# SUPPORTING INFORMATION

## *An electrochromic ionic liquid: design, characterisation and performance in a solid-state platform.*

*Andrew Kavanagh, Kevin J. Fraser, Robert Byrne and Dermot Diamond*[*]

*CLARITY: The Centre for Sensor Web Technologies, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Ireland.*

*E;mail: Dermot.diamond@dcu.ie*

*Tel: : +353 1 700 5404.*

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## Materials and Methods:

### *Chemicals and Materials:*

1-bromo-3-chloropropane, 2',4'-Dimethoxyacetophenone (DMPA), Indium Tin Oxide (ITO) coated polyethylene, methacryloxypropyltrimethoxysilane (MAPTMS), Methacrylic acid (MAAH), Aluminium tri-iso-propoxide (AlO), poly(octylthiophene) (POT) and 1-heptyl-4-(4-pyridyl)pyridinium bromide (*herein referred to as "mono-alkylated viologen" (MAV))* were used as purchased from Sigma-Aldrich® Ireland Ltd. Trioctylphosphine and trihexyltetradecylphosphonium chloride ($[P_{6,6,614}][Cl]$) were generously donated by Cytec® industries. $[P_{6,6,614}][Cl]$ was purified via washing with both water and hexane, followed by further column cleansing using basic alumina, as previously published[1].

### *Instrumentation:*

Differential Scanning Calorimetry analysis was performed using a Q200 series calorimeter under the convention that endothermic is up and exothermic is down. All scans were performed using a 5 $^0$C-heating rate in the range from -80 to 100 $^0$C (in triplicate).

Thermogravimetric analysis was conducted using a TA® Q50 in a flowing dry nitrogen atmosphere (50 mL / minute) between 25 and 800 °C, with a heating rate of 10 °C / min. Sample sizes ranged between 10 to 20 mg. The instrument was calibrated using the Curie points of three reference materials, Aluminium, iron and nickel. Platinum pans were used in all experiments.

Spectroelectrochemistry was performed using a Cary 50 Probe® UV/Vis spectrophotometer and a CHI® Instruments 660A potentiostat in tandem. The voltage range for all the experiments performed was between -3 - +3 V using scan rates varying from 100 to 10 mV/s. (More detailed experimental parameters can be found in the relevant sections of the main text).

Electrochemical Impedance Spectroscopy (EIS) was performed using a CHI® Instruments 660A potentiostat. The frequency range scanned ranged from 1 MHz to 1 Hz, and the perturbation signal applied was 100 mV. A platinum and Ag/AgCl were used as the reference and counter electrodes, respectively, and a nF capacitance shunt bridge was used in order to reduce high frequency noise. A 0.1 M KCl solution was used as the supporting electrolyte and in house screen-printed, carbon paste silver electrodes were used as the working electrode, as described previously[2]. The working electrodes were initially dropcast with a layer of POT ($10^{-2}$ M in chloroform) and allowed to dry in order to aid the transfer of ionic to electronic conduction. 40 μL of the ionogel to be analysed was then drop-cast and photo-polymerised for 5 minutes onto the POT layer.

Ionogel polymerisation was performed using a Electro-lite ®UV Bondwand (365 nm, 20W).

Ionogel thickness was measured using Mitutoyo® vernier calipers calibrated to a resolution of 1 μm.

D.C. solid-state platform experiments were performed using an Isotech IPS1603D D.C. power supply in the voltage range from 1 to 1.8 V.

