The quaternisation of phosphines:

A blank canvas reaction for the generation of smart materials for electrochemical devices.

Andrew Kavanagh

University College Dublin
8th August 2012.

Talk Outline

Introduction

- NCSR
- CLARITY
- Adaptive Sensors Group

Andrew Kavanagh

- Ionic Liquids
- Ionogels
- Ionic Liquid Synthesis

Electrochemical Devices

- **Device Complexity**

Electrochromic Displays

- **Leaching of electrolyte**

Polymeric Ionic Liquids

- **Device Sensitivity**

2-photon lithography

Conclusions & Acknowledgements

National Centre for Sensor Research

- Housed in the campus of Dublin City University.
- Multidisciplinary research institute invested in the advancement of sensor science.
- Over 260 full time researchers and support staff.
- Investments and income since 1999 now approaching € 100 million.

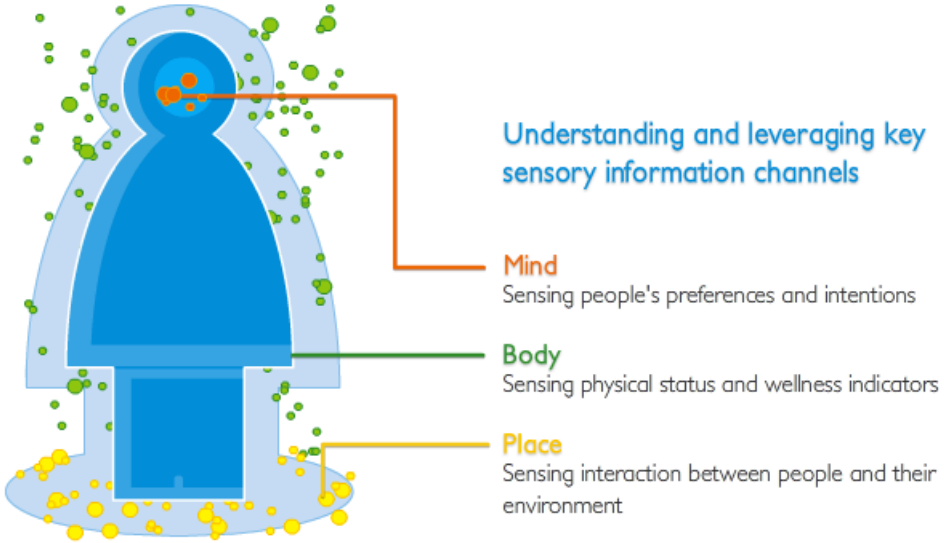
CLARITY
The Centre for Sensor Web Technologies

CLARITY – SFI CSET

CLARITY
clarity-centre.org

Vision: Sensing Mind, Body & Place

sfi Science Foundation Ireland

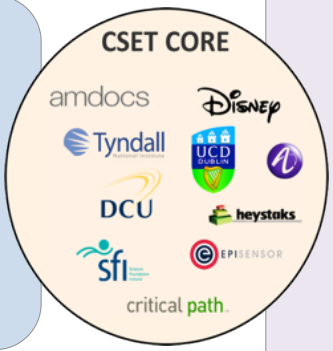


- 5-year, €16.4 million research program to develop next generation Sensor Web Technologies with significant environmental focus.
- Brings together fundamental materials science, functional polymers, device prototyping, energy management, adaptive middleware, wearable sensors, distributed environmental monitoring.

CLARITY Centre & Ecosystem

CLARITY
clarity-centre.org

SOCIAL/AGENCY COLLABORATORS



INDUSTRY COLLABORATORS

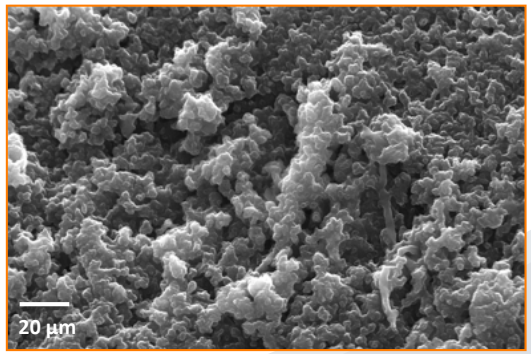
The Adaptive Sensors Group

- Chemical Sensor element of CLARITY.
- Group Leader: Professor Dermot Diamond.

- Contains >20 researchers engaged in:

Microfluidics
Electronic Engineering
Platform Testing (Analytical Chemistry)
Novel Materials Synthesis

Prof. Dermot Diamond



www.adaptivesensors.com

The Adaptive Sensors Group

Modus Operandi

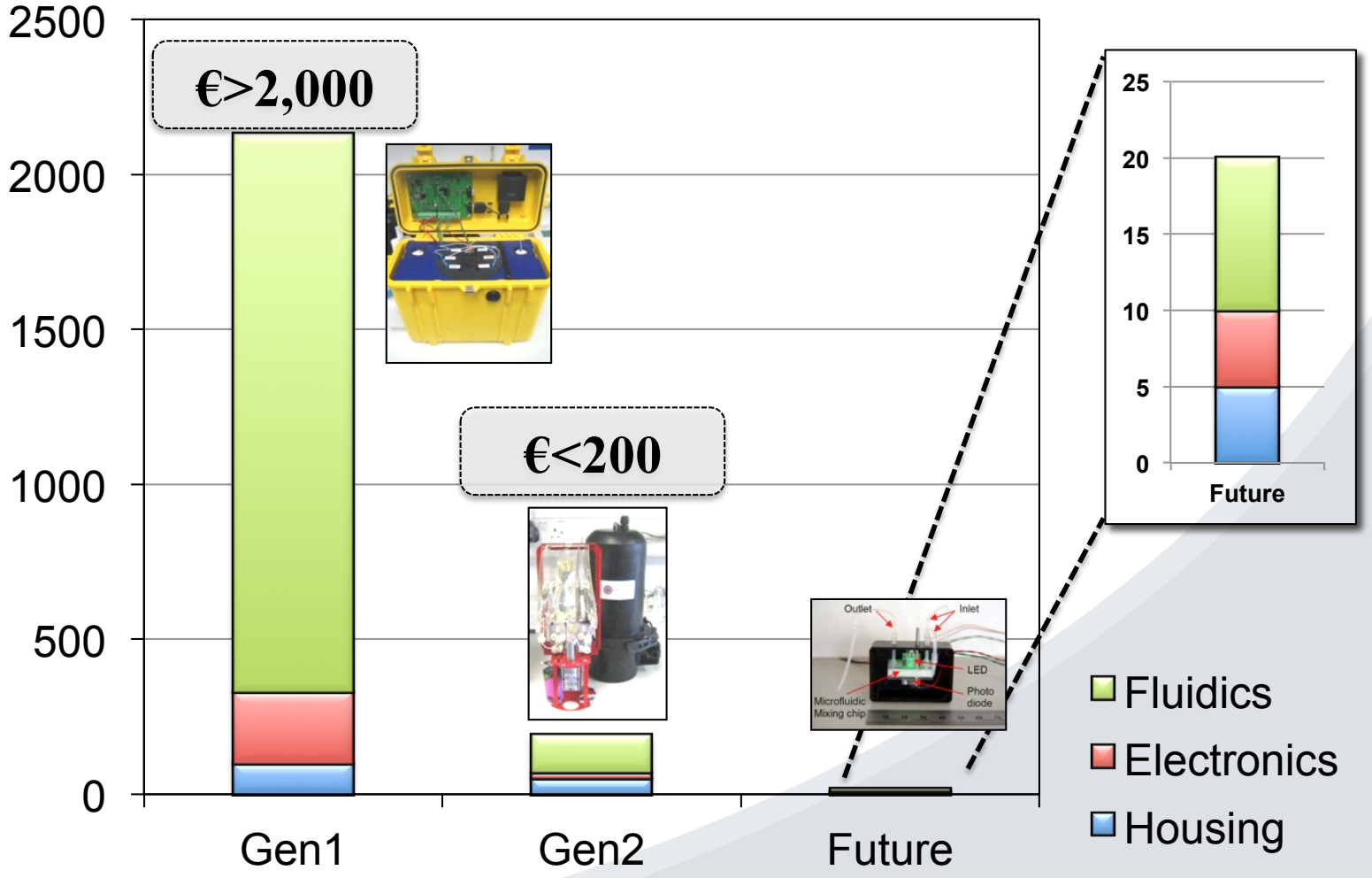
A two-pronged approach to improve the quality of autonomous environmental chemical analysers [1].

