Supporting information for:

Ion Jelly: a tailor-made conducting material for smart electrochemical devices†

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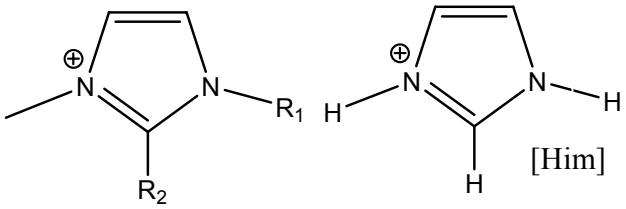
Contents

Materials and Methods

All ionic liquids based on the imidazolium cation and were provided by Solchemar. The tri-n-octyl-methylammonium chloride (Aliquat 336®) ionic liquid was provided by Sigma-Aldrich. 1-ethyl-3-methylimidazolium-2-(2-methoxyethoxy)ethylsulfate [emim][$MDEGSO_4$] - ECOENG™21M was provided by Solvent Innovation. ITO glass was obtained from ICE. Gelatin (Cultimed, Panreac), $K_3[Fe(CN)_6$ (Aldrich, ACS reagent, ≥99.0%) $FeCl_3.6H_2O$ (Riedel-de Haën, puriss. p.a., ≥99%), HCl (Panreac reagent grade), KCl (Merk), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate (PEDOT/PSS, Aldrich conductive grade) were used as received.



[Hmim] R_1= H ; R_2=H

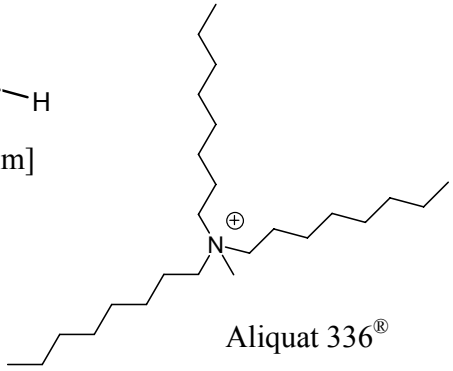
[emim] R_1= Et ; R_2=H

[bmim] R_1= *n*-Bu ; R_2=H

[omim] R_1= n-octyl ; R_2=H

[C_{10}mim] R_1= *n*-decyl ; R_2=H

[bdim] R_1=*n*-Bu ; R_2=CH_3



Prussian Blue (PB) film preparation

PB films were electrogenerated on glass indium tin oxide transparent electrode. The electrochemical polymerization was performed in a conventional three-electrode cell. An aqueous solution of 5 mM $K_3[Fe(CN)_6$, 5 mM $FeCl_3.6H_2O$, 5 mM HCl and 0.2 M KCl was used as PB polymerization solution. Electropolymerization conditions: constant applied voltage of 0.55nV (*vs.* Ag/AgCl), for 300 s. After deposition, the electrode was gently rinsed with distilled water.

Electrochromic Window Assembly

The electrochromic window set-up was constructed using two ITO glasses, each one covered with a different electrochromic layer, of PB and of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate (PEDOT/PPS), respectively. The ion jelly was spread over PEDOT/ITO using a pipette, forming a homogenous film. The film was left to jellify before being covered with PB/ITO. The window was then sealed with epoxy glue.

Electrochemical and spectroscopic measurements

Electrochemical polymerization and choronocoulometry/chronoabsorptometry were performed with a conventional three-electrode cell using a computer controlled computerized potentiostat-galvanostat Model 12 Autolab, from Eco-Chemie Inc. The collection of data was controlled by GPES Version 4.9 Eco Chemie B.V. Software (Utrecht, The Netherlands). Working electrode: PEDOT/ITO. The PB/ITO electrode functioned both as auxiliary and reference electrode. UV/Vis absorbance chronoabsorptometry spectra were recorded in a Shimadzu UV2501-PC spectrophotometer. All spectroscopic measurements of the electrochromic cell were done *in situ*.

Conductivity measurements

The conductivity of several ion jelly films was measured using an impedance analyzer (Alpha-N Analyzer from Novocontrol GmbH), covering a frequency range from 0.1 Hz to 1 MHz. Films were placed between two gold-plated electrodes (diameter 20 mm) of a parallel plate capacitor. The temperature control, with a precision of ± 0.1 K, was assured by the QUATRO Cryosystem also supplied by Novocontrol GmbH. Frequency dependent ionic conductivity of the different gel films was measured from -110 to 40ºC.

