Photopatternable ionogels for electrochromic applications

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Introduction:

Class two sol-gel materials are particularly attractive for research purposes as they exhibit both the intrinsical characteristics of glassy substances, but also the flexibility of organic based polymers.
By performing the chemistry needed to synthesise these sol-gels in the presence of Ionic Liquid's (IL's), so called *"Ionogels"* are formed which the exhibit characteristics typical of the IL within a solid medium.
Of relevance to this work is the fact that some ionogels can exhibit impressive ionic conductivities.
If these materials are to be used in future technologies, then the ability to spacially define their exact physical conformation represents an challenging incentive.
Herein this works describes the structural encapsulation, intrinsic ionic conductivity characterisation and the direct photopatterning of hybrid organic/inorganic ionogels

Experimental:

•IL's chosen in this study are shown in Figure 1. These particular liquids were chosen as they exhibit relatively low viscosities, which is more favourable for electrolyte applications.

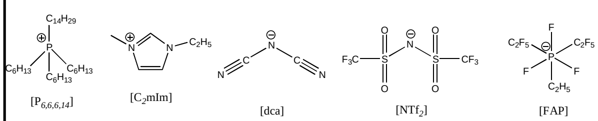

Figure 1: The cations and anions used in this study: (i) trihexyl(tetradecyl)phosphonium, (ii) 1-ethyl-3-methylimidazolium, (iii) dicyanamide, (iv) bistrifluoro(sulfonyl)imide and (v) *tris* (pentafluoroethyl)trifluorophosphate.

Ionogel Synthesis:

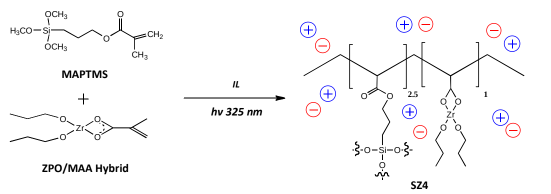

Figure 2: Synthesis and possible structure of hybrid, photopatternable ionogels.

• *Methacryloxypropyltrimethoxysilane (MAPTMS)* is a hybrid precursor which permits classical sol-gel chemistry but also radical polymerisation via a tethered acrylate moiety.

•Addition of a Zirconium based methacrylic acid complex (ZPO/MAA) increases the rate of polymerisation leading to a dry transparent surface.

• An IL can be encapsulated within this gel network via simple mixing with the precursors and direct UV polymerisation, generating the hybrid ionogel SZ4.

Results & Discussion:

Electrochemical Impedance Spectroscopy (EIS)

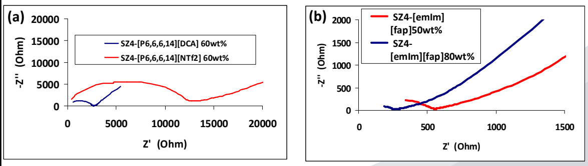

Figure 4: Nyquist plots obtained for *(a)* 60 wt% [$P_{6,6,6,14}$] [DCA] and [NTf_2] in SZ4 ionogel, *(b)* [emIm][fap] at 50 and 80wt% in SZ4 ionogel.

• EIS demonstrates the change in *Resistance of Charge Transfer* of the ionogel as a function of:
(a) the anion of the IL and;
(b) the effect of an increase in IL concentration in the ionogel composition.

Ionogel Structuring:

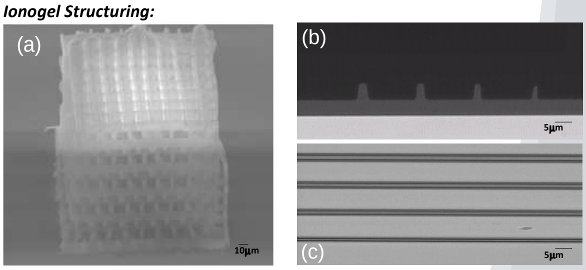

Figure 4: *(a)* SEM images of three-dimensional woodpile structures from SZ4-20wt% [$P_{6,6,6,14}$][DCA]; *(b)* and *(c)* direct laser photopatterning of SZ4-20wt% [$P_{6,6,6,14}$][DCA].

• 2-photon polymerisation (2PP) is a powerful instrumental technique which allows direct photopolymerisation as a function of the tri-axial movement of an incident laser source (λ 780 nm) .

•Fabrication of a 3D woodpile structure with sub-micron resolution *(a)* was achieved.

•Direct UV laser writing (λ 325 nm) of the ionogels was also performed, resulting in structures similar to optical waveguides *(b)* and *(c)*.

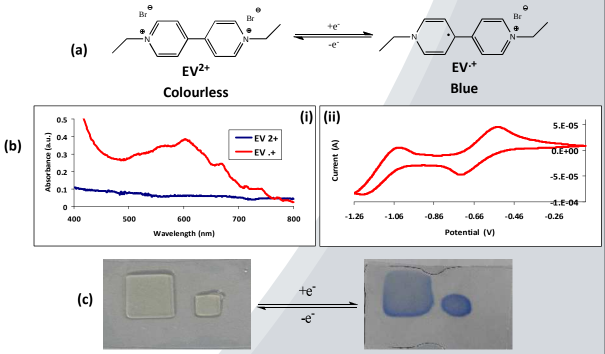

Figure 5 : *(a)* The voltaic equilibrium of the electrochromic dye *ethyl viologen dibromide (EV)* used in this work; *(b)* Spectroelectrochemistry obtained of EV doped ionogel. *(c)* Patterned ionogels on Indium Tin Oxide coated polyester exhibiting both coloured and bleached states of EV in a solid state device.

• EV is easily incorporated into the ionogel; which allowed the classical spectroelectrochemistry of EV to be obtained *(a)* and *(b)*.
• The first step to construct a solid state electrochromic device was to pattern the doped ionogels into squares using a UV filter chrome mask *(c)*. The original ionogel was then used as a supporting electrolyte around the squares to facilitate the prospective current being passed through it.

Conclusion:

A particular attractive quality of these ionogels is the ability to spatially define their precise location and structure by optical exposure. We believe there is a great potential for these materials to fulfill roles in future optoelectronic devices.
The ionogels studied also exhibited ionic conductivity which facilitated the construction of a fully functional solid state device. This demonstrates that these materials have equal potential to function as transparent and flexible electrochromic displays.

Further Reading:

A. Kavanagh, R. Copperwhite, M. Oubaha, J. Owens, C. McDonagh, D. Diamond and R. Byrne, *"Photopatternable Ionogels for Electrochromic Applications", J.Mater.Chem, 2011, 21, 8687-8693*.

Acknowledgement:

The authors would like to thank both Prof. B. Chichkov and Dr. A. Ovsianikov from the Laser Zentrum in Hannover for access to the 2PP instrument as well as both Cytec and Merck industries for the generous donation of the IL's used in this study.

Funding Acknowledgement
This work is supported by Science Foundation Ireland under grant 07/CE/I1147 including the SFI-funded National Access Programme (NAP) grant NAP210 and by Enterprise Ireland grant 07/RFP/MASF812, which is part of EU-MATERA initiative.

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