## Supporting Information Figures:

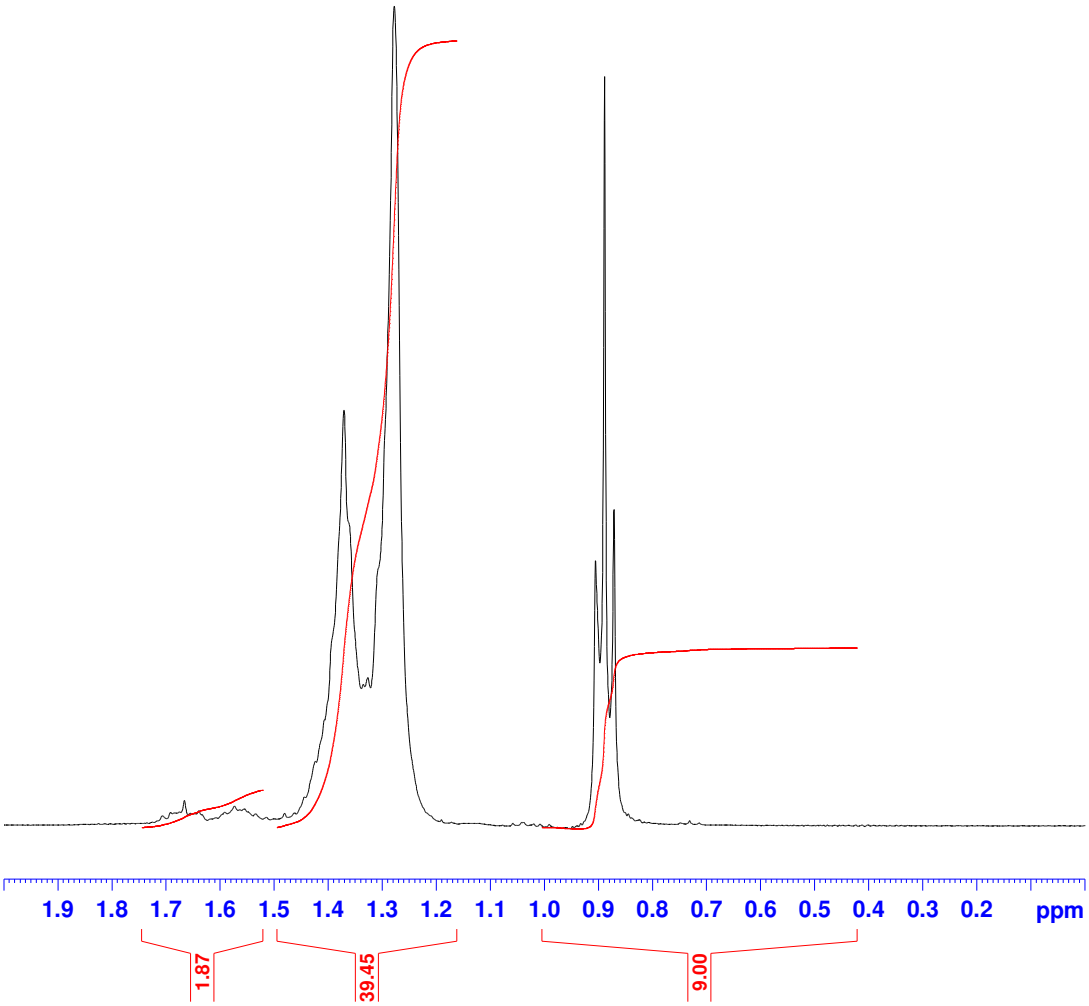



**Figure S1 (i):** $^{1}$H NMR spectrum obtained for trioctylphosphine.

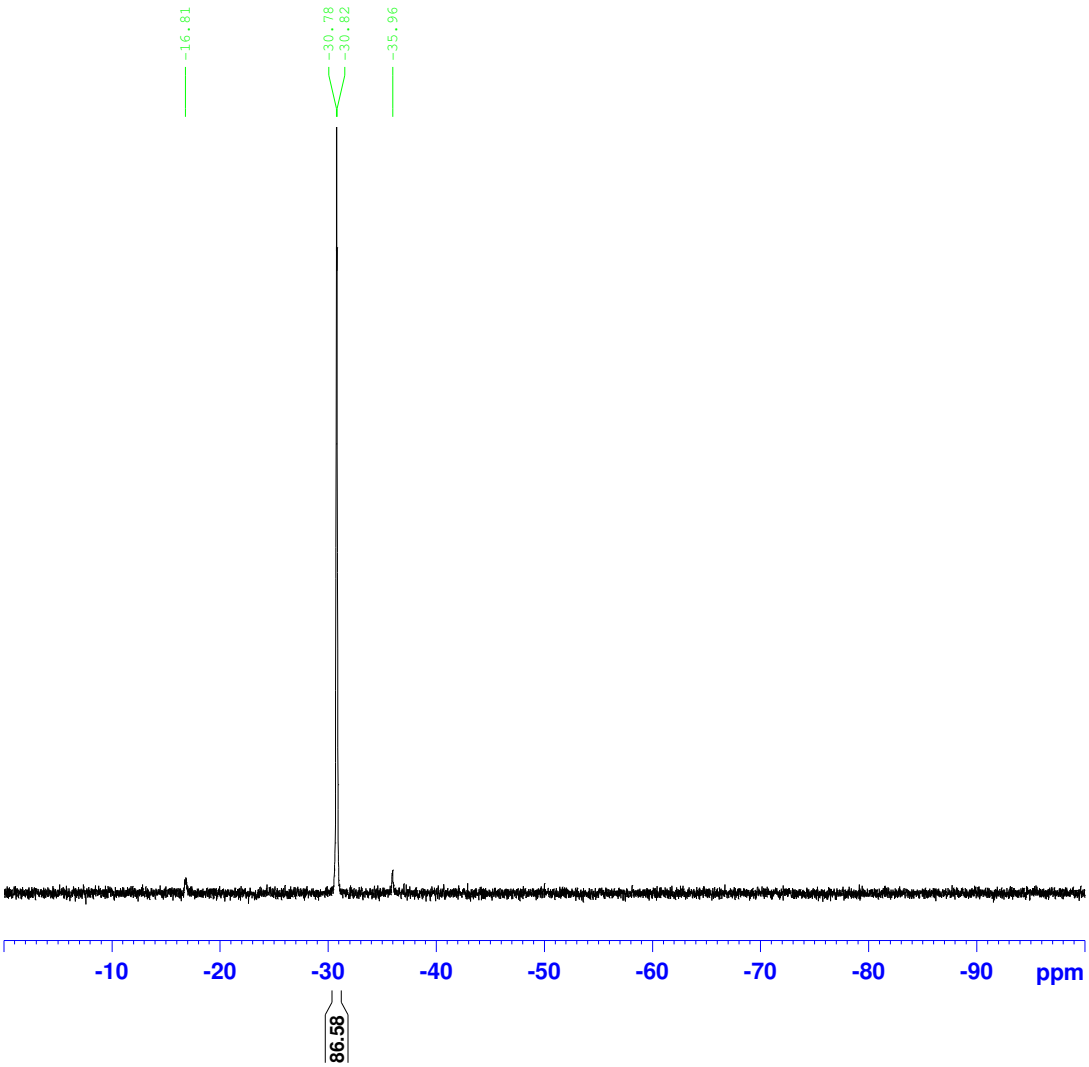



**Figure S1 (ii):** $^{31}$P NMR spectrum obtained for trioctylphosphine.

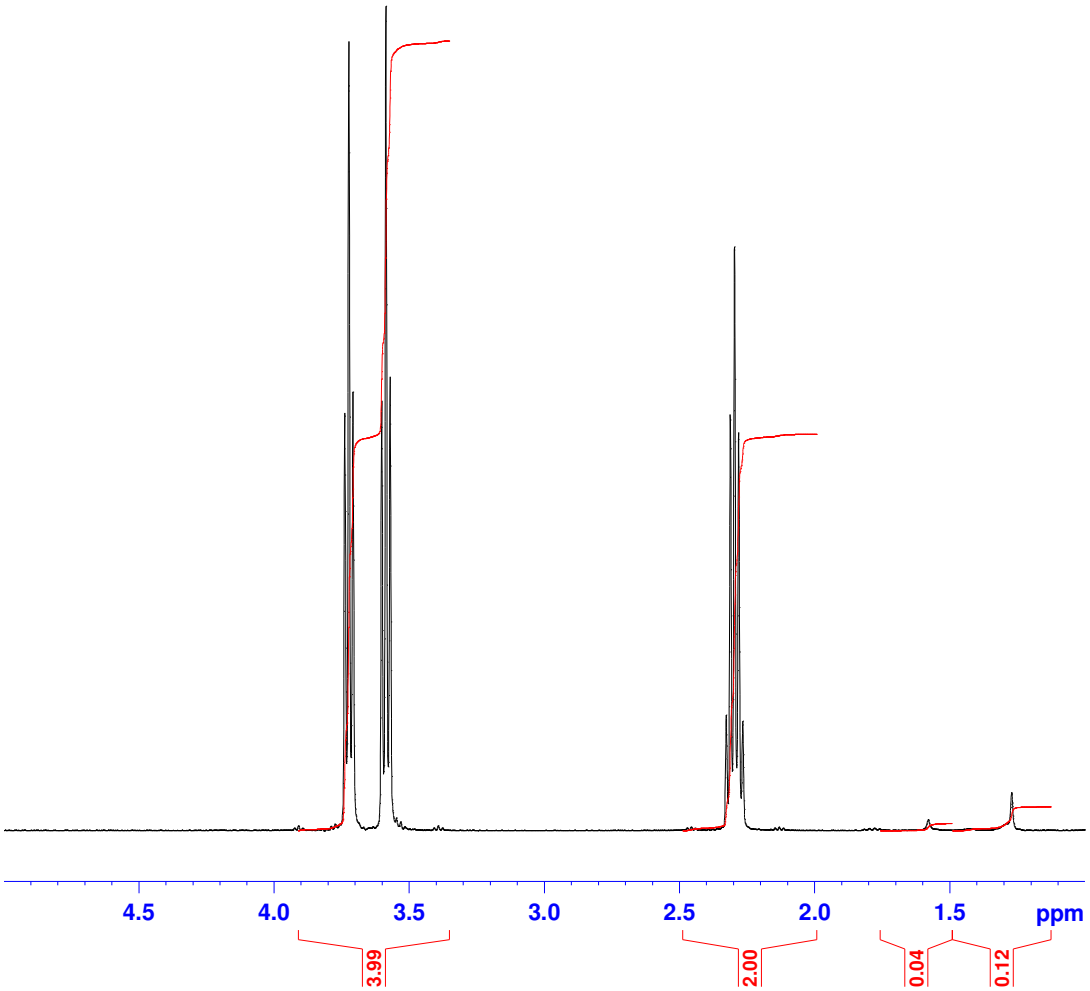