1. ***Evolutionary:*** Drive down the cost of analysers through clever engineering.

2. ***Revolutionary:*** Develop disruptive technologies based on break-throughs in fundamental materials science.

1. R. Byrne, C. Ventura, F. B. Lopez, A. Walther, A. Heise and D. Diamond, *Biosensors & Bioelectronics*, 2010, **26**, 1392-1398.

Platform Evolution: Autonomous Analyser for Phosphates in River Water



Current Industry Standard Instrument for Phosphate analysis costs in the region of € 15,000.

Mé Féin: Part of the Revolutionary Team!

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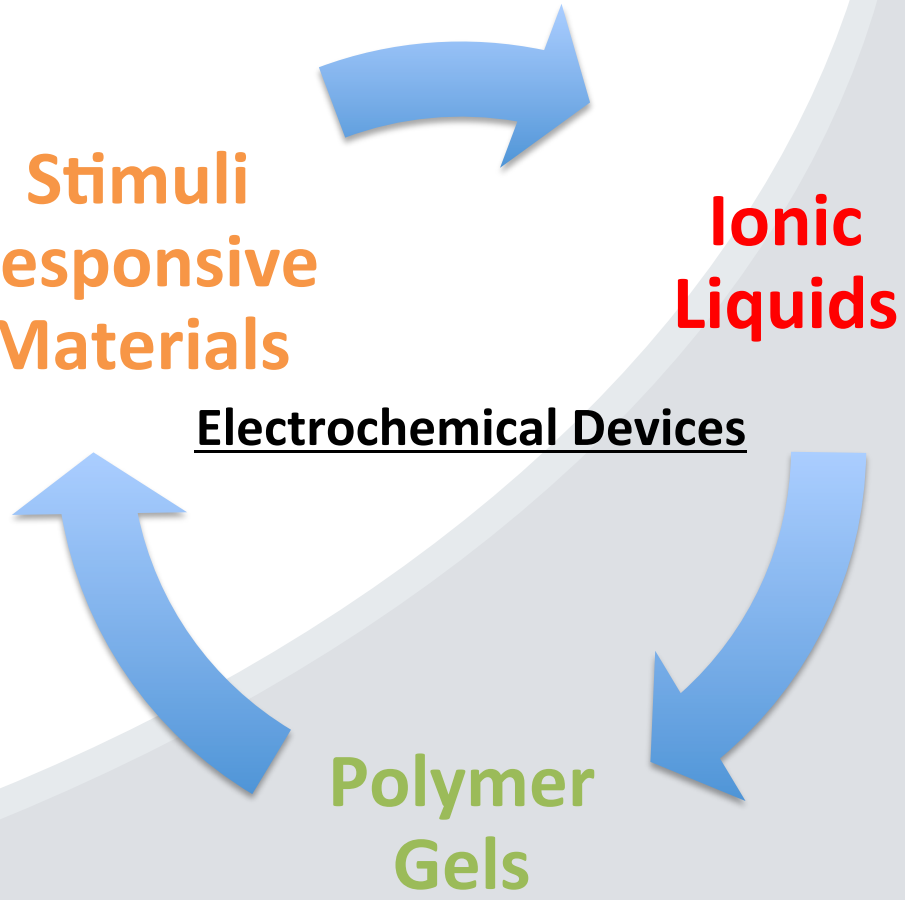
Research Interests:

- Thermal Actuators
- Lithography
- Optical Sensing
- Materials Synthesis
- Photodynamic Surface/Liquid control



Ionic Liquids

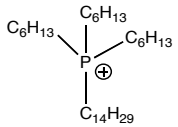
- **Organic liquids composed solely of ions.**[2]

- **Important liquid properties such as density, viscosity and melting point can be altered by variation of the ion pair.**[3]

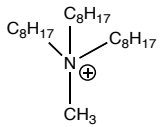
- **Ionic Liquids exhibit good ionic conductivity and stable electrochemical windows.**[4]

2. P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, WILEY-VCH, Weinheim, 2003.
3. R. E. Del Sesto, C. Corley, A. Robertson and J. S. Wilkes, *Journal of Organometallic Chemistry*, 2005, **690**, 2536-2542.
4. C. Zhao, G. Burrell, A. A. J. Torriero, F. Separovic, N. F. Dunlop, D. R. MacFarlane and A. M. Bond, *Journal of Physical Chemistry B*, 2008, **112**, 6923-6936.