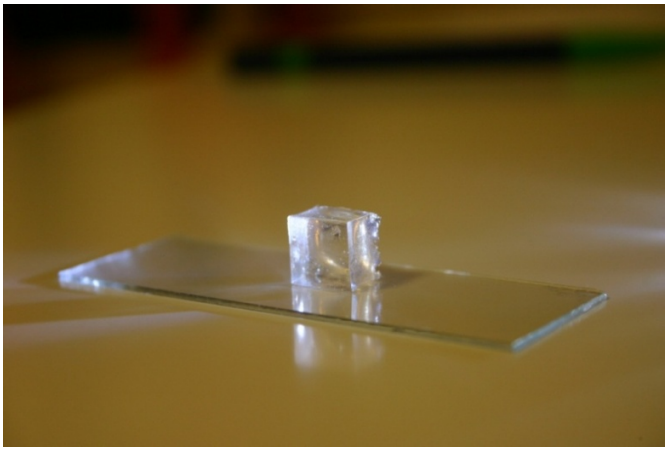
X-ray diffraction

The X-ray diffraction measurements were carried out on a Enraf-Nonious X-ray generator equipped with a Cu-Rotating anode. The diffraction patterns were collected, by rotating the sample 360° with a step size of 1° and an exposure time of 1h, with a detector to sample distance of 90 mm.

General ion jelly synthesis

100-300 µL of ionic liquid was heated to 40 ºC and under magnetic stirring 1 equivalent mass of gelatin was added. The amount of added water depended on the hydrophilicity and initial water content of the ionic liquid used, as measured through Karl-Fischer titration. In the case of water-miscible ionic liquids, a water content of 10 % was used, whereas non water-miscible ionic liquids were used water-saturated. The mixture was kept stirring at 40 ºC until gelatin was completely solubilized (1 to 24 hours). The solution was then spread over a glass surface or used to fill a mold. Jellification occurred at room temperature. “R” indicates ionic liquid/gelatin mass ratio (w/w). Different types of material formed are shown in Figure S1.

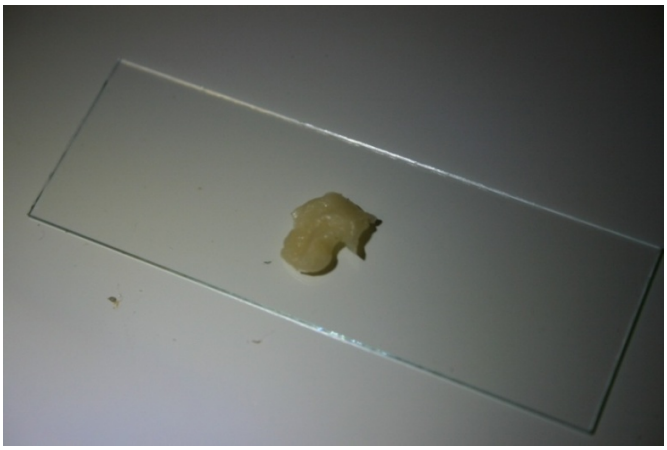
Pictures of ion jelly materials



(a)

Figure S1- Type of material formed upon combining an IL with gelatin. (a) - solid transparent block of [bmim] $[(CN)_2N]$ $R_{(IL/gelatin)}$=3; (b) - solid transparent film of [emim] $[EtSO_4]$; (c) - solid rigid block of [bmim] $[BF_4]$.

(b)



(c)

Ion jelly synthesis table

Table S1. Selected cation and anion combinations that led to the formation of an ion jelly.

Cation	Anion	Il/gelatin ratio (w/w)	Water-miscible	Type of material formed
[bmim]	[N $(CN)_2$]	1:1	YES	Solid Transparent films
		3:1	YES	Solid Transparent films
		6:1	YES	Liquid gel
[omim]	[N $(CN)_2$]	1:1	YES	Solid Transparent films
		1:3	YES	Solid Transparent films
Aliquat 336®	[N $(CN)_2$]	1:1	NO	No Ion Jelly formation
[Him]	[Cl]	1:1	YES	Solid Transparent films
[Him]	[Cl]	1:3	YES	Solid Transparent films
[Hmim]	[Cl]	1:1	YES	Solid Transparent films
		1:3	YES	Solid Transparent films
[bmim]	[Cl]	1:1	YES	Solid Transparent films
		1:3	YES	Solid Transparent films
[omim]	[Cl]	1:1	YES	Solid Transparent films.
		1:3	YES	Solid Transparent films.
[C_{10}mim]	[Cl]	1:1	YES	Solid Transparent films
[bdim]	[Cl]	1:1	YES	Solid Transparent films
		1:3	YES	Solid Transparent films
Aliquat 336®	[Cl]	1:1	NO	No Ion Jelly formation
[bmim]	[saccharin]	1:1	YES	Solid Transparent films
		1:3	YES	Solid Transparent films
Aliquat 336®	[saccharin]	1:1	NO	No Ion Jelly formation
[bmim]	[PF_6]	1:1	NO	No Ion Jelly formation
[bmim]	[BF_4]	1:1	YES	Compact rigid solids
[bmim]	[PTSA]	1:1	YES	Solid Transparent films
		1:3	YES	Solid Transparent films
[bmim]	[NTf_2]	1:1	NO	No Ion Jelly formation

