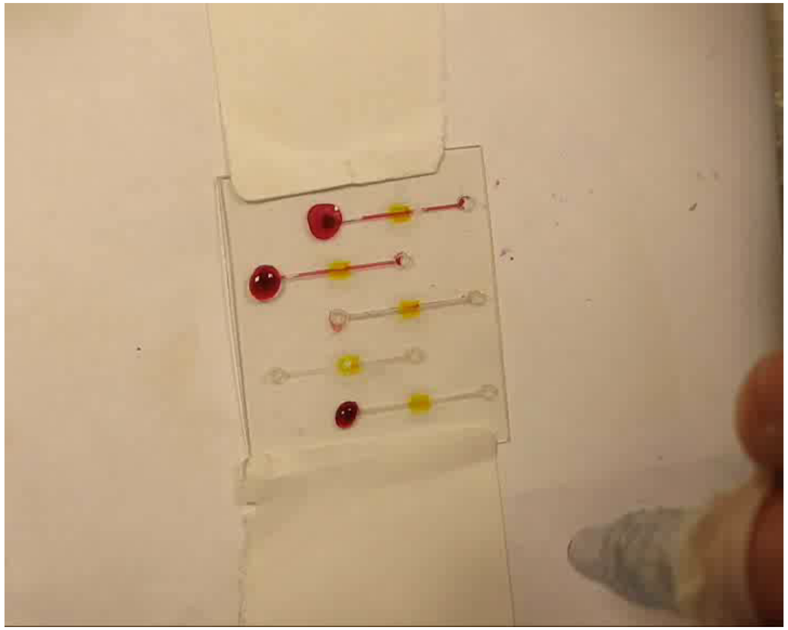
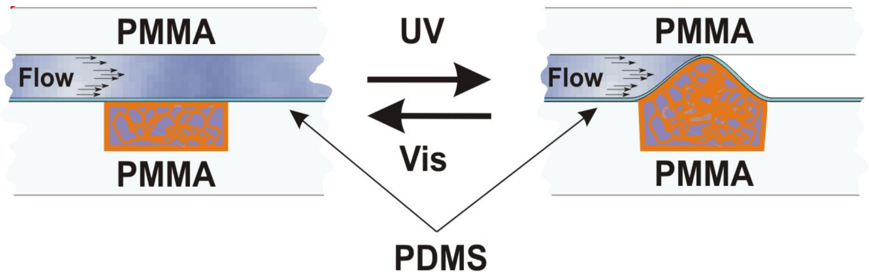
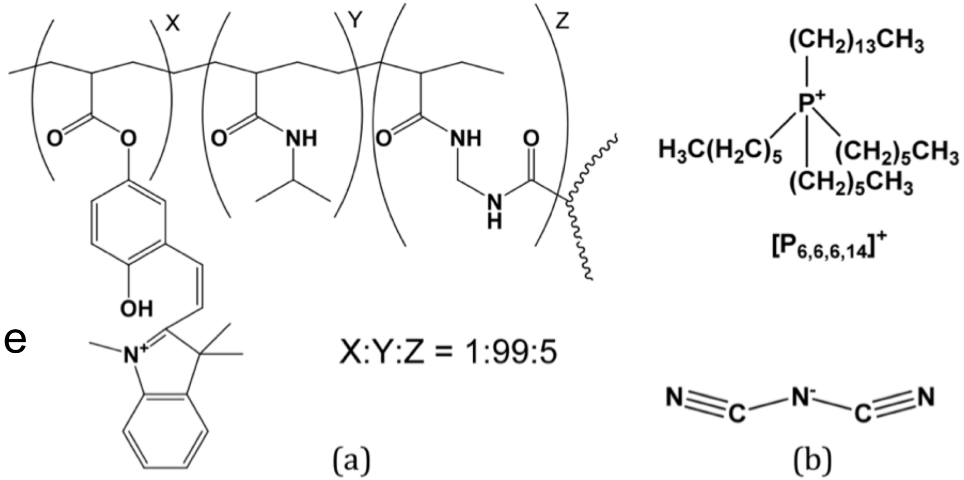






trihexyltetradecylphosphonium dicyanoamide
[P6,6,6,14][dca]