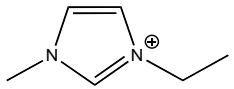
Cations



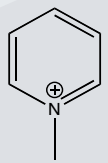
(i) $[P_{6,6,6,14}]^+$



(ii) $[N_{1,8,8,8}]^+$

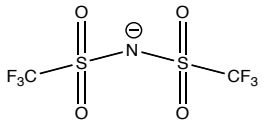


(iii) $[C_2mIm]^+$

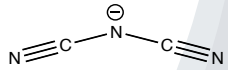


(iv) $[mpyr]^+$

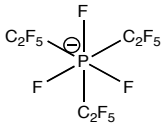
Anions



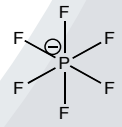
(v) $[NTf_2]^-$



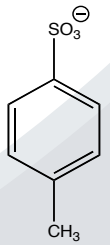
(vi) $[DCA]^-$



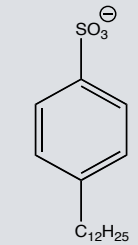
(vii) $[FAP]^-$



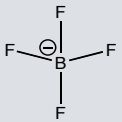
(viii) $[PF_6]^-$



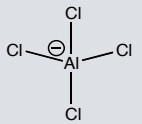
(ix) $[TOS]^-$



(x) $[DBSA]^-$

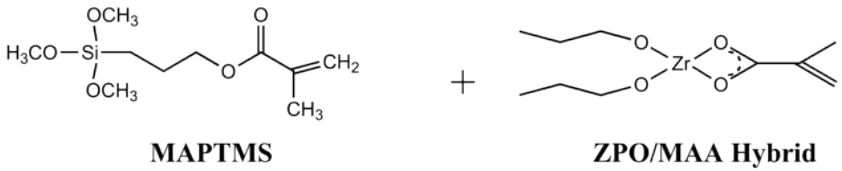


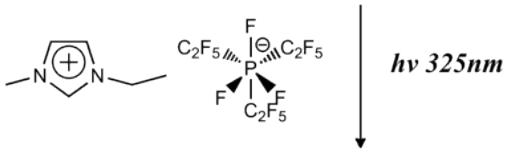
(xi) $[BF_4]^-$

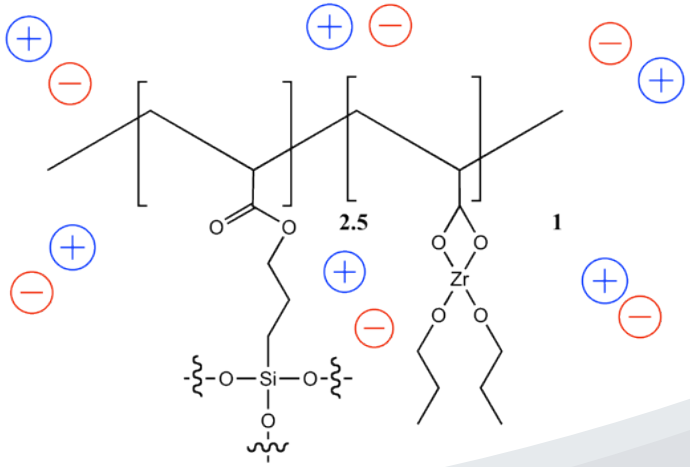


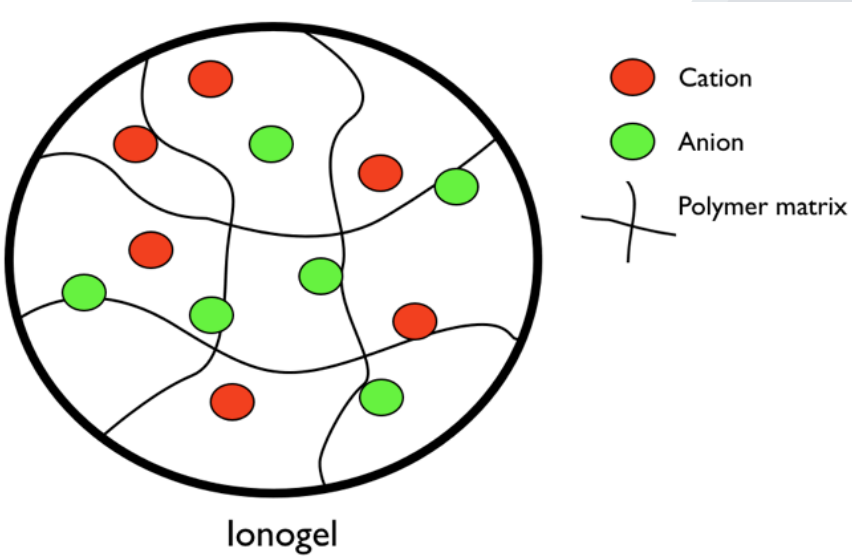
(xii) $[AlCl_4]^-$

IL encapsulated within a polymer network: *Ionogel*

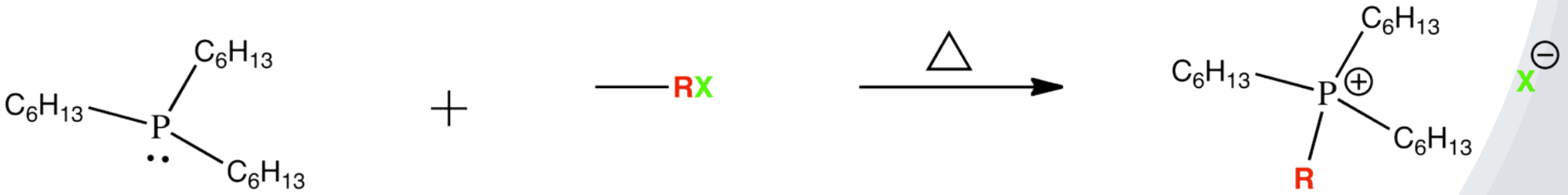






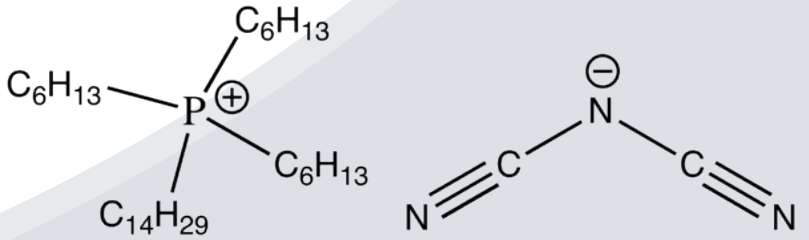


The blank canvas!



- Direct nucleophillic addition of a trialkyl phosphine with an alkyl halide to form a phosphonium salt.

- When: **R** = $C_{14}H_{29}$ and **X** = DCA^-….



Liquid at room temperature salt
η = 256 mPa's
T_{deg} = 395 ^0C [5]

5. K. J. Fraser and D. R. MacFarlane, *Australian Journal of Chemistry*, 2009, **62**, 309-321.

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- **Device Complexity**

Electrochromic Displays

- **Leaching of electrolyte**

Polymeric Ionic Liquids

- **Device Sensitivity**

2-photon lithography

Conclusions & Acknowledgements

Electrochemical Devices (ECD's)

3 Key Issues To Address:

1. **Device complexity**: Some electrochemical devices can contain multiple components, each with their own defined role relating to device performance.

2. **Leaching of electrolyte:** Loss of electroactive components dramatically reduces device lifetime!

3. **Device Sensitivity:** For electrochemical sensors in particular, increased sensitivity of device components can dramatically improve sensor performance.

Ionic Liquids have the answer!!

Device Complexity:

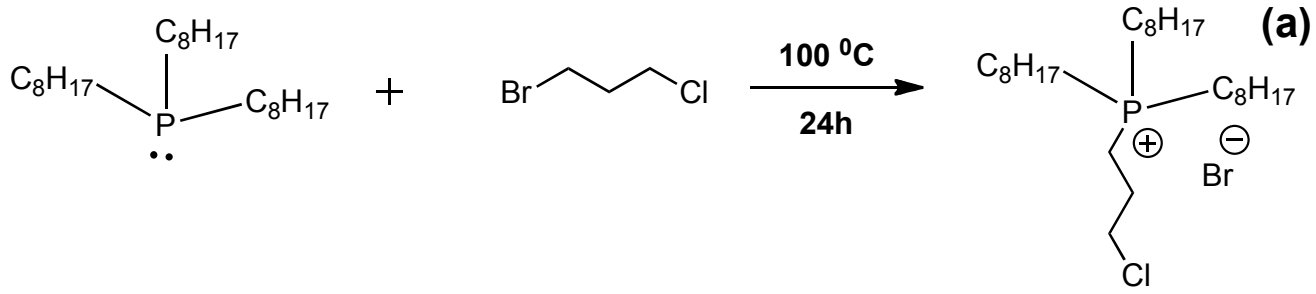
Electrochromic Devices

- **Electrodes** Source of charge, site of electrochemical reaction
- **Electrolyte** Facilitates charge transfer between the electrodes
- **Electrochrome** Redox active material which undergoes a change in optical properties in response to the applied voltage
- **Polymer** Inert matrix to house active sensing components
- **Plasticizer** Lowers T_g of polymer to produce solid film

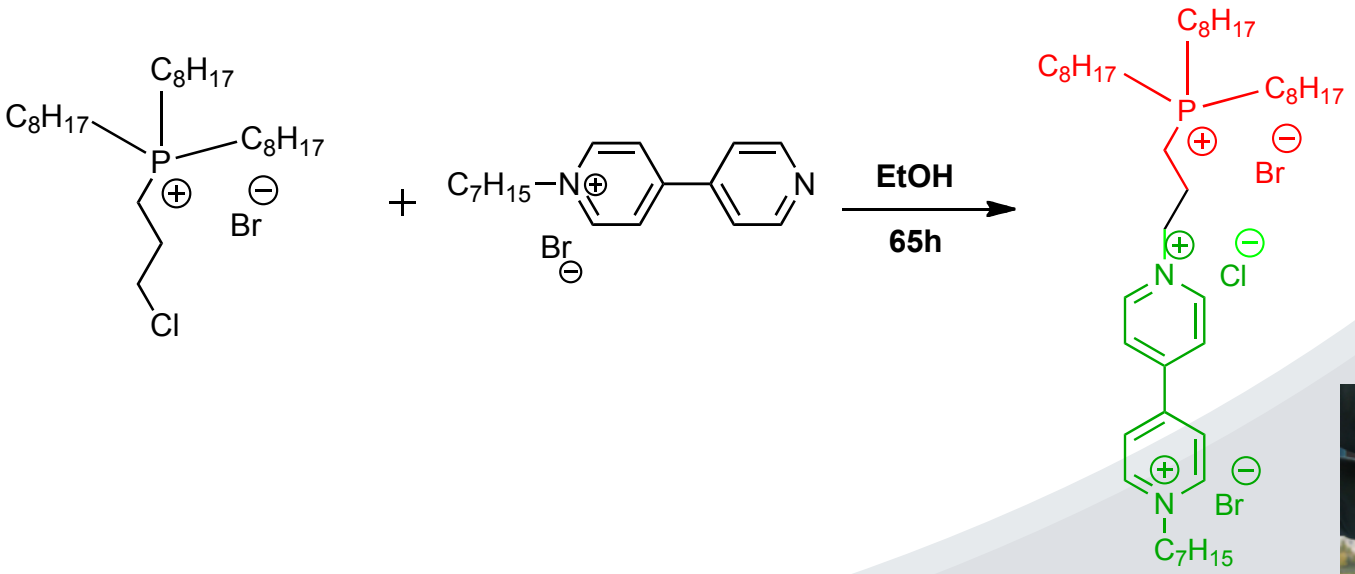
Rich variation in optical properties of PEDOT based ECD's. [6]