[emim]	$[EtSO_4]$	1:1	YES	Solid Transparent films
		1:3	YES	Solid Transparent films
		1:6	YES	Liquid gel
[emim]	$[MeSO_4]$	1:1	YES	Solid Transparent films
		1:3	YES	Solid Transparent films
[emim]	$[MDEGSO_4]$	1:1	YES	Solid Transparent films
		1:3	YES	Solid Transparent films

X-ray diffraction patterns

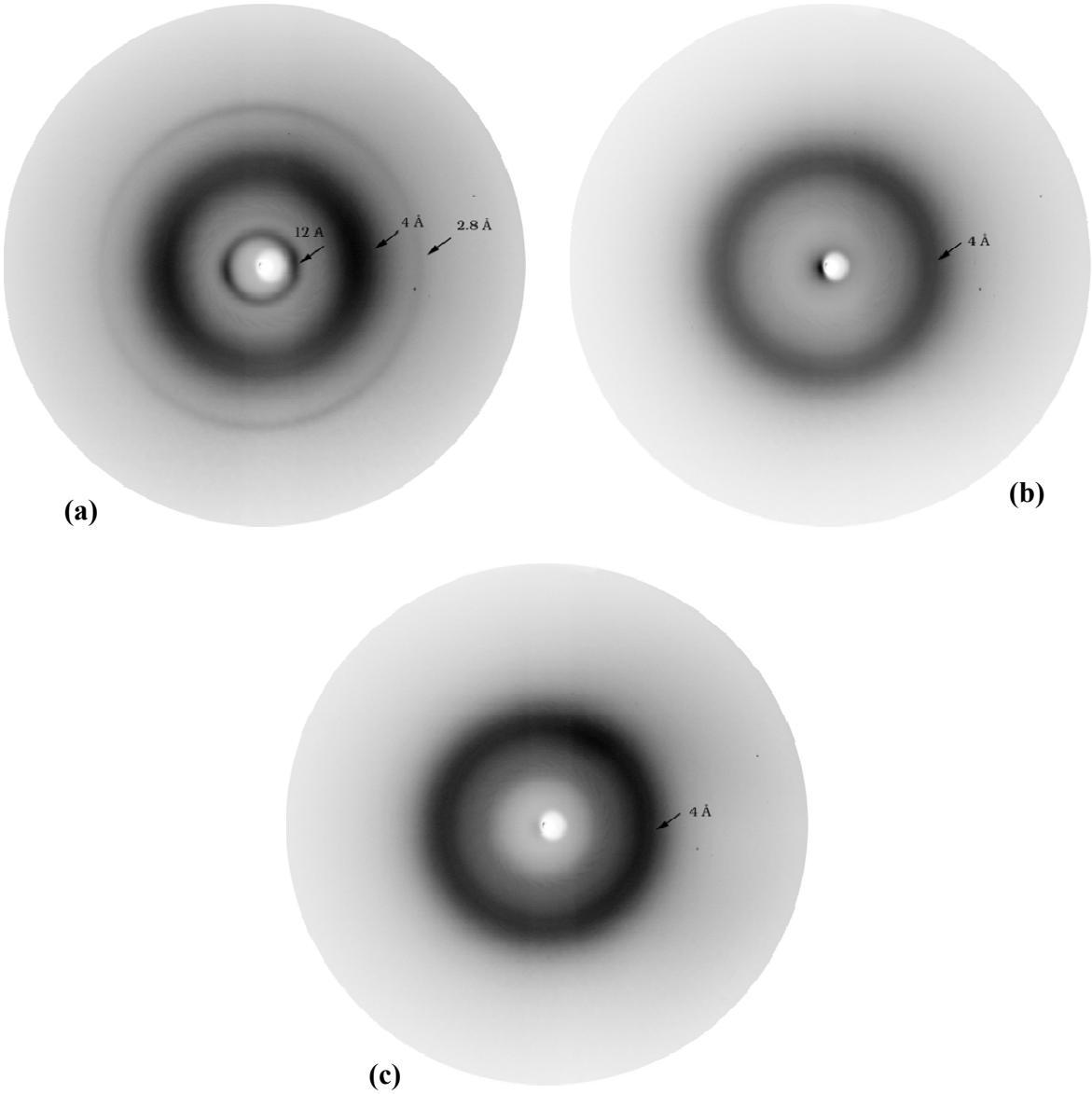


Figure S2 – X-ray diffraction patterns. (a) – Water-based gelatin gel ; (b) – Ion jelly with [bmim][$N(CN)_2$] ($R_{RTIL/gelatin}$ = 3) ; (c) – Ion jelly with [emim][$EtOSO_4$] ($R_{RTIL/gelatin}$ = 3).