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

Mobile platforms with chemical actuation: No external power required

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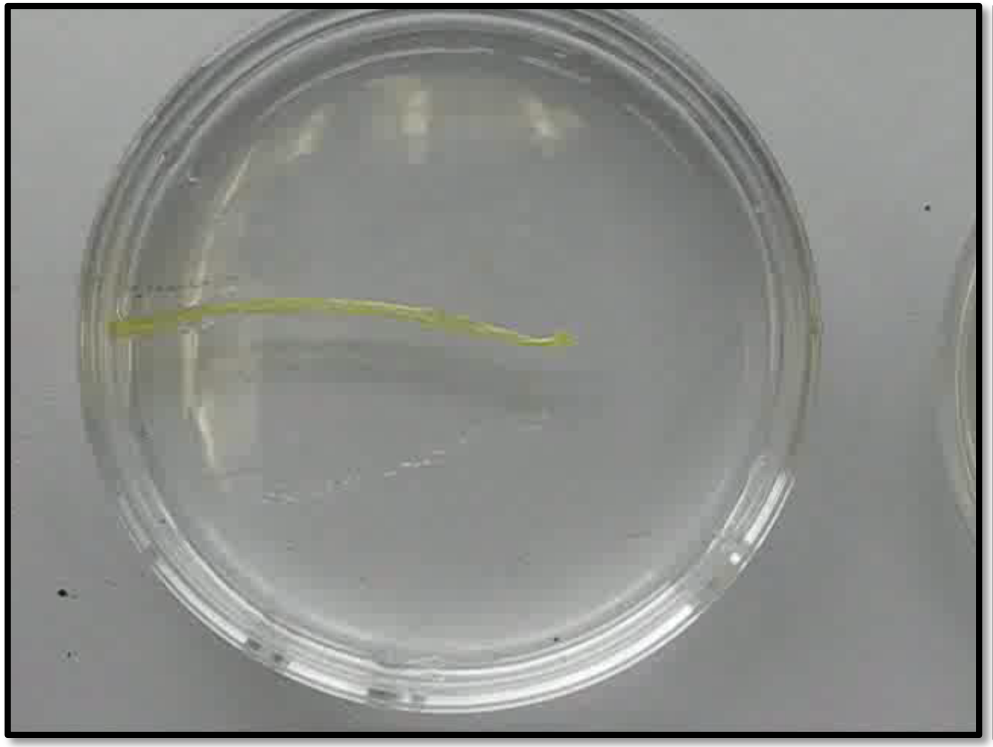

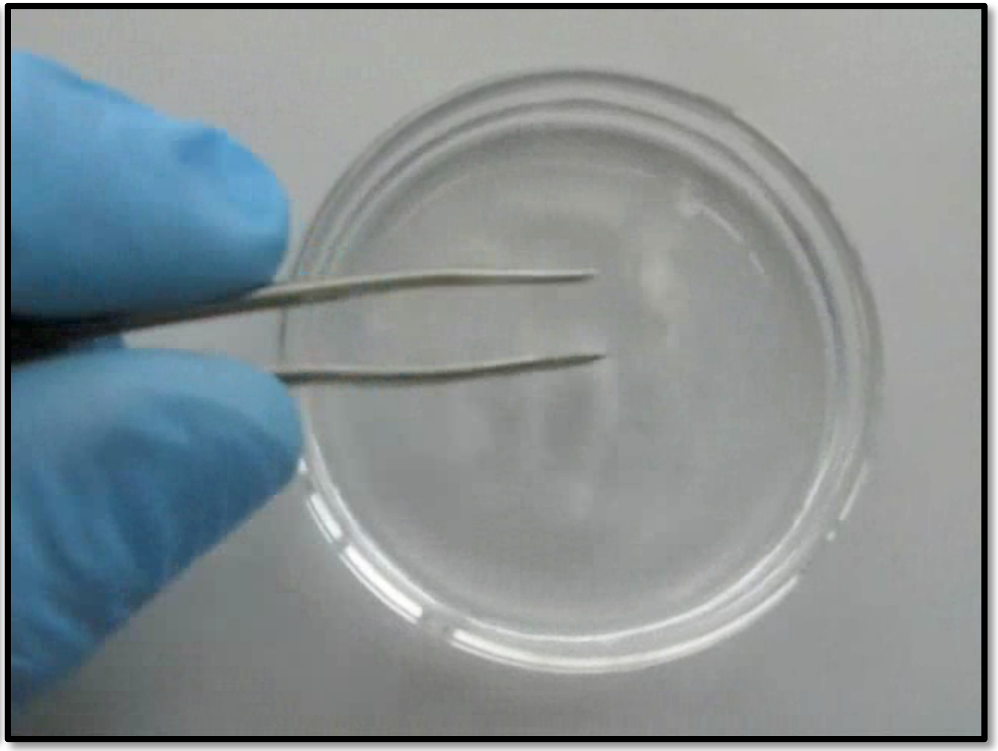

Based on solvent exchange within ionogel (water/ethanol)

Robert Byrne and Fernando Lopez

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Conclusions

- Switchable materials open the way to devices with radically different behaviour – much of which can be applied to analytical flow systems
  - Biomimetic polymer pumps and valves
  - Photocontrolled actuation
  - Photocontrolled uptake and release
  - Movement of loaded particles and structures
  - Very low power flow systems
  - …….

Very exciting possibilities for developing next generation analytical devices including separations targeting many environmental and pHealth applications

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