6. S. A. Sapp, G. A. Sotzing and J. R. Reynolds, *Chemistry of Materials*, 1998, **10**, 2101-2108.

Phosphonium based, electrochromic ionic liquid

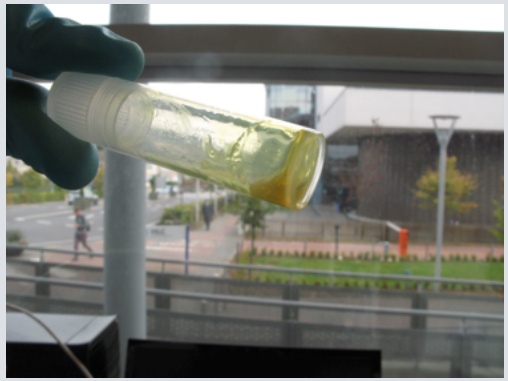


(a): $[P_{3Cl,8,8,8}][Br]$

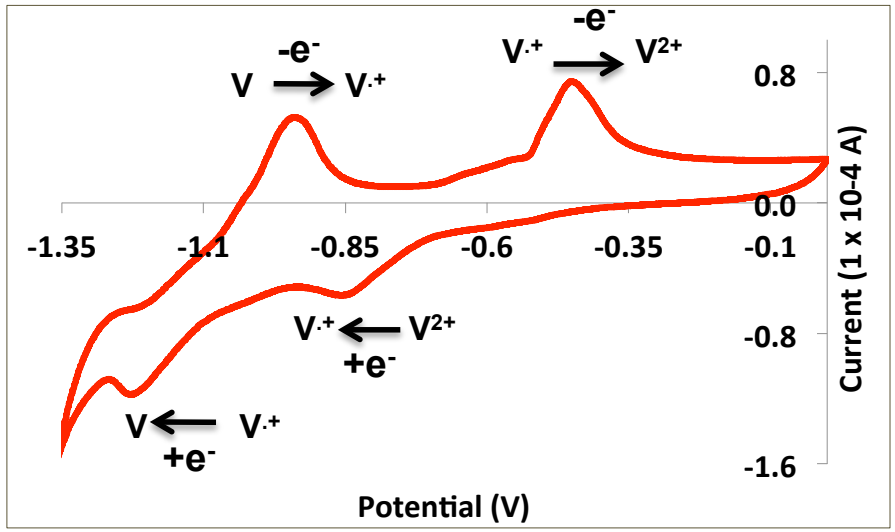


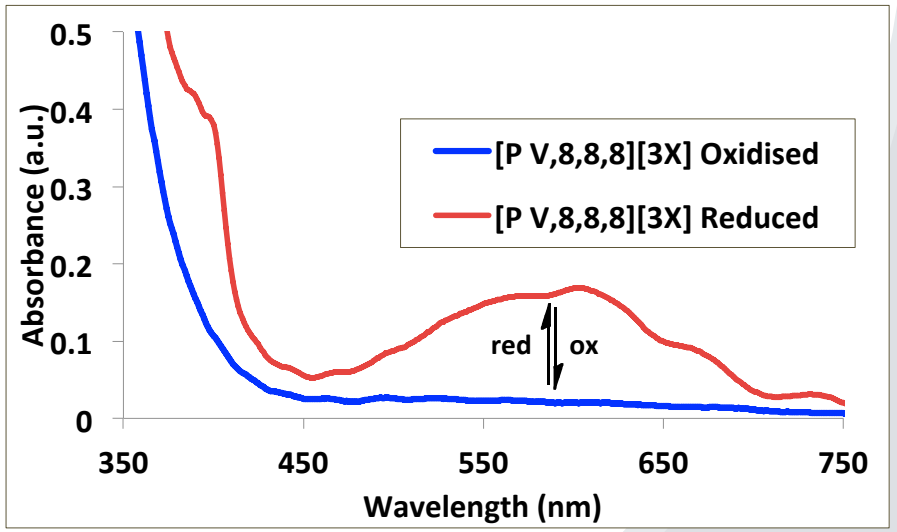
Electrolyte

Electrochromic

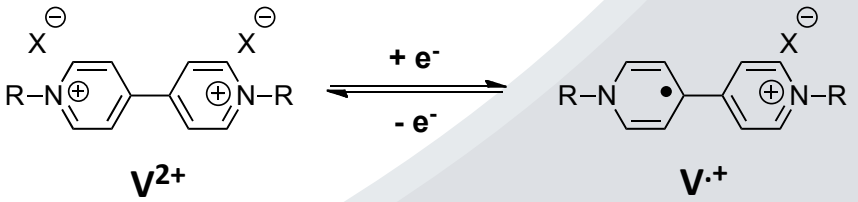


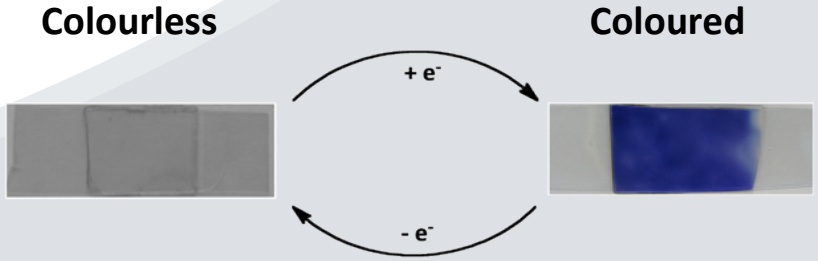
Spectroelectrochemistry





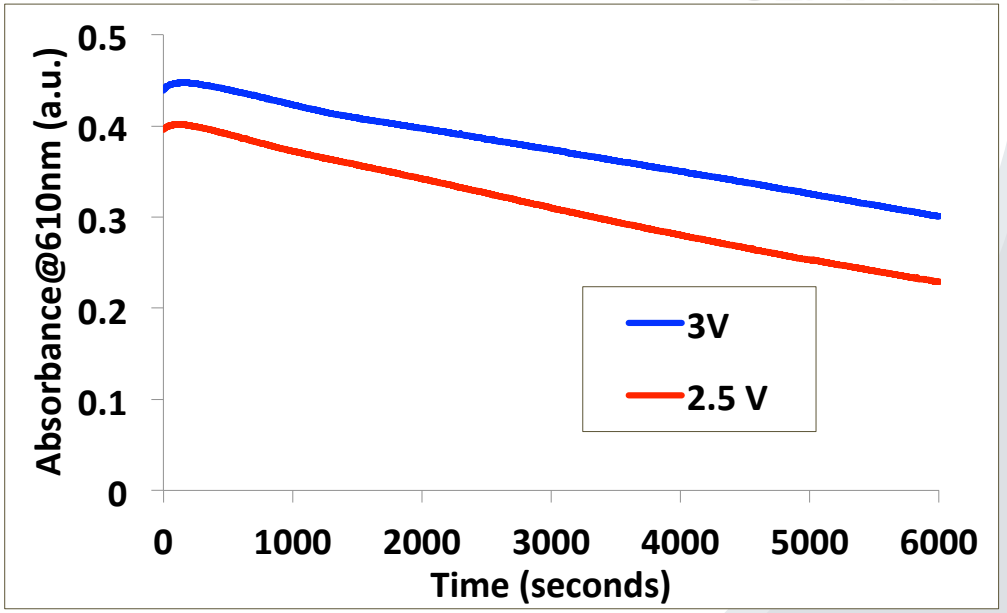
- Electrochromic device fabricated from an ionogel containing the Electrochromic IL.



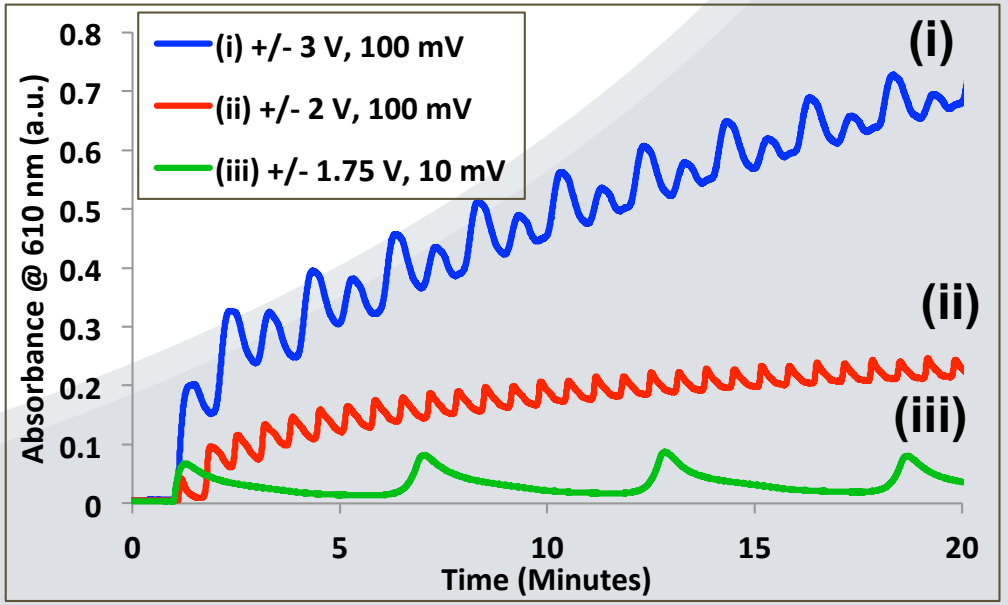


Device Output

- **DC Current:** ~ 60 % of device coloration is maintained after 100 minutes under open circuit.