Differential scanning calorimetry analysis

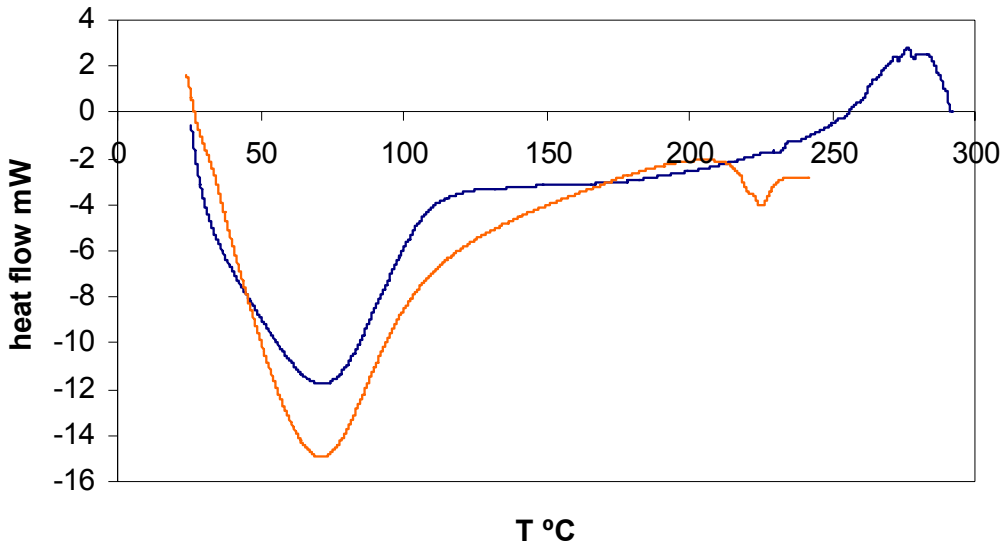


Figure S3 - Differential scanning calorimetry analysis. Blue – ion jelly with [bmim][$N(CN)_2$] ($R_{RTIL/gelatin}$= 1); Orange – water-based gelatin gel.

Conductivity of ion jelly films

Table S2 – Conductivity of ion jelly films at three different frequencies.

Film	Conductivity [S.cm^{-1}] at 25ºC		
	10^{-1} Hz	**10^{3} Hz**	**10^{6} Hz**
$[bmim][N(CN)_2]_{(R=1)}$	6.12 E^{-6}	1.51 E^{-4}	1.63 E^{-4}
$[bmim][N(CN)_2]_{(R=3)}$	2.71 E^{-7}	2.17 E^{-5}	8.62 E^{-5}
$[bmim][Cl]_{(R=1)}$	2.67 E^{-6}	7.52 E^{-5}	8.47 E^{-5}
$[Hmim][Cl]_{(R=1)}$	7.09 E^{-6}	8.94 E^{-5}	1.13 E^{-4}
$[C_{10}mim][Cl]_{(R=1)}$	6.58 E^{-8}	1.99 E^{-7}	1.34 E^{-6}
$[emim][EtSO_4]_{(R=1)}$	5.30 E^{-7}	1.23 E^{-4}	2.50E^{-4}
[Him][Cl]	2.43 E^{-5}	6.42 E^{-5}	6.85E^{-5}

Table S3 - IL conductivity.

IL	Conductivity at 25ºC [S cm^{-1}]
bmim][$N(CN)_2$]	1.1 E^{-2} [S1]
[bmim][Cl]	3.0 E^{-2} [S2]
[emim][$EtSO_4$]	8.0 E^{-2} [S2]

[S1] -Yoshida, Y., Baba, O., Larriba, C. , Saito G. (*2007), J. Phys. Chem. B ,111,* 12204.
[S2] - Sigma-Aldrich ionic liquids