**Figure S1 (iii):** $^{1}$H NMR spectrum obtained for $C_3H_6BrCl$.

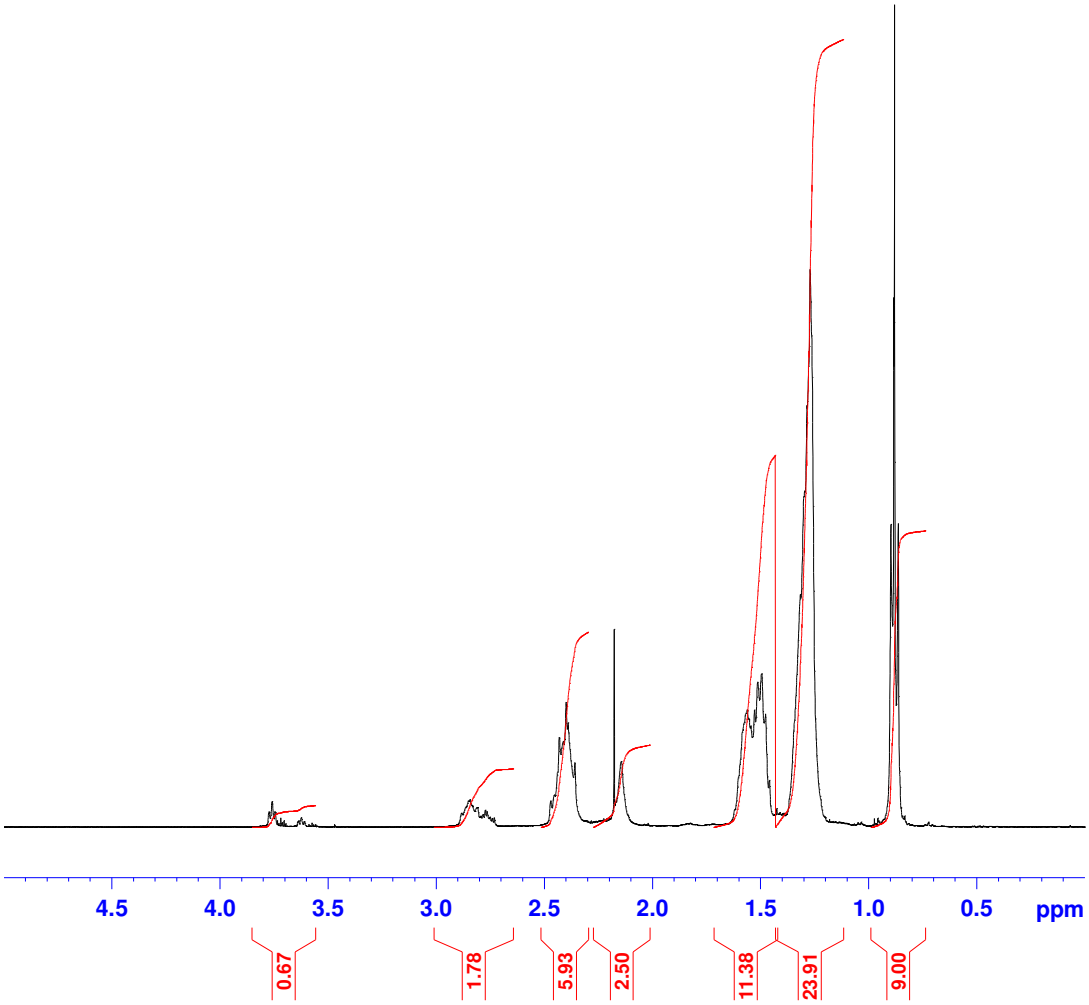



**Figure S1 (iv):** $^{1}$H NMR spectrum obtained for $[P_{3Cl,8,8,8}][Br]$.

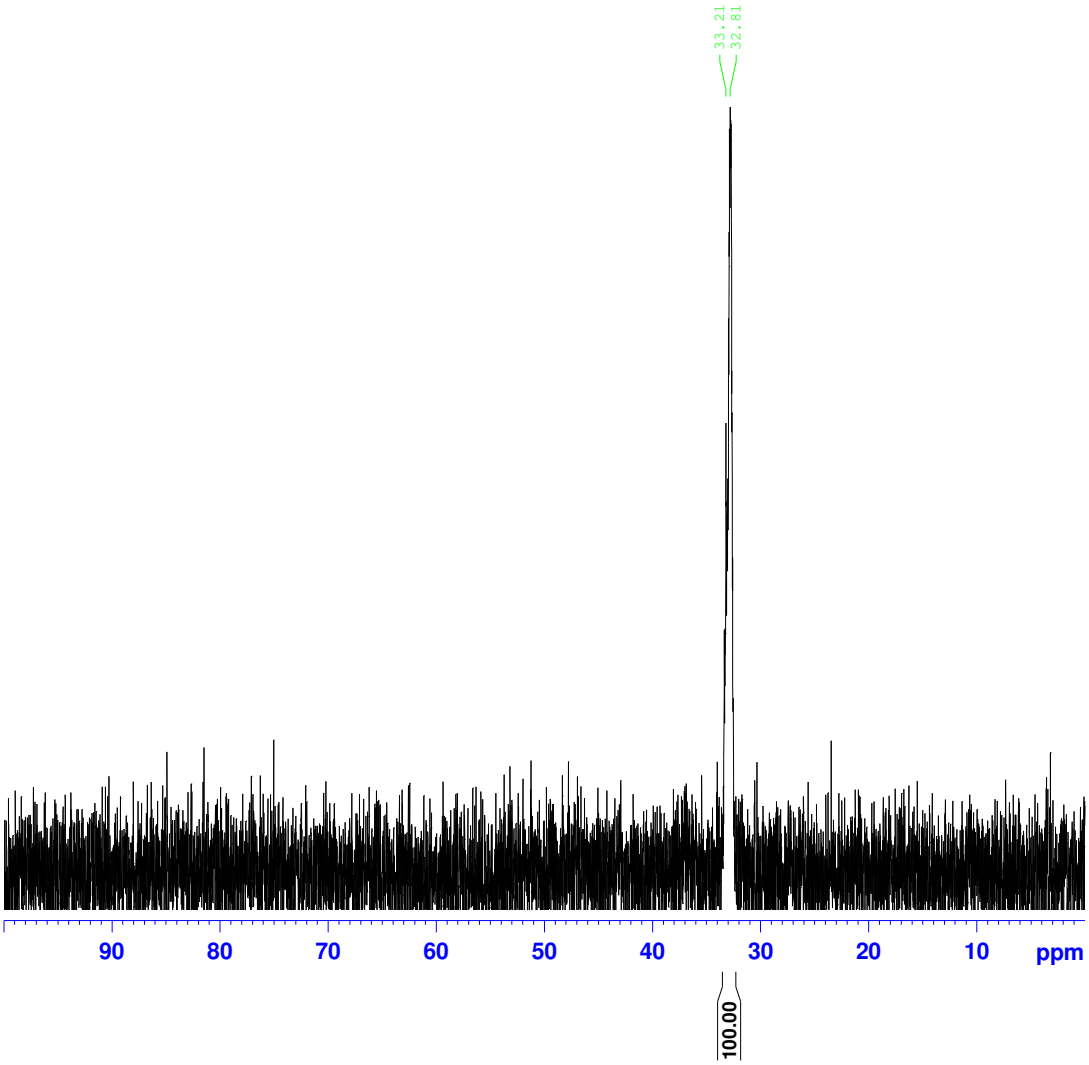



**Figure S1 (v):** $^{31}$P NMR spectra of $[P_{3Cl,8,8,8}][Br]$.

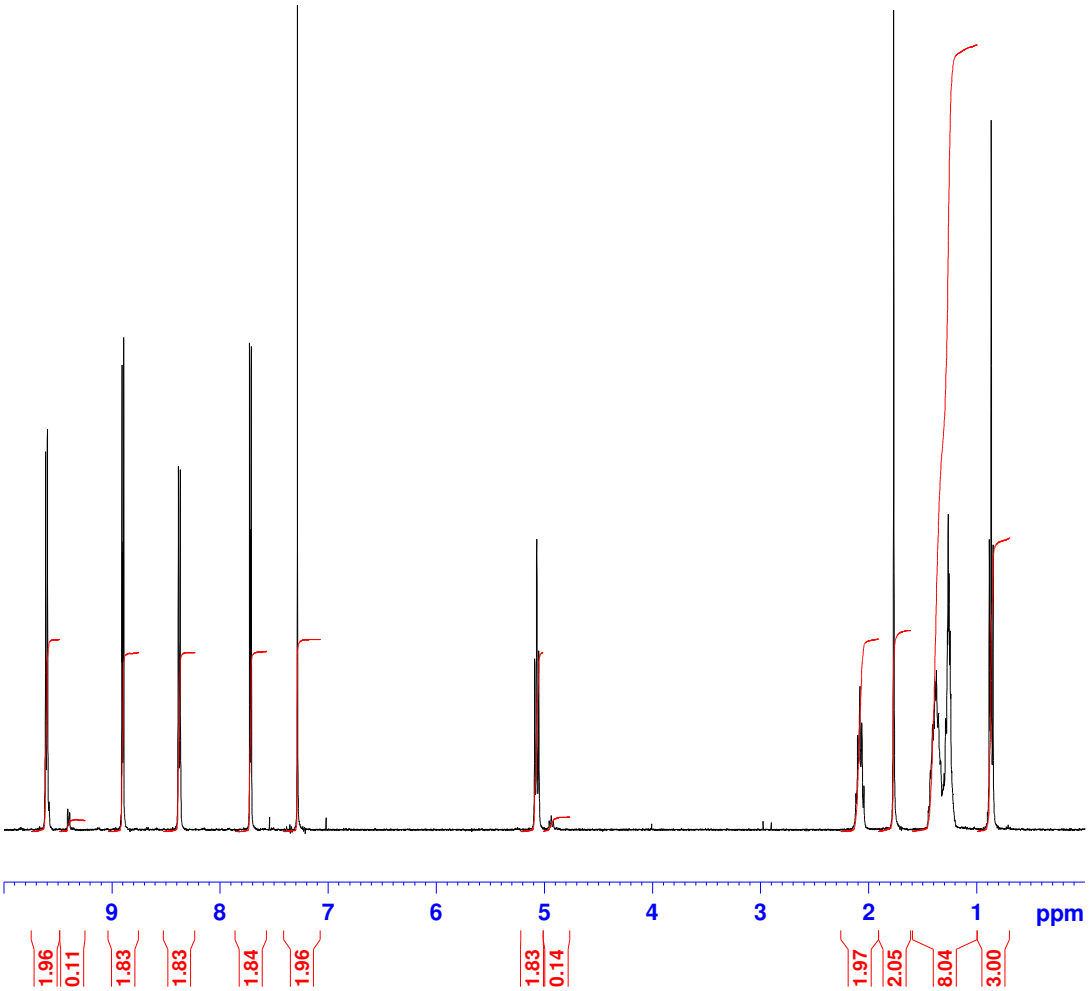



**Figure S1 (vi):** $^{1}$H NMR spectrum obtained for MAV.

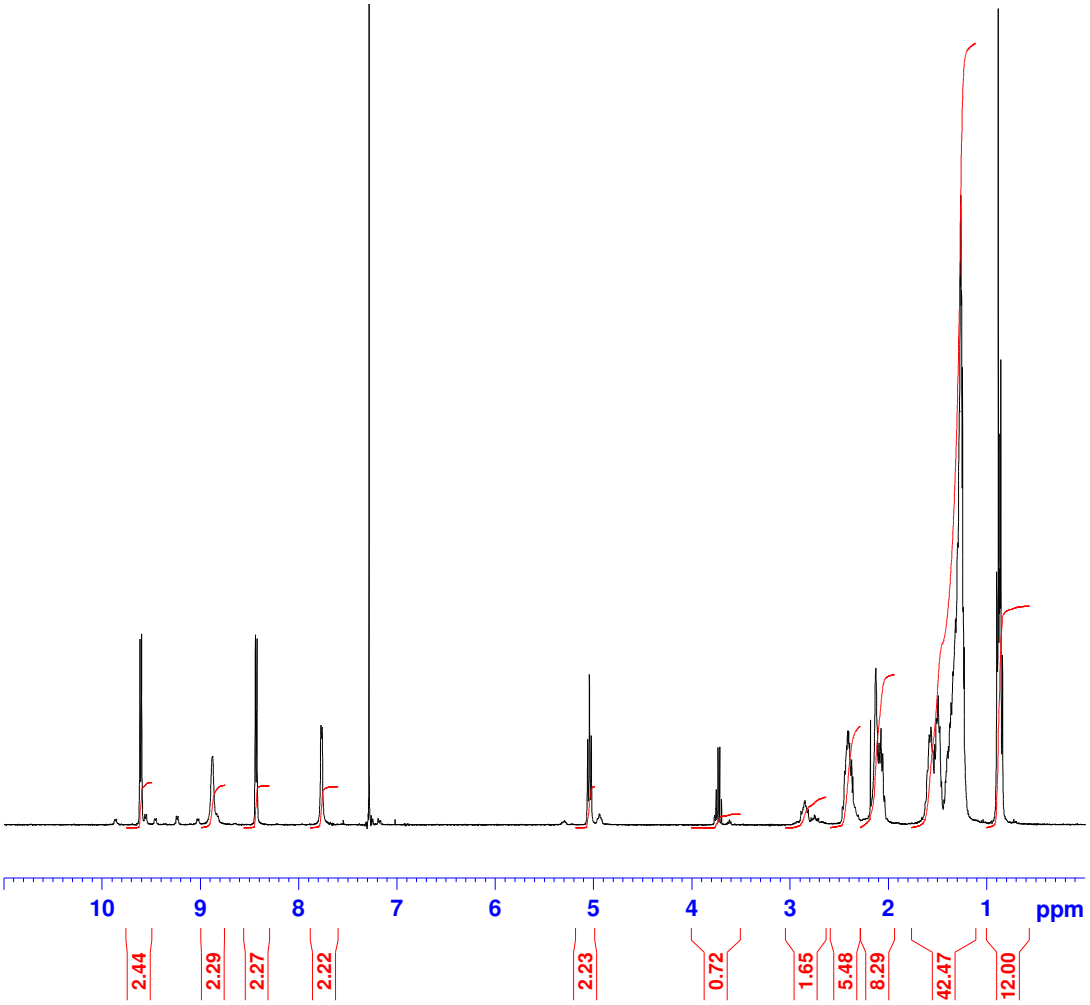