- **AC Current:** Device can switch between transparent and coloured states under the right cycling conditions.



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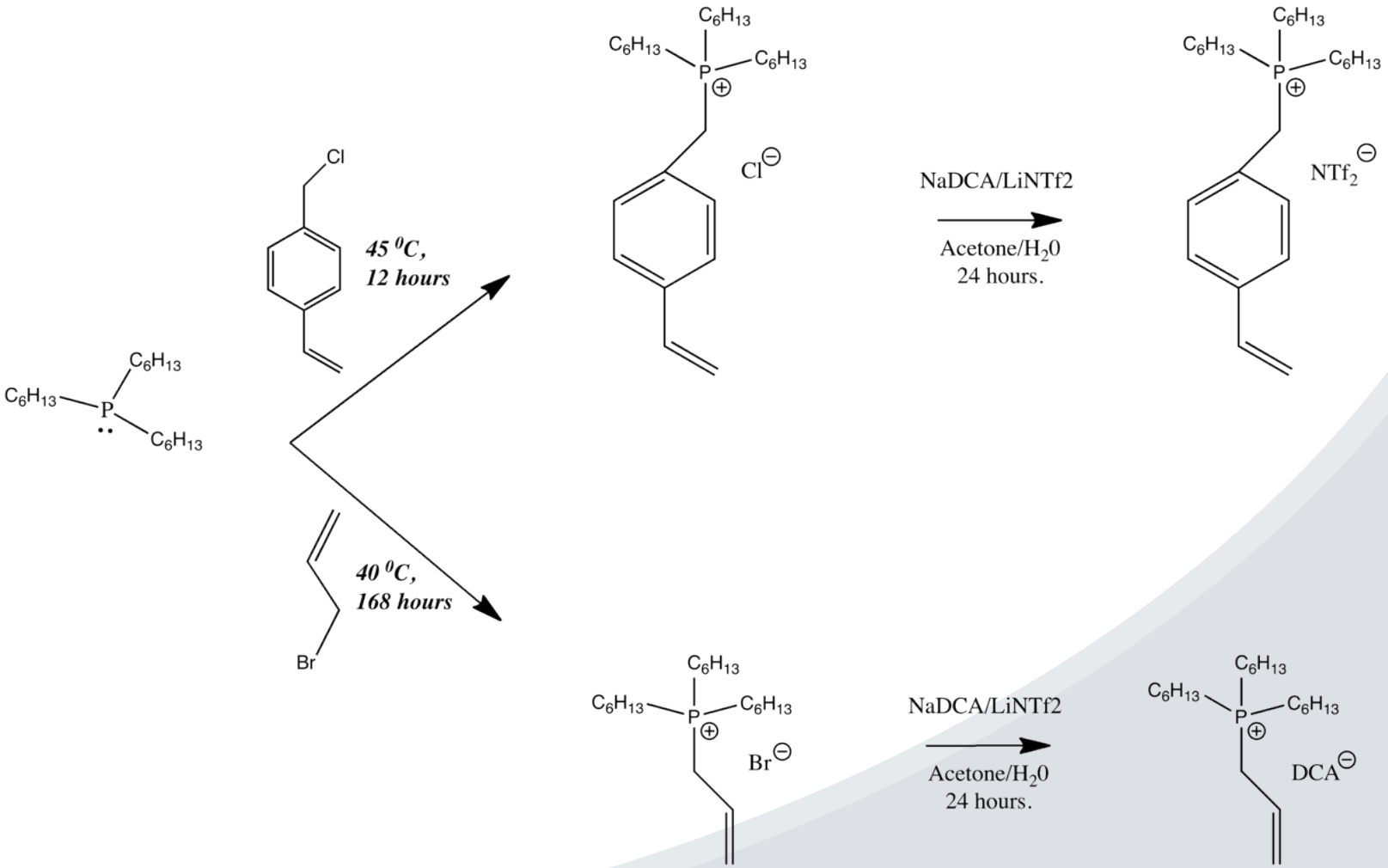
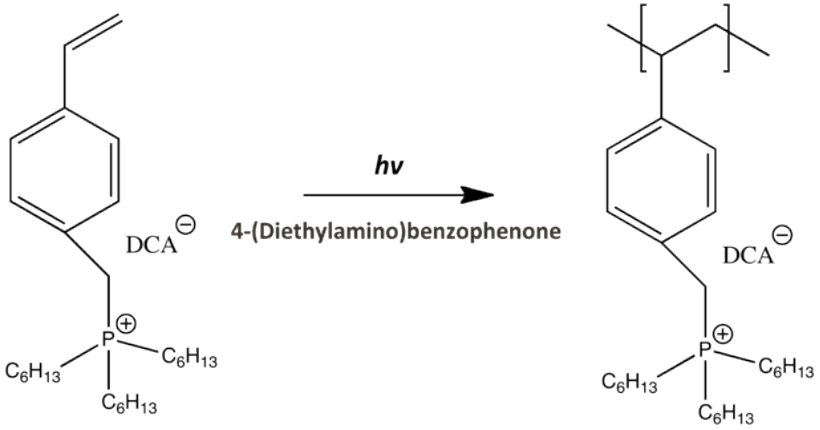
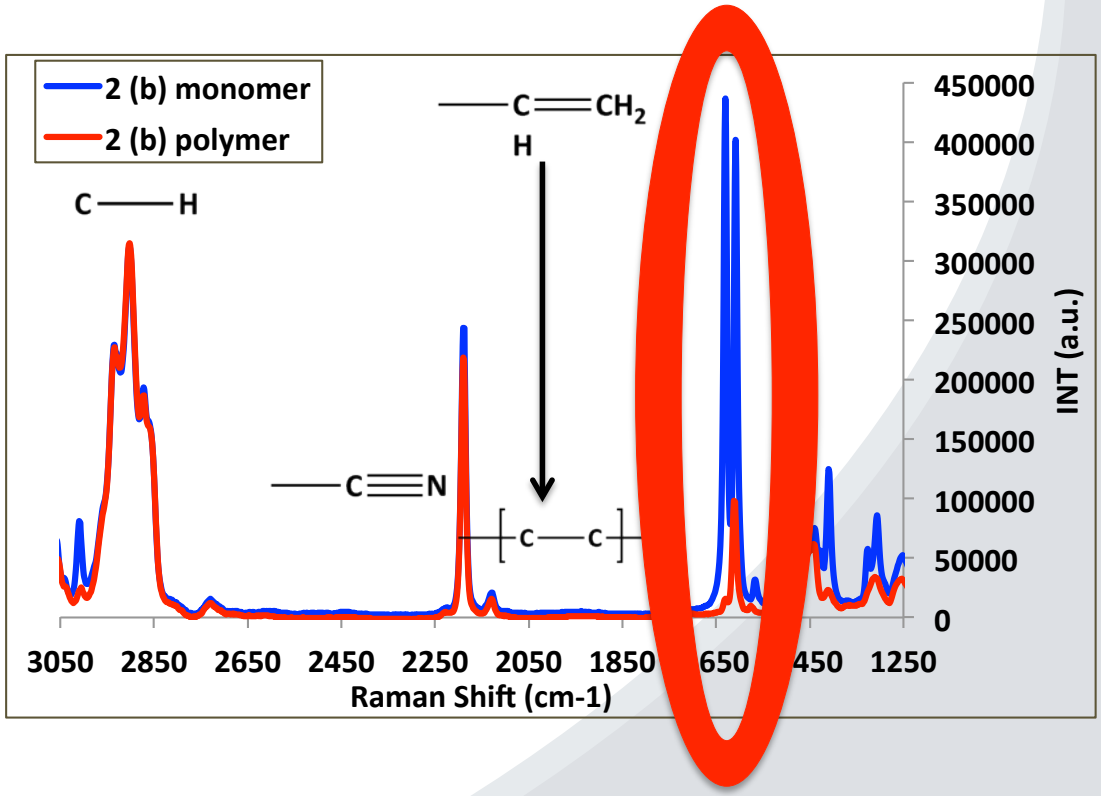
Device Leaching