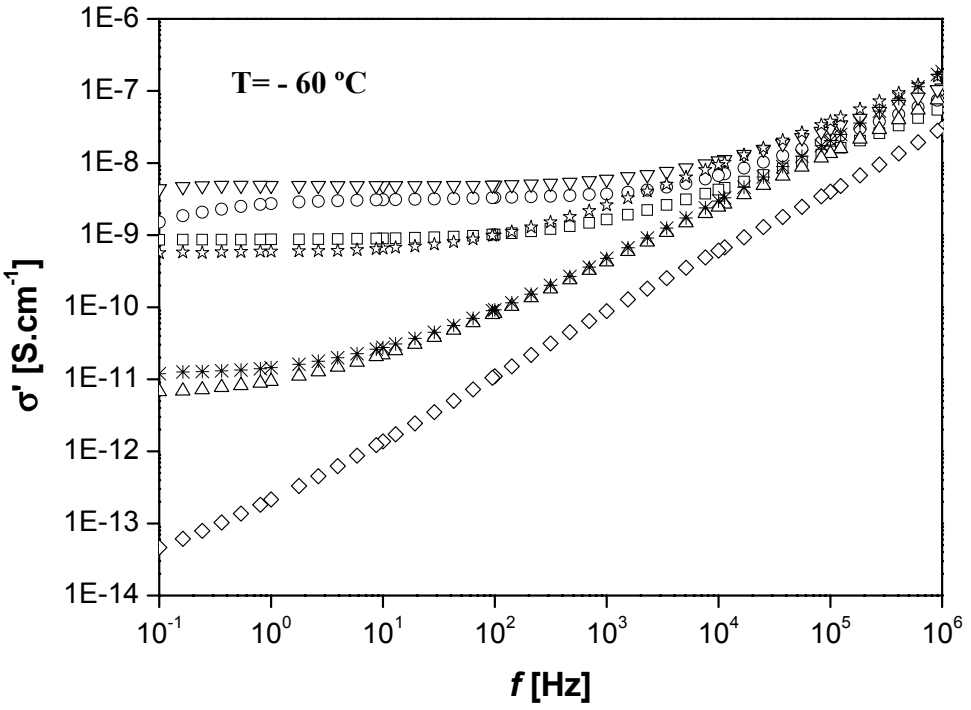


Figure S4 - Conductivity spectra of ion jelly films at -60ºC
□ $[bmim][N(CN)_2]_{(R=3)}$; ○ $[bmim][N(CN)_2]_{(R=1)}$;
△ [bmim][Cl](R=1); ❋ $[Him][Cl]_{(R=1)}$;◇$[C_{10}mim][Cl]_{(R=1)}$;
▽ $[Hmim][Cl]_{(R=1)}$; ☆ $[emim][EtSO_4]_{(R=1)}$; $R=m_{IL}/m_{gelatin}$.

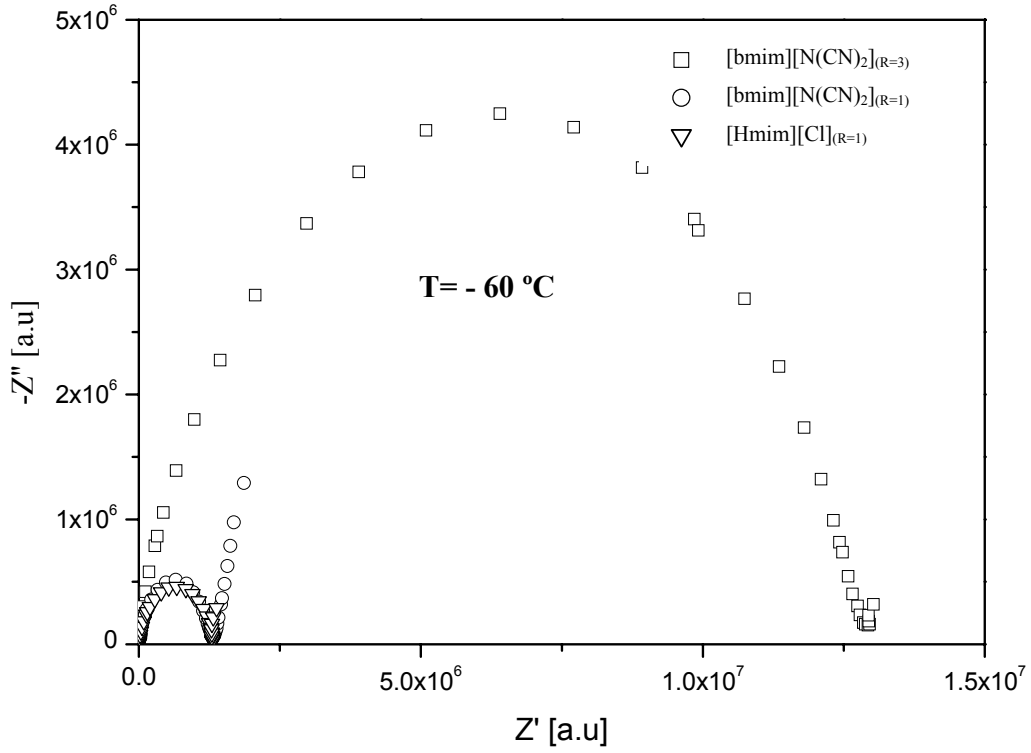


Figure S5- Nyquist plots of ion jelly films: $[bmim][N(CN)_2]_{(R=3)}$; $[bmim][N(CN)_2]_{(R=1)}$; $[bmim][Cl]_{(R=1)}$ at -60ºC