**Figure S1 (vii):** $^{1}$H NMR spectrum obtained for the electrochromic IL.

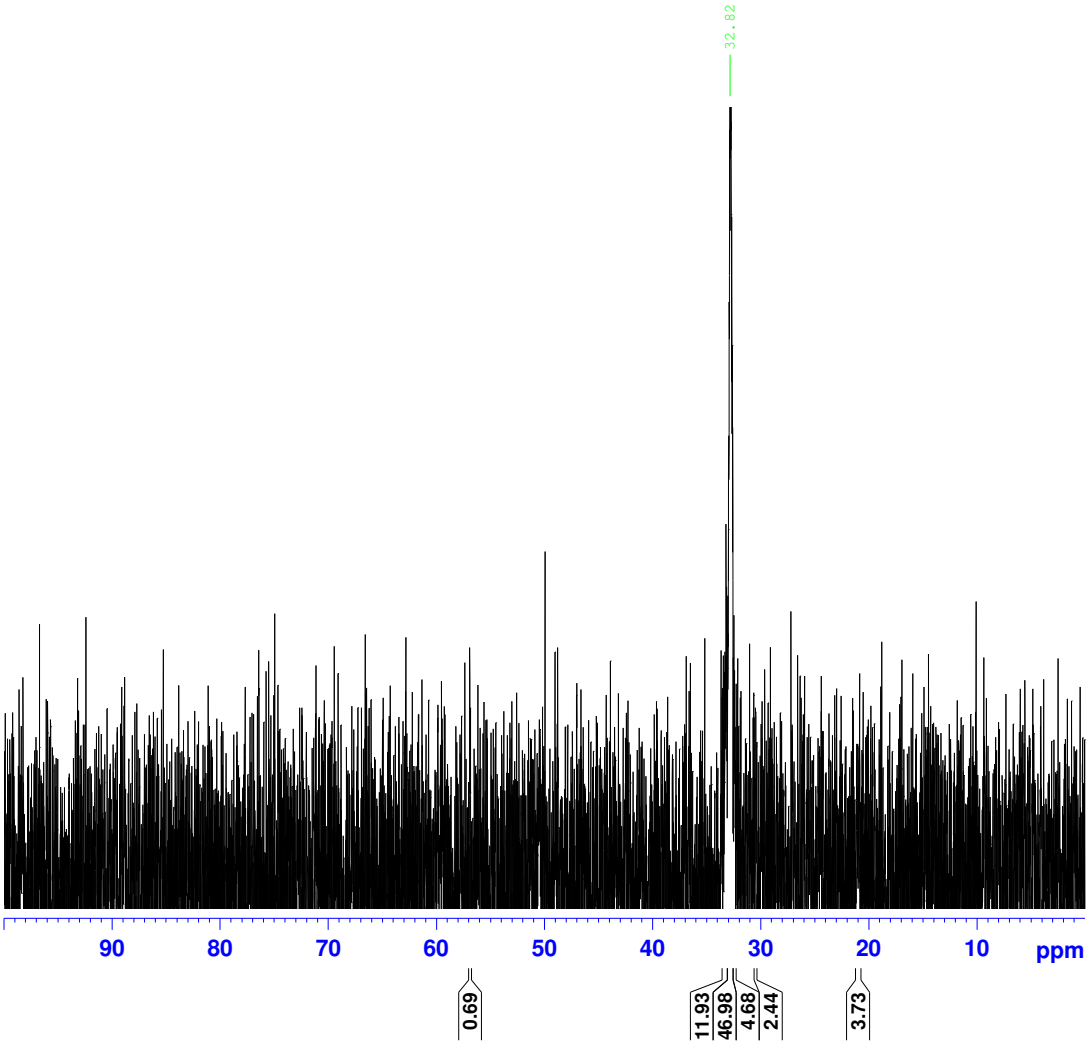



**Figure S1 (viii):** $^{31}$P NMR spectrum obtained for the electrochromic IL.

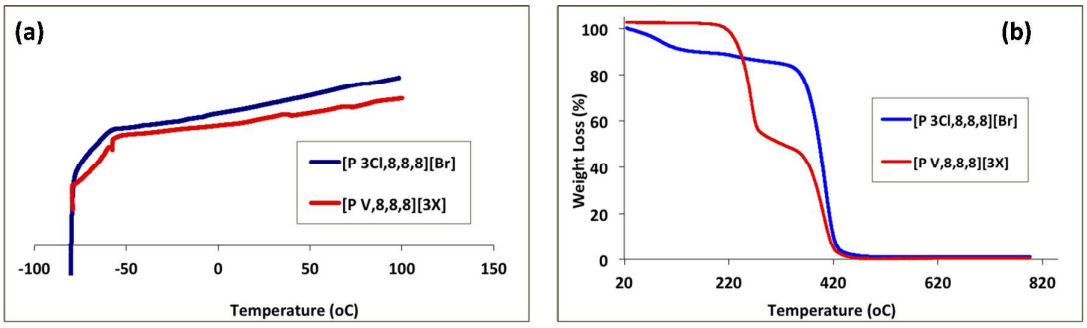
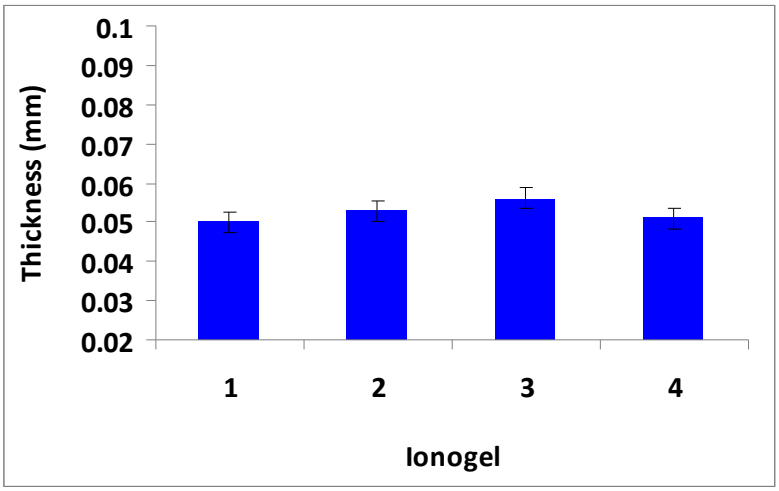