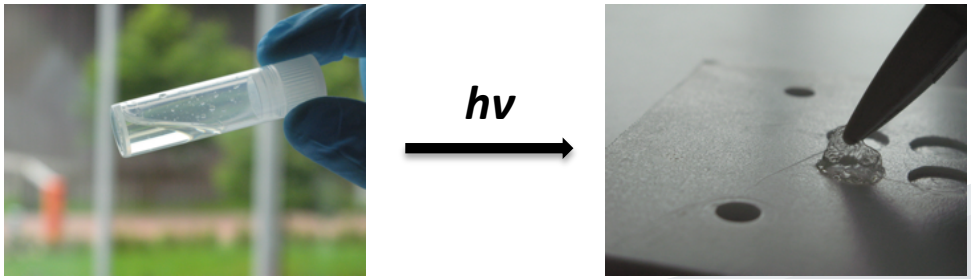


9 Monomeric ILs synthesised in total.

Poly IL characterisation







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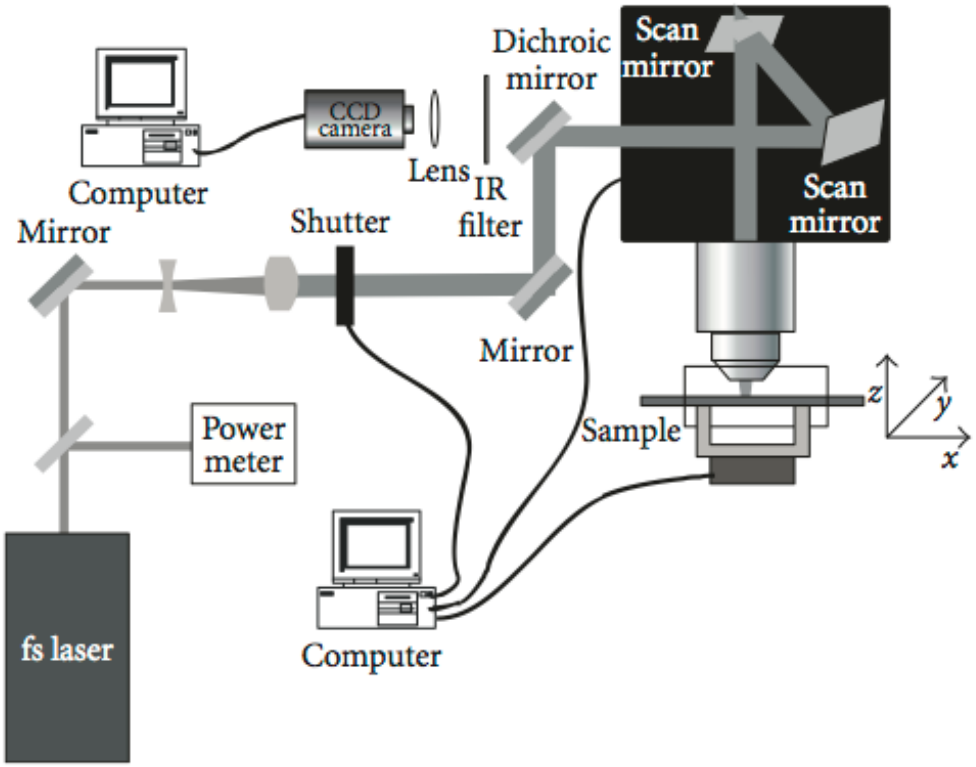
Material sensitivity

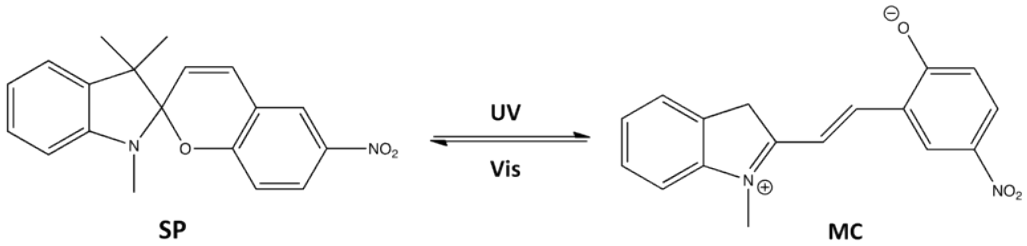
2-photon polymerisation: a direct laser lithographic technique.



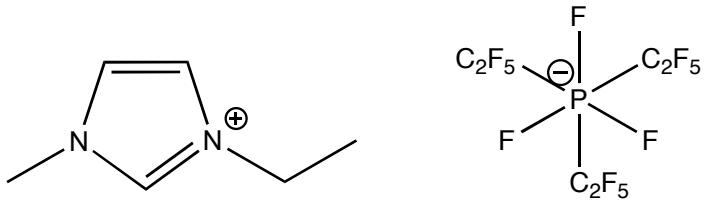
- **High frequency laser impulses are passed through high aperture lensing.**
- **Results in the two photon effect, i.e. Initiator in liquid resin absorbs two photons instead of one.**
- **Piezoelectric motor controls the movement of the resin in three dimensions. [7]**

7. A. Ovsianikov, A. Gaidukeviciute, B. N. Chichkov, M. Oubaha, B. D. MacCraith, I. Sakellari, A. Giakoumaki, D. Gray, M. Vamvakaki, M. Farsari, C. Fotakis, *Laser Chemistry*, 2008.

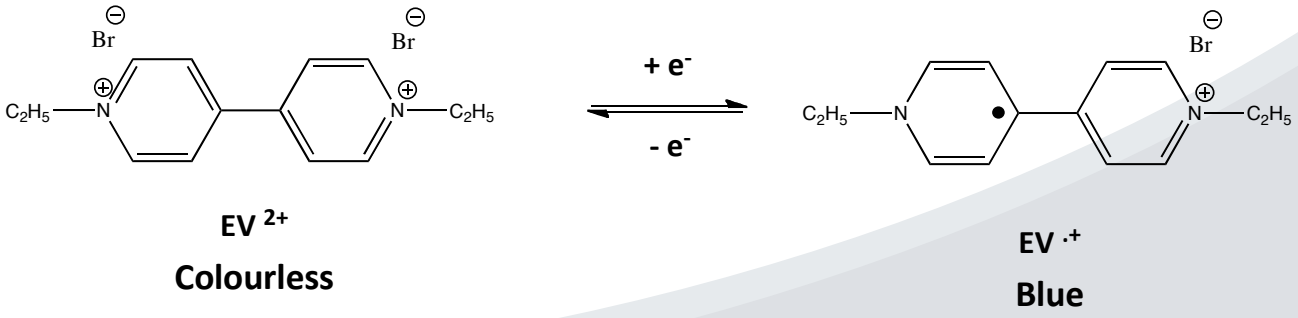
Direct, 3-D laser printing of stimuli responsive materials