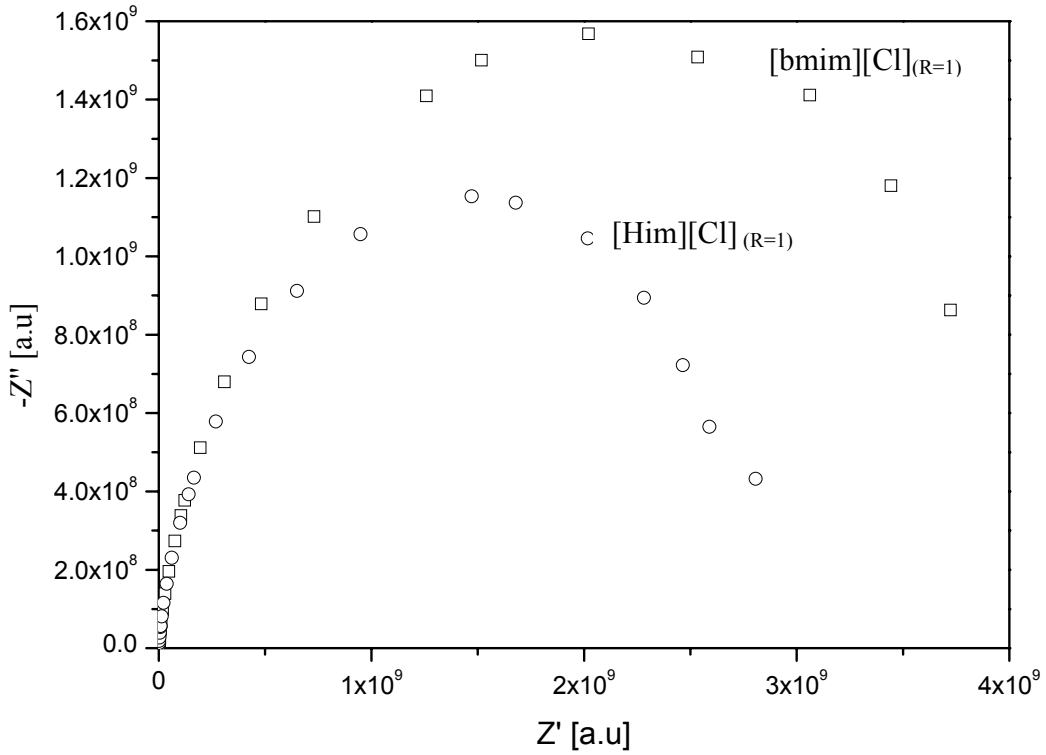


Figure S6- Nyquist plots of ion jelly films:; $[bmim][Cl]_{(R=1)}$; $[Him][Cl]_{(R=1)}$ at -60ºC