**Figure S2:** Thermal properties of novel synthesized ILs: **(a)** DSC traces -80 $^{o}$C to 100 $^{o}$C, **(b)** Decomposition profile of ILs in the region of 25 – 800 $^{o}$C.




| *Device* | *Ionogel + electrodes (mm)* | *Ionogel (mm)* |
|---|---|---|
| 1 | 0.307 | 0.05 |
| 2 | 0.31 | 0.053 |
| 3 | 0.313 | 0.056 |
| 4 | 0.308 | 0.051 |
| | average thickness (mm) | 0.0525 |
| | SD | 0.002645751 |

**Figure S3:** Platform thickness reproducibility analysis.

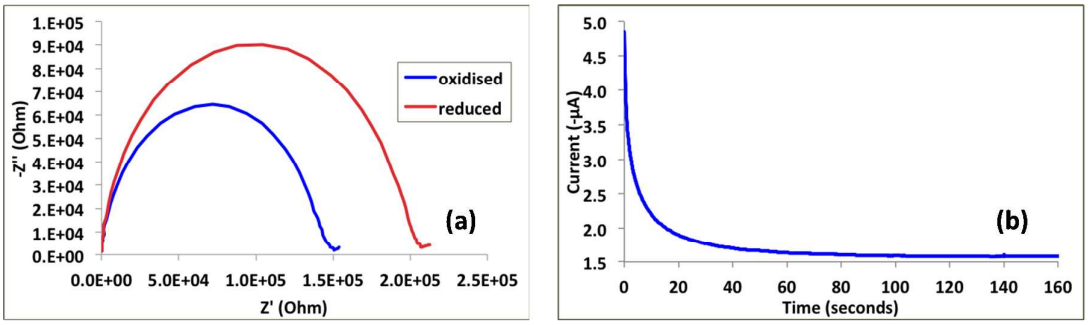



**Figure S4:** **(a)** Nyquist plots obtained for $[P_{v,8,8,8}][3X]$ in the oxidised ($V^{2+}$) and reduced state ($V^{\cdot+}$); **(b)** amperometric i-t curve used to generated the reduced state ($V^{\cdot+}$).

| | $R_{CT}$ (Ohm) | G (S) | Conductivity ($S/cm^2$) |
|---|---|---|---|
| **Oxidised** | 148,000 | 6.75676E-06 | 5.65315E-07 |
| **Reduced** | 205,000 | 4.87805E-06 | 4.0813E-07 |

| | | |
|---|---|---|
| **Conductance:** | 1/G | |
| **Conductivity:** | G*L / A | |
| **Average thickness: (L)** | 0.0753 | cm |
| **Electrode Area: (A)** | 0.9 | $cm^2$ |

**Figure S5:** Summary of data and equations used to estimate the impedance of the ionogel on a working electrode.

# References:


(1) Ramnial, T.; Taylor, S. A.; Bender, M. L.; Gorodetsky, B.; Lee, P. T. K.; Dickie, D. A.; McCollum, B. M.; Pye, C. C.; Walsby, C. J.; Clyburne, J. A. C. *J. Org. Chem.* **2008**, *73*, 801.

(2) Morrin, A.; Killard, A. J.; Smyth, M. R. *Anal. Lett.* **2003**, *36*, 2021.