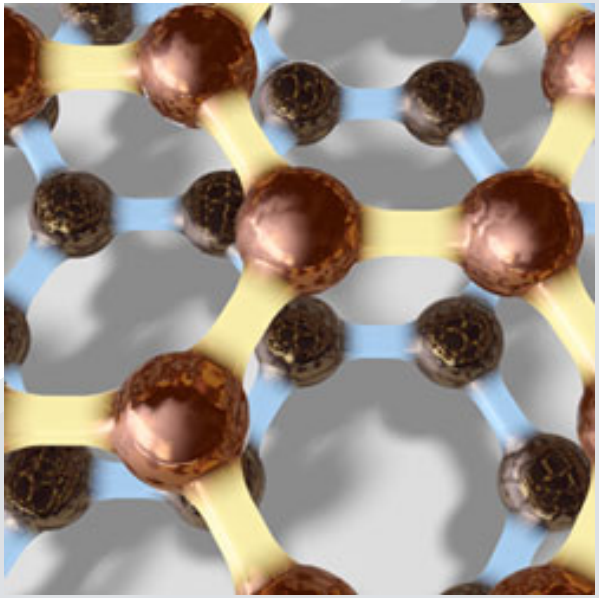
Photochromics - *Spirocyclics*



Ionic Liquids

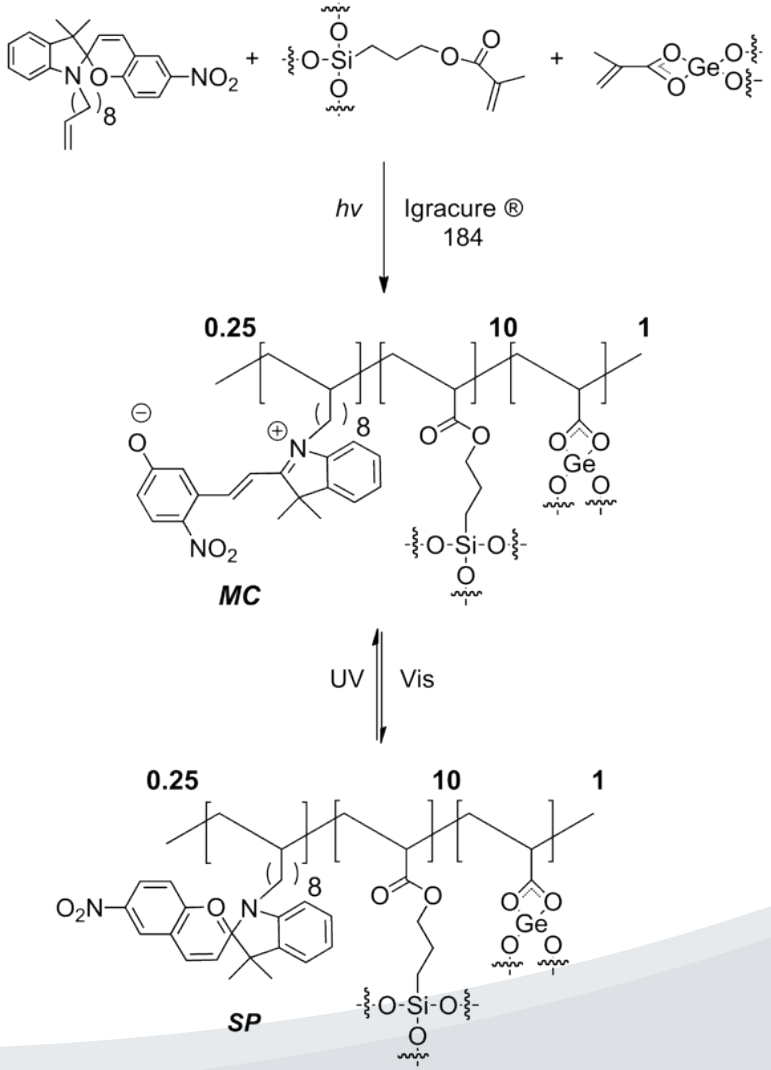


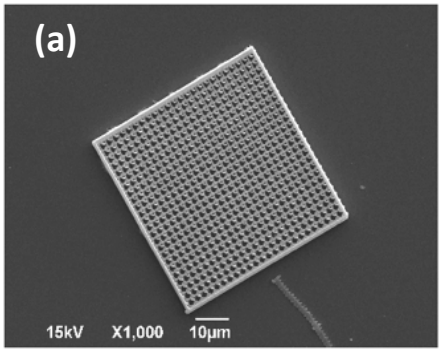
Electrochromics - *Viologens*

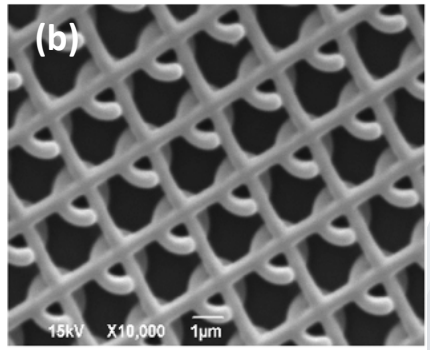


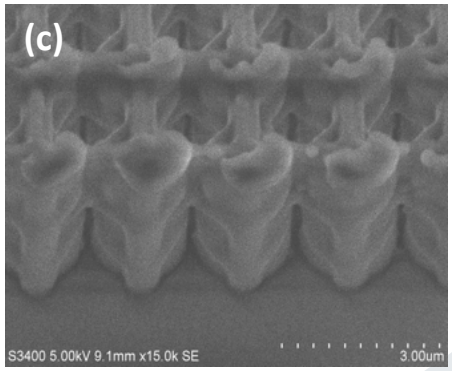
Dispersed graphene sheets

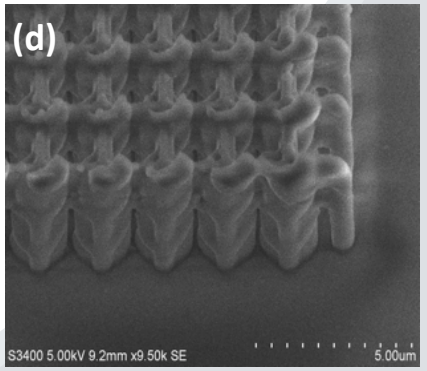
Sub-micron, photoresponsive structures

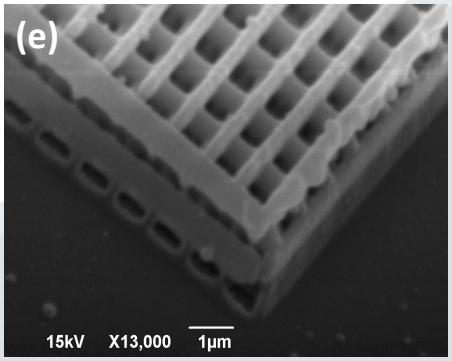


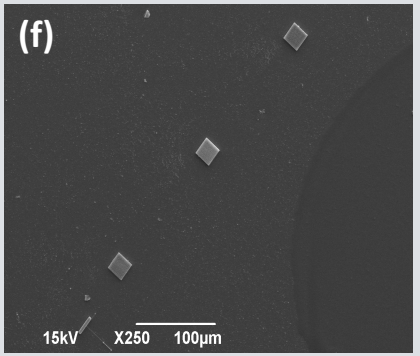




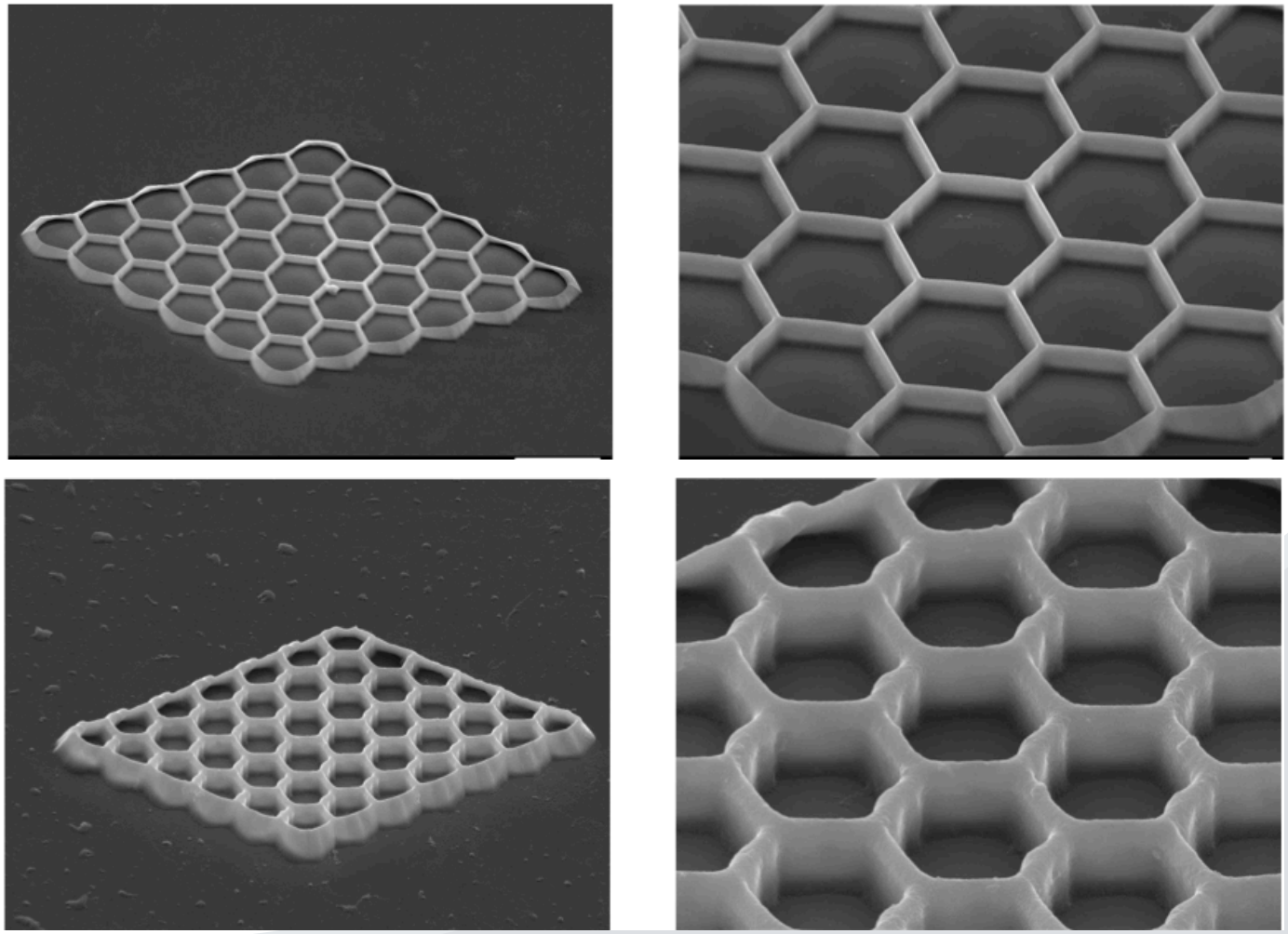






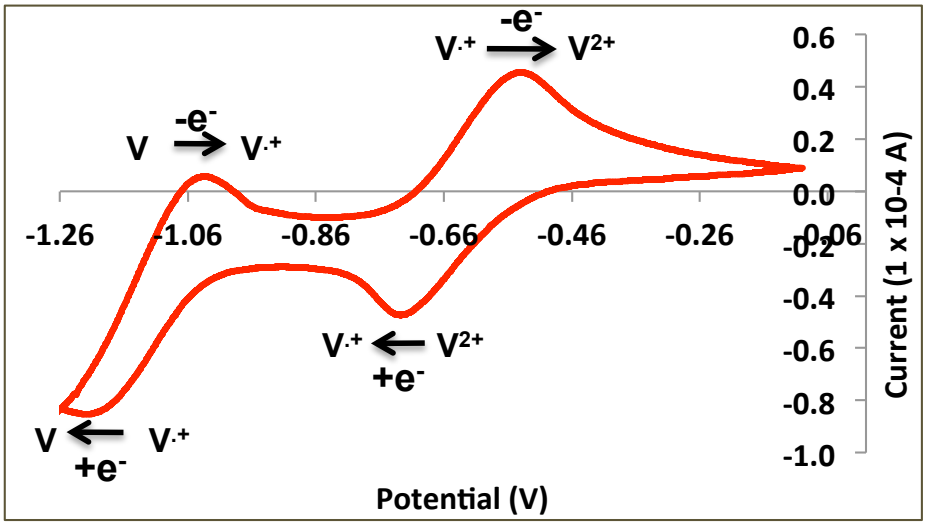


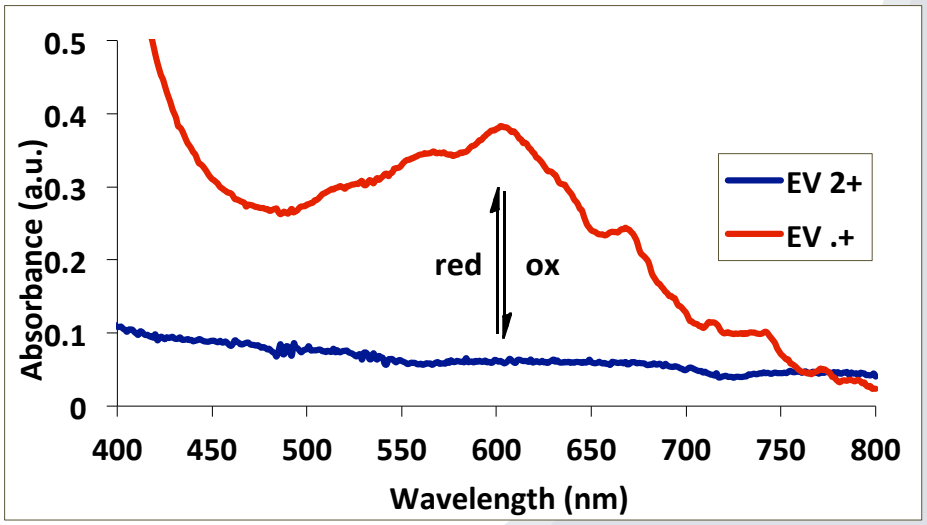
Photopatterned, graphene dispersed ionogels



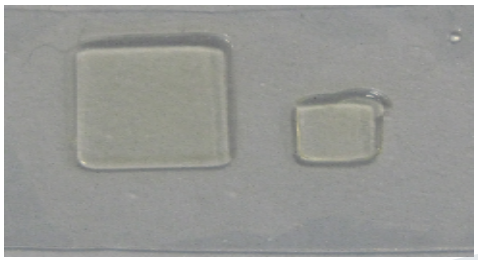
- 8 µm honeycomb diameter
- 2 µm honeycomb diameter

Photopatterned, electrochromic device





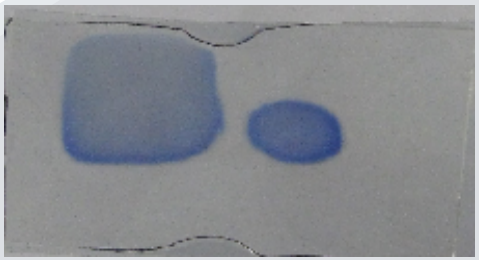
EV^{2+}



$+e^-$, E_{red}: -1V

$-e^-$

$EV^{\cdot+}$



λ_{max} 610 nm

Conclusions

- **Device Complexity:** Synthesised Electrochromic IL acts as the electrolyte and the electrochrome when encapsulated between two electrodes.

- **Leaching of Electrolytes:** Synthesised polymeric Ionic Liquids form flexible, conductive films.

- **Material Sensitivity:** 2 - photon lithography is an attractive technique for the generation of high resolution structures *in situ.*

Further Reading

1. **Andrew Kavanagh**, Kevin J. Fraser, Robert Byrne and Dermot Diamond *"An electrochromic ionic liquid: design, synthesis, characterisation and performance in a solid-state platform"*, **Chemistry of Materials, 2012 (Article Submitted).**