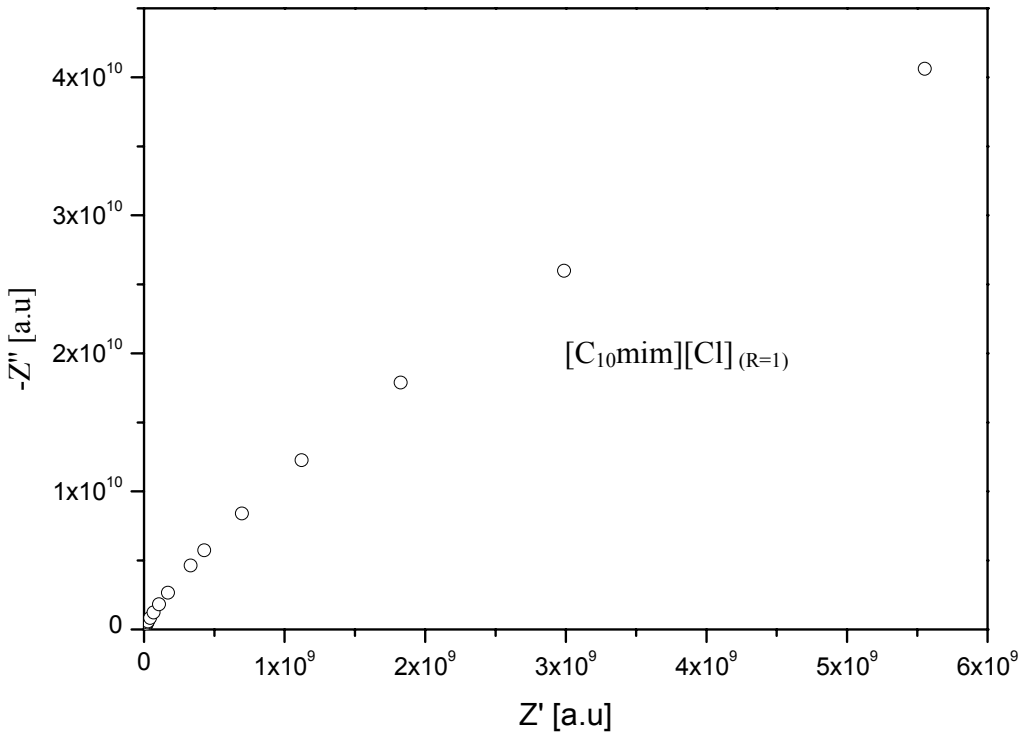


Figure S7- Nyquist plots of ion jelly films:,$[C_{10}mim][Cl]_{(R=1)}$ at -60ºC

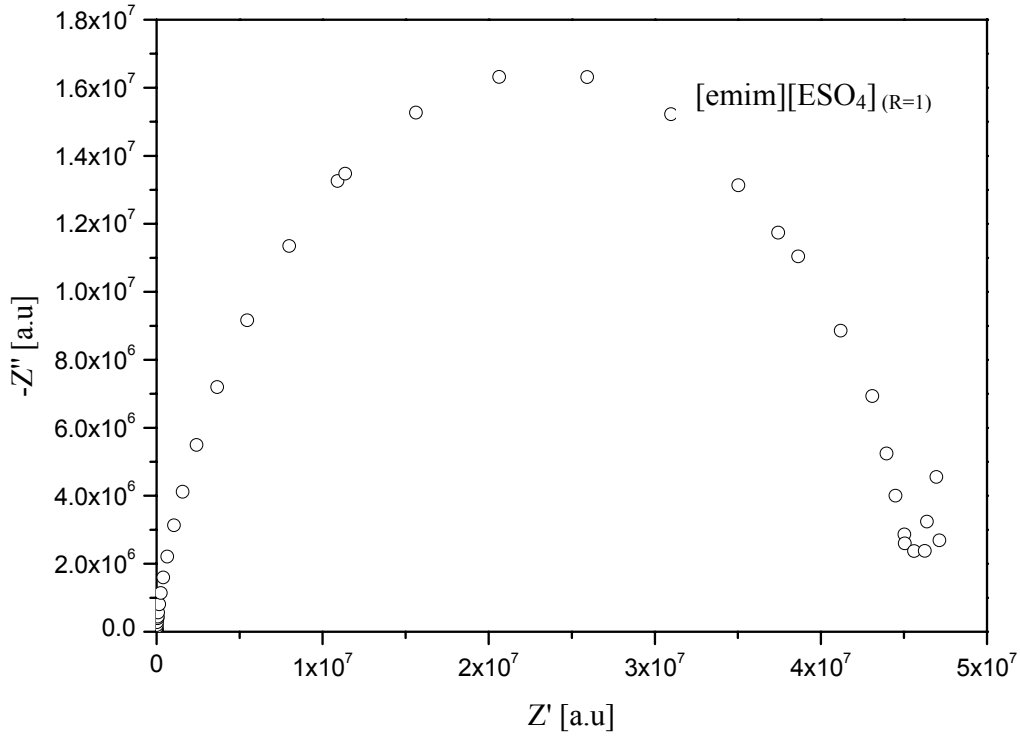


Figure S8- Nyquist plots of ion jelly films:,$[emim][ESO_4]_{(R=1)}$ at -60ºC

In situ **spectroelectrochemical cycling data for Glass – ITO/PEDOT/ion jelly/PB/ITO – Glass, ion jelly wire**

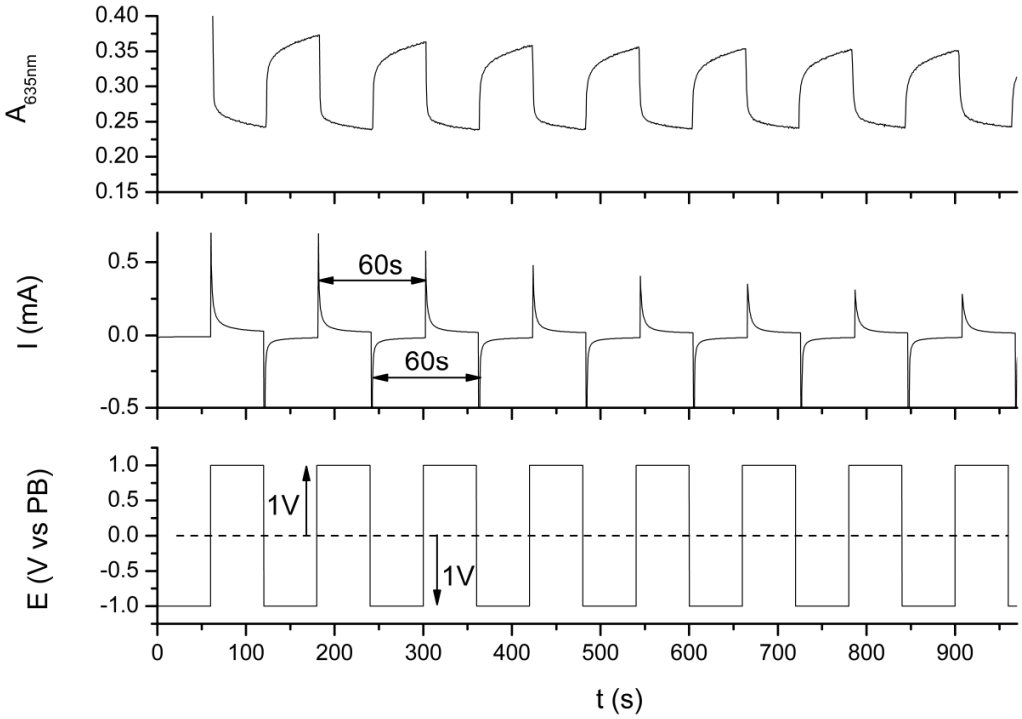


Figure S9 – *In situ* spectroelectrochemical cycling data for Glass-ITO/PEDOT/ion jelly/PB/ITO-Glass. A - Chronoabsorptometry recorded at 700nm; B - Square-wave switching between -1V (step duration 60 s) and +1, V (step duration 60 s) (vs. PB);

Ion jelly wire

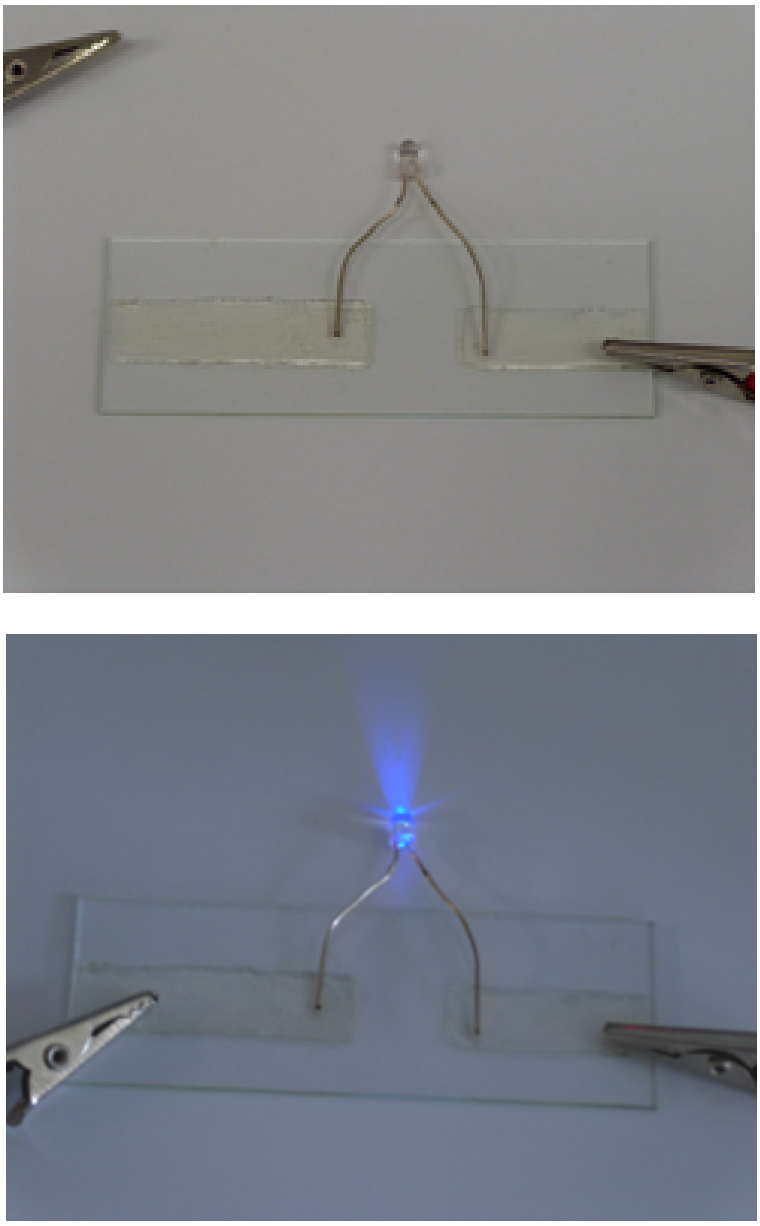


Figure S10 – Ion jelly wire. The electron transfer in mediated by the ion jelly conducting material.