2. Mohamed Oubaha**, Andrew Kavanagh**, Arnaud Gorin, Gabija Bickauskaite, Robert Byrne, Maria Farsari, Richard Winfield, Dermot Diamond, Colette McDonagh and Robert Copperwhite**,** *"Graphene-doped photo-patternable ionogels: tuning of conductivity and mechanical stability of 3D microstructures"***, Journal of Materials Chemistry, 2012, 22, 10552-10559.**
3. **Andrew Kavanagh,** Robert Byrne Dermot Diamond and Kevin J. Fraser**,** *"Stimuli Responsive Ionogels for Sensing Applications - An Overview"* **- Membranes, 2012, 2, 16-39. Review contribution as part of special edition entitled "Stimuli Responsive Polymers".**
4. **Andrew Kavanagh,** Matthias Hilder, Noel Clark, Aleksandar Radu and Dermot Diamond**,** *"Wireless Radio Frequency Detection of Greatly Simplified Polymeric Membranes based on a Multifunctional Ionic Liquid"***, Electrochimica Acta, 2011,56, 8947-8953.**
5. Dimitrije Cicmil, Salzitsa Anastasova**, Andrew Kavanagh,** Dermot Diamond, Ulriika Mattinen, Johan Bobacka, Andrzej Lewenstam and Aleksandar Radu**,***"Ionic Liquid based, Liquid Junction Free Reference Electrode"***, Electroanalysis, 2011, 23(8), 1881–1890.**
6. **Andrew Kavanagh**, Robert Copperwhite, Mohamed Oubaha, Jessica Owens, Colette McDonagh, Dermot Diamond and Robert Byrne**,** *"Photopatternable Ionogels for Electrochromic Applications"***, Journal of Materials Chemistry, 2011, 21, 8687-8693.**
7. **Andrew Kavanagh,** Robert Byrne, Dermot Diamond and Aleksandar Radu**,** *"A two component optode membrane based on a multifunctional ionic liquid"***, Analyst, 2011, 136, 348-353.**

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Thanks for listening!!